

Modern Materials for Adsorption Heat Energy Storage – A Mesoporous Silica Matrix

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Modern Materials for Adsorption
Heat Energy Storage -
A Mesoporous Silica Matrix
by

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A thesis submitted for the degree of Doctor of Engineering
in the
Interdisciplinary Graduate School of Engineering Sciences
Department of Energy and Environmental Engineering

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Declaration of Authorship

I, FRANTIŠEK MIKŠÍK, declare that this thesis titled, “Modern Materials for Adsorption Heat Energy Storage - A Mesoporous Silica Matrix” and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
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“Getting a doctoral degree did not in fact make me to understand more about my topic, it mostly made me to realize how deep my ignorance was.”

Abstract

Energy storage is one of the key components for effective utilisation of renewable sources of energy. The necessary storage capacity is not limited only to the electric energy but can be applied to thermal energy as well, since the consumption of thermal energy exceeds the electric energy in general. This work introduces the concept of adsorption thermal energy storage (aTES) technology with the main focus on the storage matrix in the combination with water as a working medium. The energy in aTES is stored in a form of adsorption potential when the heat is released upon contact and adsorption of the vapours of the working medium with the surface of the storage substrate. The pressure drop in the whole system coupled to this vapour adsorption on the substrate drives further evaporation of the working medium and hence creating an active cooling part as well as heating. Because the energy release is given by the contact of the working fluid vapours with the substrate only, the energy release can be postponed indefinitely creating a lossless energy storage. This work analyses the potential of nano-tailored and highly structured artificially produced mesoporous silica materials based on a deep material analysis. For the purpose of this work six specimens of an industrially manufactured mesoporous silica from the TMPS family, with 4 of the samples enhanced with aluminium, were selected for evaluation as a potentially suitable substrate material for adsorption heat transformation technologies.

The first part of this dissertation focuses on the common properties of the selected materials and compares them with more common representatives of the tailored mesoporous silica group the SBA-15 and MCM-41. The mean pore diameter of the samples was found out starting at 1.8 nm up to 4 nm with wall thickness around ≈ 1.5 nm. The XRD, FTIR, SEM/EDS, DSC analysis were performed to measure the physical parameters. It was found out that the basic properties of the TMPS samples are closer to the MCM-41 family rather than the wide pore SBA-15. The thermal stability analysis conducted on TGA did not reveal any significant changes in the structure up to 800 °C proving high stability of the TMPS group. Next chapter of this thesis is focused on actual water adsorption properties of the studied mesoporous silica materials. The main points of interests were effective capacity, working region of the relative pressure and modelling of the adsorption properties. The effective working relative pressure (P/P_0) of the total uptake was found out in a wide range up to 0.3 P/P_0 for the lowest TMPS-1.5A up to 0.75 P/P_0 for the highest TMPS-4R. The recommended effective working region 0.05

to $0.3 P/P_0$ for the adsorption heat transformation applications was successfully fitted by TMPS-1.5 and TMPS-1.5A samples. A significant part of the uptake in this region was also observed in case of TMPS-2A, making these three specimens potential candidates for a direct use. The adsorption isotherm was modelled by Henry-Sips (HS) combined model and Langmuir-Freundlich-Gauss (LFG) model as an original attempt of this work. The higher compatibility of the LFG model was observed in the majority of the samples and especially for samples with the majority occurring adsorption higher than $>0.5 P/P_0$.

The theoretical properties of the examined mesoporous silica materials for the use as an adsorption substrate in the aTES were critically examined on the pretext of temperature lift, pressure reduction and storing capacity. The isosteric heat of adsorption was calculated based on the Clausius-Clapeyron equation and shows strong dependency on pore size and aluminium presence. The isosteric heat was then used as a theoretical base for the energy storing capacity. The highest storing capacity was naturally achieved by the samples with the highest effective pore volume TMPS-4A and TMPS-4R, however their temperature lift and coupled pressure reduction were found out not sufficient. A sufficient heating and cooling capacity was calculated for the TMPS-1.5 and TMPS-1.5A with a plausible use of TMPS-2A as well. The cooling and heating capacity of the best performing TMPS-1.5A was calculated as low as $T_{C25} = 4.1^\circ\text{C}$ and heating capacity of $T_{H10} = 31.3^\circ\text{C}$ at 50 % uptake capacity with driving temperatures of $T_D = 25^\circ\text{C}$ and $T_D = 10^\circ\text{C}$, respectively.

A possible composite material is elaborated in the last part based on TMPS-4A with three inorganic salts inside its porous matrix. CaCl_2 , MgCl_2 , and MgSO_4 were integrated into the pores from 25 % solutions and adsorption properties were measured at 288.15 K, 298.15 K, and 308.15 K. All three combinations show an improvement in the overall properties when the best values were achieved by TMPS-4A+ MgCl_2 . The temperature lift in case of TMPS-4A+ MgCl_2 was in fact doubled to $\Delta T \approx 16\text{ K}$ at 50 % filling compared to the sole TMPS-4A respective to the cooling and heating capacity at the driving temperature of $T_D = 10^\circ\text{C}$ for heating and $T_D = 40^\circ\text{C}$ for cooling. Furthermore, the observation of the isotherm data on the second measurement did not reveal any significant loss of the salt from material and safe containment of the salt solution inside the pores. Hence, the observed values show significant enhancement compared to the plain material proving this method to be a suitable technique for the highly ordered TMPS-4A materials and possibly for the other members of the TMPS family as well.

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Abbreviations

AAD	A verage A bsolute D eviation
BET	B runauer E mmett T eller
BJH	B arrett J oyner H alenda
COP	C oefficient O f P erforamce
CTMABr	C etil T ri M ethyl A mmonium B romide
DFT	D ensity F unctional T heory
DH	D ellimore H eal
DSC	D ifferential S canning C alorimetry
EDS	E nergy D ispersive X -ray S pectroscopy
H/J	H arkins/ J ura
IEA	I nternational E nergy A gency
IPD	I ntra- P article D iffusion
IUPAC	I nternational U ion of P ure and A ppled C hemistry
LDF	L inear D riving F orce
LFG	L angmuir F reundlich G auss
MCM-41	M obil C omposition of M atter No. 41
MOF	M etal O rganic F ramework
MPS	M esoporous S ilica
PCM	P hase C hange M aterials
PFO	P seudo F irst O der
PFO2	P seudo F irst O der M odified
PSO	P seudo S econd O der
SBA-15	S anta B arbara A morphous-15
SEM	S canning E lectron M icroscopy
TES	T hermal E nergy S torage
TG	T hermo G ravimetry
TG-DSC	T hermo G ravimetry - D ifferential S canning C alorimetry
aTES	A dsorption T hermal E nergy S torage

TMPS	T aiyo K agaku M esoporous S ilica
XRD	Powder X-Ray D iffraction

Physical Constants

Avogadro constant	N_A	=	$6.022\,140\,86 \times 10^{23} \text{ mol}^{-1}$
Gas molar volume	V_{GSP}	=	$22\,414 \text{ cm}^3 \text{ mol}^{-1}$
Nitrogen density	ρ_{N_2}	=	$0.806\,06 \text{ g cm}^{-3}$
Nitrogen molar weight	Mr_{N_2}	=	$28.0134 \text{ g mol}^{-1}$
Nitrogen surface density	γ_{N_2}	=	8.8737 mN m^{-1}
Pi	π	=	$3.141\,592\,653\,59$
Silica density (amoprhous)	ρ_{SiO_2}	=	2.196 g cm^{-3}
Universal gas constant	R	=	$8.314\,459\,8 \text{ J K}^{-1} \text{ mol}^{-1}$
XRD source wavelength	λ	=	$0.154\,06 \text{ nm}$

Symbols

a	Pore distance	m^2
a	Linear regression parameter	
A	Arrhenius pre-exponential factor	
A_p	Pore area	m^2
b	True Temkin's paramater	J mol^{-1}
b	Linear regression parameter	
B	Temkin's isotherm parameter	
C	BET constant	
C_{BET}	BET constant	
C_{ipd}	IPD model's non-zero coverage constant	g g^{-1}
C_p	Specific heat	$\text{J g}^{-1} \text{K}^{-1}$
d_{100}	Planar distance	nm
d_{110}	Planar distance	nm
d_G	Pore cylinder diameter	nm
d_p	Pore diameter	nm
D	Pore diameter	nm
D_0	Particle diffusivity	m s^{-1}
e	Euler's number	
e_{DFT}	Pore size	nm
E_a	Activation energy	J mol^{-1}
E_L	Heat of liquefaction	J mol^{-1}
E_1	Adsorption heat of the first layer	J mol^{-1}
$f()$	A function f	
ΔG	Gibbs energy change	J
h	Lenght of a side oh a hexagon	
H	Meniscus curvature	m^{-1}
ΔH_H	Henry's isotherm adsorption enthaply at zero coverage	kJ mol^{-1}

ΔH_S	Sips' isotherm adsorption enthalpy at zero coverage	kJ mol^{-1}
ΔH	Enthalpy change	J
ΔH_{st}°	Isosteric heat of adsorption	J g^{-1}
i	Parameter of a linear function	
k_{ft}	Pseudo-first order rate constant	s^{-1}
k_{ipd}	IPD model's rate constant	s^{-1}
k_L	PFO2 rate constant	s^{-1}
k_{LDF}	LDF model's rate constant	s^{-1}
k_{st}	Pseudo-second order rate constant	s^{-1}
k_P	Pressure driving kinetics rate constant	s^{-1}
K_F	Freundlich's constant	
K_H	Henry's constant	
K_L	Langmuir's constant	
K_{LF}	Langmuir - Freundlich constant	
K_{LF0}	Langmuir - Freundlich constant's pre-exponential factor	
K_{LF1}	Langmuir - Freundlich constant's exponential factor	
K_S	Sips' constant	
K_{TH}	Toth's constant	
K_{TM}	Temkin's constant	
K_{0H}	Henry's pre-exponential factor	
K_{0S}	Sips' pre-exponential factor	
L	Pore cylinder length	m
m	Parameter of a linear function	
Mr	Molar weight	g mol^{-1}
n	Exponential factor	
n	Number of points	
n_1	Linear regression factor of the exponential parameter	
n_2	Linear regression factor of the exponential parameter	
N_A	Avogadro's constant	
P	Absolute pressure	kPa
P_e	Pressure at equilibrium	kPa
P_t	Pressure at time	kPa
P_0	Saturation pressure	kPa
q_0	Maximum adsorption	g g^{-1}
q_e	Adsorption at equilibrium	g g^{-1}
q_m	Adsorption of monolayer	g g^{-1}

q_t	Adsorption quantity at time	g g^{-1}
q^e	Isosteric adsorbed amount at equilibrium	g g^{-1}
q_{ea}	Regular adsorption amount at equilibrium	g g^{-1}
q_{ec}	Capillary condensation adsorption amount at equilibrium	g g^{-1}
Q_{ads}	Adsorption heat (released)	W
Q_{des}	Desorption heat (consumed)	W
Q_{cond}	Condensation heat (released)	W
Q_{evap}	Evaporation heat (consumed)	W
x	A universal variable	
r_0	Particle radius of the adsorbent	m
r_k	Critical pore radius	m
r_p	Actual pore radius	m
R	Universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
R^2	Coefficient of determination	
ΔS	Entropy change	J K^{-1}
S_{BET}	Surface area calculated by the BET model	$\text{m}^2 \text{g}^{-1}$
S_m	Surface area calculated by the BET model	$\text{m}^2 \text{g}^{-1}$
t	Time	s
t	Film thickness	m
ΔT	Temperature lift	K
ΔT_C	Temperature lift for cooling	K
T	Absolute temperature	K
T	Relative temperature	$^{\circ}\text{C}$
T_D	Driving temperature	$^{\circ}\text{C}$
T_H	Temperature cooling capacity	$^{\circ}\text{C}$
T_H	Temperature heating capacity	$^{\circ}\text{C}$
Ths	Heat source/sink temperature	$^{\circ}\text{C}$
V_e	Adsorbed volume at equilibrium	$\text{cm}^3 \text{g}^{-1}$
V_l	Molar volume	$\text{cm}^3 \text{mol}^{-1}$
V_M	Molar volume	$\text{cm}^3 \text{mol}^{-1}$
V_m	Monolayer volume	$\text{cm}^3 \text{g}^{-1}$
V_{mes}	Mesopore volume	$\text{cm}^3 \text{g}^{-1}$
V_p	Pore volume	$\text{cm}^3 \text{g}^{-1}$
V_{SiO_2}	Volume of silica	cm^3
V_T	Total pore volume	$\text{cm}^3 \text{g}^{-1}$
y	Measured value	

y'	Predicted value	
y_{ex}	Measured value	
y_{cl}	Predicted value	
$y()$	A function y	
α	Molar change compensation	
α	Magnitude compensation	
α_E	Elovich kinetic model's parameter	
α_S	Sips' isotherm parameter	
β	Henry/Sips Connecting parameter	
β_E	Elovich kinetic model's parameter	
β_S	Sips' isotherm parameter	
β_S	Henry/Sips connecting parameter's exponential	
β_1	β_S exponential factor	
β_2	β_S exponential factor	
γ	Surface tension	N m ⁻¹
Δ	Change in quantity	
χ^2	Chi-Square test	
μ	Mean pore diameter in normal distribution	nm
μ	Mean relative pressure of capillary condensation	
μ_0	Mean relative pressure pre-exponential factor	
μ_1	Mean relative pressure exponential factor	
π	Pi	
ρ	Tap density	cm ³ g ⁻¹
ρ_l	Density of a liquid	kg l ⁻¹
ρ_{SiO_2}	Density of silica	kg l ⁻¹
ρ_Q	Energy density	MJ kg ⁻¹
σ	Distribution parameter	
σ_{est}	Regression error	
σ_{N_2}	Cross-sectional area of nitrogen molecule	nm ²
σ_R	Residual standard deviation	
σ_1	Distribution linear regression factor	
σ_2	Distribution linear regression factor	
θ	Adsorption ratio	
2θ	Diffraction angle of the XRD method	deg

For a better world.

Disclaimer

The text of this thesis is based on the following published or unpublished work at the moment of submission.

Some text used in **Chapter 1** and **Chapter 2** was based on these publications: **Mikšík, F.**, Kotlík, J., Miyazaki, T., Levek, P., Půčková, H. High Density Adsorption Heat Energy Storage in Energy Management for Renewable Sources of Energy Balancing. In: 40 Non-conventional Sources of Electrical Energy NZEE. Vemyslice, Czech Republic: Czech Electrotechnical Society; 2019. p. 53–6.

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Chapter 6

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Chapter 1

Introduction

1.1 Heat energy storage

With the progress in the field of renewable sources of energy and their rapid expansion there is an imminent need for sufficient energy management. The necessity arises from the non-continuous production characteristics of the renewable energy sources as their typical trait. To properly solve this problem and further enhance the efficiency and sustainability of the renewable sources of energy, it is essential to introduce to the energy systems some elements which will be capable of storing energy overflows and input them back in case of need. Most of the current technologies are intended for the storage of electric energy [2], however, if we consider that most of the necessary energy we consume is in fact heat energy [3] the direct storing of heat energy becomes more apparent.

According to the International Energy Agency (IEA) the energy expenditures for space heating averages in the residential sector around 51 % for the world, while the more equator-distant countries reach values around 70 % in general. This is further followed by the energy required for preparation of domestic hot water contributing to the energy budget by approximately 17 % on average in 2014 [3]. Furthermore, during the past years the importance of air-conditioning, which is from the thermodynamic point of view just opposite flow of heat energy, is being discussed in connection to the comfort of living and increase of electricity use

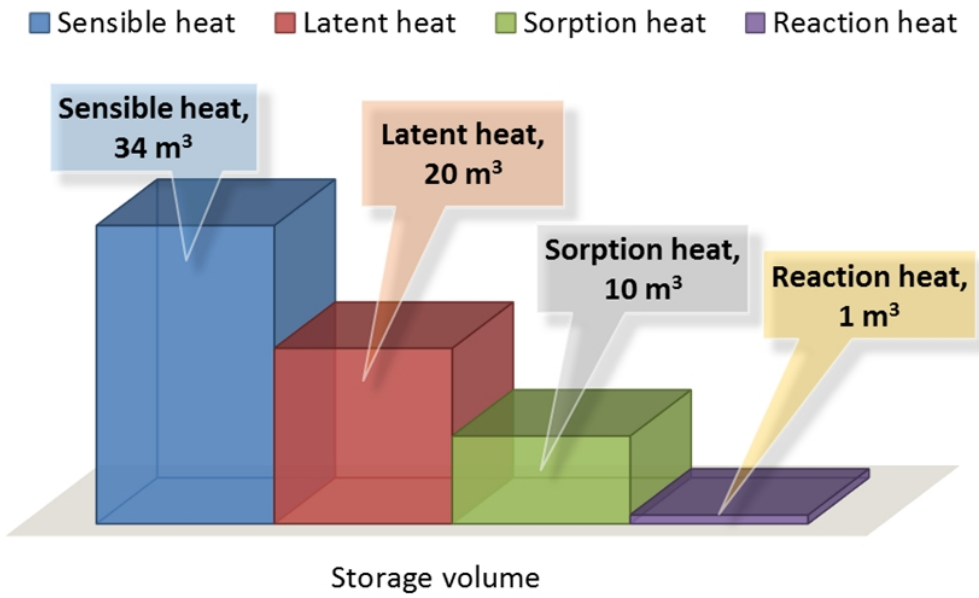


FIGURE 1.1: Necessary system volume for storing of 1.85 MWh of heat energy[1]
(At 70 °C and 25 % heat losses)

[4]. That meaning, with increasing expectations of quality of life the demands for air-conditioning are rising even in countries which have been traditionally in low need for space cooling thanks to the geographical position such as the Czech Republic. That is not only the case of the commercial sector but also the residential sector. Together the yearly increase of installed units in 2017 compared to 2016 was over 8 % [5]. This development creates additional stress on the distribution grid together with the increase of connected renewable sources of energy. To this point, many different solutions have been proposed [6] and are in practical use to mitigate this issue. One of the most obvious and to the date wide-spread solutions is energy storage, which can be found in various types and shapes.

Storing of thermal energy can be accomplished by several methods with the most common and simplest in the form of sensible heat in the way of heat capacity (or specific heat). However, despite the fact that this method has many advantages, the usage is severely limited by the energy density and reachable temperatures. Graphical comparison of basic methods for storing of thermal energy is shown in Fig. 1.1. From the comparison is apparent that the sensible heat has the lowest

possible energy density and the density is growing in the fashion of Sensible heat < Latent heat < Sorption heat < Reaction heat. Because the reaction heat can be difficult to control and the durability of the systems together with high loading temperatures and usually high corrosivity of the filling[7] pose a significant problem to environment, these applications are usually left for special use where the energy density is crucial. In this work the focus is on the second and third option which are Latent heat and Sorption heat. Latent heat is in research focus for long time and a significant progress has been accomplished in the field of PCM (Phase Change Materials)[8] in the late years. The last not-mentioned method, which is also gaining momentum by the rapid renewable energy progress, is sorption heat-based thermal energy storage.

The main objective of this thesis is analysis and evaluation of mesoporous silica matrix as an potentially new material for thermal storage. The work is based on industrial grade mesoporous silica with the name of TMPS (Taiyo Kagaku Co., Ltd.) with the variety of pore sizes and material composition, specifically aluminium addition. Some of the results are compared to the laboratory prepared SBA-15 and MCM-41 mesoporous silica with 2D hexagonal structure. The focus was especially given to material properties, water adsorption characteristics and energy and temperature evaluation for a potential use in adsorption thermal storage or adsorption heat pump applications.

Chapter 2

State of the Art

2.1 Sorption storage

Adsorption thermal energy storage (aTES) technology is based on adsorption as a surface phenomenon and from the perspective of energy storing processes it is a system on the boundary of latent and sorption heat utilisation. Compared to conventional way of storing heat energy, such as sensible heat storing, adsorption storage does not show any significant energy losses over a long periods of time and can be used for storing of both positive and negative thermal potentials [9, 10]. Schematic of a typical system is provided in Fig. 2.1.

The adsorption aTES uses the adsorption process to store and release the thermal energy as described in a simple schema in Fig. 2.2. In the first step the system is charged by introducing thermal energy to the adsorption chamber and elevating its temperature. By this process the equilibrium is disrupted and the adsorbate is being desorbed (evaporated) followed by recondensation in the condenser and there it is stored for the next steps. The opposite process of energy release is built on reintroducing the adsorbate into the adsorption chamber. Because this process is directly dependent on the relative pressure of the adsorbate, by simply closing the valve between the adsorption chamber and the storage compartment, we can store the energy in form of the adsorption potential almost indefinitely without any losses. Furthermore, during the adsorption process the pressure drops significantly driving the evaporation process in the storage compartment. This pressure

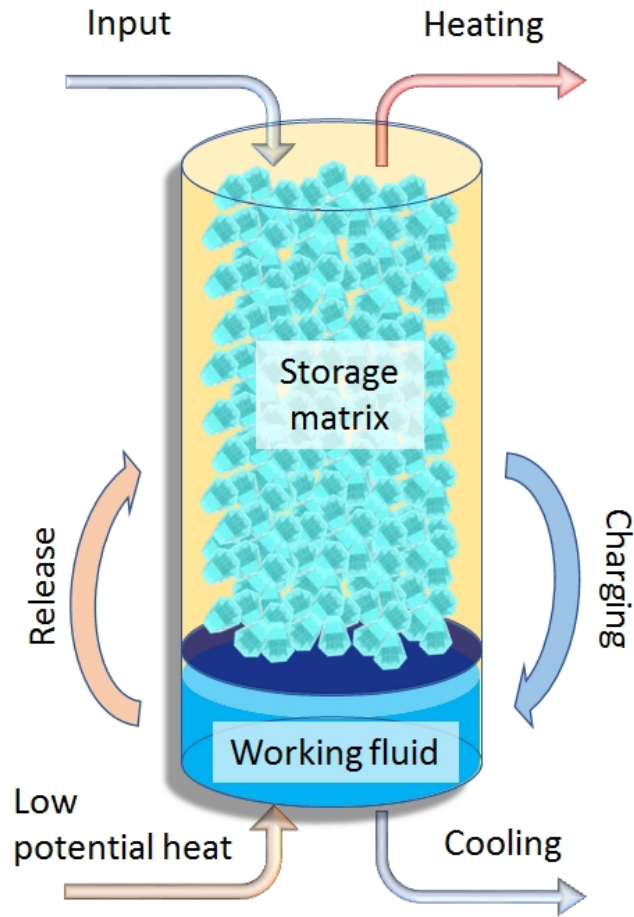


FIGURE 2.1: Adsorption heat energy storage cell - Heat energy battery (closed system).

drop can be further used to low-pressure evaporation which will cause temperature drop in the liquified adsorbate and can be used as a cooling source. From the standpoint of the presence of the working fluid inside the system we then talk about open and closed systems. The open systems have the advantage of collecting the vapours of the working fluid (in this case is used almost only the water present in the air in the form of air humidity) further simplifying the system. However, these systems are usually thermodynamically disadvantageous with very low COP.

The basic for the function of the aTES is in fact reflected from the adsorption heat pump systems, which are actually more common and widespread [9, 11–14]. The only difference is in the reciprocating continuous work of the heat pump system as shown in Fig. 2.3. However, it is this reciprocating function that makes this system more complex and more difficult to develop. From this point, the aTES

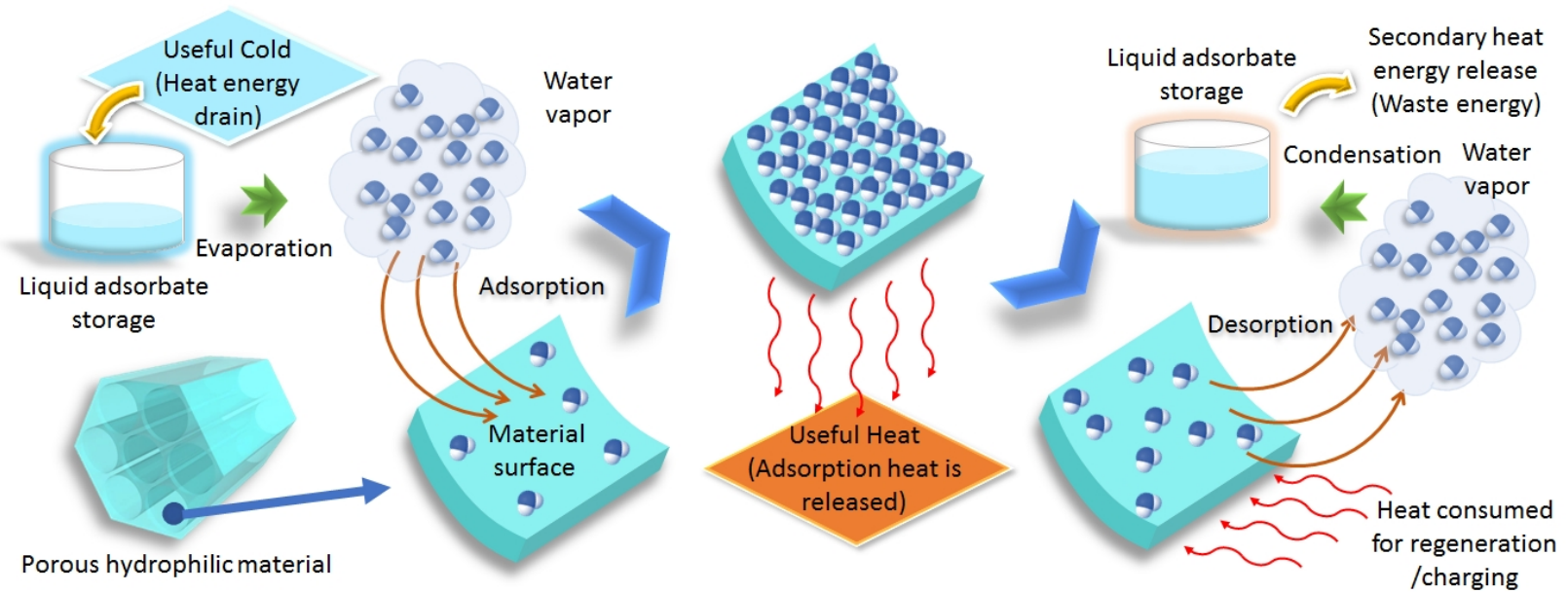


FIGURE 2.2: Schema of an adsorption process for adsorption heat pump and adsorption heat energy storage.

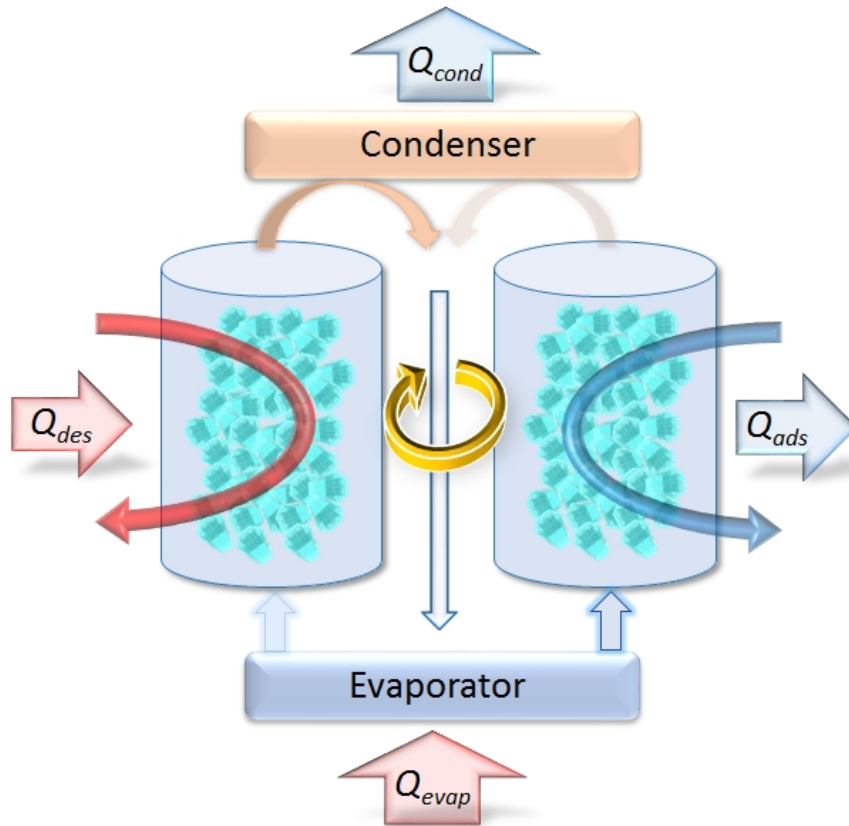


FIGURE 2.3: Adsorption heat pump.

is simplified adsorption heat pump with all its advantages and limiting some of the disadvantages. With only one chamber the system can operate only with one valve between the storage tank and working fluid tank which significantly reduces the complexity of the system and allows for more 'dense design'. Nevertheless, both systems share one significant impediment which is the lack of an affordable, durable, and efficient adsorbent material.

The sorption systems are typically thermally driven and as an energy source can be used practically any source of energy with high preferences for renewable sources of energy. Especially the combination with solar thermal systems has been extensively studied by many [13, 15–19]. These systems can be especially useful for evenly spreading the electricity demands for air-conditioning through the day, since they do not consume electric energy during discharging and can provide cooling or heating on demand. A typical schema of such combination is shown in Fig. 2.4.

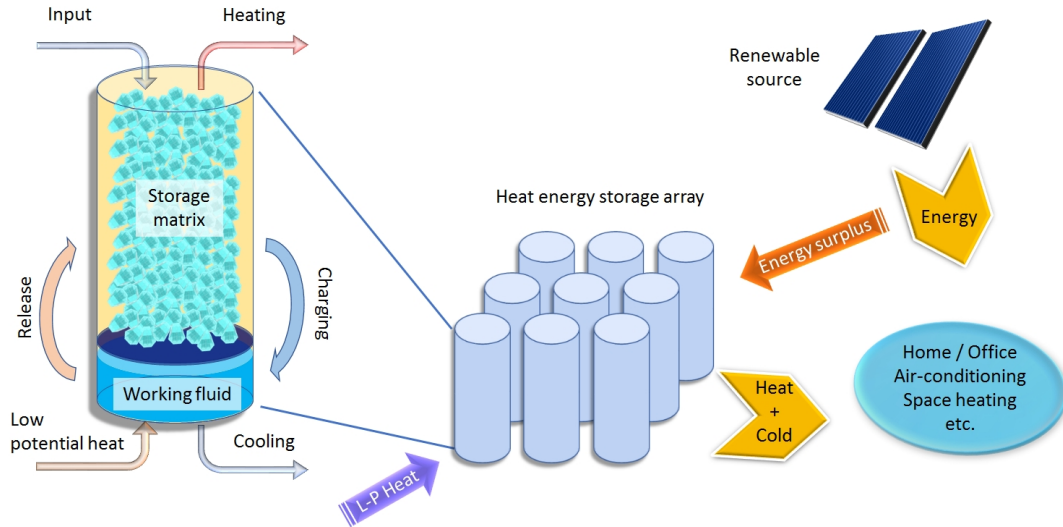


FIGURE 2.4: Adsorption heat energy storage system connected to renewable source of energy.

2.2 Materials and adsorption pairs overview

From the perspective of material usage we can separate the thermal storage and heat pump systems using the adsorption+latent heat into categories based on the materials in use. Systems using pure materials for true adsorption and systems using composite materials for combination of absorption and adsorption or simply called sorption, or chemisorption as well. A separate problematic are systems using latent heat only, based on phase change materials (PCM)[20], which, although not included in the topic of this work, can utilize similar mesoporous silica matrix as a carrier (encapsulation shell) for the working PCM material[21–24]. However, in this work is dealt with adsorption and absorption processes only. While absorption is a bulk process typical for physicochemical process occurring inside of a material sometimes connected to certain chemical changes (e.g. salt hydration), adsorption is strictly a surface phenomenon usually extended to porous solids.

One of the first problems that any new system has to solve is a selection of a working pair. The main requirements are connected to the specific application where the temperature requirements, energy density and durability are usually the main topic. From this perspective, it is necessary to address the issue of the

working pair application-wise.

2.2.1 Working pairs for sorption-based heat transformations

In the literature one can mostly encounter three groups of systems distinguishable by the working fluid which are using water, ethanol/methanol, and ammonia. The last listed ammonia is mostly used only in special applications and it is usually considered as a thermochemical sorption using the coordination reaction of ammonia with inorganic salts[25]. The specificity of these systems is high energy density of the chemical reaction, however, at the expense of high aggressive substrate, high loading temperatures and of course toxicity of the ammonia, limiting the use significantly.

More common use have ethanol/methanol working fluids mostly with a connection to the activated carbon matrix. The topic of activated carbon and carbon fibres adsorption properties with ethanol was extensively studied by a research group of Saha et al.[26, 27] and El-Sharkawy et al.[28, 29], dealing mostly with the application for adsorption chillers and air conditioning. That is of course a logical application for ethanol which has very low temperature of freezing and it is ideal for temperatures reaching 0°C and below. Recently, the possibility of ethanol adsorption onto metal organic frameworks has been also studied by Saha et al. [30], however, the practical use of MOFs is still very far which will be explained later. Nevertheless, the technology of activated carbon production is well known and reasonably affordable, hence, the adsorption chillers based on activated carbon are also extensively studied in combination with some other refrigerants as working fluids at high pressures such as carbon dioxide[31], R134a[32] and several others. Even though the application of the activated carbon and ethanol, and other refrigerants, are vast, their applicability for heat storage is somehow limited. That is caused by the low latent heat of the compatible refrigerants and the actual capacity of the activated carbon which is characteristic mostly by its supreme surface area, however, not the volumetric adsorption capacity. Furthermore, for

TABLE 2.1: Some of the materials for adsorption heat storage and the properties of their systems

Material	Charging T ($^{\circ}\text{C}$)	Storage density (Wh kg^{-1})	Material density (kg m^{-3})	Ref.
Zeolite 4A	150-180	140-179	700	[33]
Zeolite 13X	160-180	108-149	739	[16, 34]
Zeolite MgNaX	180	175	732	[16]
Silico-aluminophosphate 34	95	203	-	[13]
Aluminophosphate 18	95	243	-	[13]
AQSOA FAM-Z02	75-90	280	~ 650	[35]
Microporous silica gel	90	35	710	[34]
Macroporous silica gel	90	24	620	[34]
MOF MIL-101	90	684	-	[13]

high capacity storage system a certain amount of the working fluid is required and the highly flammable ethanol, methanol or the other refrigerants with low boiling point pose a not negligible risk. Hence, from the perspective of the basic working fluid for the adsorption thermal energy storing, the most suitable substance and currently most used is water by far.

2.2.2 Pure materials for water adsorption in adsorption thermal energy storage

Possibly the most studied materials for water adsorption regarding aTES are various zeolitic types materials, molecular sieves and silica gel. Already in 1979 the problematic of aTES with water adsorption was studied by Shigeishi et al. [36] on the example of charcoal, activated alumina, silica gel and zeolites 4A, 5A and 13X concluding advantageous properties of these materials, however, burdened by high price. To overcome the high price of the artificiality produced materials some natural zeolitic tuffs were studied by Aiello et al. [37] with results more likely to

TABLE 2.2: General properties of the most used water-adsorptive materials for aTES

Material	Adsorption heat (kJ kg ⁻¹)	Typical desorption temp. (°C)	Material density (kg m ⁻³)	Specific heat (kJ kg ⁻¹ K ⁻¹)	Typical cycle uptake (g g ⁻¹)
Silica gel	160-180	50-80	650-700	≈0.85	≈0.1
Zeolites	50-300	70-350	650-900	≈0.9	≈0.2
Alumino-phosphates/ silicates	250-300	60-90	800-900	≈0.9	<0.25
Composite materials	50-250	60-90	300-600	≈1.0	<0.8
MOFs (potentially)	20-200	60-150	1000-2000	≈1.0	<0.4

Reference Vasta et al. [42]

lead to dehumidifying applications from the current point of view.

In the recent years a new development can be seen in the field of heat storage connected to new materials and rapidly progressing evolution of renewable sources of energy desperately looking for some new ways of energy storage. This new effort can be seen in the vast amount of reviews published on the current state of the aTES technology. Most of the work is naturally done on the pretext of using solar energy for heat storage[13, 17, 18, 34, 38] solar cooling[13, 19, 39] and many general overviews as well[9, 40–42] such as is this. A brief overview of some currently tested materials for thermal energy storage is listed in Table 2.1.

Some crucial properties of the currently most employed materials are summarized in Table 2.2 according to Vasta et al. [42]. Storing capacity expressed as adsorption heat is very important, but itself it is only a part of the whole picture. Furthermore, the adsorption heat expressed in the units of kJ kg⁻¹ is directly dependent on the actual uptake the material can exchange during a typical cyclic operation. This is especially limiting factor for silica gel systems with only 0.1~0.2 g g⁻¹ of

useful loading. Zeolites show better performance in all aspects because the natural zeolites does not feature enough adsorption capacity, as was mentioned before, and the artificial ones are usually too expensive. The only exception is the AQSOA zeolitic aluminophosphate series from Mitsubishi Plastics, developed particularly for the adsorption heat transformation applications and has been extensively studied by many specifically for adsorption heat pumps and chillers[9, 43, 44], desiccant wheels[45, 46] and limitedly for aTES purposes as well [35, 47]. The main advantage is usually seen in the well defined working region and step-like adsorption properties in the working region of 0-0.3 P/P_0 . However, the capacity is at 0.2 g g⁻¹ in the case of AQSOA FAM-Z01 and 0.3 g g⁻¹ AQSOA FAM-Z02 still lacking, even though that the actual energy capacity is higher than most of the tested materials. More promising in the aspect of total capacity are showing composite materials based on the combination of porous materials with inorganic salts which are developing recently together with new hydrothermally stable porous materials, which can handle the corrosive properties of the ion-rich environment. The problematic of composite materials with inorganic salts so called *salt inside porous matrix* is presented in Chapter 6.

2.2.3 New trends - MOFs

A new emerging group included in the Table 2.2 of materials is from porous coordination polymers family called metal-organic frameworks (MOFs). Thanks to their high variability consisting of large surface area and tunable pore size they have attracted considerable amount of attention in the applications of adsorption heat transformations. A very thorough work on the water adsorption properties of various MOFs was reported by Furukawa et al. [48] identifying and comparing 23 samples which 20 of them were actual MOFs. Among them many had high uptake (≈ 0.4 g g⁻¹) in the the working region of 0.1 to 0.3 P/P_0 suitable for adsorption heat transformation processes. Investigations on adsorption properties with other working fluids such as ethanol can also be find in the literature[30]. In general, many author consider the the MOFs as very promising materials for adsorption heat transformations and storage[13, 18, 40, 42], but all of them are

pointing out several yet overcome shortcomings. The probably most important one is the hydrothermal stability reported in general[49], and in connection to the thermal transformation applications[50], has been a strong topic in the recent years. Many hydrothermally stable MOFs have been prepared[51–53] so far, but any durability study on the continuous adsorption/desorption cycle for adsorption driven heat transformation or storage applications was yet published. Nonetheless, the main factor for any reasonable usage of these materials lies in the production which is so far almost only limited to laboratory preparation and highly specialized application.

2.2.4 Mesoporous silica

In the previous sections the topic of mesoporous silica was purposely avoided to summarize the current progress in one section. Mesoporous silica is a general term signifying lately a group of materials based on silica (SiO_2) with organized mesoporous structure. Artificially prepared nano-structured (tailored) mesoporous silica materials are used in many fields as molecular sieves[54–56], catalyst carriers[57, 58] or drug carriers[59]. Lately, the mesoporous silica materials are also referred to as powerful sorption materials for thermal energy and air conditioning applications such as adsorption heat pumps[12, 14], energy storage[22, 41, 60] and desiccants[61, 62]. However, because the applications for thermal energy conversion and conservation are using the materials in large quantities, the utilization is strongly constrained by the production capacities of laboratories and manufacturers. To a certain degree, this influences the technological progress and limits the mesoporous silica materials so far to be used only in the aforementioned specialized industries. The limited studies that are investigating adsorption properties in connection to thermal management of the mesoporous silica are mostly focused on typical representatives such as SBA-15[22, 63] or MCM-41[60] as their properties are well documented and described. The uniting factor of these studies is that they are using these materials prepared directly in the laboratory in small quantities and the practical impact can be only estimated.

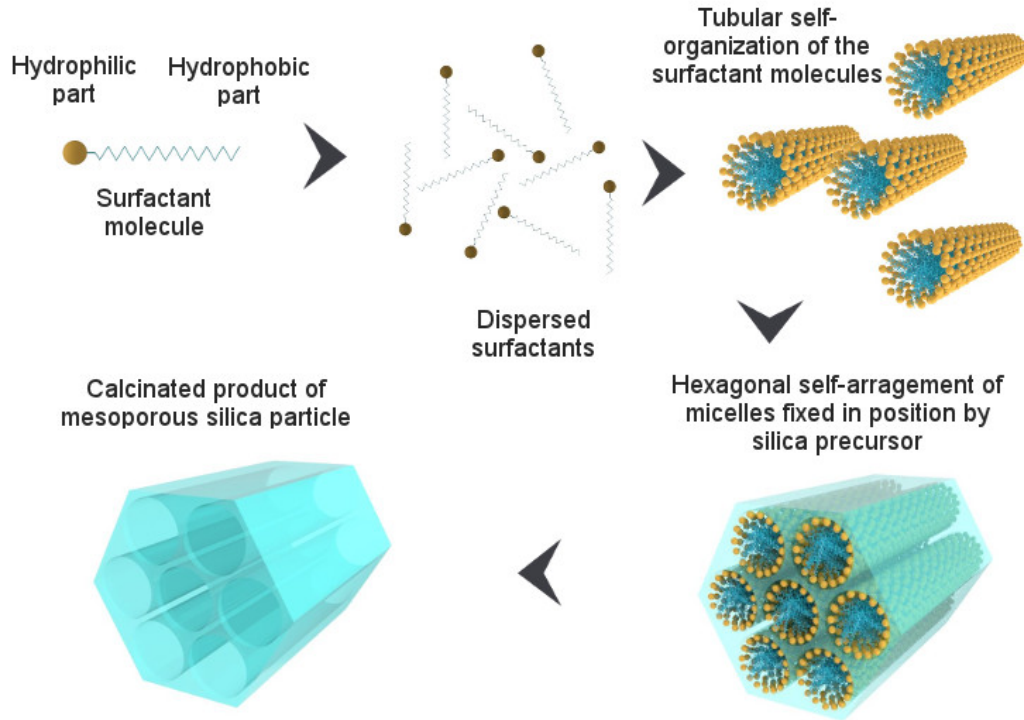


FIGURE 2.5: Schema of a typical preparation process of mesoporous silica

Since the re-discovery of the mesoporous silica in the 90s a significant progress in the manufacturing processes has been achieved and currently a laboratory preparation is a matter of basic chemical equipment and some of the mesoporous silica materials can be produced on daily basis[64]. The typical preparation procedure of mesoporous silica is shown in Fig. 2.5. Nevertheless, it is important to add that any significant industrial production has yet to be established. Therefore, any manufacturer which is capable of bulk production of mesoporous silica is deemed as highly desirable and the produced materials have to be thoroughly investigated.

2.2.5 Adsorption thermal energy storage with mesoporous silica matrix

As has been said, the basic properties and operational conditions of adsorption aTES are decided by its adsorption pair. Research on several mesoporous materials from the family of mesoporous silica has been done with various success [18, 41]

with the more current research focusing on composite materials with inorganic salts impregnation [65–67] as well as phase change material encapsulation [22–24]. However, the bulk usage, necessary for energy applications, of mesoporous silica materials such as infamous SBA-15 or MCM-41 is strongly constrained by the production capacities and price. Currently (March 2019), there is only a handful of manufacturers of mesoporous silica and they are focusing on high grade products used as catalysts and pharmaceutical industry[64]. Thanks to that, most of the development of the silica materials for energy/air conditioning applications in the mesoporous region has been done so far on silica gel[16, 68–72], which is produced considerably cheaper and in large quantities, however, with usually low adsorption capacities and insufficient temperature lift. The objective of this work is to investigate the possibility of utilisation of a new industrially manufactured mesoporous silica material from the family of TMPS, developed and manufactured by Taiyo Kagaku Co., Ltd. Japan for the application of adsorption thermal energy storage and other adsorption heat transformation applications as a first study of this kind.

2.3 Adsorption equilibria and kinetics models

To fully and correctly evaluate the system properties the work usually begins with the evaluation of the raw material for adsorption. In this section will be introduced most common methods for the adsorption evaluation from the perspective of adsorption equilibrium and adsorption kinetics. The explanation about individual approach for the material used in this work will be then provided in the beginning of the chapter in concern.

2.3.1 General models

Adsorption in contrast to absorption is solely a surface phenomenon. Spontaneous adsorption, as similar to spontaneous chemical reaction, is strictly an exothermic process. Most of the adsorption processes can be described by the shape of the

adsorption isotherm. According to the IUPAC recommendation there are 6 different isotherm types describing adsorption process of gases and vapours on solid materials [73]. These isotherms are shown in Fig. 2.6, each with its distinguishable shape for certain or prevalent adsorption process. The Type I usually describing monolayer adsorption or microporous adsorption. Subtypes (a) and (b) are then to further distinguish the adsorption based on the pore size when (a) is dedicated for materials with only micropores. Type II and Type III describe multilayer adsorption when Type II further describes stronger interaction of adsorbent/adsorbate. Similarly Type IV and Type V describe mesoporous materials with occurring capillary condensation with its typical desorption hysteresis as shown by the arrows in Fig. 2.6. Similarly to the Type II, the Type IV describes higher surface adsorption potential towards the adsorbate. Here again, the adsorption isotherm Type IV can be further distinguished based on the pore size when the Type IV(b) is typical for microporous materials. The last Type VI describes more uncommon and complex adsorption process such as adsorbing methane on magnesium oxide under cryogenic conditions [74].

To describe the adsorption process many mathematical models have been developed over the years. Many of them are trying to explain the adsorption process from the perspective of energies and interaction between the adsorbent/adsorbate and adsorbate/adsorbate. However, because the behaviour of many of the adsorption pairs is too complex, several empirical models are used as well to fill up the gap and to allow mathematical description of the adsorption processes otherwise not solvable.

The simplest adsorption model is described by **Henry's adsorption isotherm** [75, 76], named after William Henry thanks to the formal resemblance to the Henry's law.

$$q_e = K_H \frac{P}{P_0} \quad (2.1)$$

where K_H is the Henry's constant and P/P_0 is the relative pressure. The format

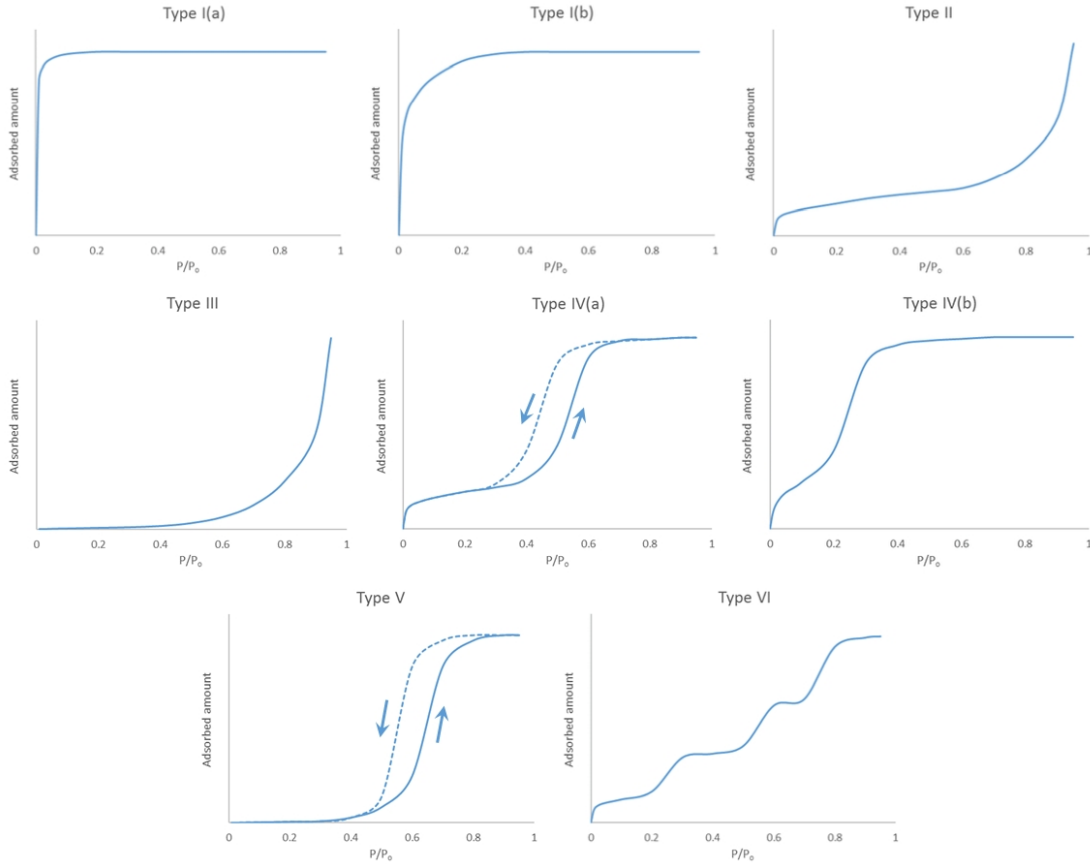


FIGURE 2.6: Adsorption isotherm types according to IUPAC.

of the equation shows strictly linear dependence as the model uses only one constant with the variable pressure. The validity of this model is usually at least of a partial subject of many isotherms at low surface coverages, when the adsorption energy is still independent on the actual coverage. That is, no influence from the already adsorbed particles. Through its simplicity, the actual use is limited to special cases or in combination with other models.

One of the first proper models used for adsorption calculations is **Freundlich adsorption isotherm** model [77, 78]. The Freundlich adsorption isotherm can be used for gas adsorption and for adsorption in solutions as well, due to its empirical nature. However, as the Freundlich adsorption isotherm is an empirical model it holds only a limited amount of information about the observed system and for thermodynamic explanation of the adsorption process different models are

typically used.

$$q_e = \frac{\text{adsorbate}}{\text{adsorbent}} = K_F \left(\frac{P}{P_0} \right)^{1/n} \quad (2.2)$$

In the equation 2.2 is shown the Freundlich isotherm, where the q_e is the adsorption amount at the equilibrium per adsorbate unit, P/P_0 is the relative pressure, or can be substituted for concentration in adsorption in solutions, and n and K_F are constants specific for an adsorption pair at a given temperature for the Freundlich isotherm.

More rational approach was employed by Langmuir in his **Langmuir adsorption isotherm** model. The Langmuir equation was developed to describe gas adsorption on solid surfaces as it had been described by Irving Langmuir in his original paper from 1916 and later on in 1918 [79].

$$\theta = \frac{q_e}{q_0} = \frac{K_L \left(\frac{P}{P_0} \right)}{1 + K_L \left(\frac{P}{P_0} \right)} \quad (2.3)$$

The Greek letter θ in the Langmuir equation, as well as in many other adsorption models, is used for the relative adsorption or adsorption fraction. The relative adsorption is obtained from the expression q_e/q_0 where q_e is the adsorption amount at the equilibrium and q_0 is the maximum adsorption amount, which, in the case of Langmuir isotherm, is equivalent to the monolayer amount q_m . In the right part of the equation the K_L is the Langmuir constant and P/P_0 states for the relative pressure at the given temperature. From the shape of the equation is apparent that the adsorbed amount is limited by the adsorption capacity of the material and has to be known for the calculation or, by fitting the data to the model, it can be found out from the equation. This is based on the Langmuir theory which considered the true adsorption only as a direct adsorbent/adsorbate interaction by the means of monolayer formation. Langmuir knew, that the surface of the solids is not smooth, and even for completely flat crystal surfaces there is a certain amount of potential difference between individual sites caused by the chemical structure.

The curve shape of the Langmuir isotherm is therefore a derivation of the statistical distribution of those adsorption potentials caused by local differences on the adsorbent surface [79]. And this is truly the case for many adsorption pairs. Nonetheless, the application is limited mostly to the Type I adsorption isotherm with the prevalent effect of adsorbent/adsorbate through the adsorption process.

The third most known adsorption model is possibly the **BET model** named after the names of its creators S. Brunauer, P. H. Emmett and E. Teller [80]. The BET model is build on the same principles as the Langmuir model, however it brought for the first time the problematic of multilayer-adsorption, thus, it accounts for the adsorbate/adsorbate interaction as well. Typically, the BET model corresponds to the adsorption processes equivalent to the Type II adsorption isotherm described by IUPAC recommendation, however, because of the apparent similarity to the Langmuir isotherm, it can be partially used for Types I, II, and IV. This is used with advantage in the region $P/P_0 = 0.05 - 0.35$ where the BET isotherm takes a linear form in case of monolayer adsorption and many important information about the system can be obtained. The regular BET equation is written as follows:

$$\frac{1}{q_e \left(\frac{P_0}{P} - 1 \right)} = \frac{C - 1}{q_m C} \left(\frac{P}{P_0} \right) + \frac{1}{q_m C} \quad (2.4)$$

where the C is the BET constant and with the rest of the variable being the same as for the Freundlich and Langmuir models. The constant C is directly connected to the adsorption energy and is expressed as

$$C = e^{\frac{E_1 - E_L}{RT}} \quad (2.5)$$

where E_1 is the adsorption energy of the first layer and E_L is the energy of consecutive layers typically equal to the condensation energy of the adsorbate. To obtain a linear form of the BET model for calculation of the surface area from the Eq. 2.4 the adsorption amount is plotted against the relative pressure according

to the following expression:

$$f\left(\frac{P}{P_0}\right) = \frac{1}{q_e\left(\frac{P_0}{P} - 1\right)} \quad (2.6)$$

The adsorbed amount of the monolayer is then calculated according to the resulting linear expression fitted to the output of the Eq. 2.6.

$$y(x) = mx + i \quad (2.7)$$

In the Eq. 2.7 the m and i are simple linear function parameters. The adsorbed amount on the monolayer is then calculated from the Eq. 2.7 as:

$$q_m = \frac{1}{m + i} \quad (2.8)$$

The surface area of the monolayer S_{BET} according to the BET model is finally calculated based on the knowledge of the adsorbed amount of the monolayer and geometrical properties of the adsorbate:

$$S_{BET} = \frac{q_m N_A \sigma_{N_2}}{Mr} \quad (2.9)$$

where N_A is the Avogadro constant, q_m is the monolayer adsorbed amount in g g^{-1} , Mr is molar weight of the adsorbate and σ_{N_2} is the cross-sectional area of the adsorbate, in this case nitrogen.

Temkin adsorption isotherm also builds on the Langmuir model on the basis of the surface coverage but directly deals with the problematic of adsorbate/adsorbate interaction [81, 82]. Although the primary application of the Temkin isotherm is for adsorption on solids in solutions, the generalized form can be used for the adsorption of gases on solids as well, described by pressure rather than concentration [83]. The Temkin isotherm at the equilibrium adsorption q_e can be written in the following form:

$$q_e = B \ln(K_{TM}P) \quad (2.10)$$

where B and K_{TM} are Temkin parameters for given adsorbent/adsorbate system and P is the adsorbate pressure. The parameter B is a measure of the adsorption heat and is usually translated as $B = RT/b$, where b is the true Temkin parameter for sorption heat calculation (J mol^{-1}) [84]. The Temkin Eq. 2.10 can be also written in a linear form as:

$$q_e = B \ln K_{TM} + B \ln P \quad (2.11)$$

In the Langmuir model the adsorption energy is constant during the adsorption process, while the Temkin model assumes that the adsorption energy is decreasing linearly with the increasing surface coverage [85, 86].

Another empirical modification of Langmuir isotherm is represented by **Toth adsorption isotherm** [87].

$$\theta = \frac{q_e}{q_0} = \frac{K_{TH}P}{[1 + (K_{TH}P)^n]^{1/n}} \quad (2.12)$$

The Toth isotherm described by Eq. 2.12 works with two fitting parameters. The K_{TH} constant is related to the adsorbate/adsorbent interaction and it is specific for the material pair, the same as for Langmuir isotherm. The exponential factor n in the Eq. 2.12 is then a measure of the heterogeneity of the surface. From the Eq. 2.12 is apparent that when the exponential heterogeneity factor $n = 1$, the equation takes the format of the original Langmuir isotherm and the surface is regular with Langmuir distribution. Hence, the farther from unity is the factor, the more the surface is irregular [88, 89]. For better fitting the Eq. 2.12 can be also written in a linear form:

$$\ln \frac{q_e^n}{q_0^n - q_e^n} = n \ln K_{TH} + n \ln P \quad (2.13)$$

where all the parameters are identical to the Eq. 2.12.

Sips adsorption isotherm is yet another adsorption model building this time on

both Langmuir and Freundlich adsorption models [90]. The basic Sips isotherm is written as

$$q_e = \frac{q_0 K_S \left(\frac{P}{P_0}\right)^{\beta_S}}{1 + \alpha_S \left(\frac{P}{P_0}\right)^{\beta_S}} \quad (2.14)$$

where the K_S is the Sips' adsorption isotherm constant. The resemblance with the both Langmuir and Freundlich models is given by using of the addition parameters α_S and β_S . These parameters are usually added as an empirical extension and should serve as a measure on the heterogeneity of the adsorption surface. However, for the modelling purposes, this modification can fit very well to many systems and it is widely used for both liquid and gas systems [89, 91–94].

This list represents the most common modification used for gas/solid adsorption, however, it is just a small part from the possible alterations that are used in the current literature for adsorption in general [84]. However, to avoid unnecessary repetition, the other non-suitable modifications are omitted on the pretext that they are not considered in this work further on.

2.3.2 Adsorption kinetics models

For many adsorption processes, just the isothermal results at the equilibrium are not sufficient to predict the behaviour of the system. Due to the spontaneous energy transfer a necessary factor is also the speed of the adsorption, which greatly affect any system's performance.

From the perspective of adsorption kinetics, adsorption can be compared to a chemical reaction:



where $[A]$ is an adsorbate molecule/atom and $[S]$ is a vacant adsorption site. We know, that for the process to be spontaneous, the Gibbs free energy ΔG has to be negative. Thanks to the similarity with chemical reactions the energy change

during the adsorption process can be written in the same way:

$$\Delta G = \Delta H - T\Delta S \quad (2.16)$$

where ΔH is the enthalpy of adsorption, T is absolute temperature and ΔS is the entropy. Strangely enough, in case of adsorption this equation is not completely true. Because the adsorption process in fact does not increase the degree of disorder but decreases it, the entropy will take negative sign and the result will be positive.

$$\Delta G = \Delta H + T\Delta S \quad (2.17)$$

Therefore, to obey the rules of thermodynamics, for the adsorption to be spontaneous and exothermic, the enthalpy of the adsorption process has to be negative and the following has to be true:

$$|\Delta H| > |T\Delta S| \quad (2.18)$$

Because of all these similarities the basic rules of chemical reaction kinetics apply to adsorption kinetics as well and can be easily deduced from them. However, from the perspective of main driving force responsible for the adsorption speed another processes have to also be considered [95].

Pseudo-first order rate model (PFO) was firstly introduced by Sten Lagergren in his original work from 1898 [96] and it is primarily used for pure adsorption. The model builds on the same base as the first order chemical reaction rate, however, it was modified for sorption rate description because the sorption process basically follows the same mechanism as chemical reaction. The derivative form takes in account the states of the system before and after adsorption and any state in-between can be assessed by the time and rate constant:

$$\frac{dq_t}{dt} = k_{ft}(q_e - q_t) \quad (2.19)$$

where q_e is the adsorption at the equilibrium, k_{ft} is the pseudo-first order rate

constant, q_t is the adsorption at a given point in time and t is the time. From the equation is apparent that once the $q_t = q_e$ the equilibrium is reached and there is no more change of the adsorbed amount. After the integration we get practical form of the equation:

$$\ln(q_e - q_t) = \ln q_e - k_{ft}t \quad (2.20)$$

often found in the literature in the form of a common logarithm:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ft}}{2.303}k_{ft}t \quad (2.21)$$

The pseudo-first order for adsorption is used the same way as the first order for chemical reaction. Basically, it is intended for one step precesses as shown by Eq. 2.15. In case that the adsorption process is more complex and the adsorption speed is constrained by secondary action such as film diffusion, condensation etc., many other models are used regularly.

Pseudo-second order rate model (PSO) counts with two step process, similarly to its chemical equivalent [97] and the equation is hence very similar to the PFO model.

$$\frac{dq_t}{dt} = k_{st}(q_e - q_t)^2 \quad (2.22)$$

where the parameters are identical to the Eq. 2.19, just the k_{st} is used instead as a rate constant to avoid confusion. It is obvious that the basic equation build on the same theoretical ground, however, the product of integration is different.

$$\frac{t}{q_t} = t \frac{1}{q_e} + \frac{1}{k_{st}q_e^2} \quad (2.23)$$

In both cases of PFO and PSO one can obtain a linear dependence by simple arithmetical rearranging.

Elovich model is another direct adsorption model, primarily used for chemisorption purposes. The original relation was proposed in 1934 by Roginsky and Zeldovich[98, 99] but it is more known from the work of Elovich [95, 100] and in the

literature we can encounter only this name. The Elovich model is widely used for many adsorption processes with a gas or liquid adsorbate [97, 101–103]. The equilibrium is described by the Elovich equation in this way:

$$\frac{dq_t}{dt} = \alpha_E \exp(-\beta_E q_t) \quad (2.24)$$

where α_E and β_E are the constants for a given case. The α_E is considered as an initial rate constant, as the equation solution approaches α_E with q_t approaching 0. Considering $q_t = q_t$ at $t = t$ and $q_t = 0$ at $t = 0$ the integrated form will be the final form of the Elovich relation:

$$q_t = \frac{1}{\beta_E} \ln(\alpha_E \beta_E) + \frac{1}{\beta_E} \ln t \quad (2.25)$$

The so far mentioned models describe many adsorption processes with high precision and sufficient simplicity. However, in many cases, especially with higher adsorption amounts, the adsorption rate can be govern by different physical phenomena than just adsorption and different approach has to be chosen.

Intra-Particle Diffusion model (IPD) introduced by Weber and Morris [97, 104] takes in account different process deciding the adsorption rate. In the intra-particle model the adsorption itself is considered as a fast step of the whole process, however, due to the limited number of adsorption sites directly accessible from the surroundings, filling of deeper parts by the adsorbent is governed by different process, diffusion. Thus, during the adsorption, only a limited area of the adsorbent interacts with the adsorbate through actual adsorption and the rest of the adsorbent is filled by moving of the adsorbate on the surface of the adsorbent. This process is fundamentally different from the adsorption, however, the basic mathematical expression follows the same way:

$$q_t = k_{ipd} t^{1/2} + C_{ipd} \quad (2.26)$$

where k_{ipd} is the rate constant of the diffusion process and C_{ipd} is the additional

constant sometimes used to express the non-zero coverage prior to the adsorption or as measure for film diffusion assessment [105], although, it is necessary to add that its practicality was previously questioned [95].

Linear Driving Force model (LDF) similarly to the intra-particle diffusion model considers diffusion as an important factor for the adsorption dynamics. For simplification, it is usually described on a porous spherical particles. The original relation of the LDF model is written similarly to the pseudo-first order rate model[106, 107]:

$$\frac{d\bar{x}(t)}{dt} = k_{LDF} (x^* - \bar{x}(t)), k_{LDF} > 0 \quad (2.27)$$

where $\bar{x}(t)$ is the average adsorbate concentration/amount in the particle of adsorbent and x^* is the adsorbate concentration/amount at the final equilibrium. The effective LDF mass transfer coefficient k_{LDF} is then typically given as follows [108]:

$$k_{LDF} = \frac{15D_0}{r_0^2} \quad (2.28)$$

where D_0 is the intra-particle diffusivity of the adsorbate and r_0 is the particle radius of the adsorbent. The whole relation is also based on the temperature uniformity through the volume of the particle at all times [109]. This means that not only the system isothermal conditions have to apply but local as well.

The use of the LDF has proven to be very convenient because of its physical consistency and simplicity [107], however, it is generally considered as only an approximation and for complex systems, and in simulations, more rigorous approach such as Fickian Diffusion is usually recommended for better accuracy and results [110]. The studied form of an adsorption on a non-fixed adsorbent in this work allows for use of the LDF model while maintaining high accuracy.

Chapter 3

Material Selection and Characterisation

3.1 Introduction

In this chapter the industrially produced nano-structured mesoporous silica from Taiyo Kagaku Co., Ltd. is fully analysed for its properties. The main objective is to investigate in detail surface area, pore volume, pore diameter, pore distribution, thermal conductivity, specific heat and thermal stability. The samples selected for the analysis in this work are TMPS-1.5, TMPS-1.5A, TMPS-2A, TMPS-2.7A, TMPS 4A and TMPS 4R. The materials were used in their original form as received from the manufacturer without any additional treatment. To compare the properties of the materials with regular laboratory-prepared mesoporous silica were used two typical representatives of the mesoporous silica family the SBA-15 and MCM-41. The selected TMPS samples pore size varies from 1.8 nm to 4.2 nm as stated by the manufacturer with the standard individual particle size around 50 nm to 200 nm which is putting these materials on the boundary of nanomaterials.

3.2 Experimental

3.2.1 Materials

The SEM images of the materials are provided in Fig. 3.1. From the images is apparent high uniformity of the materials' particles. The basic size of an individual spherical cell is almost constant for all of the selected materials with an average around 200 nm. These individual cells are the most apparent for TMPS-1.5 and TMPS-1.5A in 3.1. Observed materials are generally prone to aggregation and form strong clusters. This behaviour is especially noticeable in the case of TMPS-4R, where the clusters are the most developed and regular with the size around 30 μm to 100 μm containing over 95 % of the material's cells. This behaviour can also be observed in other selected materials, however on a much smaller scale and with an irregular appearance suggesting more random formation during the later treatment of the materials.

The SBA-15 for the comparison was prepared according to synthesis route based on non-ionic surfactant Pluronic P123. To achieve the smallest possible pore diameter, closer to the observed materials, the synthesis process was adjusted according to the work of Sayari et al.[111]. The process in their work sets the temperature of the micelle stabilisation phase to $T = 35^\circ\text{C}$ (for 20 hours). In this work, the subsequent growth phase has been successfully reproduced by the temperature setting of $T = 100^\circ\text{C}$ (24 hours). The result was standard rod-like cells with a diameter of 200 nm to 300 nm and length of about 1 μm . The preparation of the MCM-41 was based on cationic surfactant CTMABr in ammonia solution as described by Grün and his co-workers[112]. The method was adjusted to create a smaller pore size by limiting the ammonia volume to 3 mL with keeping the rest of the volumes untouched. The resulting spherical cells had diameter spanning from 100 nm up to 2 μm on average. Both the SBA-15 and MCM-41 were used in the original state without any modifications after the calcination process.

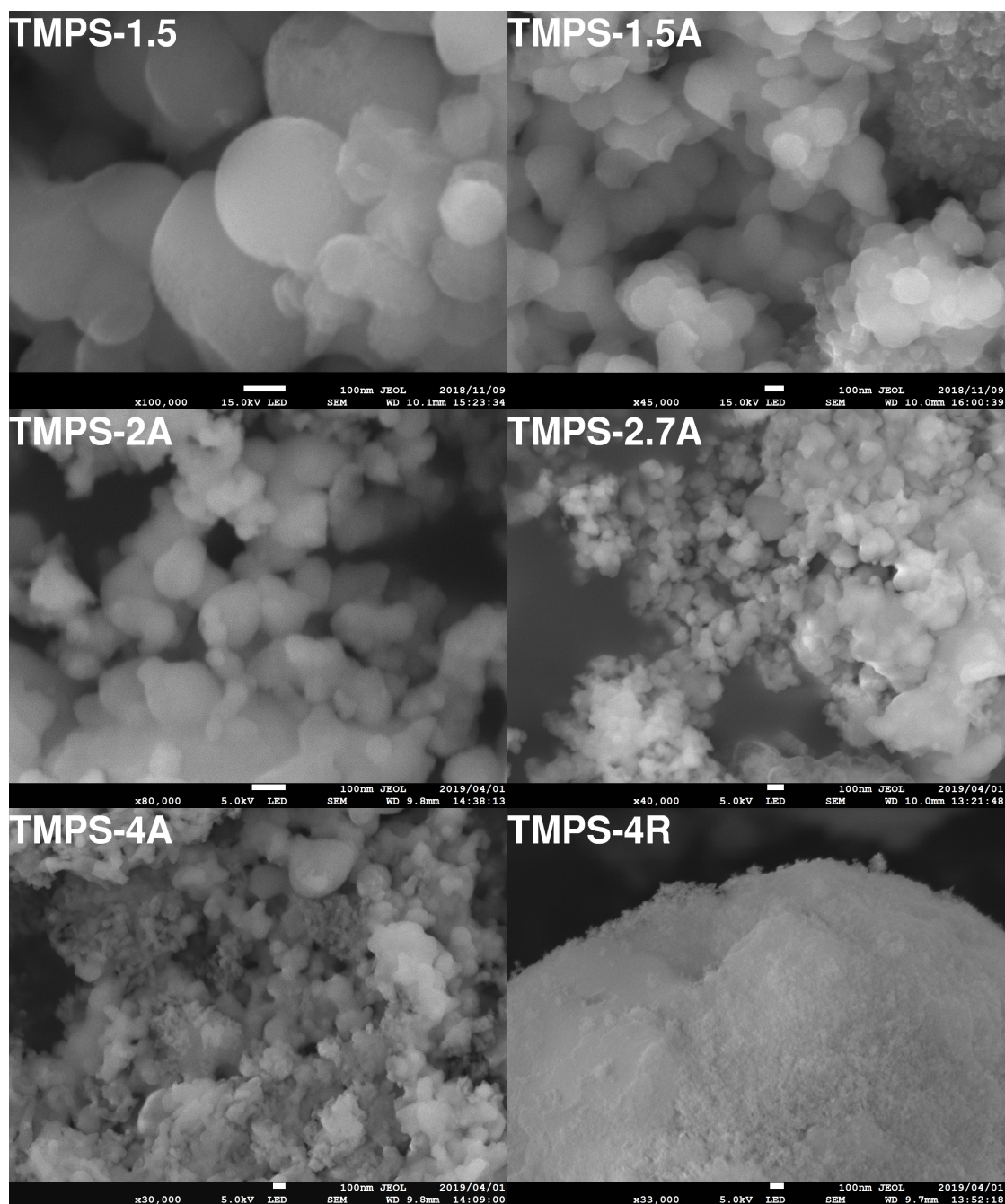


FIGURE 3.1: SEM images of the TMPS mesoporous silica samples

3.2.2 Methods and equipment

The standard basic material properties such as surface area, pore volume, pore diameter and pore distribution according to pore diameter and pore surface area were established by nitrogen adsorption at the boiling point of nitrogen ($T = 77.4\text{ K}$) at atmospheric pressure. The adsorption/desorption data were measured by the 3Flex instrument (Micromeritics Instrument Corp., US). Prior to the measurement, the materials were dried at $200\text{ }^{\circ}\text{C}$ for 24 hours in high vacuum ($P < 0.01\text{ Pa}$). The temperature was chosen in respect to the intended application of adsorption thermal energy storage to protect the silanol (Si-OH) groups from condensation. The isothermal data of the adsorption/desorption process were then fitted to standard adsorption models.

The measurement of the pore structural distances was conducted on X-ray powder diffraction (XRD) instrument, an automatic X-ray diffraction system SmartLab 9kW AMK (Rigaku, Japan). The materials were measured in the region from 0.5° to 10° of 2θ . The SmartLab instrument was used for the small-angle XRD with $\text{CuK}\alpha$ X-ray source in Bragg-Brentano geometry.

The specific heat was determined by a differential scanning calorimeter (DSC) DSC-60A (Shimadzu, JAPAN). To exclude the influence of humidity on the determination of the specific heat the materials were dehumidified at $200\text{ }^{\circ}\text{C}$ in an oven for 12 hours prior to the actual measurement. The measurement of specific heat was measured in the nitrogen atmosphere. The temperature range was set to $T = (25\text{ to }150)\text{ }^{\circ}\text{C}$ with the heating and cooling rate of 10 K min^{-1} .

Thermal stability was defined by the simultaneous thermal analyzer (TG-DSC) STA 449 F3 Jupiter (Netzsch, Germany) operated in TG/DSC mode. To establish the thermal stability the samples were heated during the measurement to $800\text{ }^{\circ}\text{C}$ at the rate of 10 K min^{-1} .

The tapped bulk density (envelope density) was established by GeoPyc 1360 (Micromeritics Instrument Corp., US) instrument. The size of the inner tube was 19.1 nm and the consolidation force was set to 10 N.

3.3 Results and discussion

3.3.1 Basic properties

The adsorption isotherms of nitrogen are presented in Fig. 3.2 and directly show the difference in the pore size and volume. The full adsorption and desorption dependencies of nitrogen are provided in the Appendix A.

Specific surface area measurement was based on the isothermal data of nitrogen adsorption and was calculated according to the standard BET model which is applicable to the mesoporous and some microporous materials. To calculate the surface area the BET model was used in its linearised form:

$$\frac{1}{V_e \left(\frac{P_0}{P} - 1 \right)} = \frac{C - 1}{V_m C} \left(\frac{P}{P_0} \right) + \frac{1}{V_m C} \quad (3.1)$$

where V_e is the actual (at equilibrium) adsorbed volume of the adsorbate, P and P_0 are the absolute and saturation pressure, respectively, V_m is the adsorbed volume of the monolayer, and C is the BET constant. The usual applicability range of the BET model is usually stated as $P/P_0 = 0.05$ to 0.35 [80], however, this range has to be adjusted and fitted according to the actual data. For materials with pore size $d_p < 2$ nm a smaller relative pressure is typically fitted to the linearised fitting. Alternatively, a single point approach for mesoporous materials can be selected as well, however, the precision is poor on the boundary of the microporous and mesoporous region around $d_p = 2$ nm, thus it was avoided in this work. The results of the BET analysis are summarized in Table 3.1. Residual standard deviation σ_R of the data fit was calculated as:

$$\sigma_R = \sqrt{\frac{\sum (y - y')^2}{n - 1}} \quad (3.2)$$

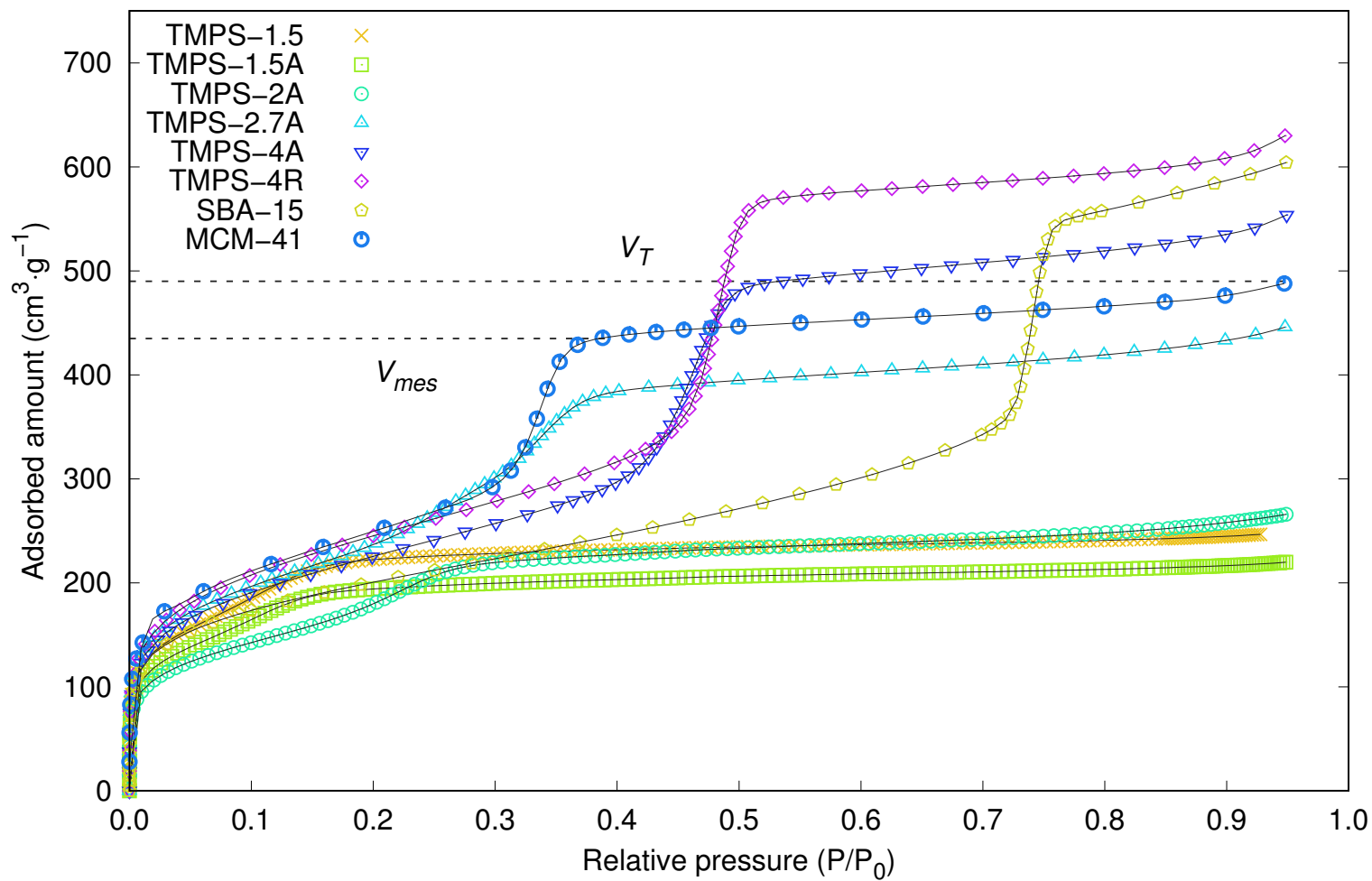


FIGURE 3.2: Adsorption isotherms of nitrogen at $T = 77.4\text{ K}$ on TMPS materials

TABLE 3.1: Total surface area S_m (BET), total pore volume V_T , mesopores pore volume V_{mes} , and properties of BET analysis with the residual standard deviation σ_R of the linear fitting

Sample	Total surface area S_m ($\text{m}^2 \text{g}^{-1}$)	Total pore volume V_T ($\text{cm}^3 \text{g}^{-1}$)	Mesopores pore volume V_{mes} ($\text{cm}^3 \text{g}^{-1}$)	Monolayer volume V_m ($\text{cm}^3 \text{g}^{-1}$)	C_{BET} constant	Linear range	P/P_0	σ_R
SBA-15	1101.7	1.770	1.607	303.7	282.3	0.05-0.3		5.73×10^{-6}
MCM-41	759.0	0.756	0.675	209.3	89.1	0.05-0.3		1.46×10^{-5}
TMPS-1.5	669.4	0.423	0.370	184.5	75.8	0.04-0.1		3.04×10^{-6}
TMPS-1.5A	602.0	0.380	0.334	166.0	68.7	0.05-0.1		3.03×10^{-6}
TMPS-2A	519.9	0.505	0.418	143.3	87.6	0.025-0.17		9.96×10^{-6}
TMPS-2.7A	727.8	0.691	0.592	200.7	69.3	0.05-0.23		7.28×10^{-6}
TMPS-4A	670.4	0.859	0.760	184.8	124.9	0.05-0.3		7.07×10^{-6}
TMPS-4R	725.3	0.977	0.888	200.0	137.8	0.05-0.3		8.28×10^{-6}

where y and y' are measured value and predicted value, respectively, and n is the number of selected points. The very low values of the deviations show a good fit with the model. The fitting in a graphical form is provided in the Appendix A. The total pore surface area S_m is then calculated from the mono-layer volume V_m given the linear form $y(x) = mx + i$ as:

$$V_m = \frac{1}{m + i} \quad (3.3)$$

where x represents the relative pressure P/P_0 , and m and i are the slope and constant of the linearised BET from Eq. 3.1, respectively. Defining the surface area itself is a matter of simple recalculation of the molecular cross-sectional area of nitrogen σ_{N_2} .

$$S_m = \frac{V_m N_A \sigma_{N_2}}{V_M} \quad (3.4)$$

where N_A is the Avogadro constant and V_M is the molar gas volume. Selection of the correct cross-sectional area of nitrogen is, however, more demanding. The common value is referred to $\sigma_{N_2} = 0.162 \text{ nm}^2$ [113], however, its applicability for different materials than carbon has been questioned. Mostly, because it is theoretically calculated and it is disregarding the surface effect. The theoretical value of σ_{N_2} can be obtained through the following formula:

$$\sigma_{N_2} = 1.091 \left(\frac{Mr(N_2)}{\rho_l N_A} \right)^{\frac{2}{3}} \quad (3.5)$$

where $Mr(N_2)$ is the molecular weight of nitrogen and ρ_l is the density of liquid nitrogen at the adsorption temperature. This value has been experimentally studied by Ismail[114] and the results for general carbon surfaces show only a little difference. For the silica surfaces is, however, recommended much lower value due to the dipole moment of the N_2 molecule in the contact with the oxidized SiO_2 surface. The experimental value of cross-sectional area of nitrogen on the silica surface was found out by Ismail as $\sigma_{N_2} = 0.143 \text{ nm}^2$ [114] and later on was corrected to even smaller value of $\sigma_{N_2} = 0.135 \text{ nm}^2$ by Jelinek and Kováts[115]. With the connection to the modern mesoporous silica materials an experimental investigation of the mesopores size evaluation was performed on MCM-41 by Galarneau et al.[116], proving the better performance of models using the value of Jelinek and

Kováts. Therefore, the same value of $\sigma_{N_2} = 0.135 \text{ nm}^2$ is used in this work as well. The surface area may seem therefore smaller than the available literature data, however, the comparison is complicated due to the general usage of the higher σ_{N_2} value without being stated. The data show that the surface area is not necessarily dependent on the pore size and it is rather connected to the material itself. On that account, the TMPS materials manifest properties similar to the MCM-41. That is further supported by the spherical shape of MCM-41 and TMPS particles as shown on the SEM images.

Total pore volume represents another important property of these porous materials. The simplest way how to calculate the pore volume is direct recalculation from the volume of adsorbed nitrogen. The disadvantage of this method is that the results disregard pores smaller than the nitrogen molecule. This, however, can be ignored in case of highly organized materials such as mesoporous silica, where we do not expect micropores smaller than nitrogen molecule to be present, or to have a significant effect. This practice is widely used using usually the relative pressure values of $P/P_0 = (0.95 \text{ to } 0.99)$. In this work, to avoid the overestimation due to the effect of nanoparticles, the value on the lower side of the range was selected. The nanoparticle effect is mainly apparent in the case of SBA-15 and TMPS materials with higher pore size and smaller particle size where the nitrogen can also condense in the very narrow inter-particle space. Here again, the TMPS materials exhibit values similar to the MCM-41 reference material.

3.3.2 Pore size distribution

In combination with X-ray diffraction (small-angle powder X-ray diffraction) the pore size was established by standard methods for mesoporous materials. The Barrett-Joyner-Halenda method (BJH), Dollimore-Heal method (DH), and Density Functional Theory method (DFT) were used in the appropriate form for silica surfaces. To use the regular methods an important assumption for the cylindrical

TABLE 3.2: Mean pore diameter d_p ($2r_p$) according to Barrett-Joyner-Halenda (BJH), Density functional theory (DFT), $4V/S$ method, and XRD-based geometrical method

Sample	BJH (Halsey) d_p (nm)	BJH (H/J) d_p (nm)	DFT d_p (nm)	$4V/S$ d_p (nm)	XRD d_p (nm)
SBA-15(1)	6.4	6.4	7.5	5.8	10.6
MCM-41(3)	2.9	2.8	3.3	3.5	3.5
TMPS-1.5	1.8	1.6	1.9	2.2	2.6
TMPS-1.5A	1.8	1.6	1.8	2.2	2.5
TMPS-2A	2.4	2.2	2.3	3.2	3.2
TMPS-2.7A	2.9	2.8	3.1	3.3	3.5
TMPS-4A	3.8	3.5	4.0	4.5	4.7
TMPS-4R	3.7	3.6	4.2	4.9	4.8

pore geometry calculation has to be considered.

$$r_p = r_k + t \quad (3.6)$$

In the above Eq. 3.6 the actual pore radius r_p is calculated as a sum of critical radius r_k and statistical film thickness t . That means, the pore radius is calculated through continuous addition, or reduction, of the capillary condensation and the surface adsorption/desorption. Considering the Kelvin equation as the basic mathematical expression for the capillary condensation occurrence we can write:

$$\ln \frac{P}{P_0} = -\frac{2H\gamma V_l}{RT} \quad (3.7)$$

where H is the curvature of the meniscus in the capillary, γ is the surface tension of the liquid nitrogen, V_l is the molar volume of liquid nitrogen, and R and T are the gas constant and absolute temperature, respectively. Knowing all the constant values and the fact that the curvature H is reciprocal to the critical radius of the pore $r_k = 1/H$ the Kelvin equation can be modified to find out the critical radius at which the nitrogen condenses inside the pore:

$$r_k = \frac{0.96}{\ln \frac{P_0}{P}} \quad (3.8)$$

The second parameter t , necessary to estimate the pore radius r_p from Eq. 3.6, is the layer thickness of the adsorbate on the surface of the adsorbent. Halsey model and Harkins-Jura model were used to estimate the adsorbed layer thickness. The Halsey model gives the layer thickness based on the following equation in which the 3.54 represents the monolayer thickness in Angstroms:

$$t[\text{\AA}] = 3.54 \left[\frac{5}{\ln \frac{P_0}{P}} \right]^{\frac{1}{3}} \quad (3.9)$$

The thickness model of Harkins and Jura is calculated similarly as:

$$t[\text{\AA}] = \left[\frac{13.99}{0.034 - \log \frac{P}{P_0}} \right]^{\frac{1}{2}} \quad (3.10)$$

And finally, the pore size distributions according to BJH were obtained by:

$$V_p = \left(\frac{\bar{r}_p}{\bar{r}_k + \Delta t_n} \right)^2 \left(\Delta V_n - \Delta t_n \sum_{i=1}^{n-1} \Delta A_p + \Delta t_n \bar{t}_n \sum_{i=1}^{n-1} \frac{\Delta A_p}{\bar{r}_p} \right) \quad (3.11)$$

where $\bar{r}_p$ is the average pore radius calculated according to Eq. 3.6, $\bar{r}_k$ is the average Kelvin radius according to Eq. 3.7, Δt_n is the layer thickness change, ΔV_n is the desorbed volume change, ΔA_p is the change of the pore area calculated as $\Delta A_p = 2\Delta V_p/r_p$ and $\bar{t}_n$ is the average layer thickness. The values Δt_n and $\bar{t}_n$ were then based on the equations 3.9 and 3.10 depending on which model the calculation followed. For comparison, the pore size distribution was also obtained according to DH method, as an extension of BJH method. However, because the results from the DH method are practically identical, they are omitted further on in this work. When using the Halsey and Harkins and Jura models Galarneau et al.[116] pointed out that these models overestimate the statistical thickness t by up to 0.1 nm which leads to a certain underestimation of the pore size. If we compare the results of BJH with a modern computational method such as DFT the pore size difference between the methods increases with increasing pore diameter as expected. The results of the BJH method using two different layer

thickness models and DFT are listed in Table 3.2. From the results is apparent that Halsey's model produces slightly higher pore diameters than the model of Harkins and Jura which is already apparent from their respective dependence on the relative pressure. The full results on the pore size distribution are provided in the Appendix A. For the exact calculation of the mean pore size a modified normal standard distribution function was used as the pore size distribution is expected to follow normal distribution in general. Very good fit of the data with the normal distribution function was achieved with less than 5 % of absolute average deviation (AAD(%)) in general. The normal distribution function was used in a form described by Eq. 3.12.

$$y(d_p) = \alpha \frac{1}{\sqrt{2\pi}\sigma^2} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \quad (3.12)$$

where σ is the distribution or also deviation, μ is the mean value of the pore diameter d_p , and the additional parameter α compensates for the magnitude. This approach proved to be especially advantageous in case of the DFT method, where the density of the results is not dependent on the data acquisition density but on the DFT kernel density and the actual mean pore diameter d_p has to be determined by a follow-up method. The BJH method is usually applicable for the mesoporous region where $d_p = (2 \text{ to } 50) \text{ nm}$. However, good agreement with the results of the DFT method was also achieved in the case of the TMPS-1.5 and TMPS-1.5A with the mean pore diameter $d_p = 1.7(9) \text{ nm}$ and $d_p = 1.7(6) \text{ nm}$, respectively, using the Halsey thickness model.

A more direct approach to calculate the pore diameter can be followed by using Gurvitsch rule[117, 118] also referred to as $4V/S$ [116]. If we assume that the geometry of the pore is a regular cylinder the diameter of such cylinder d_G can be calculated based on the proportion of the adsorbed mesopore volume V_{mes} over the surface area obtained for example by the BET method S_{BET} :

$$d_G = \frac{4V_{mes}}{S_{BET}} \quad (3.13)$$

TABLE 3.3: Distance of the pore plains d_{100} , d_{110} , and d_{200} , calculated pore axis pitch a by XRD and wall thickness based on DFT pore size e_{DFT} and average $\bar{a}$

Sample	$2\theta_{d_{100}}$	d_{100} (nm)	$2\theta_{d_{110}}$	d_{110} (nm)	$2\theta_{d_{200}}$	d_{200} (nm)	a_{100} (nm)	a_{110} (nm)	a_{200} (nm)	$\bar{a}$ (nm)	e_{DFT} (nm)
SBA-15(1)	0.88	10.03	1.54	5.73	1.76	10.03	11.58	11.47	11.58	11.54	4.12
MCM-41(3)	2.18	4.05	3.79	2.33	4.38	4.03	4.68	4.66	4.66	4.66	1.42
TMPS-1.5	2.76	3.20	4.58	1.93	5.16	3.42	3.69	3.86	3.95	3.83	1.84
TMPS-1.5A	2.83	3.12	4.96	1.78	5.18	3.41	3.60	3.56	3.94	3.70	1.77
TMPS-2A	2.24	3.94	4.12	2.14	4.29	4.12	4.55	4.29	4.75	4.53	2.26
TMPS-2.7A	2.26	3.91	3.97	2.22	4.47	3.95	4.51	4.45	4.56	4.51	1.38
TMPS-4A	1.82	4.85	3.24	2.72	3.40	5.19	5.60	5.45	6.00	5.68	1.58
TMPS-4R	1.80	4.90	3.11	2.84	3.56	4.96	5.66	5.68	5.73	5.69	1.48

The mesopore volume V_{mes} was obtained directly from the adsorption isotherm of N_2 as shown in Fig. 3.2 on the example of the MCM-41, where the V_{mes} symbolises the mesopore volume and the V_T the total volume.

Direct observation of the pore size was performed by the small-angle powder X-ray diffraction (XRD). In most cases, it was possible to conclusively distinguish in the XRD signal two or three peaks corresponding to the expected hexagonal structure. The diffraction as a function of the angle 2θ of all the samples is shown in Fig. 3.3. Based on the peak positions, the plane distances d_{100} and d_{110} , as shown in Fig. 3.3, can be calculated by the Bragg's law:

$$2d \sin \theta = n\lambda \quad (3.14)$$

Under the assumption of constructive interference of the X-rays, in the Eq. 3.14 the parameter d is the plane distance, θ is the beam angle, n is the plane sequence number and λ is the specific wavelength of the used X-ray beam source (see Table 3.5). Results of the XRD analysis are summarized in Table 3.3. Comparing the results of the TMPS materials an interesting pattern is revealed. The investigated samples show a pair pattern where the six samples can be divided into three groups according to pore axis a distance. This pattern, together with pore size similarity, suggests the same surfactant template precursor for pairs TMPS-1.5/TMPS-1.5A and TMPS-4A/TMPS-4R. The difference then lies mainly in the wall thickness and slight alternation of the pore diameter. This observation is further supported by the bulk (tapped) density measurement.

The pore distance a together with the measured mesopore value V_m can be used for an alternate method to calculate the pore diameter. Galarneau et al.[116] showed a simple calculation based on the volume ratio of the hexagonal array. The resulting Eq. 3.15 calculates the pore diameter D based on the pore distance

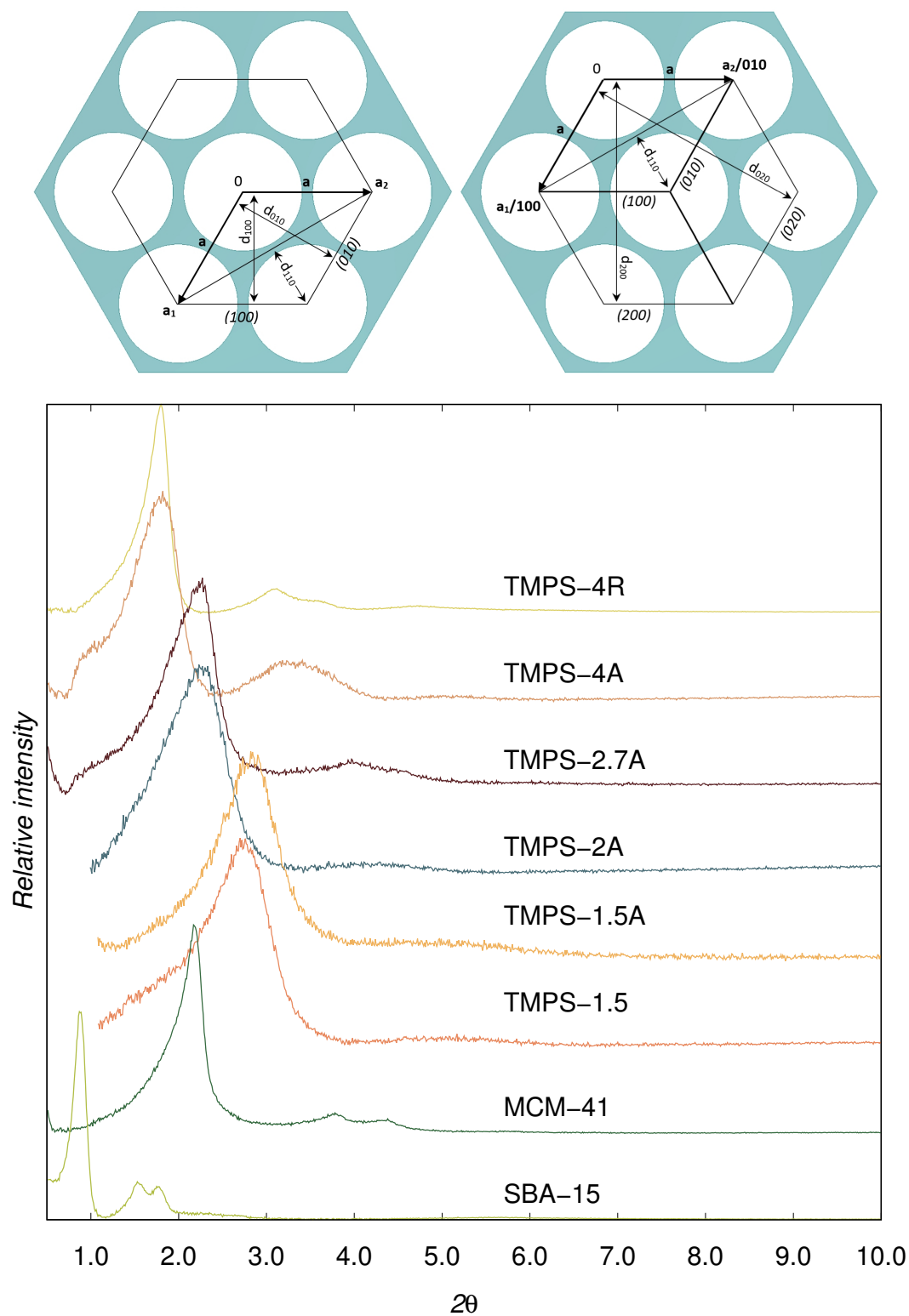


FIGURE 3.3: Small-angle XRD of the TMPS mesoporous silica samples

a measured by XRD and the density of amorphous silica ρ_{SiO_2} .

$$D = 1.05a \sqrt{\frac{V_{mes}}{V_{mes} + 1/\rho_{SiO_2}}} \quad (3.15)$$

An alternative approach based on the hexagonal array presented in here builds on the idea that the particle can be divided into individual identical hexagonal prisms with cylindrical pore in the middle and then connect them in an end-to-end fashion creating one hexagonal prism of a length L . Because the outside surface area of the prism was created artificiality it is omitted from the calculation. The total volume V_T of such prism is then, beside the general mathematical formula, a sum of the silica volume V_{SiO_2} and the mesopore volume represented by the single cylindrical pore. The hexagon side length in Eq. 3.16 is then written as h .

$$V_T = \frac{3\sqrt{3}}{2}h^2L = V_{SiO_2} + V_{mes} \quad (3.16)$$

The volume of the silica V_{SiO_2} is calculated based on the density of the amorphous silica as $1/\rho_{SiO_2}$. From the geometrical representation is apparent that the side of an individual hexagonal section h is equal to $a/\sqrt{3}$ of the pore distance. Thus, the length L will be expressed as:

$$L = \frac{1 + \rho_{SiO_2}V_{mes}}{\rho_{SiO_2}} \frac{2}{h^2 3\sqrt{3}} \quad (3.17)$$

Because the mesoporous volume is expressed as a volume of the cylindrical pore $\pi r^2 L$, if we substitute the pore length L we will get the final expression for the pore diameter d_p :

$$d_p = 2 \sqrt{\frac{V_{mes}}{\pi} \frac{a^2 \sqrt{3}}{2} \frac{\rho_{SiO_2}}{1 + \rho_{SiO_2}V_{mes}}} \quad (3.18)$$

Except for the SBA-15, the results of the geometrical method correspond to the $4V/S$ method. However, comparing the data further, it is apparent that the sample SBA-15 somehow fails the geometrical methods altogether. In general, the $4V/S$

TABLE 3.4: Tap density ρ ($\text{cm}^3 \text{g}^{-1}$) and specific heat C_p ($\text{J g}^{-1} \text{K}^{-1}$) of TMPS mesoporous silica nanoparticles, SBA-15, and MCM-41 at 25 °C

Sample	Tap density ρ ($\text{cm}^3 \text{g}^{-1}$)	Specific heat C_p ($\text{J g}^{-1} \text{K}^{-1}$)
TMPS-1.5	0.222	0.89
TMPS-1.5A	0.274	0.89
TMPS-2A	0.169	0.94
TMPS-2.7A	0.200	0.77
TMPS-4A	0.175	0.85
TMPS-4R	0.219	0.91
SBA-15	-	0.89
MCM-41	-	0.85

method tends to overestimate the pore size disregarding the difference between the outside and inside surface area and more complex structures. The significant difference in case of the observed SBA-15 is thus caused by the strong effect of microporous inter-pore connections typical for SBA-15, adding a great deal of surface beside the mesopore area.

The calculated wall thickness e_{DFT} is shown in Table 3.3 and it is calculated as a difference between the pore distance (pitch) in the perpendicular plane to the pores' hexagonal coordination face (Fig. 3.3) and pore mean diameter taken from the DFT method. As presented in Table 3.3 the wall thickness varies in case of TMPS materials in the range of $e_{DFT} = 1.3 \text{ nm}$ to 2.1 nm and does not follow any regular pattern. From the comparison to the SBA-15 and MCM-41, it seems that the wall thickness is again closer to the MCM-41, however, considering the actual ratio of wall thickness/pore size, the SBA-15 is closer to the TMPS materials over MCM-41 in this case.

3.3.3 Physical properties

Physical properties of tap density and specific heat of the TMPS materials, SBA-15, and MCM-41 mesoporous silica at 25 °C are listed in Table 3.4. The tap density was measured at consolidation force of 10 N. The results show low specific density around $\rho_{\text{SiO}_2} = 0.2 \text{ cm}^3 \text{g}^{-1}$. Because the mesoporous silica materials are

in general considered as an amorphous form of the silica the true density is equal to $\rho = 2.196 \text{ g cm}^{-3}$. Even if we consider the particles as spherical and apply the regular packing factor for random packing for spherical particles of 0.634 [119], the resulting difference is still too big. Hence, to consider the actual bulk density other two factors have to be taken into an account. The obvious one is the pore volume and the resulting density of a particle cell. The second one is the consideration of electrostatic repulsion forces hindering close packing. Pure amorphous silica is a naturally good electric insulator and the particles of the samples tested in this work show high electrostatic charge especially when fully dried. The static charge is probably not strong enough to substantially change the bulk density of the silica materials, but thanks to the combined effect of the nanoparticles it can become significant. However, the effect of static charge on the bulk density has yet to be investigated in detail. Furthermore, if we compare the data on pore distance from the XRD analysis the same correlation is visible. It is apparent that the wall thickness of the materials has an immediate effect on the tapped density. The wall thickness then directly influences the performance of the materials in correlation to the bulk performance qualities.

The specific heat of the TMPS materials was found out in the range of $0.77 \text{ J g}^{-1} \text{ K}^{-1}$ to $0.94 \text{ J g}^{-1} \text{ K}^{-1}$ at 25°C and it does not differ from the values of regular mesoporous silica samples. In the case of SBA-15 and MCM-41 prepared in this work, the specific heat was found out $C_p = 0.89 \text{ J g}^{-1} \text{ K}^{-1}$ and $C_p = 0.85 \text{ J g}^{-1} \text{ K}^{-1}$, respectively. If we compare the specific heat of the mesoporous silica with standard quartz silica some small difference is apparent. While crystalline silica has typically specific heat of $C_p = 0.74 \text{ J g}^{-1} \text{ K}^{-1}$ [120] the nano-structured silica exhibits higher values [121]. This is naturally not caused by the macroscopic structure, which in general does not have an effect on the heat capacity, but the fact that mesoporous silica is a non-crystalline form of silica i.e. amorphous silica. Values found out in this work are in agreement with available literature sources [122].

3.3.4 Infra-red analysis on the aluminium bond on the silica structure

The structural FTIR (Fourier-transform) analysis of the samples is provided in Fig. 3.4 and shows the data of the TMPS-1.5, TMPS-1.5A compared to MCM-41 sample. FTIR data on the rest of the samples are further provided in the Appendix A. From the comparison is clear that the TMPS materials are almost pure silica, the same as the SBA-15 and MCM-41. Typical adsorption bands for SiO_2 were found for all major bonds. Si-O-Si stretching at 1080 cm^{-1} , bending around 800 cm^{-1} , and rocking around 450 cm^{-1} . Although the samples were rigorously dried prior the measurement, some amount of water from the air adsorbed on the surface and it is clearly visible together with the stretching of SiO-H bond in the higher region of 4000 cm^{-1} to 2600 cm^{-1} . The EDS elemental analysis discussed later on shows that the actual amount of the doped aluminium in the TMPS samples is not higher than 4 wt% which significantly limits the effect on the spectra. For the aluminium to have any effect on the properties of the material it is to be expected as an integral part of the Si-O structure. The Al-O-Si bond bending can be found in the region around the wavenumber of 500 cm^{-1} of the spectra of the TMPS-1.5A in the contrast of the missing transmittance band in case of TMPS-1.5 and MCM-41.

3.3.5 Thermal stability

The mesoporous silica materials are typically thermally stable materials and can withstand high temperatures for prolonged time[112, 123]. Although there is no need to further investigate this matter in case of the regular mesoporous silica such as SBA-15 and MCM-41, the situation is less obvious in the case of the TMPS materials containing aluminium additive in their structure. The effect of aluminium content on the thermal durability was investigated on the example of TMPS-1.5 and TMPS-1.5A. The mass change and heat flow dependence on temperature is shown in Fig. 3.5 in the range from 25°C to 800°C . As the samples were tested directly without any preparation, in the first phase up to 100°C , the adsorbed water

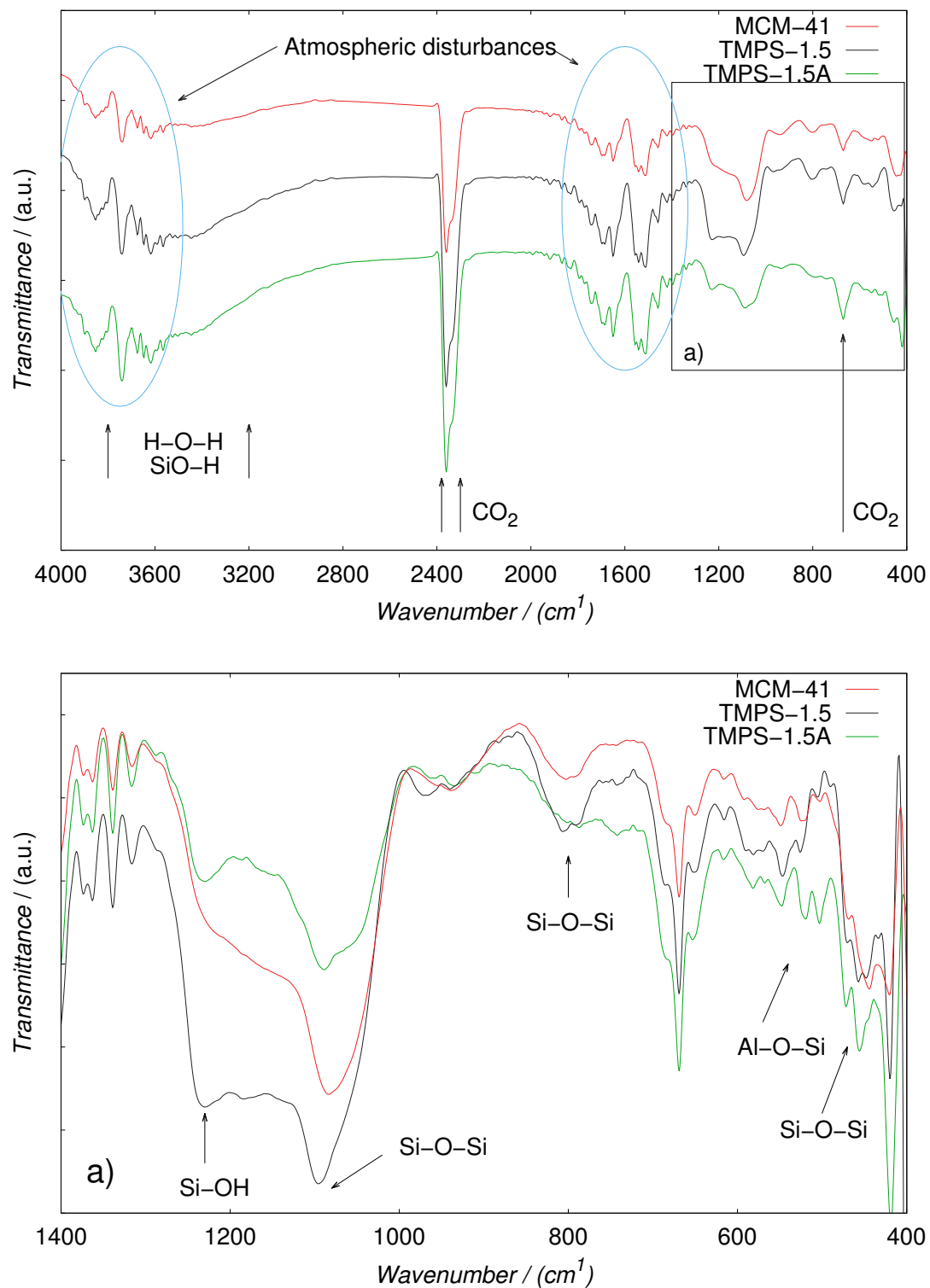


FIGURE 3.4: Infra-red spectrum transmittance of TMPS-1.5, TMPS-1.5A and MCM-41 in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1} .

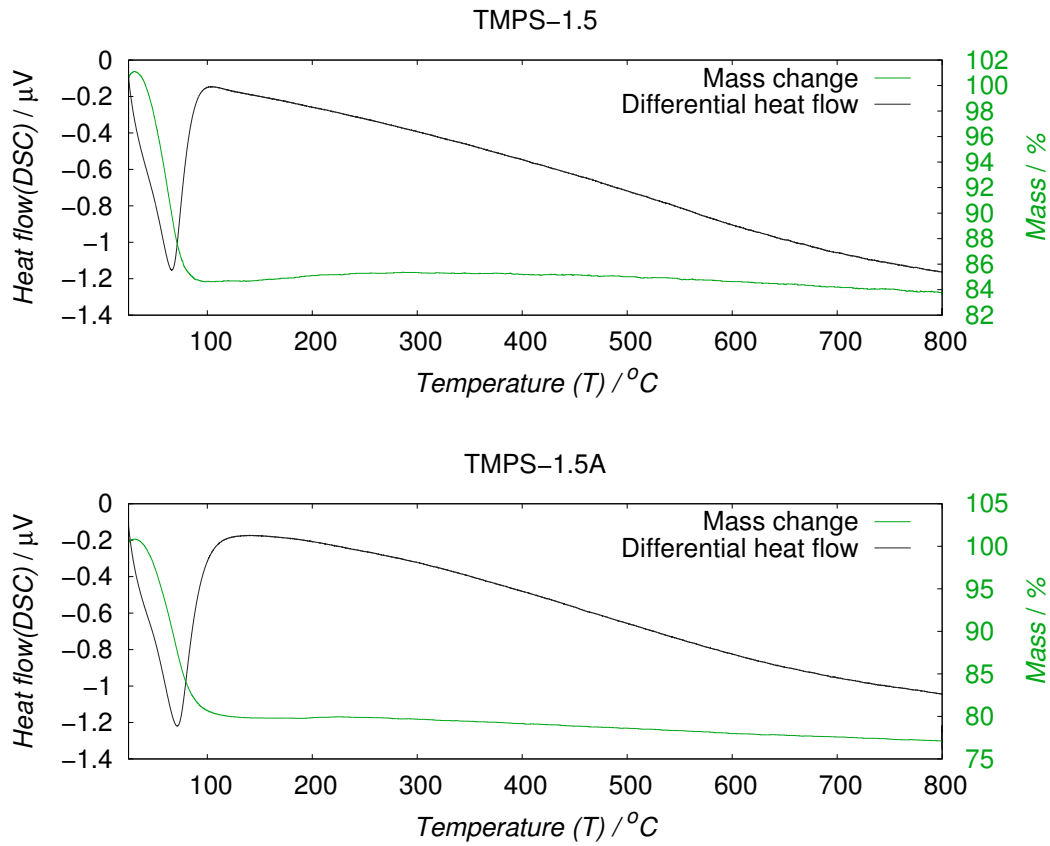


FIGURE 3.5: Thermogravimetric analysis of TMPS-1.5 and TMPS-1.5A.

and possible other low-boiling substances are desorbed. The desorption process creates a significant change in the mass and a spike in the heat flow. Because the desorption process is endothermic, the detected spike is negative. After reaching the temperature of 100 °C the situation stabilizes and remains constant until the set maximum of 800 °C. If we compare the data between the aluminium doped TMPS-1.5A and aluminium free TMPS-1.5, the only difference is in the higher affinity towards water in case of TMPS-1.5A. The higher affinity causes a higher spike in the heat flow as more energy is consumed for the desorption and the surface manifests lower willingness for water release. This is also demonstrated by the less sharp transition signifying complete water release around the boiling point of water of 100 °C at the atmospheric pressure. Further on, with the increasing temperature, the mass of the samples remains constant. Without the effect of the desorption processes, the change of specific heat capacity is clearly visible as a constant increase in the heat flow towards the samples. From the presented data

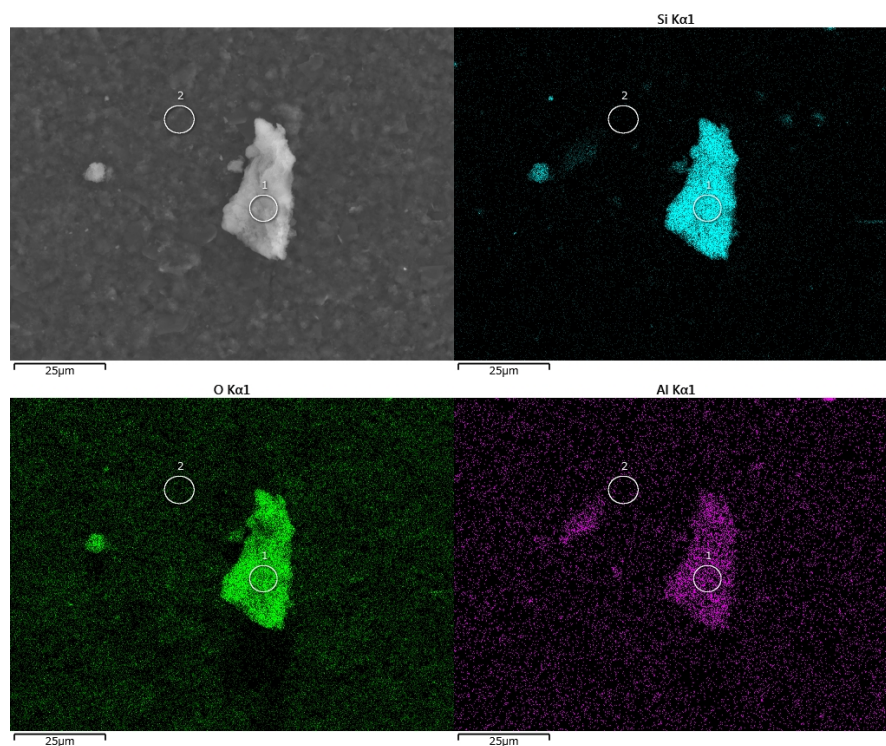
is therefore apparent that the materials are thermally stable and do not exhibit aberrations from regular silica materials. Similar findings were observed in the case of the rest of the TMPS specimens as well as shown in the Appendix A.

3.3.6 Elemental analysis by Energy-dispersive X-ray spectroscopy (EDS)

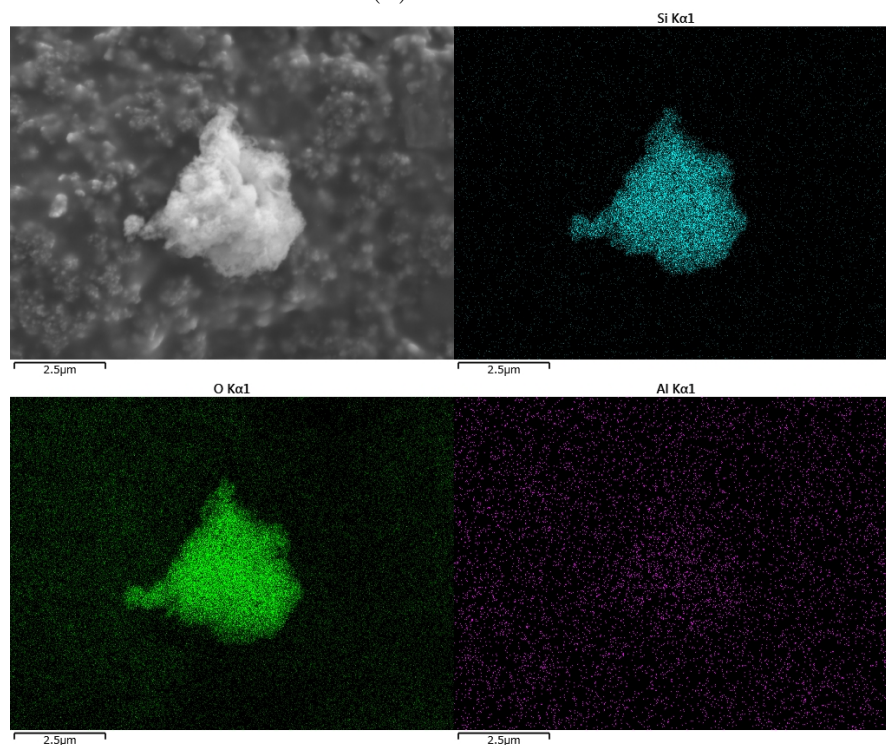
The elemental analysis of the samples was primarily focused on silica, oxygen and aluminium. The intensity maps in Fig. 3.6 clearly shows the difference between the sample with and without the aluminium addition. The intensities of individual elements in case of TMPS-4A were calculated for two different locations for comparison. The location (1) from Fig. 3.6(a) was selected on top of the sample particle and the atomic composition was 49.2 at% carbon, 36.0 at% oxygen, 13.3 at% silicon, and 1.1 at% aluminium and several trace elements with the occurrence typically less than 0.1 at%. The location (2) then exhibited the composition of the background (colloidal graphite paint). The composition was 84.9 at% carbon and 15.0 at% oxygen, with the sum of all other detected elements accounting for 0.1 at%. It is apparent that the strong presence of carbon and oxygen hinders direct evaluation and the effect of the background has to be considered or otherwise eliminated. Hence, to assess the composition of the material, we assume static ratios of Si/O and Si/Al. The silicon-based calculation then gives the exact amount of the atoms present in the samples disregarding the background effect. The additional EDS maps are available in the Appendix A. By this method, the amount of the added aluminium was found out for all of the samples provided by Taiyo Kagaku Co., Ltd. for this study practically the same as 3.5 wt% (± 0.5 wt%).

3.4 Conclusion

A detailed analysis of several samples of the nano-structured commercial mesoporous silica from the family of TMPS was conducted and compared to the regular



(A) TMPS-4A



(B) TMPS-4R

FIGURE 3.6: Elemental analysis of TMPS-4A and TMPS-4R by the means of SEM/EDS.

TABLE 3.5: Physical constant and parameters used for the calculations in this work

R (J mol ⁻¹ K ⁻¹), Gas constant	8.31446
λ (nm), XRD beam source wavelength	0.15406
σ_{N_2} (nm ²), Nitrogen cross-sectional area	0.135
N_A (mol ⁻¹), Avogadro constant	6.02214e10 ²³
Mr_{N_2} (g mol ⁻¹), Nitrogen molar weight	28.0134
ρ_{N_2} (g cm ⁻³), Nitrogen density (77.4 K)	0.80606
γ_{N_2} (mN m ⁻¹), Nitrogen surface tension (77.4 K)	8.8737
ρ_{SiO_2} (g cm ⁻³), Silica density (amorphous)	2.196

SBA-15 and MCM-41 mesoporous silica. The TMPS materials show typical properties of mesoporous silica and behaviour in a very similar fashion.

The size of the individual particle cell sizes is in the range from 50 nm to 200 nm as observed by the SEM, and aggregate into bigger particles typically in the range of units of micrometres. The nano-structured inner coordination shape and inner structure (particle cell shape, pore size) of the TMPS materials have higher similarity with the prepared MCM-41. Because of the individual particle cell, the materials can be put on the border of nanoscale materials as the size of the particles together with the material properties affect the bulk properties.

The addition of aluminium in the structure does not physically affect the basic properties however it is expected to have a significant effect on the adsorption properties. The addition of aluminium is generally used to enhance the water adsorption properties and water such as adsorption rate and adsorption energy.

Chapter 4

Water Adsorption on the Mesoporous Silica Matrix

4.1 Introduction

Pure silica materials such as silica gels are known for their good water adsorption properties and are extensively used for humidity control and related applications[124, 125]. This property is given to silica by the silanol ($-\text{SiOH}$) groups, to which the water molecules can attach directly through the hydrogen bridges[126]. Since the Si-O-H bond has different energy distribution than the H-O-H, the adsorption enthalpy can be significantly higher than the simple condensation enthalpy[70] build only on the H-O-H bond. Consequently, any similar material based on silica is expected to have similar properties and can be considered as a good candidate for water adsorption. Mesoporous silica materials also fall into this category and the water adsorption had been extensively studied on them from their rediscovery in 1992 in case of MCM-41[54, 55] and later on in 1998 in case of SBA-15[56] as typical representatives of hexagonal mesoporous silica. The mesoporous silica materials have, compared to the silica gels, highly organized structure characterized by narrow pore size distribution, which can be varied depending on the preparation process[56, 127]. This gives them more precise control over the relative pressure dependent adsorption and enhances their applicability, eg. as selective catalysts[128] or drug delivery matrix[59]. The adsorption of water on mesoporous

silica was studied shortly after the aforementioned new process was developed. In 1995 was studied the aluminophosphate type of MCM-41 by Llewellyn et al. [129] and FSM-16, which was prepared even earlier in Japan[130], was then studied by Inagaki et al. [131]. After that, many other studies started to emerge together with the significance of the new nano-tailored mesoporous silica material groups, mainly in connection to energy-related fields[60, 132–134].

Although the pure mesoporous silica materials are still intensively studied, more new adaptations have been introduced in the recent years. Some known combination of the silica doped with not-silicon atoms proved to enhance the surface hydrophilicity thus positively influencing the water-adsorptive properties. Therefore, most of the attention is naturally given to aluminium doping, although, effects of other atoms such as zirconium dopants were also extensively tested[132, 134, 135] showing some positive results in hydrothermal stability. In the case of aluminium, the main factor influencing the water adsorption is the change in the surface acidity induced by aluminium atom displacing silicon atoms and creating localised acidification enhancing attraction to polar substances. Above that, it has been reported that the aluminium addition also significantly increases the hydrothermal stability as well[136]. Thus, the aluminium-doped specimens of mesoporous silica are expected to have more suitable properties for water adsorption than pure mesoporous silica.

To introduce the aluminium atoms to the structure there are two options in general; during the formation and as a post-treatment. The post-treatment method consisting from aluminium coating reported by Kim et al. [14] shows very promising values in the aspects of adsorption properties and hydrothermal stability increase. Another post-treatment method introduced by Mokaya and Jones [137] showed the use of aluminium chlorohydrate as the source for surface aluminium doping on pure mesoporous silica MCM-41. The increase of hydrothermal stability was observed in this case through boiling in water (reflux). The effects on water

adsorption by aluminium doping into the mesoporous silica structure directly during the formation process was recently studied by Ribeiro et al. [138] with similar results as the previous publications. The influence of aluminium doping on the water adsorption and hydro-stability is therefore well known, however, actual adsorption data are still somehow limited.

The main objective of this chapter is to investigate the water adsorptive properties of the new industrially manufactured TMPS mesoporous silica. Even though many new mesoporous silica materials and composites are introduced every year, the actual industrial production is still highly limited, slowing down development of potential applications. The aim is the analysis of water adsorption for energy-related applications such as adsorption heat pumps and adsorption thermal energy storage, hence, full analysis of adsorption heat, activation energy and kinetics models is given as well.

4.2 Materials

In this chapter the same materials as from Chapter 3 are used. The aluminium doped samples in the TMPS family are signed with capital letter *A* in the end of the sample name. Again, for comparison, MCM-41 and SBA-15 mesoporous silica were prepared and measured for water adsorption as well. Similarly to the TMPS materials, both the SBA-15 and the MCM-41 were used without any modifications after the calcination process was finished. The properties of all used materials are for recapitulation shown in Table 4.1. For more detailed information please refer to the previous chapter.

4.3 Experimental

The adsorption isotherms were measured on surface characterisation analyser 3Flex (Micromeritics, US). The schematic of the measurement is provided in Fig. 4.1. Prior the measurement, the samples were thoroughly degassed at 200 °C and high vacuum (<0.01 Pa) for 5 hours before weighting. After weighting, the

TABLE 4.1: Materials properties; total surface area S_m (BET), total pore volume V_T , mesopores pore volume V_{mes} , pore diameter d_{DFT} , and pore pitch a_{XRD}

Sample	Total surface area S_m ($\text{m}^2 \text{g}^{-1}$)	Total pore volume V_T ($\text{cm}^3 \text{g}^{-1}$)	Mesopores pore volume V_{mes} ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter d_{DFT} (nm)	Pore pitch a_{XRD} (nm)
TMPS-1.5	669.4	0.423	0.370	1.9	3.6
TMPS-1.5A	602.0	0.380	0.334	1.8	3.6
TMPS-2A	519.9	0.505	0.418	2.3	4.4
TMPS-2.7A	727.8	0.691	0.592	3.1	4.5
TMPS-4A	670.4	0.859	0.760	4.0	5.6
TMPS-4R	725.3	0.977	0.888	4.2	5.6
MCM-41(3)	759.0	0.756	0.675	3.3	4.7
SBA-15(1)	583.9	0.937	0.852	7.5	11.5

samples were degassed once more at 200 °C for another 5 hours. The residual pressure over the samples in the sample cell was confirmed to be <0.1 Pa in all cases at the room temperature of 25 °C at the end of the degassing process. The drying temperature of 200 °C was selected with regard to the water adsorption properties with the presence of silanol (-Si-OH) groups. Furthermore, to sustain high reproducibility, each measurement was conducted with fresh sample. The TMPS samples were measured at 5 different temperatures $T = 278.15 \text{ K}$, 288.15 K , 298.15 K , 308.15 K and 313.15 K . The MCM-41 and SBA-15 were measured at 4 different temperatures 283.15 K , 293.15 K , 303.15 K and 313.15 K .

The vapour source was prepared from ultra-pure deionised water with standard resistivity of $>18.2 \text{ M}\Omega \text{ cm}$. The vapour source was degassed by regular procedure employing liquid nitrogen and high vacuum source, until the pressure of the vapour source was equal to referenced values within the relative error of the pressure transducer ($u = 0.05$) at the room temperature (25 °C). The data acquisition of the pressure on time were recorded directly from the 3Flex device output data stream and the pressure over time and adsorption over time plots were extracted by Python scripts written for this sole purpose.

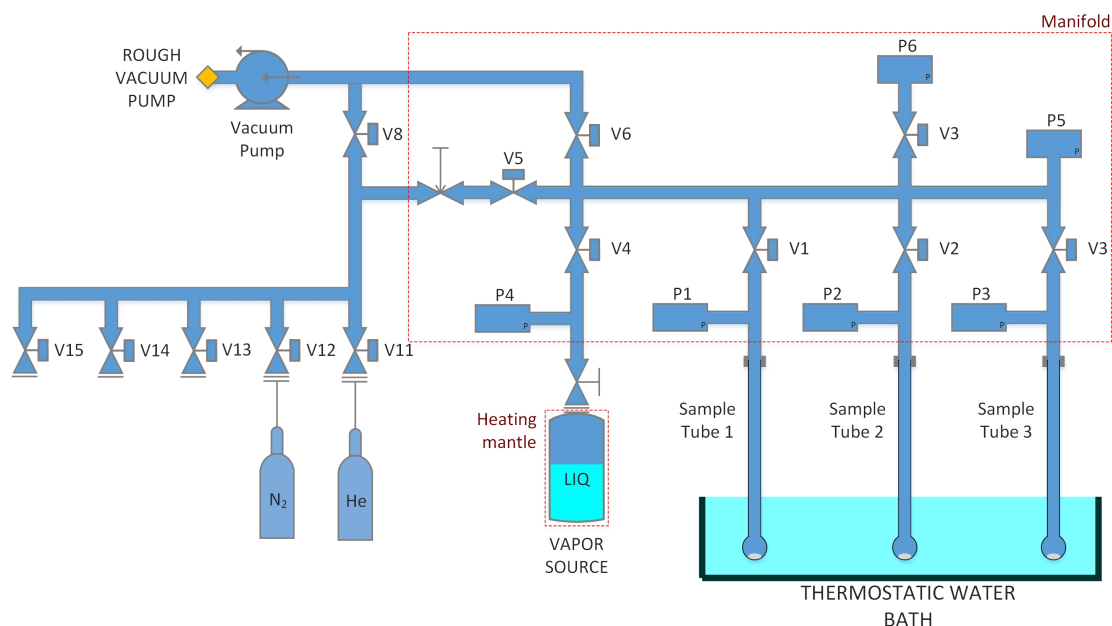


FIGURE 4.1: Schematic picture of the experimental device.

4.3.1 Adsorption models

Modelling of water adsorption curves on mesoporous materials is a subject of many research publications[74, 92, 93, 139, 140]. The adsorption isotherm of the mesoporous silica is usually identified as IUPAC Type IV or Type V depending on the surface characteristics, when Type IV corresponds to materials with surface more susceptible to adsorption of a given adsorbate, therefore, higher attraction forces and energy yield is expected. However, thanks to the nature of the adsorption process on mesoporous material, the theoretical models are difficult to apply. In the literature is only a limited amount of modelling examples of isotherm adsorption curves on mesoporous materials (Type IV and V according to IUPAC) since simple models such as Langmuir, Freundlich, BET or their algebraic combinations usually fail due to the complicated shape of the isotherm. This shape and the complication is given by the fact that the adsorption process of the mesoporous materials is a combination of two to three distinguishable processes a monolayer and multilayer adsorption, and capillary condensation.

To accommodate for such complexity a working combination of Henry and Sips model has been proposed by Kim et al. [141]. The empirical combination of the

original equations of Henry and Sips with a connecting β parameter is written in the following way:

$$q_e = \beta K_H \left(\frac{P}{P_0} \right) + (1 - \beta) \frac{q_0 \left(K_S \frac{P}{P_0} \right)^{1/n}}{1 + \left(K_S \frac{P}{P_0} \right)^{1/n}} \quad (4.1)$$

The right part of the Eq. 4.1 describes formally Langmuir-Freundlich isotherm model[90] and it can be found in literature in several modifications[94]. In the above equation the q_e is the adsorption amount at the equilibrium, q_0 is the maximum adsorption amount, and the K_H and K_S are Henry's and Sips' constants, respectively. The exponential factor n is then from the Langmuir-Freundlich model a measure of heterogeneity of the surface. The β parameter is dependent on the partial pressure through an exponential giving a final constant β_S :

$$\beta = e^{-\beta_S \frac{P}{P_0}} \quad (4.2)$$

In this form, the beginning of the adsorption is govern by site-controlled mechanism with limited adsorption at lower relative pressure. This combination was selected to describe two different process of adsorption on the example of aluminophosphate zeolite AQSOA FAM-Z02.

In this chapter two shapes based on the data from TMPS and SBA-15 and MCM-41 are shown corresponding to two isotherm types. Because of the high calcination temperature the prepared samples lack the silanol groups in general[142, 143]. This also explains the Type V shape instead of Type IV as in case of aluminium-free samples. Another problem arises from the actual pore sizes of the TMPS-1.5 and TMPS-1.5A samples which are on the boundary between microporous and mesoporous materials at 2 nm. To accommodate to this conditions some other approach has been tried as well.

4.3.2 Heat of adsorption

Heat of adsorption is an important thermodynamic property of any adsorbent/adsorbate system. To calculate the heat of adsorption or also referred to as the adsorption enthalpy ΔH° there are several options: use of a an adsorption model with defined energy calculation, calculation of equivalent isosteric heat of adsorption based on multi-isothermal experiment, and (micro)calorimetric measurement.

One of the more common methods is the isosteric heat of adsorption calculated by the conventional model often referred to as the Clausius-Clapeyron equation.

$$\Delta H_{st}^\circ = RT^2 \left\{ \frac{\partial \ln P}{\partial T} \right\}_{q^e} = -R \left\{ \frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \right\}_{q^e} \quad (4.3)$$

where R is gas constant, T is absolute temperature, P is actual adsorbate pressure and q^e is the isosteric adsorbed amount at equilibrium at which the adsorption heat is calculated. Rigorous explanation of this model was given by Sircar et al. [144]. The regression error of the isosteric lines fitting was calculated as a standard error of the estimate σ_{est} according to the Eq. 4.4.

$$\sigma_{est} = \sqrt{\frac{\sum (y - y')^2}{N}} \quad (4.4)$$

where y and y' represent the natural logarithm of pressure measured and calculated, respectively. N is then the number of individual data points which in our case represents the number of selected temperatures.

4.3.3 Kinetics models

Following the adsorption theory laid down by the classic models, the adsorption process can be described directly as a change of adsorbed amount on time. Depending on the method of introduction of the adsorbate to the system we talk about constant pressure experiment and constant or finite volume experiment. The first

mentioned is typical for gravimetric methods such as magnetic suspended balance systems, and the later describes a volumetric approach used in this work as well. The adsorption equilibrium in the isotherm experiment is typically realized in a stepwise process and the models are applied for each step individually. This allows to study the adsorption process in more details given the possibility that through the uptake the limiting factors affecting the adsorption process can change. So far the adsorption kinetics of water on microporous and mesoporous silica gel, as the closest equivalent to ordered mesoporous silica, were studied by Dawoud and Aristov [69], Aristov et al. [145], and others. The water adsorption kinetics on mesoporous silica were then studied for example by Yanagihara et al. [135] and Hwang et al. [132], however, the data on the adsorption kinetics on ordered mesoporous silica materials in the literature are scarce. To describe the adsorption process on mesoporous silica in this work, several models were selected and fitted according to the finite volume experiment described further on.

Pseudo-first order rate model (PFO) was firstly introduced by Sten Lagergren in his original work from 1898 [96] and it is primarily used for pure adsorption. The model builds on the same base as the first order chemical reaction rate, however, it was modified for sorption rate description because the sorption process basically follows the same mechanism as chemical reaction. The derivative form takes in account the states of the system before and after adsorption and any state in-between can be assessed by the time and rate constant:

$$\frac{dq_t}{dt} = k_{ft}(q_e - q_t) \quad (4.5)$$

where q_e is the adsorption at the equilibrium, k_{ft} is the pseudo-first order rate constant, q_t is the adsorption at a given point in time and t is the time. From the equation is apparent that once the $q_t = q_e$ the equilibrium is reached and there is no more change of the adsorbed amount. After the integration we get practical form of the equation:

$$\ln(q_e - q_t) = \ln q_e - k_{ft}t \quad (4.6)$$

often found in the literature in the form of a common logarithm:

$$\log (q_e - q_t) = \log q_e - \frac{k_{ft}}{2.303} t \quad (4.7)$$

This form is, however, not sufficient for the constant volume experiment and an extension has to be applied. A certain empirical consideration concerning pressure change can be added to accommodate for the pressure drop during the adsorption. We can consider that the actual adsorption rate is a ratio of the overpressure P compared to the pressure at equilibrium P_e . Based on the same relation from the pseudo-first order rate model, the pressure difference will be written as:

$$P_t = P_e e^{-\beta t} \quad (4.8)$$

The change and the influence of the pressure is decreasing with time and increasing P_e , hence the simple exponential function. The constant β then formulates the pressure change in respect to the adsorbed/desorbed amount similarly to the parameter α from Eq. 4.13. The combination of Eq. 4.7 and Eq. 4.8 will give the following relation:

$$\log (q_e - q_t) = \log q_e - \frac{k_P (P_e e^{-\beta t})}{2.303} t \quad (4.9)$$

After rearranging the final form takes the following shape:

$$q_t = q_e (1 - e^{-tk_P e^{-\beta t}}) \quad (4.10)$$

This modified model will be referred to as PFO2 further on.

Linear Driving Force model considers diffusion as the most important factor for the adsorption dynamics. For simplification it is usually described on a porous spherical particles. The derivation of the LDF model can be written as [106, 107]:

$$\frac{d\bar{x}(t)}{dt} = k_{LDF} (x^* - \bar{x}(t)), k > 0 \quad (4.11)$$

where $\bar{x}(t)$ is the average adsorbate concentration/amount in the particle of adsorbent and x^* is the adsorbate concentration/amount at the final equilibrium. The effective LDF mass transfer coefficient k_{LDF} is then typically given as follows [108]:

$$k_{LDF} = \frac{15D_0}{r_0^2} \quad (4.12)$$

where D_0 is the intra-particle diffusivity of the adsorbate and r_0 is the particle radius of the adsorbent. The whole relation is also based on the temperature uniformity through the volume of the particle at all times [109]. This means that not only the system isothermal conditions have to apply but local as well. The form of the kinetic approximation for constant volume experiment can be written:

$$f(t) = 1 - \exp\left(-k_{LDF}t \frac{1+\alpha}{\alpha}\right) \quad (4.13)$$

The additional constant α is necessary to describe the pressure change during the adsorption/desorption process. The fraction $\frac{1+\alpha}{\alpha}$ express the necessary molar quantity of adsorbate to be moved between the gas phase and the adsorbent at $t = 0$. The special case where $\alpha \rightarrow \infty$, hence $\frac{1+\alpha}{\alpha} = 1$, corresponds to the constant pressure experiments[109].

4.3.4 Error analysis and goodness of fit

To asses the quality of the model or goodness of fit, several method have been employed. As the standard method for goodness of fit was used the non-linear Chi-Square Test (χ^2) in the following form:

$$(\chi^2) = \sum_{i=1}^n \frac{(y_{cl} - y_{ex})^2}{y_{ex}} \quad (4.14)$$

where y_{cl} is the calculated value and y_{ex} is the experimentally measured value. The n then signifies the number of points. The problem with (χ^2) method is that it is supposed to be fit to data with certain distribution. In case that the model fits well and the distribution of the points is too small the results are small as well

and direct comparison can prove to be impractical.

For standard linear dependencies, the usual coefficient of determination R^2 was used to assess the correlation between the models and experimental data. The equation was used in the form:

$$R^2 = \frac{\sum (y_{cl} - y_{ex})^2}{\sum (q)} \quad (4.15)$$

To assess absolute fit of the calculated model on the experimental data an average absolute deviation (AAD(%)) was used as a direct measure for the data fitting. The AAD(%) was used in combination with generalized reduced gradient modelling method to find out the constants for non-linear models through continuous regression. The AAD(%) was used in its regular form:

$$AAD(\%) = \frac{\sum_{i=1}^n \frac{\|q_{cl} - q_{ex}\|}{q_{ex}}}{n} \quad (4.16)$$

The parameters of the function are identical to Eq. 4.14 of the χ^2 test.

4.4 Results and discussion

4.4.1 Fitting to adsorption models

The full adsorption/desorption isotherms for the analysis are provided in Fig. 4.2. Following the model from Kim et al. [141] the fitting of the adsorption model according to Eq. 4.1 is shown graphically in Fig. 4.3. The Eq. 4.1 can be further unfold to follow the thermodynamics of the adsorption depending on the pressure. It was already stated before that the connecting parameter β is an exponential function on P/P_0 with one constant β_S . The parameter β_S can be further defined

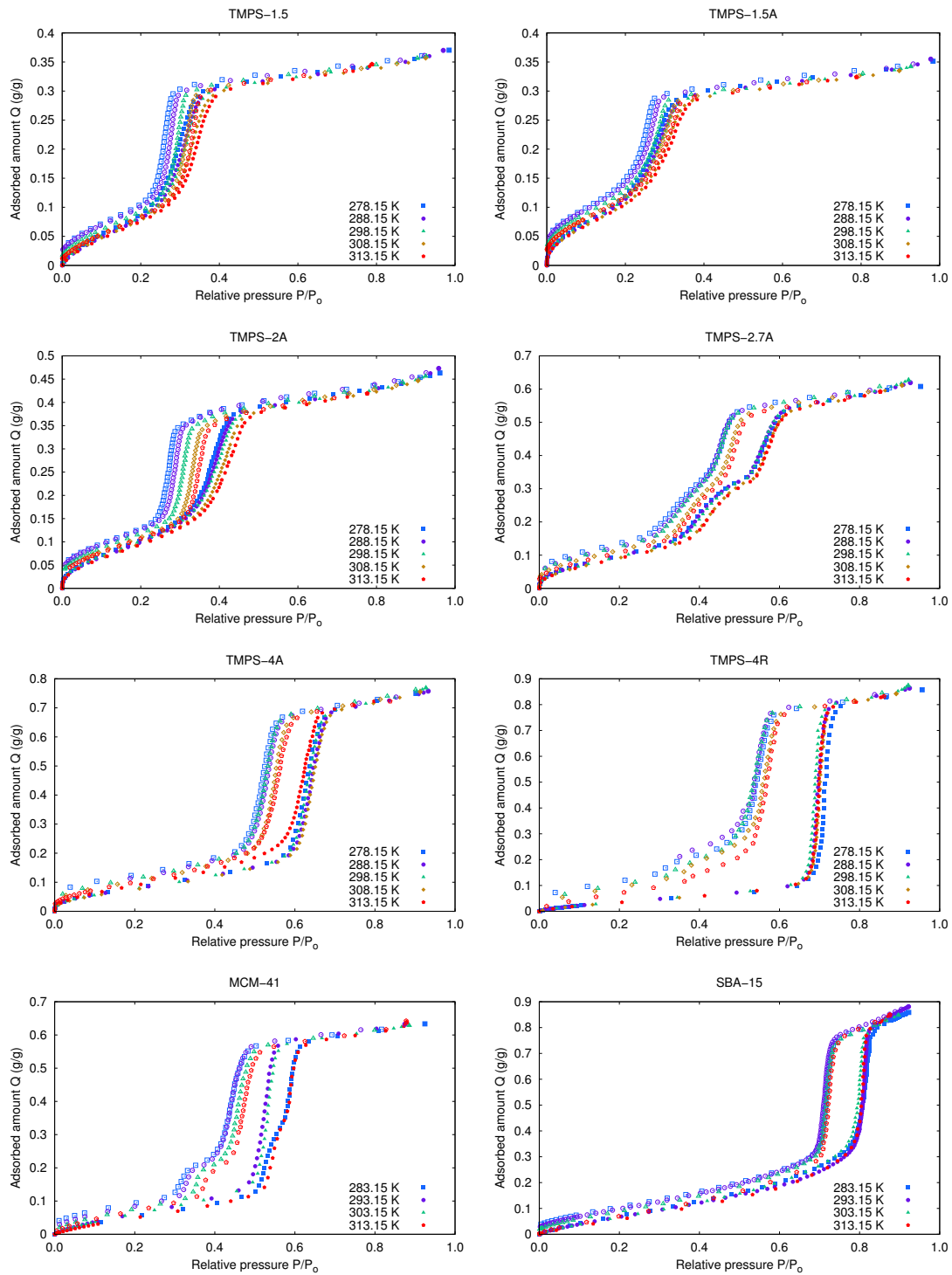


FIGURE 4.2: Adsorption isotherms of TMPS materials, and SBA-15 and MCM-41 over the relative pressure P/P_0 . Empty marks signify desorption.

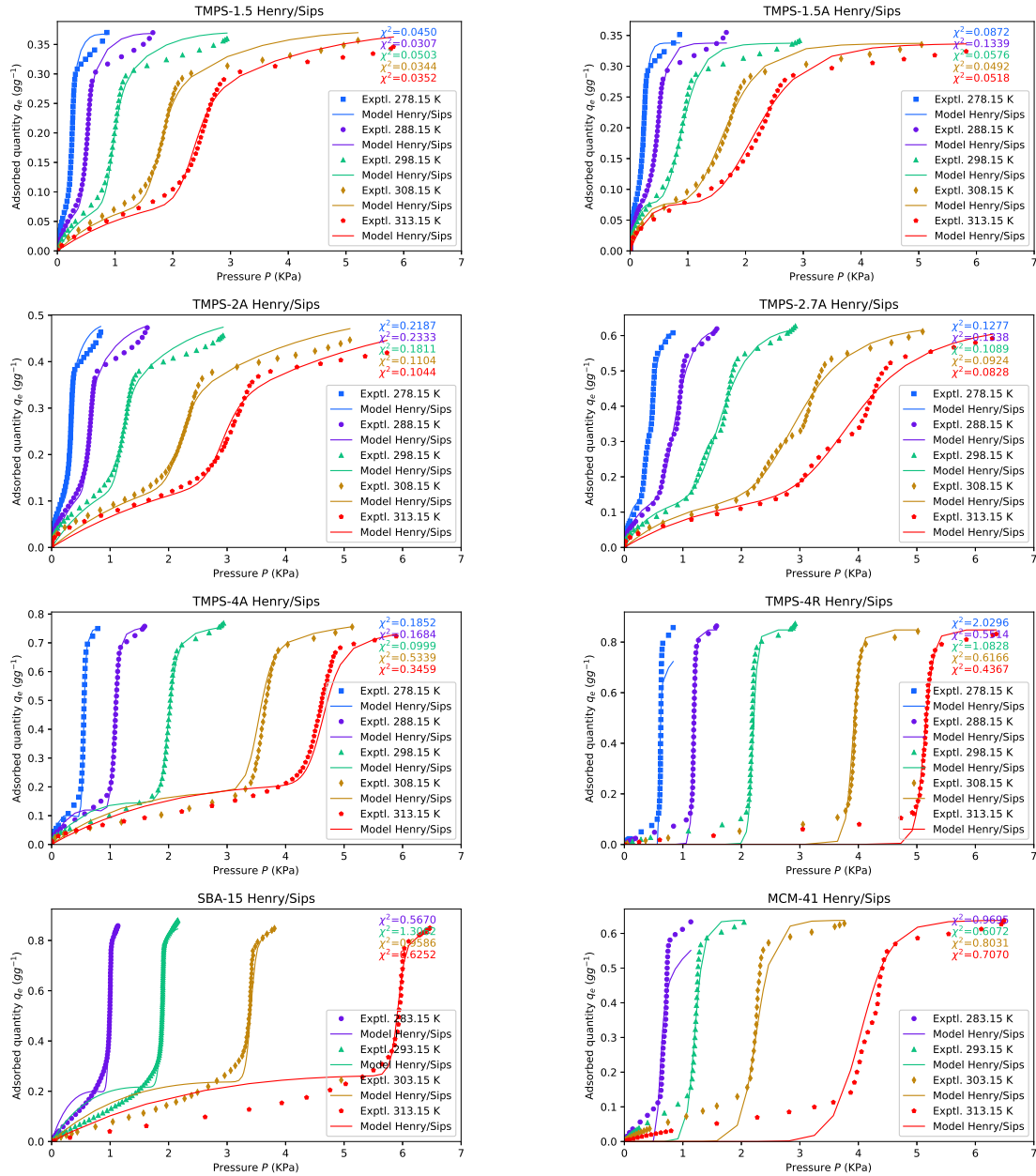


FIGURE 4.3: Fitting of the adsorption isotherm according to Henry/Sips model.

as a function of temperature T as:

$$\beta_S = e^{\beta_1 + \beta_2 \frac{T}{273.15}} \quad (4.17)$$

where β_1 and β_2 are the final fitting parameters. The Henry constant K_H and Sips constant K_S are defined traditionally based on the Arrhenius equation.

$$K_{H,S} = K_{0H,0S} e^{-\frac{\Delta H_{H,S}}{RT}} \quad (4.18)$$

where K_{0H} and K_{0S} are pre-exponential factors, and ΔH_H and ΔH_S are isosteric enthalpies of adsorption at zero loading for Henry equation and Sips equation, respectively. The exponential factor n accounting for the surface heterogeneity can be defined as a function of temperature as well:

$$n = a + \frac{b}{T} \quad (4.19)$$

where the a and b are the parameters of the linear regression. The final modelling was conducted by python script through a non-linear optimization based on least squares method implementing Levenberg-Marquardt algorithm. The maximum loading factor q_m was defined for each sample as an average value of all temperatures. The eight fitting parameters and the filling amount q_m are summarized in table 4.2.

It is apparent that the results vary significantly and that the model accuracy is decreasing with pore size. Because the model was specifically developed to accommodate the properties of aluminophosphate (AlPO) zeolites with micro pore filling the resulting goodness of fit described by χ^2 and AAD(%) is agreeable only in case of TMPS-1.5. Because the other samples are distancing further from the micropore region the applicability of Henry/Sips model becomes less accurate. As a good measure of the deviation can pragmatically also serve the Henry's and Sips' isosteric enthalpies, ΔH_H and ΔH_S , which under normal circumstances should be negative as the adsorption process is exothermic in its nature. Even though most of the samples meet this condition, except TMPS-4A and SBA-15, this is done mostly on a account of significant decrease in the fitting accuracy. Naturally, this is caused by the general application of the Sips' model which is intended to model a micropore filling as explained in the original work[141]. However, the 'S' shape of the other isotherm can be effectively modelled by this method, although, it can serve only as a certain simplification for the further modelling or simulation.

Another approach for the modelling can be taken from the perspective of the dependency of capillary condensation region and pore size distribution. Previously,

TABLE 4.2: Coefficients for Henry/Sips model

Sample	β_1	β_2	K_{0H}	ΔH_H (kJ/g)	K_{0S}	ΔH_S (kJ/g)	a	b	χ^2
Adsorption									
TMPS-1.5	11.16	-7.87	0.08	-38.75	1.10	-22.63	-0.187	79.95	0.20
TMPS-1.5A	8.54	0.59	1.54	-4.06	1.39	-19.23	0.260	-18.82	0.38
TMPS-2A	7.52	-5.48	0.18	-25.04	1.23	-15.68	-0.075	41.36	0.85
TMPS-2.7A	18.14	-14.07	0.01	-87.22	1.60	-4.45	-0.216	108.70	0.55
TMPS-4A	15.10	-11.83	0.86	0.00	1.59	0.00	-0.009	13.16	1.33
TMPS-4R	-1480	1456	-0.02	-51.04	1.38	-0.94	-0.048	20.09	4.72
SBA-15	5.35	-3.57	0.90	0.00	1.25	0.00	-0.078	27.77	3.46
MCM-41	-1410	1362	-0.03	-14.73	0.75	-19.23	0.050	3.92	3.09
Desorption									
TMPS-1.5	67.11	-56.80	0.00	229.34	0.68	33.55	-0.303	111.41	0.50
TMPS-1.5A	15.86	-4.73	0.27	47.25	0.88	30.04	0.504	-93.14	0.53
TMPS-2A	11.10	-8.36	0.11	39.47	0.39	44.04	-0.094	39.16	1.22
TMPS-2.7A	2.83	2.46	1.00	12.50	1.12	15.18	0.008	44.01	0.40
TMPS-4A	-0.19	1.84	0.74	4.22	1.07	11.70	0.067	-10.16	0.57
TMPS-4R	-2.61	4.03	1.02	0.00	1.04	11.82	-0.082	35.43	1.12
SBA-15	-0.25	1.50	0.86	0.00	1.24	2.49	-0.011	7.39	1.59
MCM-41	-0.04	1.73	0.38	16.04	0.92	18.49	-0.068	31.58	0.49

the TMPS materials were analysed on their volumetric-based pore size distribution according to DFT method and very good fit was observed with modified standard distribution function:

$$y(x) = \alpha \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (4.20)$$

where x is the pore size, α is a dimensional coefficient, and σ and μ are regular coefficients for the standard distribution function, where σ correlates to the range and μ is the position factor. Considering that the adsorption process for mesoporous materials is a combination of adsorption and capillary condensation we can write:

$$q_e = q_{ea} + q_{ec} \quad (4.21)$$

where the adsorption amount at equilibrium q_e is a sum of the regular adsorption q_{ea} and capillary condensation q_{ec} . By further developing this dependency it is possible to deduce a combination of standard adsorption model and condensation process based on the pore distribution. Firstly, it is necessary to rewrite the Eq. 4.20 into an integral form while $y(x) = q_{ec} \left(\frac{P}{P_0} \right)$:

$$\frac{dq_{ec}}{d\frac{P}{P_0}} = \alpha \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{\left(\frac{P}{P_0} - \mu\right)^2}{2\sigma^2}} \quad (4.22)$$

The boundary conditions of the Eq. 4.22 are logically stated for the states in which the isotherm is defined from $P/P_0 = 0$ to $P/P_0 = P/P_0$, while the upper limit is unity at full system saturation where $P = P_0$. The integration of this modified standard distribution then leads naturally to error function and after some algebraic manipulation we will get the cumulative condensation amount:

$$q_{ec} = \alpha \frac{1}{\sqrt{2}} \left[\operatorname{erf} \left(\frac{\frac{P}{P_0} - \mu}{\sqrt{2}\sigma} \right) + \operatorname{erf} \left(\frac{1 - \mu}{\sqrt{2}\sigma} \right) \right] \quad (4.23)$$

For the standard model have been tested the basic models such as Freundlich equation, Langmuir equation and their combination Langmuir/Freundlich equation when the best results are shown on the case of the last stated Langmuir/Freundlich model. The final combined form of the adsorption amount on relative

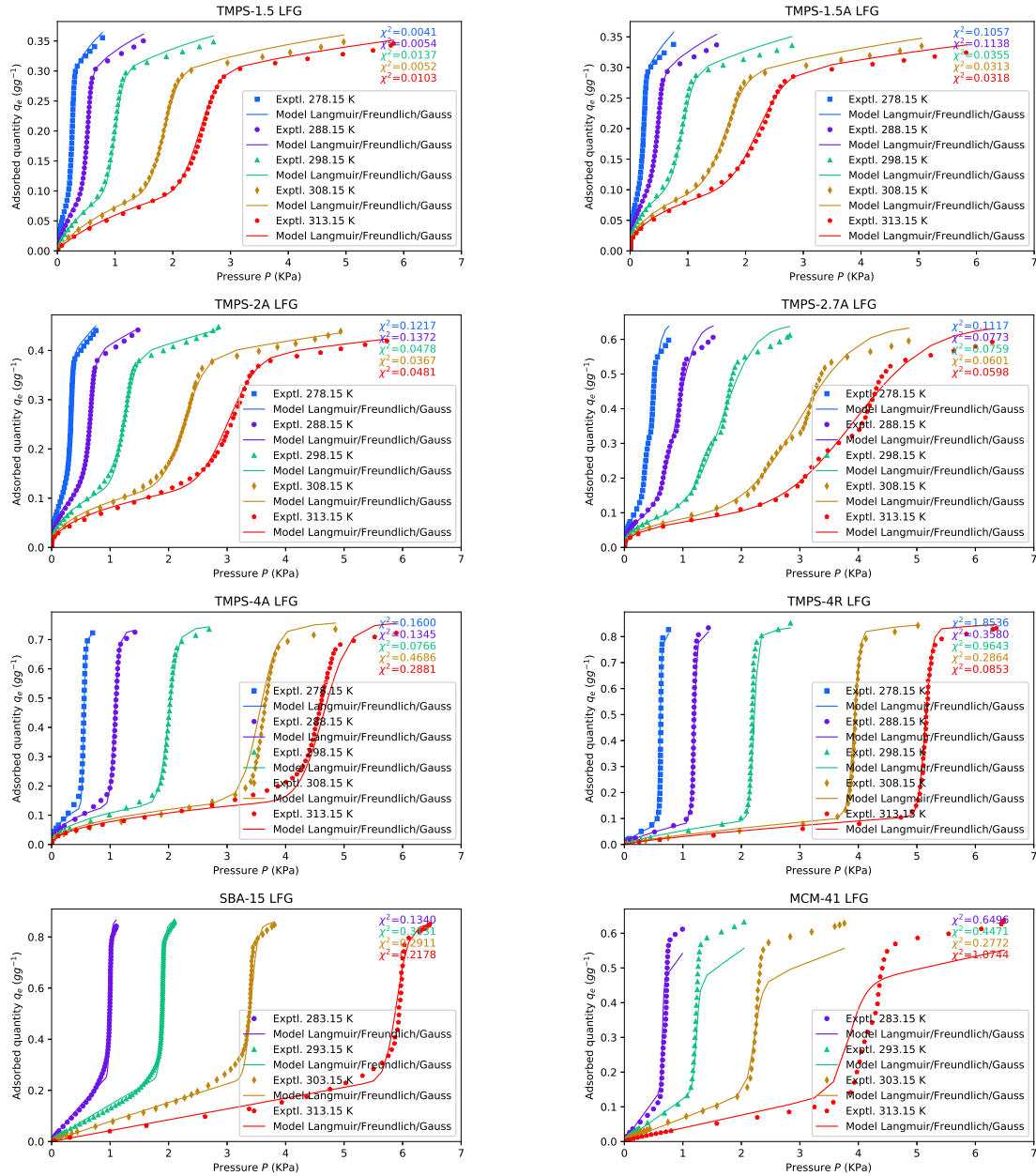


FIGURE 4.4: Fitting of the adsorption isotherm according to Langmuir-Freundlich-Gauss.

pressure then takes a form of Langmuir-Freundlich-Gauss (LFG) function:

$$q_e = \alpha \frac{1}{\sqrt{2}} \left[\operatorname{erf} \left(\frac{\frac{P}{P_0} - \mu}{\sqrt{2}\sigma} \right) + \operatorname{erf} \left(\frac{1 - \mu}{\sqrt{2}\sigma} \right) \right] + \frac{q_m \left(K_{LF} \frac{P}{P_0} \right)^{1/n}}{1 + \left(K_{LF} \frac{P}{P_0} \right)^{1/n}} \quad (4.24)$$

where the K_{LF} is the Langmuir/Freundlich constant, which serves the same purpose as the Sips' constant from Eq. 4.1. The individual constants from the Eq.

4.24 then can be given by the temperature dimension T according to their thermodynamic nature. Linear dependency can be expected from σ and n as their nature is based on the adsorbent rather than the adsorbate.

$$\sigma = \sigma_1 + \frac{\sigma_2}{T} \quad (4.25)$$

$$n = n_1 + \frac{n_2}{T} \quad (4.26)$$

The factors μ , K_{KL} describe the interaction between the adsorbent and adsorbate and their value is a thermodynamically driven, hence is their exponential nature.

$$\mu = \mu_0 e^{\frac{\mu_1}{T}} \quad (4.27)$$

$$K_{LF} = K_{LF0} e^{\frac{K_{LF1}}{T}} \quad (4.28)$$

The α and q_m are the property of the system and should independent on the temperature. However, in case of q_m it is more correct to talk about apparent maximum capacity, as it is not a true value, but rather an approximation of the model itself. The actual computation of the parameters was similar to the previous model with the only difference of adding weighting factors according to $\ln(\frac{P}{P_0})/N$, where N is the number of data point. This way a good fitting was ascertain for the regular Langmuir/Freundlich adsorption function as well.

The graphical representation of the LFG adsorption model compared to the experimental data is provided in Fig. 4.4 and the parameters are stated in Table 4.3. The visible improvement of the fitting is apparent from the χ^2 value which had been decreased in all cases. The better fitting can be also observed directly from the graphical output. Particularly good fit was achieved for samples TMPS-1.5, TMPS-1.5A and TMPS-2A which in general shows the most stable properties from the investigated samples. Poor fitting was observed in case of TMPS-2.7A which contains two distinguishable pore diameters which cannot be described by a simple individual standard distribution function in the first place.

TABLE 4.3: Coefficients for Langmuir-Freundlich-Gauss model for adsorption phase

Sample	α	σ_1	σ_2	μ_0	μ_1	K_{LF0}	K_{LF1}	n_1	n_2	q_m	χ^2
Adsorption											
TMPS-1.5	0.13	0.03	1.74	1.00	344.6	0.71	-107.4	0.58	202.24	0.37	0.04
TMPS-1.5A	0.12	0.08	-9.23	0.78	297.3	0.00	-565.3	2.37	-42.94	1.96	0.32
TMPS-2A	0.17	0.11	-19.13	0.84	225.6	0.00	-2056	2.73	-157.47	4085.0	0.39
TMPS-2.7A	0.35	0.03	33.12	0.71	90.17	0.05	-341.7	2.09	70.90	0.48	0.38
TMPS-4A	0.41	0.14	-29.29	0.62	-6.44	174	6735	-0.08	689.82	448.03	1.13
TMPS-4R	0.51	-0.13	46.02	0.68	-9.09	42.9	5984	0.01	399.84	22244	3.55
SBA-15	0.41	0.05	-7.80	0.69	-45.84	1.50	3752	-0.06	331.71	32126	0.96
MCM-41	-396	-1106	90558	0.51	7.28	2.30	56.53	0.20	-49.86	0.31	2.45

The problematic of mesopore filling is very complex and depends on many variables in general. It is clear that the fitting of the LFG model is not ideal and the thermodynamic properties of the system cannot be described by this method yet. However, the actual fitting shows very good results for using in simulation and points to an interesting direction for further development.

4.4.2 Adsorption kinetics

Fitting to adsorption kinetic models was attempted for all samples on all of their isothermal data. Altogether was analysed over 8 000 kinetic curves, over one thousand per sample. The original dependence presented in Fig. 4.5 as a function of adsorption amount q_t on time t . Due to the high density of the data and vast amount of individual steps the actual stepwise increase in the adsorption amount is barely apparent, yet still visible. From the aforementioned models in Chapter 2 only the LDF model stated in here for constant volume experiment and the PFO2 were successfully fitted to the data. An example of such fitting is shown in Fig. 4.6 corresponding to one adsorption step around the arbitrary chosen value of $q_e \approx 0.145 \text{ g g}^{-1}$ from the Fig. 4.5 for each sample. In the Fig. 4.6 can be seen on several occasions that the pressure starts below the Pe as the final pressure value at $t = t_{max}$. This is caused by the pressure sensor delay after opening the valve and it does not affect the actual adsorption process.

The data on the fitting of the models show that the better correlation was achieved by the PFO2 model. However, because the PFO2 model was not thermodynamically justified, the results needs to be carefully evaluated and the LDF model should be preferred. Because the adsorption rates k_L and k_P are given for each adsorption point it is necessary to summarize the output adequately. The cumulative graphs of the adsorption rates for each sample at at different temperatures are given in Fig 4.7 for all samples in the whole temperature rate. Four distinguishable regions are visible from the graphical representation of the adsorption rates. The first part can be differentiated in the beginning of the adsorption process and it is connected to forming of the first adsorption layer and hydration of the

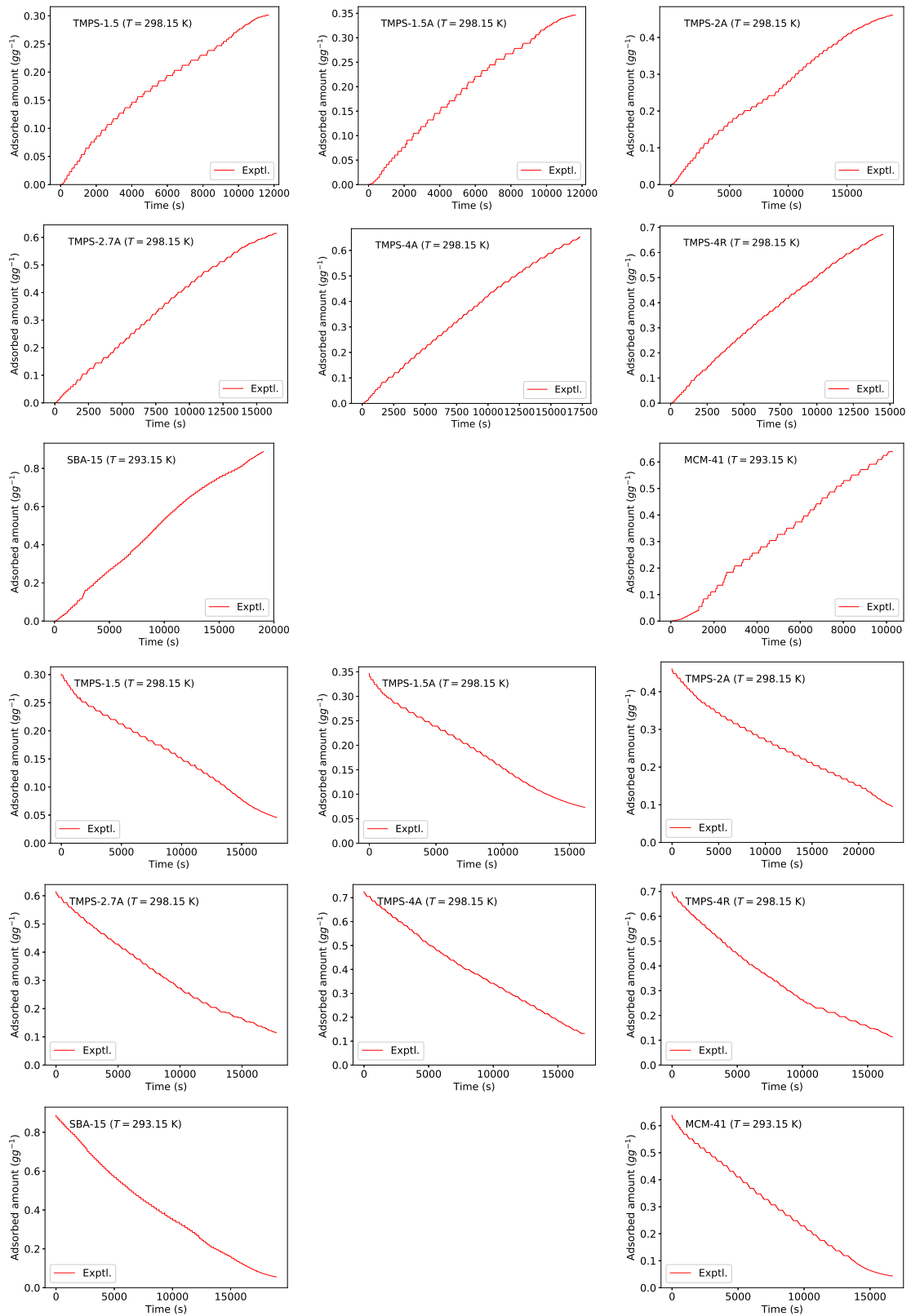


FIGURE 4.5: Dependence of step adsorption and desorption quantity on time at $T = 298.15$ K and $T = 293.15$ K (SBA-15, MCM-41)

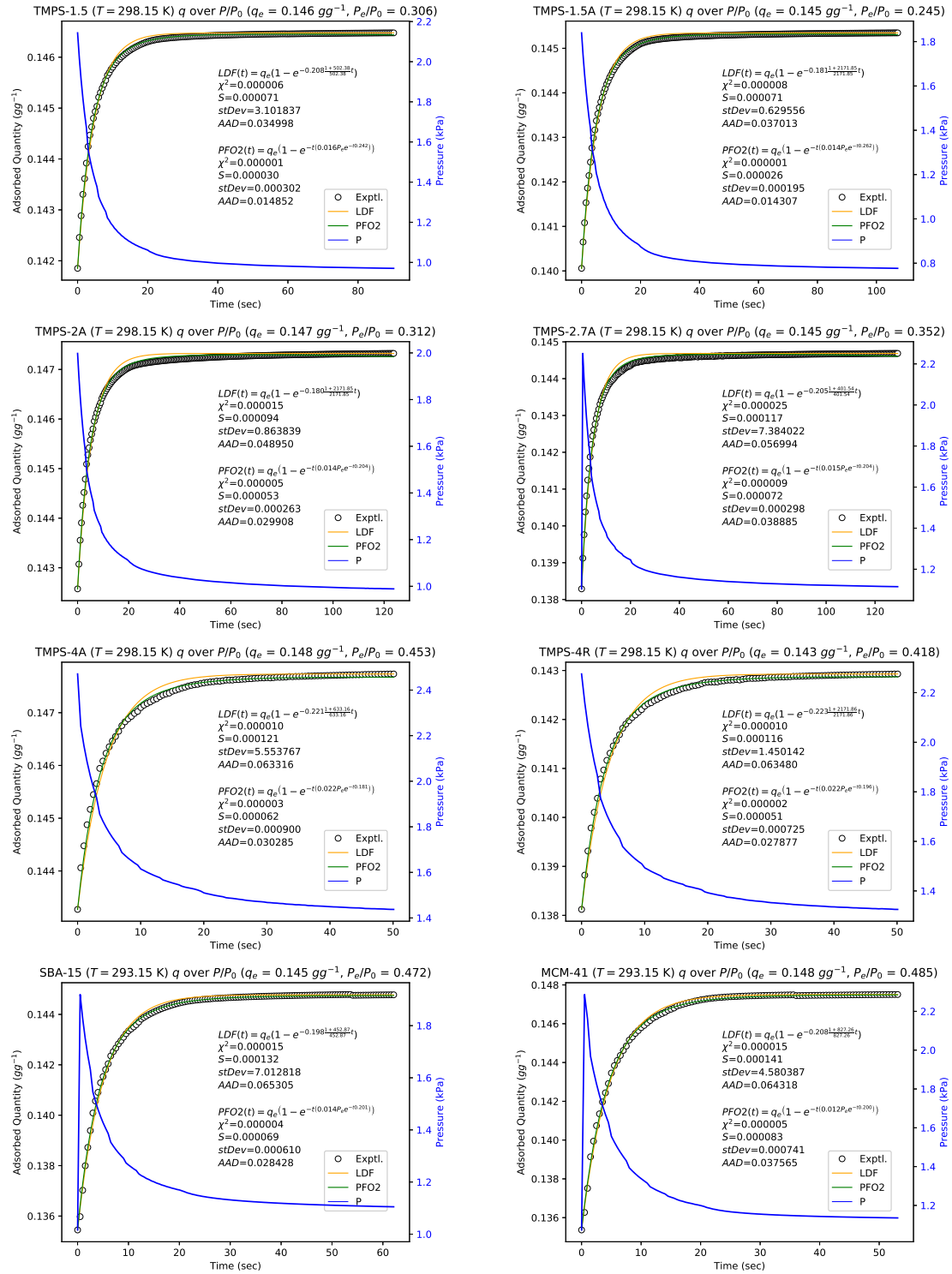


FIGURE 4.6: Isosteric heat of adsorption calculated according to the conventional CC model.

silica surface. The slow rate in the beginning can be explained by rapid heat generation during the adsorption process hindering the subsequent adsorption. The free surface of silica has considerably lower thermal capacity than water with low thermal conductivity and therefore, it can be easily saturated in the short time of the experiment (60 s to 120 s). This part is especially strong and visible for the aluminium-doped samples which in general has stronger water-adsorptive properties. After filling the part with highest adsorption potential the forming of the multilayer as the second region is signified by almost constant progress towards the capillary condensation. Third region is where the capillary condensation occurs and most of the uptake takes the place. The last, fourth, region is adsorption into bigger pores and on the plain surface of the particles. While adsorbing by small steps this region is typical by its high inconsistency in the adsorption rate. The adsorption rates were calculated for each region separately as k_{L1} to k_{L4} and k_{P1} to k_{P4} and for individual temperatures. The k_{L0} and k_{P0} are then the average values for the whole temperature range. The values are shown in Table 4.4 as natural logarithms.

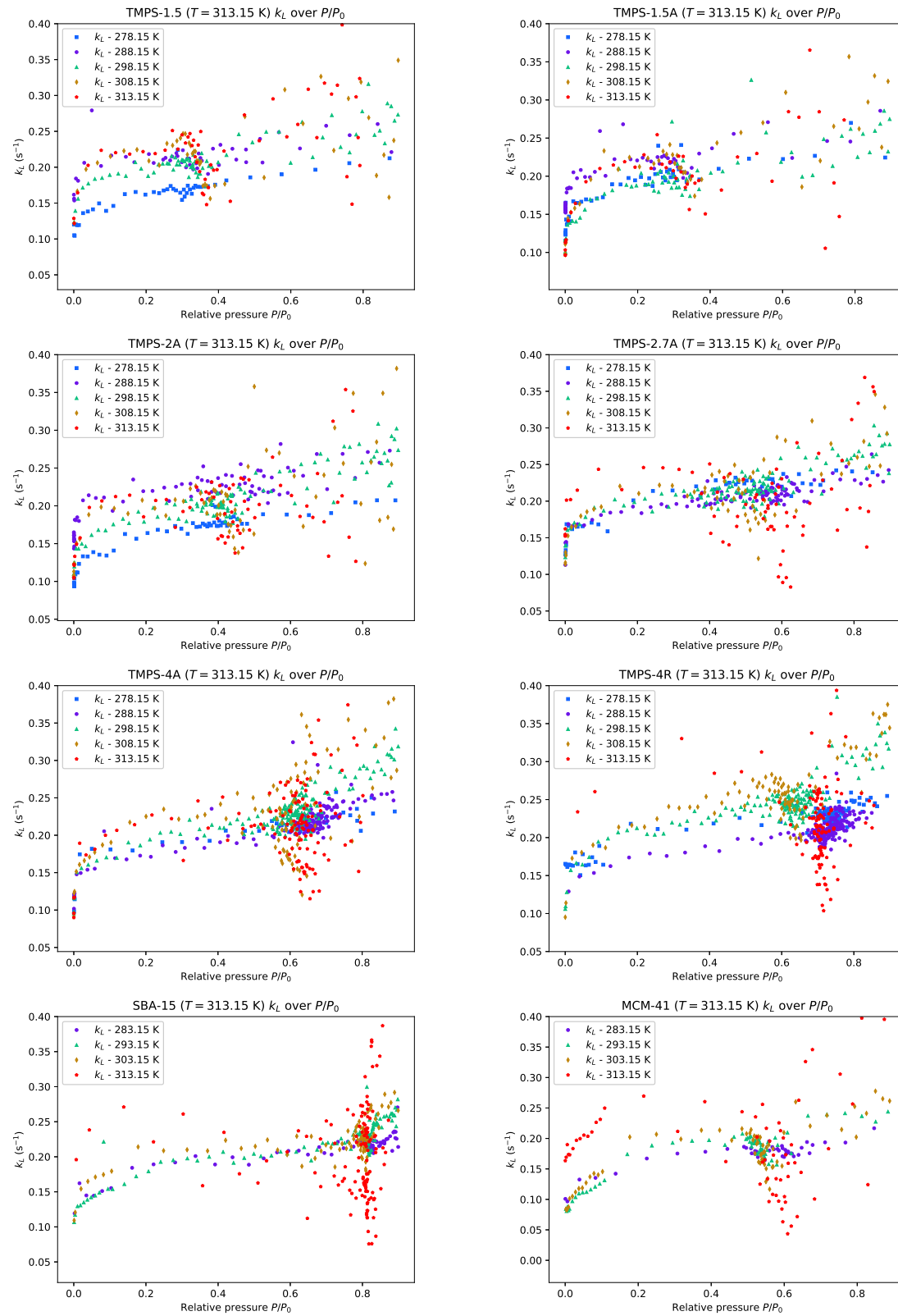
Activation energy of adsorption was attempted to calculate according to the know Arrhenius equation:

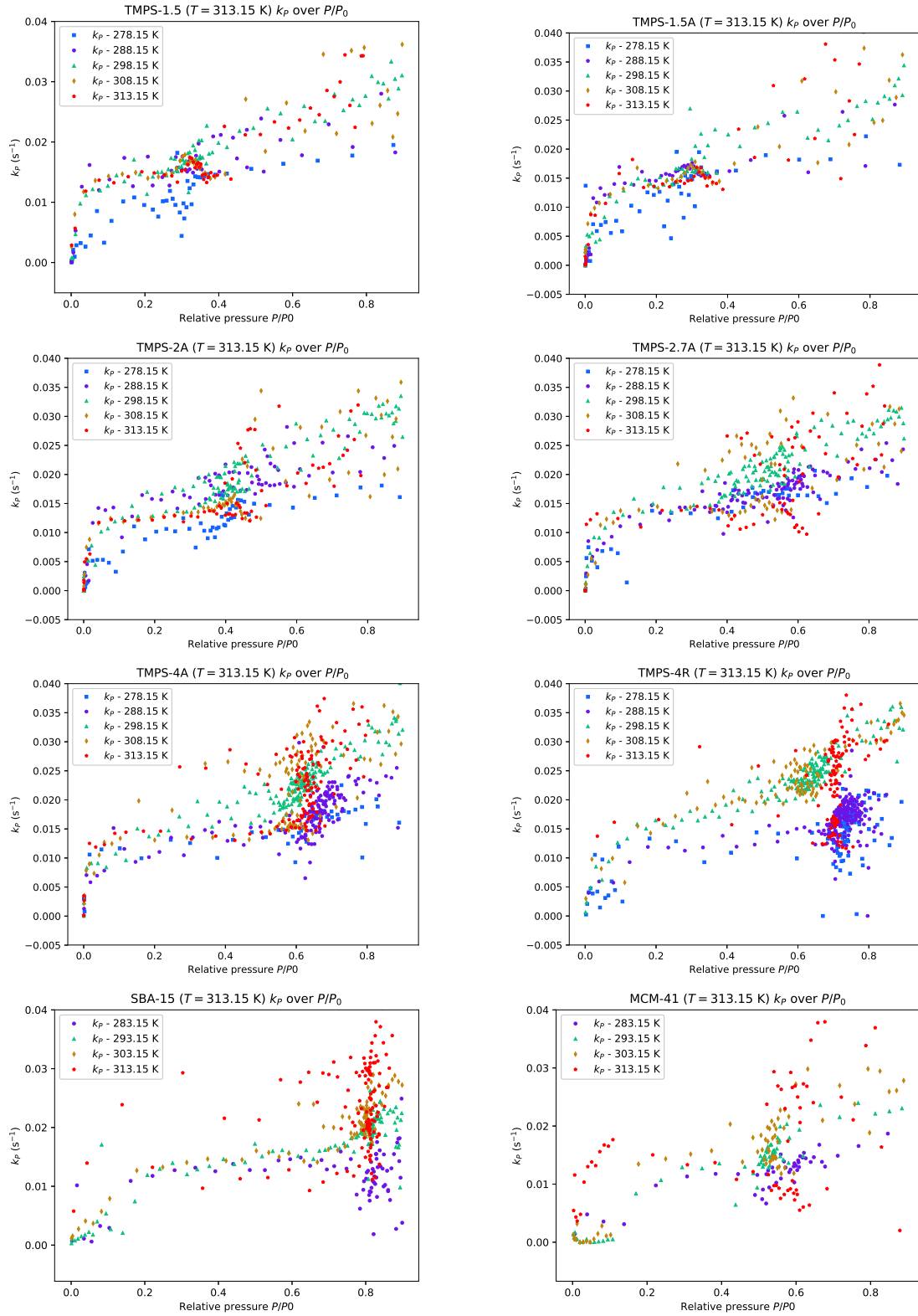
$$k = Ae^{-\frac{E_a}{RT}} \quad (4.29)$$

where k is the rate constant, E_a is the activation energy, A is the Arrhenius' pre-exponential factor, and R and T are the universal gas constant and absolute temperature, respectively. To calculate the activation energy the k_L constant based on the LDF model was used in the form:

$$\ln(k_L) = \ln(A) - E_a \frac{1}{RT} \quad (4.30)$$

The calculation was then based on the linear regression of the $\ln(k_L)$ over $1/T$. The results for the cumulative region 0 are shown in Table 4.5. Because the adsorption process is exothermic the activation energy is in negative form. The values can compare to the literature and are on the same magnitude[135]. Nevertheless, the

FIGURE 4.7: Adsorption rates k_L and k_P on the relative pressure

FIGURE 4.7: (Continued) Adsorption rates k_L and k_P on the relative pressure

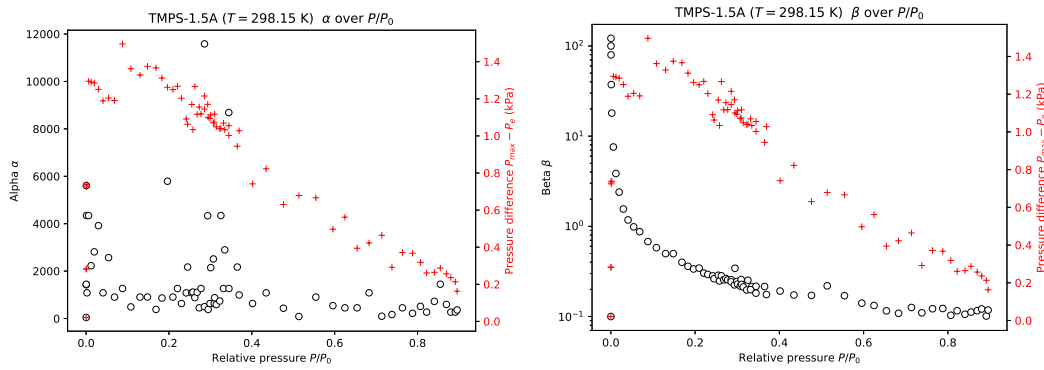


FIGURE 4.8: Comparison of α and β coefficients of adsorption rates with the initial pressure difference $P_{max} - P_e$ on the relative pressure P/P_0 for TMPS-1.5A at $T = 298.15$ K

values are fairly erratic and don't show any dependency on the pore size or a doping treatment. This is, however, understandable as the values of k_L are highly erroneous themselves. Even with the high number of adsorption steps the variation is very high and any accurate processing is unlikely. It is possible that because in the constant volume experiment the process is pressure driven the temperature dependency is disturbed and the adsorption rate does not follow the regular path. This is also supported by the resulting α values which are in no correlation to the actual pressure difference of the individual adsorption step as can be seen on the example in Fig. 4.8. From this point of view the calculation of activation energy and adsorption rate in the finite volume experiment is successful only partially and will be a subject of a future research together with constant pressure method. The graphical data output on desorption are provided in Appendix B.

4.4.3 Heat of adsorption

The calculation of the conventional model's isosteric heats of adsorption was performed on the original data and it exhibits typical values expected from silica materials shown in Fig. 4.9. Even though the acquired raw data were particularly dense for the purpose of this calculation, it is not possible to measure the adsorption at the exact point every time and the actual isosteric heats of adsorption were obtained from interpolated dataset. The univariate interpolation of the data for the purpose of Eq. 4.3 was performed by consecutive third polynomials as a cubic

TABLE 4.4: Adsorption rates k_L and k_P for different temperatures and different adsorption regions (1-4 and 0 as a average value)

T (K)	$\ln k_{L0}$	$\ln k_{L1}$	$\ln k_{L2}$	$\ln k_{L3}$	$\ln k_{L4}$	$\ln k_{P0}$	$\ln k_{P1}$	$\ln k_{P2}$	$\ln k_{P3}$	$\ln k_{P4}$
TMPS-1.5										
278.15	-1.821	-2.117	-1.882	-1.766	-1.633	-4.634	-6.361	-4.870	-4.480	-4.086
288.15	-1.549	-1.643	-1.561	-1.560	-1.474	-4.177	-5.115	-4.272	-4.135	-3.921
298.15	-1.581	-1.874	-1.652	-1.596	-1.382	-4.059	-5.217	-4.284	-4.082	-3.632
308.15	-1.513	-1.821	-1.527	-1.552	-1.377	-4.054	-4.898	-4.242	-4.153	-3.638
313.15	-1.483	-1.815	-1.510	-1.552	-1.338	-4.007	-4.991	-4.265	-4.185	-3.664
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.2	3:	0.2-0.4	4:	0.4-0.8
TMPS-1.5S										
278.15	-1.701	-1.961	-1.707	-1.594	-1.468	-4.623	-5.967	-4.729	-4.298	-3.975
288.15	-1.601	-1.777	-1.506	-1.523	-1.401	-4.409	-5.104	-4.250	-4.122	-3.915
298.15	-1.658	-2.076	-1.710	-1.626	-1.453	-4.153	-5.712	-4.358	-4.071	-3.719
308.15	-1.589	-2.055	-1.534	-1.546	-1.333	-4.208	-5.314	-4.271	-4.161	-3.693
313.15	-1.597	-2.083	-1.562	-1.591	-1.402	-4.112	-5.804	-4.246	-4.216	-3.590
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.2	3:	0.2-0.4	4:	0.4-0.8
TMPS-2A										
278.15	-1.858	-2.238	-1.861	-1.727	-1.650	-4.693	-6.530	-4.761	-4.376	-4.146
288.15	-1.554	-1.798	-1.531	-1.480	-1.445	-4.167	-5.021	-4.220	-3.988	-3.848
298.15	-1.612	-2.033	-1.691	-1.601	-1.403	-4.043	-5.659	-4.252	-3.996	-3.644
308.15	-1.610	-2.003	-1.621	-1.607	-1.379	-4.169	-5.496	-4.373	-4.130	-3.700
313.15	-1.642	-1.992	-1.606	-1.645	-1.527	-4.126	-5.523	-4.400	-4.111	-3.789
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.3	3:	0.3-0.5	4:	0.5-0.8
TMPS-2.7A										
278.15	-1.571	-1.850	-1.638	-1.497	-1.474	-4.301	-5.399	-4.583	-4.103	-4.023
288.15	-1.595	-1.887	-1.642	-1.573	-1.525	-4.148	-5.639	-4.310	-4.092	-3.924
298.15	-1.553	-1.904	-1.607	-1.537	-1.398	-3.947	-5.553	-4.151	-3.873	-3.642
308.15	-1.581	-1.911	-1.569	-1.575	-1.368	-4.050	-5.574	-4.154	-3.922	-3.776
313.15	-1.650	-1.737	-1.449	-1.664	-1.681	-3.958	-3.934	-4.315	-4.002	-3.791
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.4	3:	0.4-0.6	4:	0.6-0.8
TMPS-4A										
278.15	-1.578	-2.035	-1.609	-1.528	-1.484	-4.235	-5.445	-4.382	-4.091	-4.058
288.15	-1.550	-2.037	-1.649	-1.523	-1.447	-4.085	-5.534	-4.307	-4.037	-3.864
298.15	-1.503	-2.036	-1.538	-1.463	-1.296	-3.861	-5.323	-3.957	-3.758	-3.560
308.15	-1.508	-1.901	-1.539	-1.447	-1.324	-3.880	-5.003	-3.966	-3.717	-3.606
313.15	-1.542	-2.030	-1.520	-1.550	-1.388	-3.818	-5.270	-3.926	-3.776	-3.515
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.6	3:	0.6-0.7	4:	0.7-0.8
TMPS-4R										
278.15	-1.513	-1.798	-1.631	-1.476	-1.456	-4.345	-5.392	-4.716	-4.291	-4.092
288.15	-1.570	-1.974	-1.694	-1.577	-1.501	-4.114	-5.307	-4.413	-4.097	-4.052
298.15	-1.427	-1.930	-1.471	-1.380	-1.125	-3.786	-5.400	-3.941	-3.647	-3.416
308.15	-1.404	-1.860	-1.389	-1.418	-1.155	-3.808	-4.967	-3.866	-3.676	-3.492
313.15	-1.512	-1.453	-1.235	-1.562	-1.261	-3.770	-4.287	-3.849	-3.779	-3.540
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.65	3:	0.65-0.75	4:	0.75-0.8
SBA-15										
283.15	-1.646	-1.951	-1.641	-1.527	-1.512	-4.550	-5.523	-4.447	-4.467	-4.419
293.15	-1.648	-2.051	-1.633	-1.466	-1.439	-4.397	-6.696	-4.354	-3.915	-3.906
303.15	-1.565	-1.985	-1.578	-1.484	-1.442	-4.090	-6.038	-4.183	-3.821	-3.752
313.15	-1.583	-1.527	-1.564	-1.597	-1.571	-3.854	-4.619	-3.890	-3.736	-3.712
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.75	3:	0.75-0.85	4:	0.85-0.90
MCM-41										
283.15	-1.744	-2.166	-1.778	-1.725	-1.665	-4.453	-5.774	-4.725	-4.388	-4.199
293.15	-1.761	-2.370	-1.771	-1.682	-1.430	-4.428	-7.390	-4.882	-4.163	-3.770
303.15	-1.766	-2.310	-1.711	-1.725	-1.489	-4.265	-7.252	-4.578	-4.049	-3.726
313.15	-1.721	-1.695	-1.492	-1.903	-1.374	-4.113	-4.881	-4.240	-4.084	-3.594
P/P_0	0:	0-0.8	1:	0-0.05	2:	.05-0.5	3:	0.5-0.65	4:	0.65-0.8

TABLE 4.5: Activation energy of adsorption - average values for k_P

Sample	Slope	Intercept	E_a (kJ mol ⁻¹)	A (s ⁻¹)
TMPS-1.5	-710.69	0.8071	-106.36	2.241
TMPS-1.5A	-220.20	-0.8868	-32.95	0.412
TMPS-2A	-408.89	-0.2764	-61.19	0.759
TMPS-2.7A	(118.01)	-1.9879	(17.66)	0.137
TMPS-4A	-126.20	-1.1107	-18.89	0.329
TMPS-4R	-196.36	-0.8232	-29.39	0.439
SBA-15	-241.52	-0.7992	-36.15	0.450
MCM-41	-54.41	-1.5652	-8.14	0.209

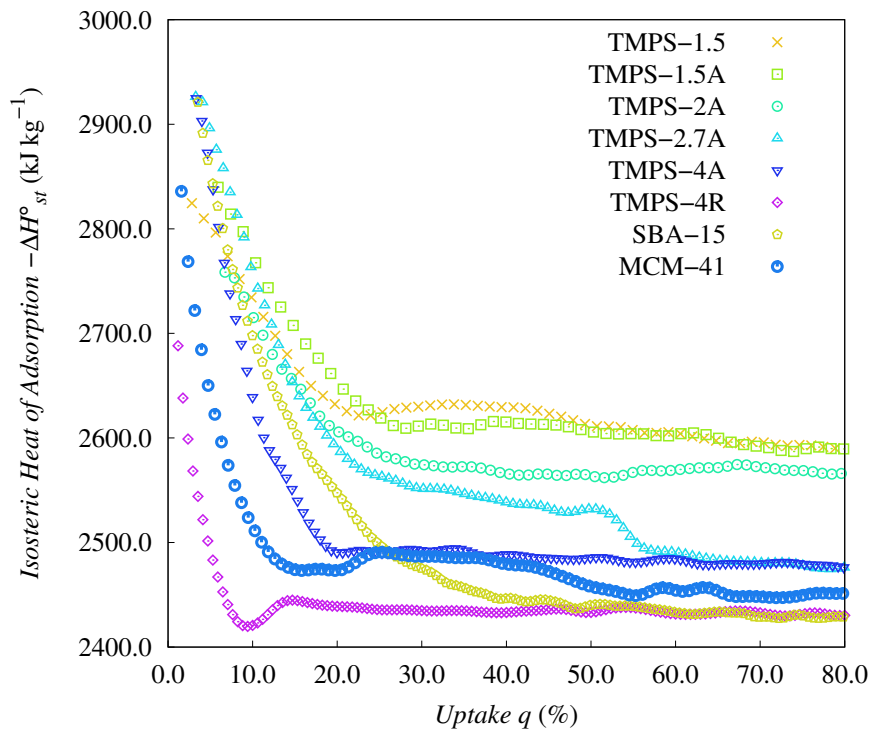


FIGURE 4.9: Isosteric heat of adsorption calculated according to the conventional CC model.

spline interpolation.

From the results is apparent that the adsorption energies are significantly higher at lower adsorption quantities. This is a natural phenomenon connected to the properties of the silica surface. The energy released during the adsorption is equal to the adsorption potential which was originally defined as an adsorbent/adsorbate interaction. The free surface of many materials has usually some excessive chemical potential build up on the boundary of the substance caused by an inequality

of chemical bonds in and out of the material. Plain surface of silica material has this property as well and depending on the actual conditions it has lower or higher potential to adsorb water molecules. The regular structure of silica on the surface can take several basic forms of condensed and hydroxylated coordination[126]. The amount of the more water-attractive hydroxylated form can significantly affect the water adsorption properties. The effect of calcination temperature on the amount of these silanol (-Si-OH) groups on SBA-15 was studied in detail by Ojeda-López et al. [143] determining the optimal calcination temperature to 450 °C. But not only the content of silanol groups affect the water affinity. As was explained before the presence of other substances, impurities, in the structure can create the desirable effect and enhancing the surface potential energy for water molecules adsorption. From this perspective, the specimens with aluminium content show higher adsorption enthalpies reaching to 3000 kJ kg⁻¹. With the progressing adsorption and fully covering the surface the prevalent interaction becomes more adsorbate/adsorbate and the isosteric heat of adsorption drops to the point where it is almost only affected by the pore diameter. Hence, the capillary condensation section is indicated by invariable energy on water uptake, while the isosteric adsorption heat is proportional to the pore diameter. This proportionality is given due to the change in surface energy caused by the curvature of the free liquid surface influencing the vapour pressure over the liquid surface as described by the Kelvin equation:

$$\ln \frac{P}{P_0} = -\frac{2H\gamma V_l}{RT} \quad (4.31)$$

where $\frac{P}{P_0}$ is the relative pressure, H is the curvature of the meniscus in the capillary, γ is the surface tension of the liquid nitrogen, the V_l is the molar volume of liquid nitrogen. The R and T are the usual universal gas constant and absolute temperature, respectively. This can be clearly observed on the example of TMPS-2.7A which contains two significant pore diameters. Once the adsorption quantity reaches the full filling of the smaller pores (the diameter is approximately 0.5 nm smaller than the main pores) at the 50 % of total filling, the isosteric heat of adsorption drops from some 2530 kJ kg⁻¹ to 2490 kJ kg⁻¹ and then slowly continues

to drop to the level of TMPS-4A. The effect of the aluminium addition can be also seen on the comparison to MCM-41. Thanks to the limited affinity towards water the MCM-41 can basically form only a thin monolayer-like layer of water molecules consequently changing the effective pore radius only a little. Thus, the MCM-41 has lower isosteric heat of adsorption compared to aluminium-doped TMPS-4A despite the bigger pore radius of TMPS-4A. The aluminium addition enhances the water affinity creating a thicker layer of water molecules which reduces the effective pore radius. Similar situation is observed on the example of TMPS-4R and technically with SBA-15 as well. The difference between aluminium-doped TMPS-1.5A and aluminium-free TMPS-1.5 at higher adsorption quantities is due to the pore size beyond the mesopore region 2 nm negligible.

An exception from the selected samples is the SBA-15 sample with the obvious presence of micropores in the wall structure. This property was observed in several studies[146, 147] and it seems that it is an integral part of the SBA-15 mesoporous silica materials prepared by triblock copolymers, such as Pluronic 123 from this work. The resulting shape of the isosteric heat of adsorption is then somehow similar to silica gel as reported by Chakraborty et al. [70] when the standard surface adsorption and micropore filling are concurrent to each other. All the samples were well above the condensation enthalpy of water which is at 40 °C approximately 2400 kJ kg⁻¹.

4.5 Conclusion

Six samples from the TMPS family of mesoporous silica were studied together with a standard SBA-15 and MCM-41 for their water-adsorptive properties. The effect of pore size, pore volume and aluminium doping was observed.

An attempt to fit the acquired adsorption isotherms into a mathematical expression was conducted on two models Henry/Sips from the work of Kim et al. [141] and combined Langmuir/Freundlich/Gauss as an original attempt of this work. The fitting of sigmoidal, or also called S-shape, isotherms is usually connected

to at least two separate adsorption processes and in this work the Type IV and Type V isotherms were positively identified on the aluminium doped and pure silica samples, respectively. The first Henry/Sips model fits well isotherms with the region of change before $0.5 P/P_0$. After that the *beta* parameter based on the exponential of P/P_0 cannot fit well and overwhelmingly preferring one model on the expenses of the other. The resulting enthalpies of Henry's isotherm ΔH_H and Sips' isotherm ΔH_S at zero coverage are then of reasonable magnitude, however without any significant correlation. Although, the enthalpy of Sips' isotherm ΔH_S exhibit a certain correlation to the pore size.

The original Langmuir/Freundlich/Gauss isotherm presented in this chapter provides significantly better fit to the experimental data and performs well in the whole region of the relative pressure. The proposed model is highly suitable for mesoporous materials with narrow pore size distribution, however, because of the nature of the model, it is not suitable for Type VI isotherm which can be seen on the example of TMPS-2.7A and partially MCM-41 showing such properties.

Kinetic data on the water adsorption in the finite (constant) volume experiment were analysed according to the linear driving force and modified pseudo-first order rate adsorption kinetic models. Despite the sufficient fitting of the LDF model and superior fitting of the modified PFO model, the resulting values provides little new information on the adsorption characteristics. The finite volume experiment and the consequent data analysis will require more attention in the future work.

Adsorption enthalpy was established based on the experimental data using the Clausius-Clapeyron equation as isosteric heat of adsorption. The volumetric apparatus 3Flex used in this work can provide in very short time very dense isotherm data points which is especially suitable for the Clausius-Clapeyron equation. For the calculation were used 5 different temperature points in case of TMPS materials and 4 temperature points for SBA-15 and MCM-41 for each isosteric regression. Because it is not practical to acquire the points at the same adsorption equilibrium

q_e for all the temperature dependencies, the differences were interpolated through an mathematical operations (consecutive third polynomials used in a cubic spline interpolation). The results show predicted behaviour, when the aluminium doped samples exhibit higher isosteric adsorption heat during the first phases of the adsorption due to the enhanced affinity towards water. The continuing heat release is then directly proportional to the effective pore size driving the pressure drop over the water surface during the capillary condensation phase.

Chapter 5

System Evaluation Based on the Pure Materials

5.1 Introduction

Ordered mesoporous silica materials have some advantages over more common silica gels in adsorption pore capacity and pore size control. When the regular silica gels have adsorption capacity of water usually around 0.3 g g^{-1} to 0.4 g g^{-1} as measured by Chua et al. [148], several researches shown [135, 149] that typical mesoporous silica can reach over 0.8 g g^{-1} of water adsorption depending on the template and preparation process. Hence, from the perspective of air conditioning an interesting trait is the possibility of adjusting the pore size, as the pore size, together with the surface properties, is responsible for the shape of the adsorption isotherm. Therefore, by adjusting the pore size we are able to adjust the temperature gain or air humidity much more precise than with regular silica gel. The versatility of the preparation process is also demonstrated by several researches reporting successful creation of doped mesoporous silica further adjusting the adsorption properties. The zircon atoms were introduced into the mesoporous silica structure by Hwang et al. [132] without significant change in the adsorption properties of water. Different approach to enhance the water adsorption properties was used by Kim et al. [14], when the aluminium was not introduced into the material

during the preparation process but rather as a post-treatment. As mentioned before, the aluminium introduced into the structure of silica creates an acidic points which then work as attraction spots for polar substances such as water [150]. The results presented by Kim et al. [14] show high water adsorption values together with increased hydrothermal stability with the used precursor MCM-41 material. In this chapter the author will show for the first time the potential of the TMPS mesoporous silica for the purpose of heat storage applications. The TMPS materials are artificially tailored ordered mesoporous silica with narrow pore size distribution with several aluminium doped specimens. The process of aluminium

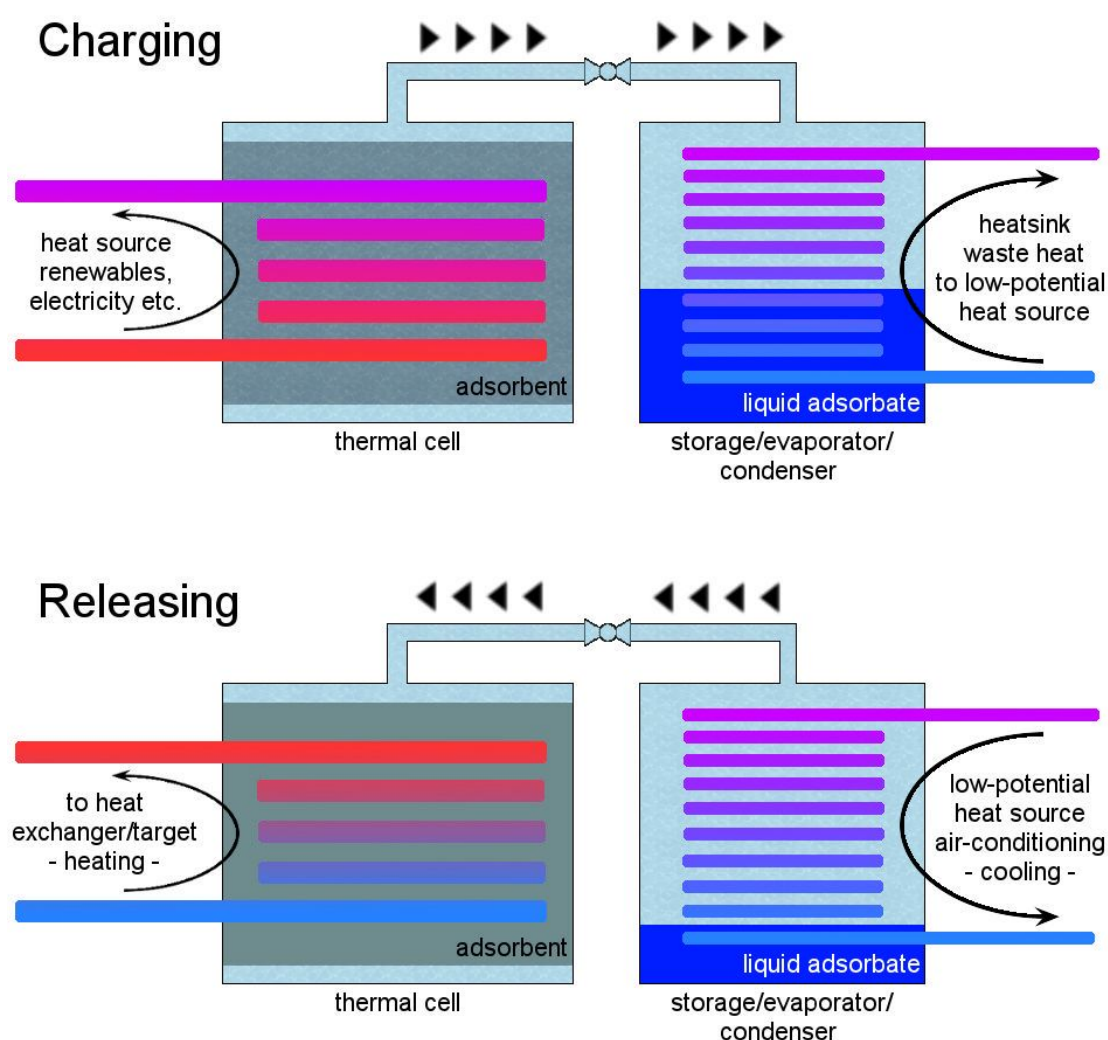


FIGURE 5.1: Working schema of adsorption thermal energy storage

doping is in the case of TMPS incorporated directly into the manufacturing process, thus creating an easier and cheaper way of doping together with claimed enhanced hydrothermal stability compared to regular mesoporous silica materials.

5.2 Materials and methods

5.2.1 Materials

The examined materials in here were TMPS-1.5, TMPS-1.5A, TMPS-2A, TMPS-2.7A, TMPS-4A and TMPS-4R. The number in the back of the material designation then roughly represents the pore size. According to the manufacturing process, the pore size can be freely changed in the range of 1.5 nm to 7 nm, however pore sizes over 4 nm are not considered in this work as practically not applicable for the purposes of heat storage in their pure form.

Here as well, all the materials were used in their original form as acquired from the manufacturer without any further adjustments. Detailed structure of the particle cells of TMPS-1.5A and TMPS-4A can be observed on the SEM images in Fig. 5.2. The appearance of all the samples was similar with a common approximate particle size of 50 nm to 200 nm and tendency to aggregate as a typical trait of non-stabilized nanoparticles.

The information on surface area, pore volume, pore size and bulk density of the used materials are listed in the previous chapter in Table 4.1. For the material characterisation were used nitrogen adsorption data measured at typical temperature of $T = 77$ K. For the surface area was used the BET multipoint approach. The pore size was calculated through density functional theory (DFT) method, and the pore volume was calculated through the maximum nitrogen adsorbed volume, disregarding the dead volume as a practically irrelevant.

Ultrapure water was used as a vapour source for the adsorbate and before the measurement was thoroughly degassed in very low temperature in liquid nitrogen.

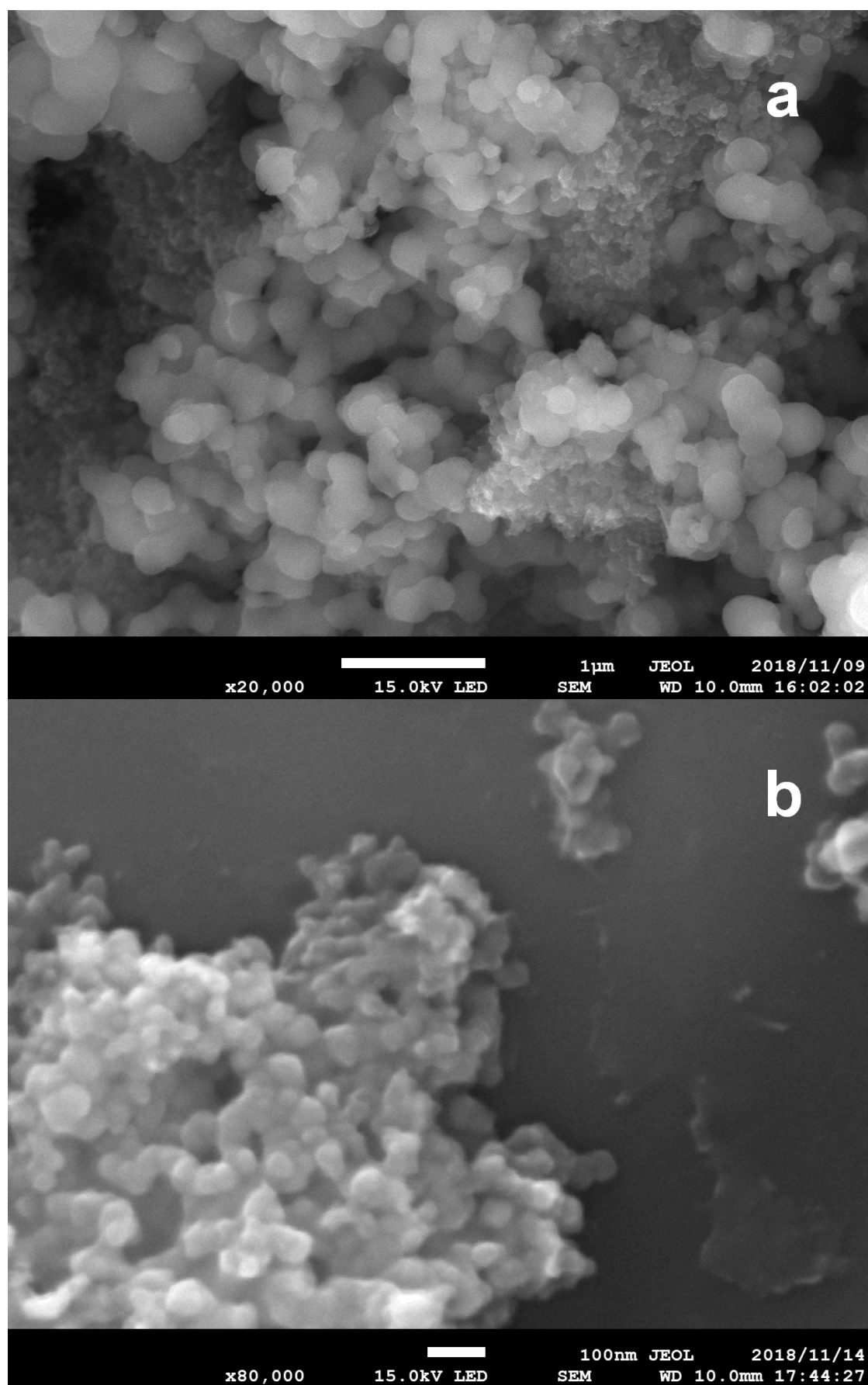


FIGURE 5.2: SEM images of TMPS-1.5A (a) and TMPS-4A (b)

The quality of the vapour source was verified by its vapour pressure at a set temperature.

5.2.2 Methods

To establish the general relations between the water adsorbate and the mesoporous silica samples the adsorption isotherms were measured volumetrically on 3Flex surface characterisation analyser (Micromeritics, US) at three different temperatures $T = 288.15\text{ K}$, 298.15 K and 308.15 K . The preparation for the measurement of the adsorption isotherms consisted of two degassing phases. In the first phase the approximate amount of the sample was inserted into weighted testing tube and degassed for 5 hours at 200°C in high vacuum (at least $p < 0.02\text{ Pa}$). After the first degassing phase the test tube was weighted again this time together with the sample and the weight of the pure and degassed material was calculated. The samples were once again degassed prior to the actual measurement for several hours at 200°C until the residue pressure of the previously adsorbed substances was $p < 0.1\text{ Pa}$ at the room temperature. For each temperature measurement a fresh sample of the material was prepared. The samples were treated in the same fashion in all cases.

The stored thermal energy was calculated based on the isosteric heat of adsorption commonly written as q_{st} representing the molar enthalpy of the adsorbate phase H_{st}° described as:

$$\Delta H_{st}^\circ = RT^2 \left\{ \frac{\partial \ln P}{\partial T} \right\}_{q^e} = -R \left\{ \frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \right\}_{q^e} \quad (5.1)$$

where R is gas constant, T is absolute temperature, p is actual adsorbate pressure and q^e is the isosteric adsorbed amount at which the adsorption heat is calculated. The regression error was calculated as a standard error of the estimate σ_{est} according to the Eq. 5.2.

$$\sigma_{est} = \sqrt{\frac{\sum (y - y')^2}{N}} \quad (5.2)$$

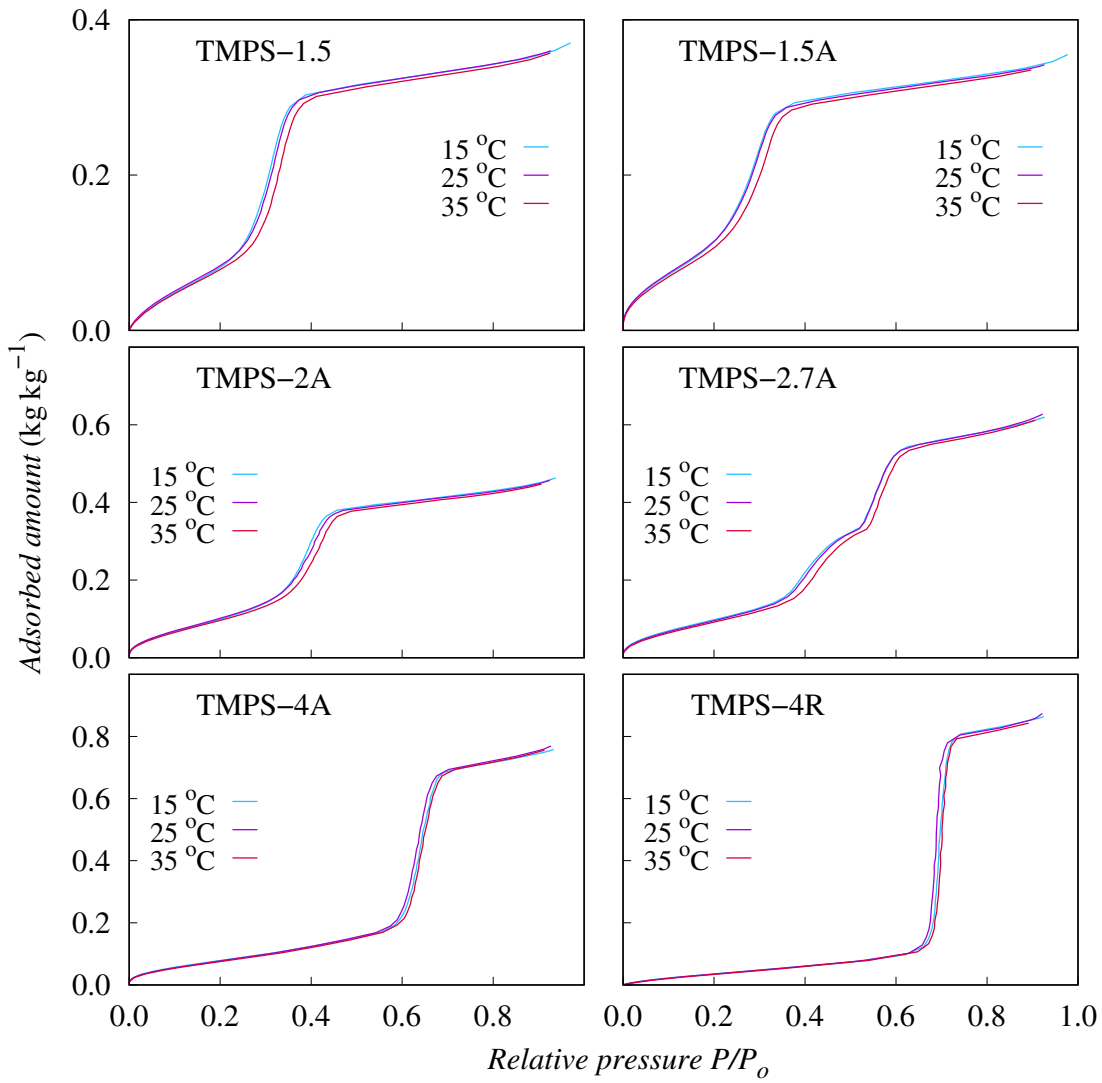


FIGURE 5.3: Adsorption isotherms of TMPS materials with water

where y and y' represent the natural logarithm of pressure measured and calculated, respectively. N is then the number of individual data points which in our case represents the number of selected temperatures.

Saturation pressures of water at given temperatures were calculated by Antoine equation in the form of:

$$\log P_0 = A - \frac{B}{C + T} \quad (5.3)$$

where p and T are the saturation pressure and temperature respectively. The constants of the Antoine Eq. 5.3 were $A = 5.40221$, $B = 1838.675$ and $C = -31.737$ [151].

5.3 Results and discussion

5.3.1 Properties on water adsorption

Presented materials are typical mesoporous representatives, thus the majority of the water adsorption occurs due to the capillary condensation. This is clearly apparent from the Fig. 5.3 where the studied TMPS materials are expressing their water adsorption isotherms as type IV and V according to IUPAC classification typical for mesoporous structures. The presented adsorption isotherms also demonstrate the main differences between the studied materials. The TMPS-1.5 and TMPS-4R are designed as a regular and pure mesoporous silica hence the little water affinity in the lower region of relative pressure and the type V shape of the measured isotherms. The TMPS-1.5A, TMPS-2A, TMPS-2.7A and TMPS-4A are mesoporous silica specimens doped with aluminium and the higher affinity towards water is signified by the type IV isotherms shape and clear formation of the first adsorbed layer in the beginning of the adsorption process. The uptakes of water onto the materials are summarized in Table 5.1. From the work of Fan et al. [72] is apparent that in the beginning at the zero coverage state not all the surface is favourable for water adsorption. Furthermore, when counting with the effect of aluminium in the silica structure an island-like dispersion of the adsorbed water over the surface in the very beginning of the adsorption process can be expected. The higher affinity of the aluminium doped samples is also clearly visible in the results of adsorption enthalpy directly calculated from the experimental data in Fig. 5.4. The high resolution of the calculation is thanks to very high density of the data in very low pressure region typically adsorbing at once less than 0.004 g g^{-1} at 5°C allowing standard pressure resolution of 3-10 Pa per step. This allows to include the main surface factor in the adsorption enthalpy simplifying the adsorption energy calculation. If we further compare the surface coverage with the full adsorption capacity of the materials it is obvious that the direct surface coverage is an imperative part of the calculated adsorption enthalpy, nevertheless, with increasing pore volume it is less important.

TABLE 5.1: Water uptakes properties of the TMPS materials

Sample	Maximum uptake (kg kg ⁻¹)	80% Uptake (kg kg ⁻¹)	P/P_0 at (80 % and $T = 35^\circ\text{C}$)	50% Uptake (kg kg ⁻¹)	P/P_0 at (50 % and $T = 35^\circ\text{C}$)
TMPS-1.5	0.355	0.284	0.37	0.178	0.32
TMPS-1.5A	0.338	0.270	0.34	0.169	0.28
TMPS-2A	0.446	0.357	0.45	0.223	0.39
TMPS-2.7A	0.613	0.490	0.60	0.306	0.50
TMPS-4A	0.751	0.600	0.68	0.375	0.62
TMPS-4R	0.850	0.680	0.72	0.425	0.68

The problematic of mesoporous silica capillary condensation and water transport inside its pores was previously studied by Yanagihara et al. [135] and more recently by Saliba et al. [152]. Yanagihara et al. [135] found that one of the constricting factors for the adsorption on these materials is a condensation of the adsorbate at the entrance to the pores. This effect was especially apparent in case of higher starting relative pressures and with samples with lower hydrophilic properties of the surface. For samples with hydrated surface or higher water affinity the adsorption rates with higher adsorption step difference were much higher suggesting faster water transport inside the pores greatly limiting the effect of the pore entrance condensation. From the isotherm data shown in Fig. 5.3 is apparent that the aluminium doped samples exhibit high water-affinity. These results suggest, similar to the finding of Yanagihara et al. [135], Saliba et al. [152], high adsorption kinetics thanks to the hydrophilic surface.

The effective uptake is accounted at 80 % of the maximum uptake measured at $P/P_0 = 0.9$. This selection has practical implications towards the ideal working cycle which borders are marked by the finish of the capillary condensation on the far end and feasible temperature driven desorption on the close end. The results show reasonably high water uptakes for all specimens relative to their pore volume ranging from $q_0 \sim 0.36 \text{ g g}^{-1}$ to 0.85 g g^{-1} with the pore size ranging from $d_p = 1.8 \text{ nm}$ to 4.0 nm . The adsorbed volumes of water are comparable to other works. Hwang et al. [132] reported adsorption amounts of $q_0 \sim 1.10 \text{ g g}^{-1}$ for the

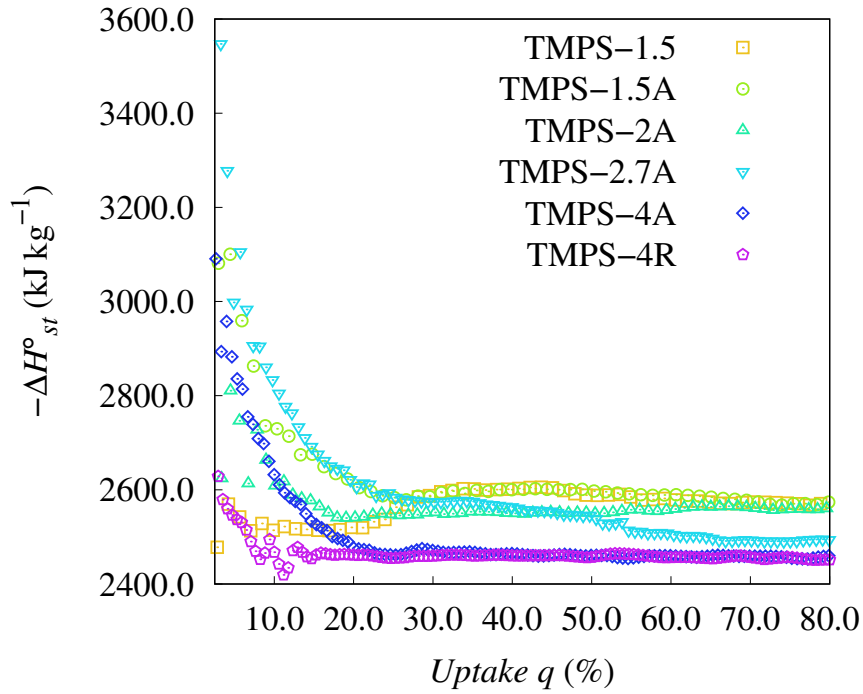


FIGURE 5.4: Isosteric heats (enthalpies) of adsorption ΔH_{st}^o of water on the TMPS materials on water uptake at $T = 308.15$ K
Water uptake q is relative to the absolute water uptake at $P/P_0 = 0.9$ for each specimen.

SBA-15 mesoporous silica with a pore size of $d_p = 9.1$ nm and $q_0 \sim 0.70$ g g⁻¹ for the SBA-15 Zr-doped mesoporous silica with a pore size of $d_p = 3.8$ nm. Kim et al. [14] studied the properties of another typical mesoporous silica material MCM-41 and reported water adsorption uptakes $q_0 \sim 0.45$ g g⁻¹, 0.60 g g⁻¹ and 0.80 g g⁻¹ for materials with pore size of $d_p = 2.4$ nm, 3.1 nm and 3.9 nm, respectively. Similar values were reached by Oh et al. [149] reaching water uptakes at $P/P_0 = 0.9$ of $q_0 \sim 0.70$ g g⁻¹ and 0.84 g g⁻¹ for MCM-41 and SBA-15 with pore size of $d_p = 3.0$ nm and 5.0 nm, respectively. Thus, from the perspective of the pore size/pore volume ratio and the water adsorption the mesoporous silica nanoparticles used in this work show slightly better performance than a regular mesoporous silica materials with the resemblance to MCM-41 group.

5.3.2 Isosteric enthalpy of adsorption

To establish the energy capacity of the material the calculations in here are based on the adsorption heat. The adsorption heat is calculated as the isosteric heat

TABLE 5.2: Coefficients for temperature gain approximation of the TMPS materials based on adsorption isotherms according to Eq. 5.4 and Eq. 5.6

Sample	a	b	σ_{aad}
80 % uptake			
TMPS-1.5	15.633	23.585	0.0121
TMPS-1.5A	15.667	24.719	0.0154
TMPS-2A	15.765	20.315	0.0158
TMPS-2.7A	15.953	15.498	0.0125
TMPS-4A	16.200	13.353	0.0114
TMPS-4R	16.282	12.227	0.0109
50 % uptake			
TMPS-1.5	15.430	25.980	0.0152
TMPS-1.5A	15.519	28.110	0.0152
TMPS-2A	15.751	22.608	0.0146
TMPS-2.7A	15.625	18.724	0.0131
TMPS-4A	16.123	14.177	0.0131
TMPS-4R	16.243	12.543	0.0114

of adsorption according to Eq. 5.1 (Clausius-Clapeyron). In the works of Builes et al. [153] and Sircar et al. [154] have been pointed out some of the limitations of this method, however, with the use of pure gas and uniform surface material this model provides sufficient properties and accuracy. The isothermal data of adsorption are normally fitted into the Eq. 5.1 through an adsorption model to avoid excessive error caused by measurement error, however, the adsorption models for mesoporous materials create even higher discrepancy for this calculation. To avoid this situation we have chosen the approach of dense data acquisition taking the reading at least every $\Delta q = 0.02 \text{ g g}^{-1}$ in the region $P/P_0 = \{0.1; 0.95\}$ up to a step size of $\Delta q = 0.004 \text{ g g}^{-1}$ below $P/P_0 < 0.1$. The points for the calculation between the measured points were then numerically extrapolated. The calculated isosteric enthalpies of adsorption are shown in Fig. 5.4. Table 5.4 then presents the average values for 80 % and 50 % of maximum uptake.

From the results is apparent the difference between the pure adsorption on the surface and forming of multilayer and subsequent capillary condensation. The start of capillary condensation is signified by constant isosteric heat of adsorption as has

been pointed out by Wang et al. [155]. The rise of the isosteric adsorption heat in the lower region of the uptake is caused by direct adsorbent/adsorbate interaction and it is more notable in the samples doped with aluminium. The later invariable progress is connected to adsorbate/adsorbate in form of capillary condensation. This behaviour is in fact typical for mesoporous materials and can be observed in other similar systems. Study of Chakraborty et al. [70] shows calculations of isosteric heat on the example of silica gel (type RD) on the same magnitude as the samples used in this work starting as high as $\Delta H_{st}^{\circ} = 3520 \text{ kJ kg}^{-1}$ and equalizing roughly around $\Delta H_{st}^{\circ} = 2670 \text{ kJ kg}^{-1}$. Similar values were also reported by Jänchen et al. [16] around $\Delta H_{st}^{\circ} \sim 2500 \text{ kJ kg}^{-1}$. The main difference between silica gels and materials from this work lies mainly in the adsorption capacity and the resulting expanded storage capacity in favour of TMPS and other structured mesoporous silica materials which will be more discussed later.

5.3.3 Theoretical temperature gain and material storage capacity

The theoretical temperature gains were calculated for heating capacity as well as for cooling capacity. Both calculations are based on pressure drop in the system caused by the condenser or the material itself and respective temperatures at the specified saturation pressures P_0 . Approximation of the temperature gain of the material (heating capacity) T_H during the adsorption at the evaporator source temperature T_{hs} was conducted based on the adsorption data following this relation:

$$T_H = a \ln P_0 + b \quad (5.4)$$

where a and b are empirically fitted constants. The saturation pressure P_0 of the evaporator was calculated by the Antoine Eq. 5.3 where the temperature $T = T_{hs}$. The deviation of the approximation according to Eq. 5.4 was calculated as average absolute deviation σ_{aad} according to Eq. 5.5. The temperature gain was calculated for two different temperatures of the heat source driving the pressure rise in the

TABLE 5.3: Pure theoretical temperature gains on the adsorbent cell and in evaporator at 80 % and 50 % of the adsorbate uptake and ideal material storage capacity at different heat-source (heating) and heat-sink (cooling) temperatures T_{hs}

Sample	Cooling capacity T_{C25} ($^{\circ}\text{C}$) ($T_{hs} = 25^{\circ}\text{C}$)	Cooling capacity T_{C35} ($^{\circ}\text{C}$) ($T_{hs} = 35^{\circ}\text{C}$)	Heating capacity T_{H10} ($^{\circ}\text{C}$) ($T_{hs} = 10^{\circ}\text{C}$)	Heating capacity T_{H25} ($^{\circ}\text{C}$) ($T_{hs} = 25^{\circ}\text{C}$)	Thermal storage capacity of the material ρ_Q (MJ kg^{-1})
80 % uptake					
TMPS-1.5	8.3	18.1	26.8	41.6	0.729
TMPS-1.5A	7.2	16.9	27.9	42.8	0.712
TMPS-2A	11.4	21.3	23.6	38.5	0.916
TMPS-2.7A	16.0	26.2	18.8	33.9	1.283
TMPS-4A	17.9	28.1	16.7	32.0	1.510
TMPS-4R	19.0	29.2	15.6	31.0	1.689
50 % uptake					
TMPS-1.5	6.1	15.8	29.2	43.8	0.454
TMPS-1.5A	4.1	13.6	31.3	46.0	0.450
TMPS-2A	9.2	19.0	25.8	40.8	0.574
TMPS-2.7A	13.0	23.2	21.9	36.7	0.823
TMPS-4A	17.2	27.3	17.5	32.8	0.957
TMPS-4R	18.7	28.9	15.9	31.3	1.056

system $T_{hs} = (10^\circ\text{C and } 25^\circ\text{C})$ denoted T_{H10} and T_{H25} , respectively.

$$\sigma_{aad} = \frac{\sum \left(\frac{T_H - T'_H}{T'_H} \right)}{N} \quad (5.5)$$

The approximations of the Eq. 5.4 demonstrate deviations less than $\sigma_{aad} < 0.02$ on average as can be observed by a very good fitting in Fig. 5.5. The calculations were made based on the measured pressures over the adsorption materials shown in Table 5.1. The full list of the values of the fitting parameters for both 80 % and 50 % of the maximum uptake of the materials is presented in Table 5.2.

Similarly, the temperature drop in the evaporator (cooling capacity) T_C was calculated on the basis of the saturation pressure, however, this time driven by the pressure drop over the adsorption material. By a simple rearranging of the previous Eq. 5.4 we will get the adsorption pressure estimation for the material and therefore the saturation pressure of the system:

$$P_0 = e^{(T_{hs}-b)a^{-1}} \quad (5.6)$$

In the Eq. 5.6 the constants are identical to Eq. 5.4 and T_{hs} states for the heat-sink temperature of the adsorption material rather than heat-source. To estimate the cooling capacity T_C of the evaporator the Antoine Eq. 5.3 was rewritten for temperature calculation. The saturation pressure P_0 was then substituted from the Eq. 5.6.

$$T_C = \frac{B}{A - \log P_0} - C \quad (5.7)$$

Calculation of the thermal energy storage capacity of the materials ρ_Q was conducted again on the basis of the practical uptake of 80 % and 50 % of the maximum uptake at $P/P_0 = 0.9$. The calculation was made on the premise of the isosteric adsorption enthalpy expressed in Table 5.4 as average isosteric adsorption enthalpy $\bar{H}_{st}^\circ$ for given uptakes. The transformation of the isosteric adsorption enthalpy of the adsorbate to the adsorbent is simply done by multiplying the adsorption amount at certain point (80 % and 50 % from Table 5.1) with the average enthalpy

TABLE 5.4: Average isosteric heats of adsorption of TMPS materials

Sample	$-\Delta\bar{H}_{st}^{\circ}(\text{kJ kg}^{-1})$ 80 % uptake	at	$-\Delta\bar{H}_{st}^{\circ}(\text{kJ kg}^{-1})$ 50 % uptake	at
TMPS-1.5	2568.0		2562.8	
TMPS-1.5A	2633.5		2665.1	
TMPS-2A	2569.3		2576.1	
TMPS-2.7A	2617.2		2687.8	
TMPS-4A	2515.8		2550.8	
TMPS-4R	2484.6		2487.4	

value up to that point. The adsorption step for the calculation of the average isosteric adsorption enthalpy was set to 0.005 g g^{-1} .

$$\rho_Q = \Delta\bar{H}_{st}^{\circ} \cdot uptake \quad (5.8)$$

The results on the temperature gain and thermal energy storage capacity are summarized in Table 5.3.

The theoretical calculations show how difficult it is to reach practically useful values in these systems which is supported by many laboratory tests and experiments as summarized by Yu et al. [18], Scapino et al. [41]. In this work, the temperature gain is calculated on the basis of sustainable rather than reachable temperature and the gains can seem to be reaching rather unexceptional results. That is, however, to be expected in relation to the sustainable temperature. As was mentioned before, the detailed examination of the data in the lower adsorption region shows that the TMPS materials containing aluminium exhibit much higher water affinity and subsequently showing higher adsorption enthalpy, typically up to 20 % of the total adsorption capacity. Here, the main objective is to show the high energy density and high potential for further development based on these materials.

The heating and cooling capacities listed in Table 5.3 are showing natural behaviour of higher temperature lifts for smaller pore diameters and lower gains for bigger pore diameters. The main limiting factor of the samples with small pore

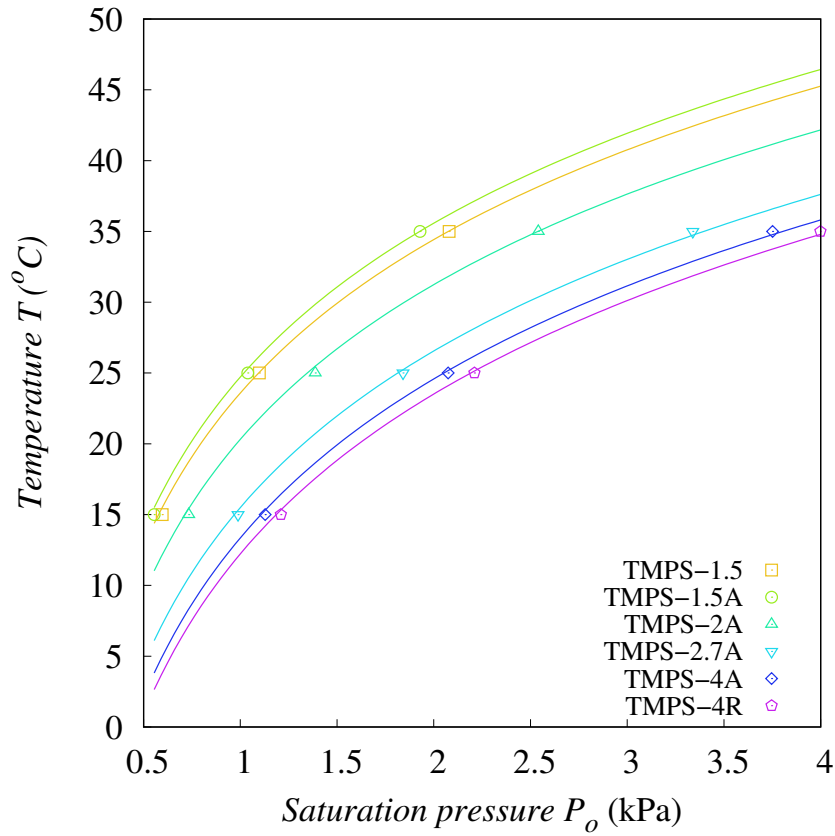


FIGURE 5.5: Pressure equilibrium (saturation) approximation at 80 % of the total uptake according to Eq. 5.4 showed as continuous line compared to measured point values at $T = 15^\circ\text{C}$, 25°C and 35°C

size is the total capacity. That is in contrast with the theoretical high average temperature gains through the whole uptake where the best performing TMPS-1.5A reaches the temperature difference of $\Delta T = 17.8^\circ\text{C}$ for cooling and $\Delta T = 22.8^\circ\text{C}$ for heating with the heat source/sink temperature of $T_{hs} = 25.0^\circ\text{C}$ at the 80 % of the total uptake. The values are slightly higher for 50 % of uptake, however, the growth is not that significant as most of the uptake is realised in a very narrow window of relative pressure change. The regular silica gel (mesoporous) cannot normally reach such high values for more than its limited surface capacity[12, 156]. Another problem is connected to its low maximum uptake and wide pore size distribution causing big part of its adsorption capacity to be over $P/P_0 > 0.5$, thus the resulting storage capacity is usually very low. However, thanks to the great commercial availability of these regular silica gel materials, the silica gel is still

intensively studied in this context mostly as an easily comparable material or impregnated with inorganic salts[18, 70, 157]. More favourable properties for direct use can be found in case of microporous silica gel. Thanks to the pore size distribution mainly in the micropore region, the majority of the adsorption amount of the microporous silica gel is situated below $P/P_0 < 0.1$. This value is promising high temperature gains ΔT and rapid kinetics as shown by Dawoud and Aristov [69]. However, as has been shown by several studies[12, 156, 158] the microporous silica gels have usually very low adsorption capacity bordering the value of 0.2 g g^{-1} . Thus, even with higher adsorption enthalpy as shown by [148] on the example of Type A silica gel, the energy capacity of microporous silica gel is somehow lacking for the purpose of energy applications.

In the terms of the energy capacity of the studied TMPS materials, it is almost a direct equivalent of the pore volume. Therefore, the storage capacity is naturally the highest for TMPS-4R, $\rho_Q = 1.689 \text{ MJ kg}^{-1}$, as the sample with the highest pore volume. This value may seem very high, however, the practical implications of the temperature gain render the pure material as unusable. Different situation is for the samples with smaller pore size, generally below $d_p < 3.0 \text{ nm}$. Although the storage capacity is below $\rho_Q < 1.0 \text{ MJ kg}^{-1}$ it is still sufficiently high enough and on the par with zeolite and zeolite-like materials which are mostly considered for this use and significantly higher than silica gel. Jänchen et al. [16] reached storage densities of $\rho_Q = 0.536 \text{ MJ kg}^{-1}$ for type 13X zeolite and $\rho_Q = 0.810 \text{ MJ kg}^{-1}$ for LiX type zeolite, while Henninger et al. [13] measured the storage density for aluminophosphate AlPO-18 as high as $\rho_Q = 0.875 \text{ MJ kg}^{-1}$ with the discharge temperature of $T_D = 40^\circ\text{C}$. If we compare the values of TMPS TMPS-1.5A and TMPS-2A, we can see that the theoretical storage densities of $\rho_Q = 0.712 \text{ MJ kg}^{-1}$ and $\rho_Q = 0.916 \text{ MJ kg}^{-1}$, respectively, at 80 % show a certain potential especially with the low loading temperatures around 80°C to 90°C .

5.4 Conclusion

Six TMPS materials from the group of mesoporous silica nanoparticles were studied on their perspective as thermal energy storage materials.

The TMPS materials show high water uptakes proportional to their pore size thanks to the capillary condensation.

The high water uptakes are in contrast with low temperature gains following the natural drive of the pore size as the main factor for the condensation in the mesopores.

The advantageous properties of the samples doped with aluminium are perceived in better water uptake in lower relative pressures and consequently smaller effective pore radius when the adsorbed monolayer is fully formed before the capillary condensation occurs. This is also demonstrated by the isosteric enthalpy of adsorption calculated on the basis of Clausius-Clapeyron relation which shows higher values of released heat during the adsorption process in the lower regions of relative pressure proving stronger interaction between adsorbent-adsorbate in the case of aluminium doped materials.

The thermal energy storage capacities were calculated on the basis of 80 % and 50 % of total uptake and integral isosteric enthalpy and are on the level of currently investigated materials with high potential.

Chapter 6

Composite Materials of TMPS-4A Mesoporous Silica Impregnated with Inorganic Salts

6.1 Introduction

The limitations of the pure mesoporous silica were exploited in the previous chapter, where was clearly shown that the practical usage of mesoporous materials is tightly connected to the effective pore size. For the adsorption heat transformations the effective range where the transformation makes any sense is generally considered around 0 to 0.3 of the relative pressure, when discussing water as a working fluid[40]. To achieve this range the effective pore size should not be bigger than $2 \sim 3$ nm. By effective pore is meant the diameter when the capillary condensation occurs but not necessarily the physical pore diameter. By introducing aluminium into the structure or by coating the silica surface, the additional adsorbed layers of water prior to the capillary condensation can reduce the effective pore size as well. The problematic of aluminium addition to structure and its effect on water adsorption was recently summarized and studied on the example of SBA-15 by Ribeiro et al. [138]. Aluminium coating was also successfully studied with effective shift of the working region by Kim et al. [14]. Nevertheless, beyond this partial success, the creation of a mesoporous silica with sufficiently small pore

TABLE 6.1: Basic properties of TMPS-4A

Mean Pore diameter ¹	Total pore volume ²	Surface area ³	Density ⁴	Heat of adsorption (water) ⁵
4 nm	0.859 cm ³ g ⁻¹	804 m ² g ⁻¹	0.175 g cm ⁻³	43.7 kJ mol ⁻¹

¹DFT method based on adsorption of N₂ at 77.4 K; ²Maximum adsorption volume of N₂ at P/Po = 0.95 and 77.4 K; ³BET multipoint method based on adsorption of N₂ at 77 K; ⁴Tapped bulk density; ⁵At 80 % of total filling capacity.

size has proved to be a challenging matter. Thus, another route is extensively studied in present which hopes to combine the mesoporous matrix with inorganic salts.

The combination of inorganic salts and porous materials for enhancement of water adsorption properties is not new and has been studied already on various silica gels[9, 157] and other porous materials[16, 66, 159]. Recently, many researchers started to focus on the possibility to include in this endeavour the mesoporous silica materials with organized structure as well. Ponomarenko et al. [65] has studied the possibility of the combination of SBA-15 and CaCl₂ with good results relatively to the use of a bulk CaCl₂. The combination of SBA-15 and MCM-41 with LiCl investigated by Zheng et al. [160] for the application on desiccant cooling system also achieved better properties than what the separate individual materials usually preform.

In this chapter are investigated the changes in water adsorption properties of TMPS-4A mesoporous silica which has been examined in this work together with other representatives of the TMPS family, impregnated with three different inorganic salts. The main objective is to compare the positive effect on the adsorptive properties and potential improvement for the use in adsorption thermal energy storage systems. The motivation for this work is based on the new availability of industrially produced TMPS mesoporous silica materials, which has not yet been tested in this context and this extent.

6.2 Experiment

6.2.1 Materials

The main material evaluated in this chapter is TMPS-4A. The basic properties of the TMPS 4A are recapitulated in Table 6.1. It is clear that the pore size is sufficiently spacious to engulf most of the available inorganic salts normally used for the adsorption properties enhancement. Here, the CaCl_2 , MgCl_2 and MgSO_4 are used in their pure form for the impregnation of TMPS-4A. The salts were procured from Sigma Aldrich in their anhydrous state with the purity of $>99\%$. First, the TMPS-4A sample was dried in oven for 48 h at 160°C to fully for desorb any impurities from the surface. The salts were dissolved in distilled water in concentration of 25 wt% and tempered to the room temperature. The standard addition of the TMPS sample was about 1 g per 100 mL of the salt solution. The impregnation period was 24 h at room temperature while agitated by a magnetic stirrer. After that, the TMPS-4A was vacuum filtered from the solutions and twice fast rinsed with distilled water to remove any remnants of the salt from the surface of the particles. The impregnated TMPS-4A was then slowly dried sequentially at 60°C , 80°C and finally 120°C to avoid rapid vapour evolution inside the pores, which could cause an outpouring of the contained solution out of the pores. The prepared and dried materials were then contained in hermetically sealed containers.

6.2.2 Measurement

Prepared materials were measured for their properties of water adsorption at 288.15 K, 298.15 K and 308.15 K. The water adsorption isotherms were measured on a volumetric surface characterization analyzer 3Flex (Micromeritics, USA). Prior the measurement, all the materials were dried and degassed twice at 200°C for at least 5 hours at high vacuum. After the first degassing period the sample weight was measured for the experiment. The second degassing was continued until the vapour pressure of the adsorbed residues was less than $P < 0.1\text{ Pa}$. The

temperatures 298.15 K and 308.15 K were measured on the same samples to observe change of the properties on adsorption desorption cycle.

6.3 Results and discussion

In the Fig. 6.1 is demonstrated that a significant enhancement of working properties was achieved in all three cases. However, it is also apparent that the total mesopore capacity was diminished by approximately 10 %. That is naturally understandable as the space was taken by the salt mass. The reduction is actually smaller than expected as the used solution was 25 wt%. The smaller reduction in the capacity is attributed to the water rinse after the impregnation process, when some of the salt solution inside the pores was partially diluted. The shape of the adsorption isotherms is fully conserved inside the mesopore area and it is possible to assume with high degree of confidence that the salt solution leakage out of the pores is negligible up to $0.8 P/P_0$. The salt solution leakage out of the pores is in fact apparent on the case of TMPS-4A+MgCl₂ and slightly also TMPS-4A+CaCl₂ at $T = 298.15$ K when the relative pressure of the adsorbate surpassed $0.85 P/P_0$. However, the desorption process and subsequent measurement at 308.15 K did not show any significant or noticeable change in the adsorption properties.

To evaluate the thermodynamic properties of the composite material the isosteric heat of adsorption was calculated and compared to the pure TMPS-4A. The isosteric heat was again calculated according to the Clausis-Clapeyron relation describing the change of enthalpy of the vapour during the condensation (vaporisation) in dependence on pressure and temperature change according to:

$$\Delta H_{st}^o = RT^2 \left\{ \frac{\partial \ln P}{\partial T} \right\}_{q^e} = -R \left\{ \frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \right\}_{q^e} \quad (6.1)$$

where R is gas constant, T is absolute temperature, P is actual adsorbate pressure and q^e is the isosteric adsorbed amount at which the isosteric heat is calculated. The comparison and results are shown in Fig. 6.2. It is clear that the salt addition

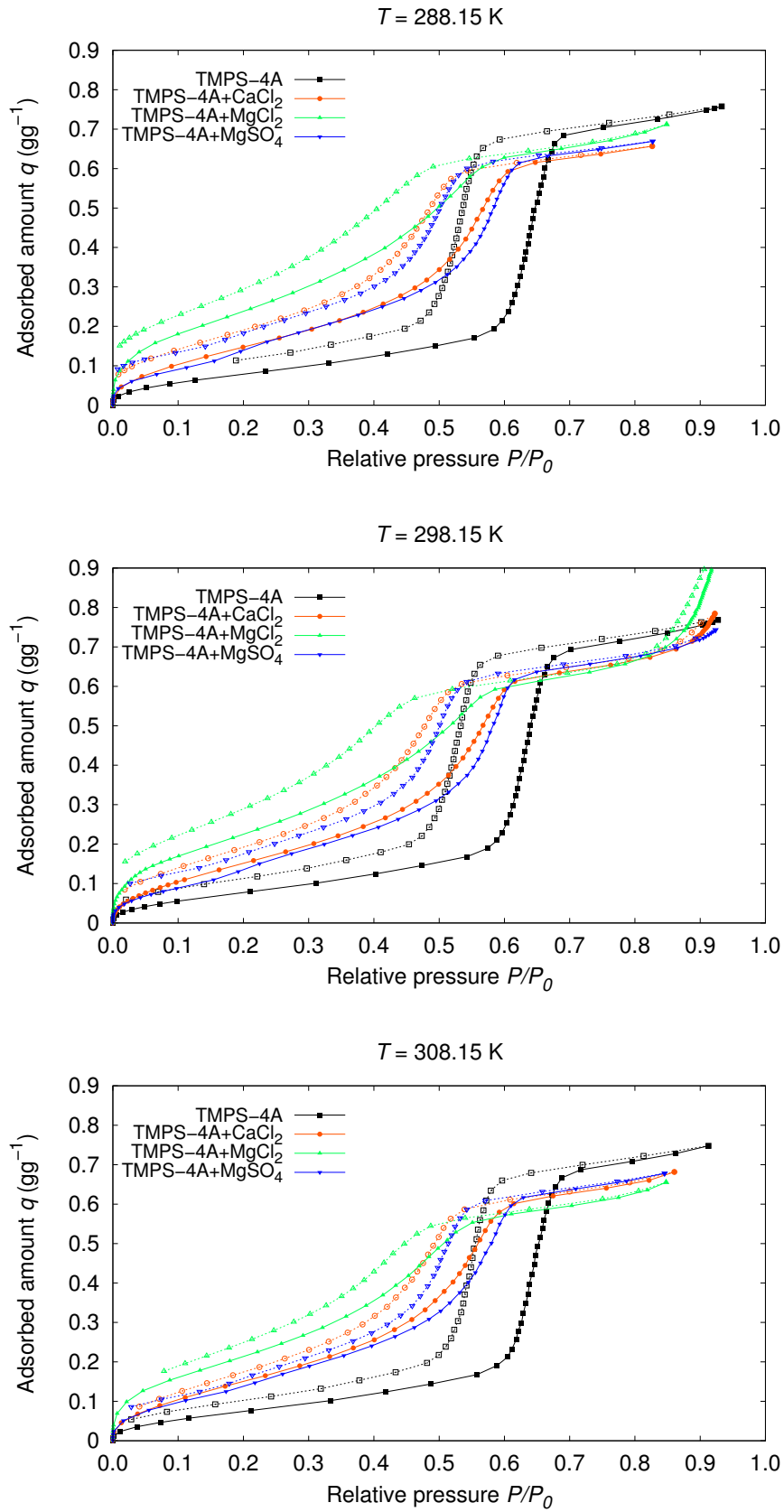


FIGURE 6.1: Adsorption isotherms for the materials at $T = 288.15 \text{ K}$, 298.15 K and 308.15 K

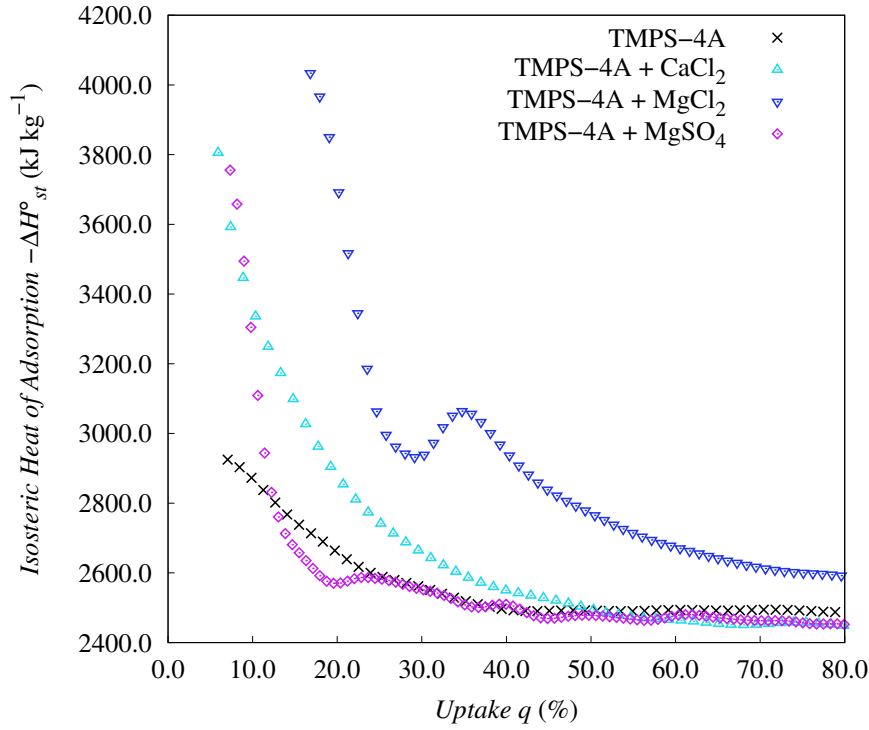


FIGURE 6.2: Isosteric heat of adsorption of the composite materials compared to the untreated TMPS-4A

improved the energy output significantly in all three cases. In the case of TMPS-4A+CaCl₂ and TMPS-4A+MgSO₄ the improvement was localised on the beginning of the adsorption uptake and equalized with the pure TMPS-4A around 40 % to 50 % of filling of the total uptake capacity. Surprisingly, the TMPS-4A+MgCl₂ increased the values of the whole capacity proving to be a strong candidate for future considerations.

To quantify the quality of the enhancement of the adsorption properties a comparison on the theoretical temperature lift (pressure reduction potential) was also attempted. The temperature dependence of the temperature lift T_H on the saturation pressure P_0 over the adsorbent was calculated based on the experimental equilibrium adsorption data according to the following relation:

$$T_H = a \ln P_0 + b \quad (6.2)$$

where a and b are the fitting parameters. This relation is possible because the

temperature lift and the pressure reduction of the adsorbate vapour bound to the adsorbent follows the same physical route for adsorption as for plain condensation of water. Once this relation is established, the recalculation of the saturation pressure reduction can be calculated by rearranging the equation to give the potential temperature necessary to drive the adsorption which is the cooling side of the system T_{hs} in the same way as in the previous chapter :

$$P_o = e^{(T_{hs}-b)a^{-1}} \quad (6.3)$$

The difference between the driving temperature T_D and the source T_H (heating side of the adsorbed) or the heat sink T_{hs} (cooling side of the water evaporation) then gives $\Delta T_{heat}, \Delta T_{cool}$ as a working range of the system. The driving temperature is then calculated based on the pressure and temperature of the system compared to the saturation pressure and temperature of water.

$$\Delta T_{heat} = T_H - T_S \quad (6.4)$$

$$\Delta T_{cool} = T_S - T_C \quad (6.5)$$

The summary of the temperature lifts is shown in Table. 6.2. The results demonstrates again an improvement in the driving force for cooling and heating for all salts composites. It is shown that the difference between 50 % and 80 % of filling of the total capacity is not that different for the simple TMPS-4A. The results show values of the temperature lift about ≈ 7 K for cooling and heating at 80 % of filling and around ≈ 8 K at 50 %. The change is caused naturally by the difference of adsorption equilibrium on the relative pressure. In the case of the composites, the TMPS-4A+MgSO₄ and TMPS-4A+CaCl₂ show similar improvement of about ≈ 1 K to ≈ 1.5 K and ≈ 3 K to ≈ 4 K at 80 % and 50 % compared to the simple TMPS-4A, respectively. Higher difference in case of TMPS-4A+CaCl₂ is also demonstrated by the higher isosteric heat of adsorption compared to the TMPS-4A+MgSO₄. Significant improvement then exhibits the TMPS-4A+MgCl₂ composite further enhancing the TMPS-4A for another ≈ 3 K at 80 % filling and doubling the values at 50 % compared to the plain TMPS-4A. Considering these

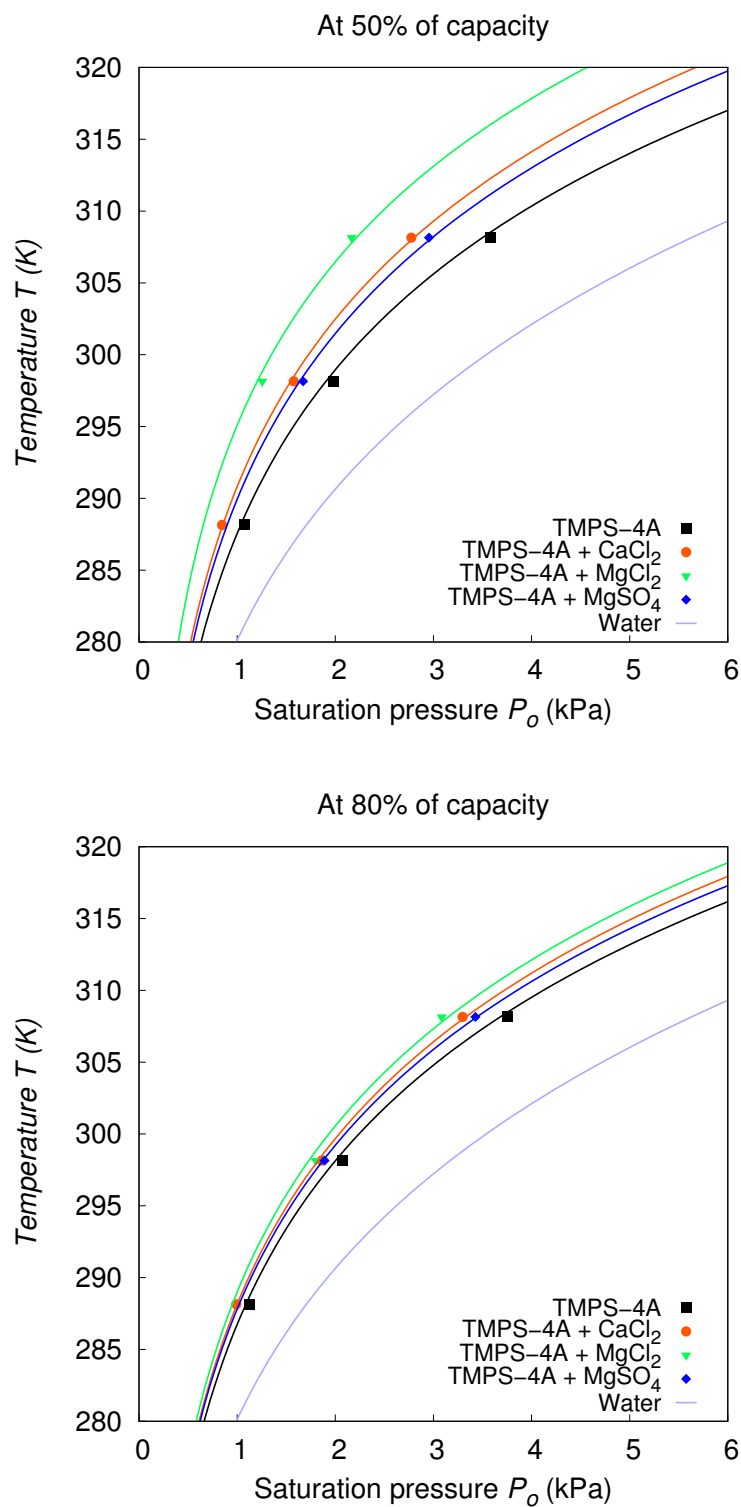


FIGURE 6.3: Temperature elevation (pressure drop) of the composite materials at 50 % and 80 % of the capacity compared to the untreated TMPS-4A

TABLE 6.2: Temperature lifts for cooling ΔT_{cool} and heating ΔT_{heat} for the TMPS-4A and salt composites, and fitting parameters for Eq. 6.2 and Eq. 6.3

Sample	Full capacity	Specific uptake (80/50%)	a	b	ΔT_{heat} (source 10 °C)	ΔT_{heat} (source 25 °C)	ΔT_{cool} (heatsink 25 °C)	ΔT_{cool} Cooling (heatsink 40 °C)
80% uptake								
TMPS-4A+CaCl ₂	0.68	0.55	16.618	15.006	8.4	9.2	8.9	9.0
TMPS-4A+MgCl ₂	0.70	0.56	16.676	15.849	9.3	10.1	9.8	10.0
TMPS-4A+MgSO ₄	0.69	0.55	16.450	14.661	8.0	8.6	8.5	8.3
TMPS-4A	0.75	0.60	16.425	13.593	7.0	7.5	7.5	7.1
50% uptake								
TMPS-4A+CaCl ₂	0.68	0.34	16.814	17.667	11.1	12.1	10.8	12.0
TMPS-4A+MgCl ₂	0.70	0.35	16.410	21.937	15.3	15.9	14.2	15.9
TMPS-4A+MgSO ₄	0.69	0.35	16.638	16.788	10.2	11.0	9.7	10.9
TMPS-4A	0.75	0.37	16.438	14.406	7.8	8.4	8.3	8.0

values and the isosteric heat of adsorption it can be summarized that the storage capacity will be also increased not negligibly, however the increase will be diminished by the decrease of the total pore capacity.

The last question which was not fully addressed in here is the problematic of the desorption. With the increase of the water affinity of the adsorbent, the increase in the temperature for desorption is an issue necessary to watch and it will be an important part to be established in the future study.

6.4 Conclusion

Three different salts were successfully impregnated into the mesoporous structure of the TMPS-4A mesoporous silica. The selected inorganic salts CaCl_2 , MgCl_2 , and MgSO_4 shows significant improvements in the adsorption properties with reasonable stability inside the pores. One of the problems concerning the salt impregnation on a porous matrix is the leakage of the salt outside of the pores, or external filling when we talk about coverage. This has been clearly demonstrated on the example of $\text{TMPS-4A} + \text{MgCl}_2$. However, this process can be controlled by simply limiting the end-point's relative pressure of the adsorption, which was the case of the subsequent measurements. From the shape of the adsorption curve it is obvious that the majority of the adsorption in the TMPS-4A impregnated with selected salts happens inside the pores and under controlled adsorption the salt leakage is kept to absolute minimum. Furthermore, even though that the filling capacity is reduced by about 10%, the heat of adsorption has increased by far more especially in case of $\text{TMPS-4A} + \text{MgCl}_2$ for the whole uptake capacity.

It has been shown that compared to the plain TMPS-4A the salt composites exhibits superior properties for the use in adsorption heat transformation applications, especially from the view of temperature lift and pressure reduction. The Calculated values show temperature lift of up to $\Delta T = 15.9 \text{ K}$ against the driving temperature of 40°C and 25°C for cooling and heating, respectively.

Some negative effect can be, however, also expected in the connection to the elevated desorption temperature and certain drop in the total capacity of the material. Nevertheless, the improvement in the temperature and pressure driving force of these new composites together with enhanced energy capacity far outperforms the negative aspects.

Chapter 7

Summary and Conclusion

7.1 Material Selection and Characterisation

A full and detailed analysis of six samples from the family of TMPS mesoporous silica was performed on their key properties. These values were compared to the regular SBA-15 and MCM-41 mesoporous silica samples.

Analysis through nitrogen adsorption revealed pore size distribution calculated according to BJH method and DFT method. The results on the pore size distribution from the DFT method were then mathematically analysed by standard distribution function well fitted to the model to establish the mean pore size. The values of the pore size of the TMPS series were found out in the range of 1.8 nm to 4 nm and correspond to mesoporous materials with the smallest part belonging on boundary between meso and micro pore region as specified by IUPAC. The prepared MCM-41 was within the same range as the TMPS materials while SBA-15 was found out with much higher value of 7.5 nm. The values were compared to some less elaborate techniques such as $4V/S$ and a new geometry-based model was proposed for simplified and easy to use purposes comparable to the $4V/S$ method. Additional method for structural analysis such as powder low angle XRD was used to measure the inter pore distance and wall thickness was established as well around 1.3 nm to 2.1 nm for the TMPS materials, and 4 nm and 1.1 nm for SBA-15

and MCM-41, respectively. The pore thickness is an important value for estimating the pore volume/bulk material volume ration and it is expected to affect the thermal stability of the materials as well.

The size of the individual particle cell sizes was found out from 50 nm to 200 nm as observed by the SEM aggregating into bigger particles typically in the range of units of micrometres. The nano-structured inner coordination shape and inner structure (particle cell shape, pore size) of the TMPS materials have higher similarity with the prepared MCM-41.

Thermal stability was discussed on the data from a TG analysis measured in the range of 25 °C to 800 °C when all the specimens were stable through the whole temperature region. The aluminium was present in the TMPS-1.5A, TMPS-2A, TMPS-2.7A, and TMPS-4A in units of wt%. The addition of aluminium is generally used to enhance the water adsorption properties, as well as enhancing the hydrothermal stability of the mesoporous silica materials. The presence of Al-O-Si bonds was observed by FTIR analysis and the aluminium itself by SEM/EDS. The enhanced water adsorption due to the presence of aluminium also significantly affects the effective pore diameter during the water adsorption, as the main topic of the next chapter.

7.2 Water Adsorption on the Mesoporous Silica Matrix

The working water adsorption region of the TMPS materials was found out from 0.3 to 0.7 P/P_0 depending on the effective pore diameter. The effect of aluminium doping on the effective pore size is clearly visible on the case of pairs TMPS-1.5/TMPS1.5A and TMPS-4A/TMPS-4R with the same physical pore size, however, different effective pore size for water adsorption. In the case of the pair TMPS-1.5 and TMPS-1.5A the effect is visible on more "tight" adsorption isotherms of TMPS-1.5A and slight shift of the adsorption to the lower values of

the relative pressure. The positive effect on the working region of relative pressure is much more visible on the case of TMPS-4A compared to the same pore sized TMPS-4R when the decrease of the relative pressure of the end of the capillary condensation is moved from 0.75 to 0.65 P/P_0 .

An attempt to fit the acquired adsorption isotherms into a mathematical expression was conducted on two models Henry/Sips from the work of Kim et al. [141] and combined Langmuir/Freundlich/Gauss as an original attempt of this work. The fitting of sigmoidal, or also called S-shape, isotherms is usually connected to at least two separate adsorption processes and in this work the Type IV and Type V isotherms were positively identified on the aluminium doped and pure silica samples, respectively. The first Henry/Sips model fits well isotherms with the region of change before 0.5 P/P_0 . After that, the β parameter based on the exponential of P/P_0 cannot fit well overwhelmingly preferring one model on the expenses of the other. The resulting enthalpies of Henry's isotherm ΔH_H at zero coverage were found out on a reasonable magnitude levels, however without any significant correlation to the studied mesoporous silica specimens. The enthalpy of Sips' isotherm ΔH_S exhibit a certain correlation to the pore size, which is understandable when we realize that the Sips' isotherm is used to describe the mesoporous area adsorption in this case.

A new original adsorption isotherm model presented in this chapter builds on the fact of the normal distribution found out in the previous chapter and tries to accommodate the capillary condensation into a limited region where the condensation physically occurs inside the pores. It was shown that the new Langmuir/Freundlich/Gauss provides significantly better fit to the experimental data and performs well in the whole region of the relative pressure. The proposed model is highly suitable for studied mesoporous materials with narrow pore size distribution, however, because of the nature of the model, it is not suitable for Type VI isotherm which can be seen on the example of TMPS-2.7A and partially MCM-41 showing at least two distinguishable areas with different pore sizes or properties.

Because of the limitations of the Langmuir/Freundlich isotherm the future work will attempt to combine the Gauss model to some multilayer isotherms such as n-BET model and its modifications which are not suitable alone for the presented materials.

Adsorption enthalpy was established based on the experimental data by the Clausius-Clapeyron equation as isosteric heat of adsorption. The volumetric apparatus 3Flex used in this work can provide in very short time very dense isotherm data points which is especially suitable for the Clausius-Clapeyron equation. For the calculation were used 5 different temperature points in case of TMPS materials and 4 temperature points for SBA-15 and MCM-41 for each isosteric regression. Because it is not practical to acquire the points at the same adsorption equilibrium q_e for all the temperature dependencies, the differences were interpolated through mathematical operations (consecutive third polynomials used in a cubic spline interpolation). The results show predicted behaviour, when the aluminium doped samples exhibit higher isosteric adsorption heat during the first phases of the adsorption due to the enhanced affinity towards water. The continuing heat release is then directly proportional to the effective pore size driving the pressure drop over the water surface during the capillary condensation phase.

7.3 System Evaluation Based on the Pure Materials

The perspective use of the TMPS materials was critically evaluated in this chapter for their working region, potential temperature lift and pressure decrease drive, and theoretical storage capacity. Thanks to the capillary condensation region the mesoporous silica materials show high adsorption uptakes, much higher than other silica materials. However, it is important to point out that the adsorption uptake is only one part of the necessary evaluation process. Especially for adsorption heat transformation technology the actual pressure drive and temperature lift are more

important values.

The region of practical use is commonly reported to 0.05 to 0.3 of P/P_0 and has direct implications for the temperature lift. The best performing materials were found out TMPS-1.5 and TMPS-1.5A with relative ΔT for cooling from the driving temperature of $T_{hs} = 10^\circ\text{C}$ as $\Delta T_C = 19\text{ K}$ and $\Delta T_C = 21\text{ K}$, respectively at the uptake of 50 % which is reaching the levels of aluminophosphates. The high water uptakes of the other TMPS samples are then in contrast with low temperature gains following the natural decrease of the pore size as the main driving factor for the condensation in the mesopores described by the Kelvin equation. Hence, the only materials that can be perceived for direct use are the TMPS-1.5 and TMPS-1.5A, possibly TMPS-2A for very low temperature applications. The advantageous properties of the samples doped with aluminium is again clearly demonstrated in better water uptake in lower relative pressures and consequently smaller effective pore radius when the adsorbed monolayer is fully formed before the capillary condensation occurs.

The thermal energy storage capacities were calculated on the basis of 80 % and 50 % of total uptake and integral isosteric enthalpy of adsorption. From this point of view the highest energy is achieved by the samples with higher pore capacity. Comparing the values calculated in this chapter with available literature it is apparent that the values reached in here are higher than for equivalent systems. At this point it is necessary to emphasise that some of those values are based on real working examples, and in here are presented mostly theoretical values. Practically speaking the author of this thesis does not expect reaching more than 60 % of the values calculated in here based on practical experience. The practical COP of the aTES systems does not reach usually more than 0.5-0.6 due to various losses connected to heat transformation processes and other losses during the heat transfer between different places of storing, heat production and places of consumption. However, despite these losses, the aforementioned TMPS-1.5, TMPS-1.5A, and

TMPS-2A performs better than silica gel and some of zeolites and aluminophosphate based on the water adsorption results. Development of direct use of these materials is therefore open, especially thanks to their bulk availability as a completely unique trait to any other mesoporous silica material with similar qualities.

7.4 Composite Materials with TMPS-4A mesoporous silica impregnated with inorganic salts

Three different salts were successfully impregnated into the mesoporous structure of the TMPS-4A mesoporous silica. The selected inorganic salts CaCl_2 , MgCl_2 , and MgSO_4 shows significant improvements in the adsorption properties with reasonable stability inside the pores. One of the problems concerning the salt impregnation on a porous matrix is the leakage of the salt outside of the pores, or external filling when we talk about coverage. This has been clearly demonstrated on the example of TMPS-4A+ MgCl_2 . However, this process can be controlled by simply limiting the end-point's relative pressure of the adsorption, which was the case of the subsequent measurements. From the shape of the adsorption curve it is obvious that the majority of the adsorption in the TMPS-4A impregnated with selected salts happens inside the pores and under controlled adsorption the salt leakage is kept to absolute minimum. Furthermore, even though that the filling capacity is reduced by about 10 %, the heat of adsorption has increased by far more especially in case of TMPS-4A+ MgCl_2 for the whole uptake capacity.

It has been demonstrated that compared to the plain TMPS-4A the salt composites exhibit superior properties for the use in adsorption heat transformation applications, especially from the view of temperature lift and pressure reduction. The calculated values show temperature lift of up to $\Delta T = 15.9\text{ K}$ against the driving temperature of 40°C and 25°C for cooling and heating, respectively.

Some negative effect can be, however, also expected in the connection to the elevated desorption temperature and certain drop in the total capacity of the material. Nevertheless, the improvement in the temperature and pressure driving force of these new composites together with enhanced energy capacity far outperforms the negative aspects.

Chapter 8

Future work

In the future endeavours the author would like to focus on design and development of the actual aTES system for experimental purposes to practically test the properties of the selected TMPS-1.5A and possibly a composite materials based on TMPS-4A or TMPS-2A. However, for such design many challenges has be addressed individually.

A serious problematic for the design of an aTES is presented by the geometry of the storage tank itself. Because porous materials are from their nature very good thermal insulators, the geometry and scattering of heat energy through the tank is essential. This, together with the necessity of good accessibility for adsorbate vapour is a demanding engineering problem which is being studied by many research teams across the world with more or less success. The most basic solution lies in deposition of the adsorbent material straight on the surface of a heat exchanger. This simple solution is suitable for adsorption heat pumps and dehumidifiers but for storage purposes is too bulky and significantly limits usable volume of the storage. Solving this problem will be one of the main tasks of future research. Ideal packing is compressing the material with binder, but compression and binder usage dramatically slows down the whole adsorption process and leads to massive losses and the heat transfer between heat exchanger and this tightly packed material is poor due to the small contact area. The goal is to find good compromise between heat transfer, volume, capacity and kinetics.

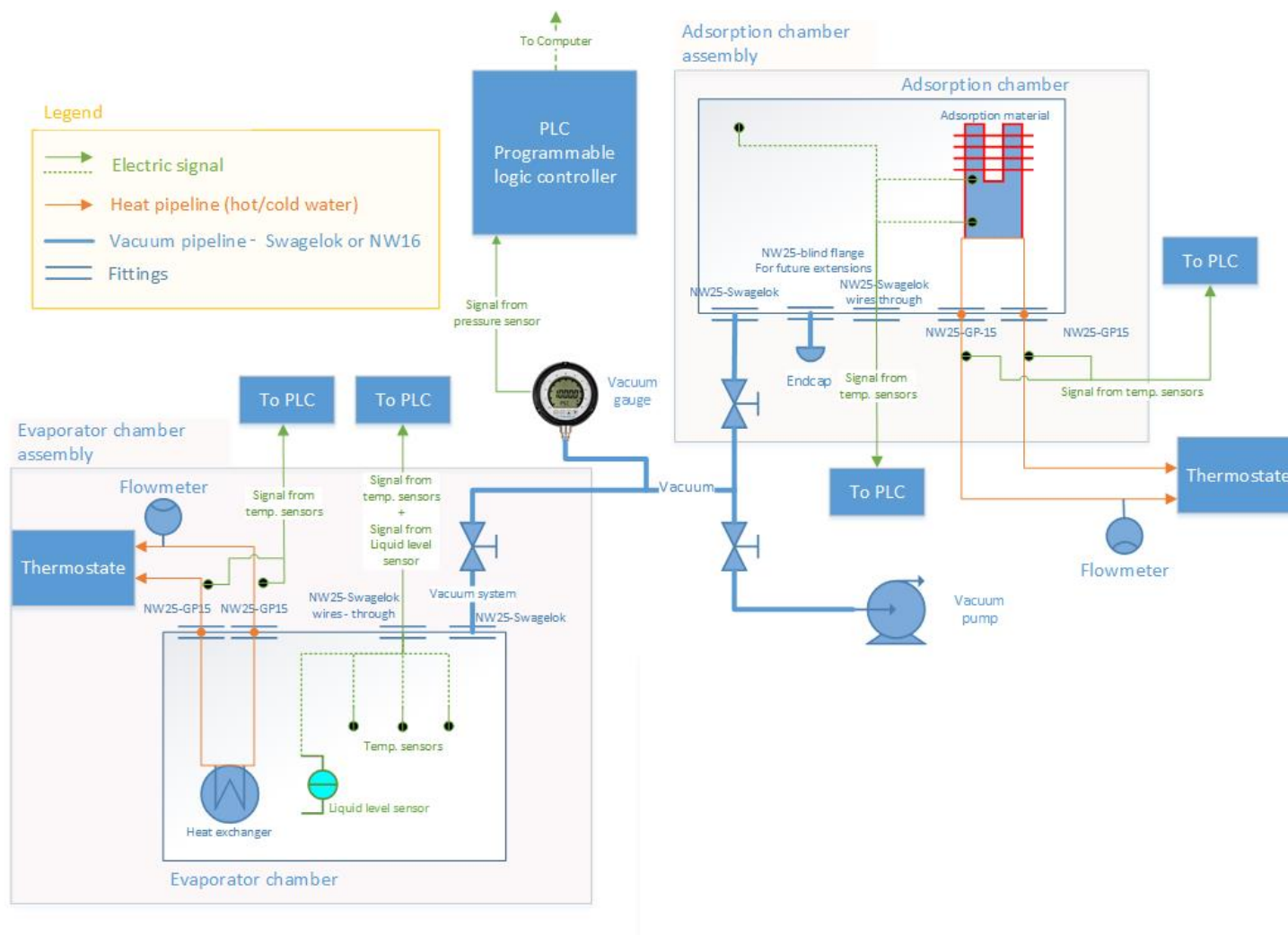


FIGURE 8.1: Adsorption heat energy storage experimental system schema.

With the whole set of the measured practical data the next step will also lead to simulation of the new design and for the construction of the system. The system has been already proposed and is currently under construction. The simplified system schema is presented in Fig. 8.1. The system being constructed for maximum load of 1 kg of adsorbate (approximately 400 W h of heat storage depending on the substrate) with the focus on measurement of section temperatures, pressures and heat fluxes. Although smaller amounts will be possible as well, higher amounts will significantly reduce the resulting errors through various heat losses in the system. The experimental unit will also focus on simplified design and will be suitable for solving of the main engineering task concerning the geometry of the storage area and minimizing of movable parts as one of the big advantages of the aTES systems. The storage area design will be variable for testing different approaches for filling of the adsorption materials and heat transfer design. As the system is generally self-pressure driven, no compressor or pump will be necessary. The main purpose of this experimental unit will be testing of different adsorption materials and geometries of the storage compartment and studying of key properties of such system in controlled environment. The presented design is therefore a wide combination of efforts from several fields for energy conversion and draws a significant amount of knowledge and expertise from different research topics. The results on the bulk usage of mesoporous silica on this scale will be completely unique to the best current knowledge of the author.

The follow-up research will be focused on a long-term research activity of developing a functional prototype adsorption heat storage unit and material development. As was mentioned in the Chapter 2, new materials are emerging every year and the progress in the last couple of year on the field of aTES is astonishing. However, for a vast majority of the new materials in research in the last decade in the field of adsorption energy storage scarcely ended with a prototype unit. The ultimate goal than may be a practical utilization of this technology with commercialisable product. The whole design, however, presents at this point a substantial

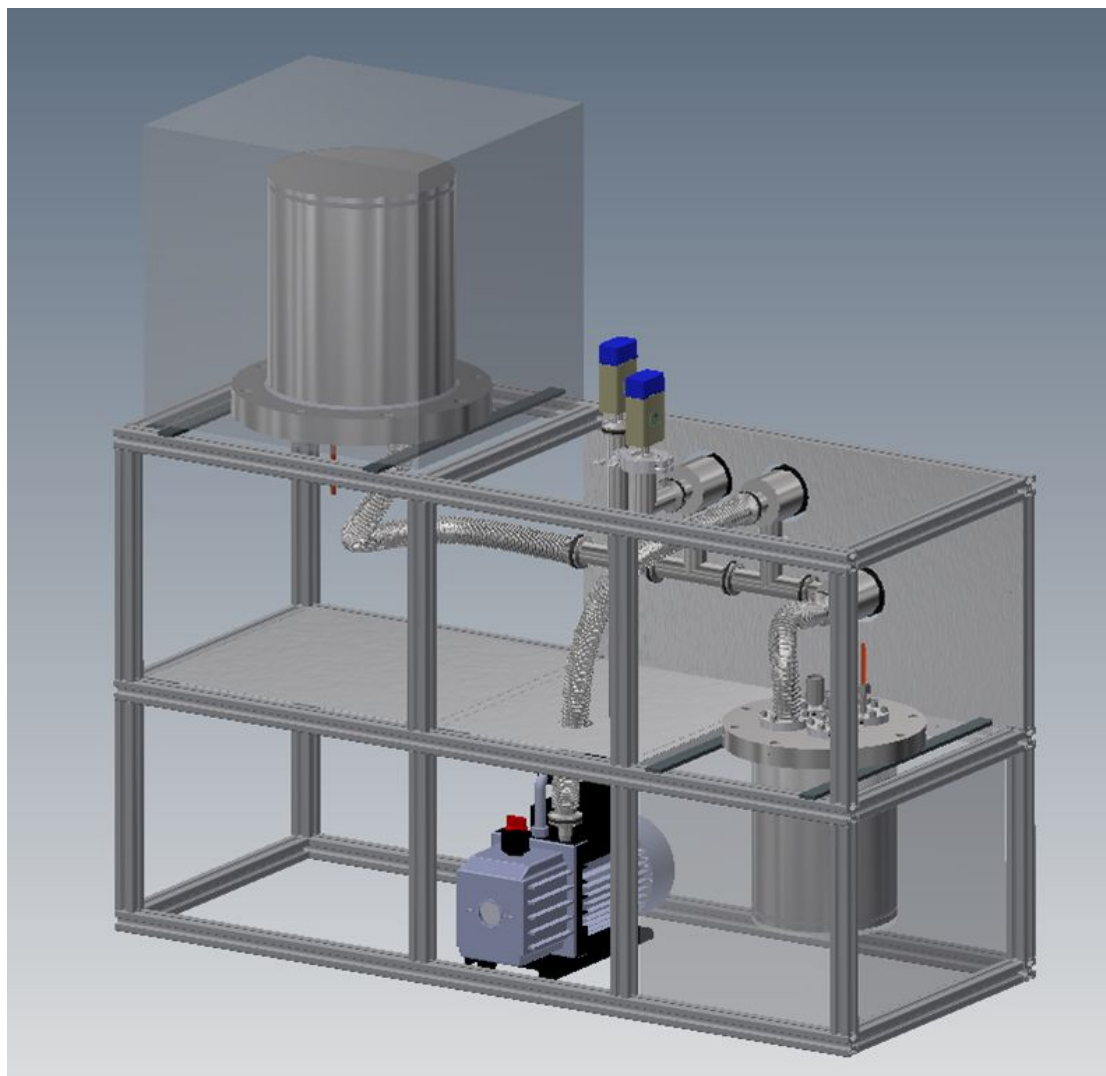


FIGURE 8.2: 3D visualization of the experimental heat storage system.

challenge in the terms of construction and operating parameters and entails several topics from variety of scientific disciplines and this is also one of the reasons, that despite the longevity of this field, practical application are still highly limited.

Together with the application development a material development and research will be absolutely necessary to constantly look for new option and progress. The highly intruding MOFs as a potentially next generation materials for adsorption heat transformations will be studied as well and once the industrial production will be available the potential can be father evolved. From this perspective a cooperation on development of new materials and production methods will be crucial for a successful design and application.

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Appendix A

Additional graphical material on
the properties of the TMPS
materials, SBA-15, and MCM-41

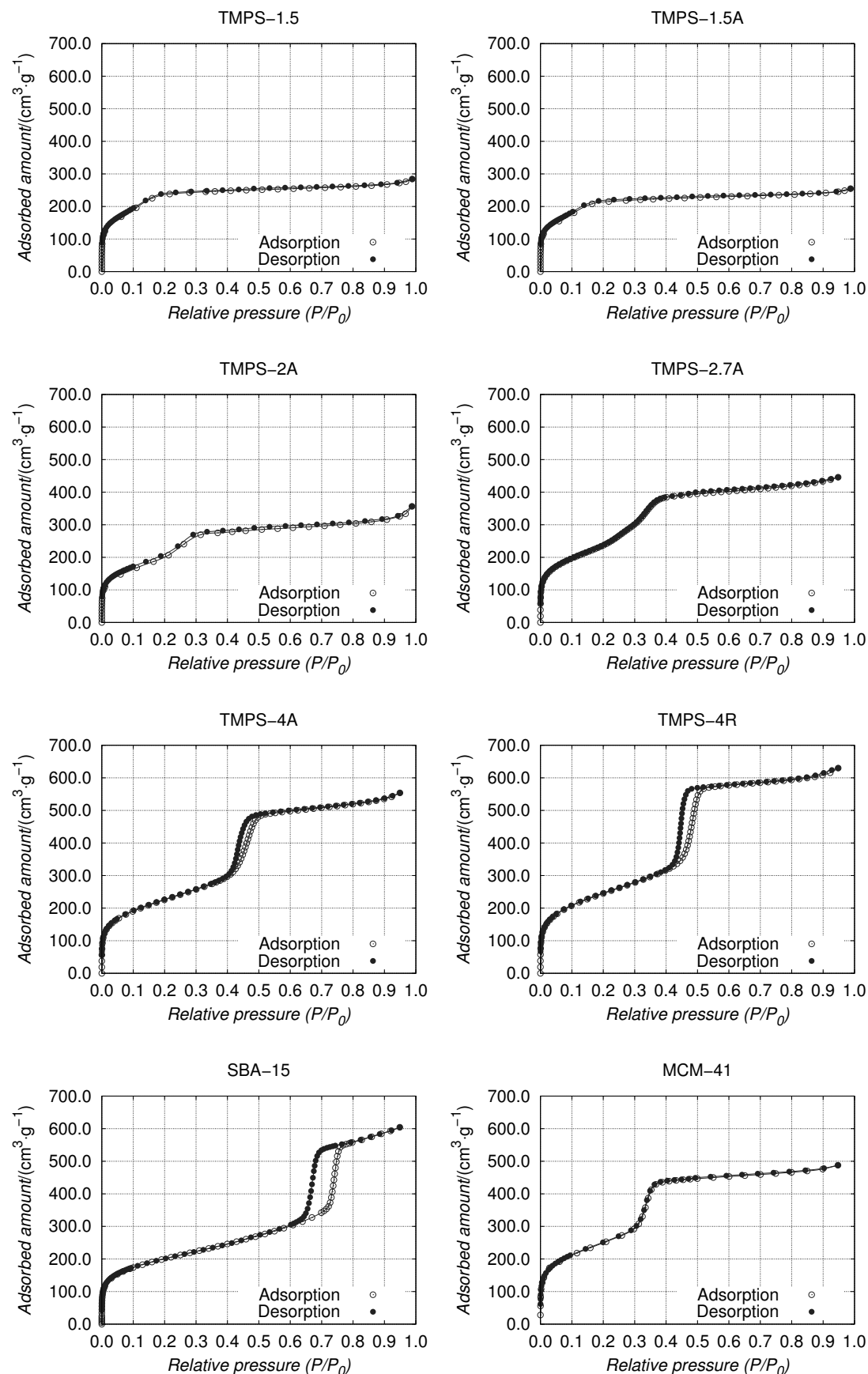


FIGURE A.1: Full adsorption-desorption cycle of nitrogen on the TMPS materials and regular mesoporous silica SBA-15 and MCM-41

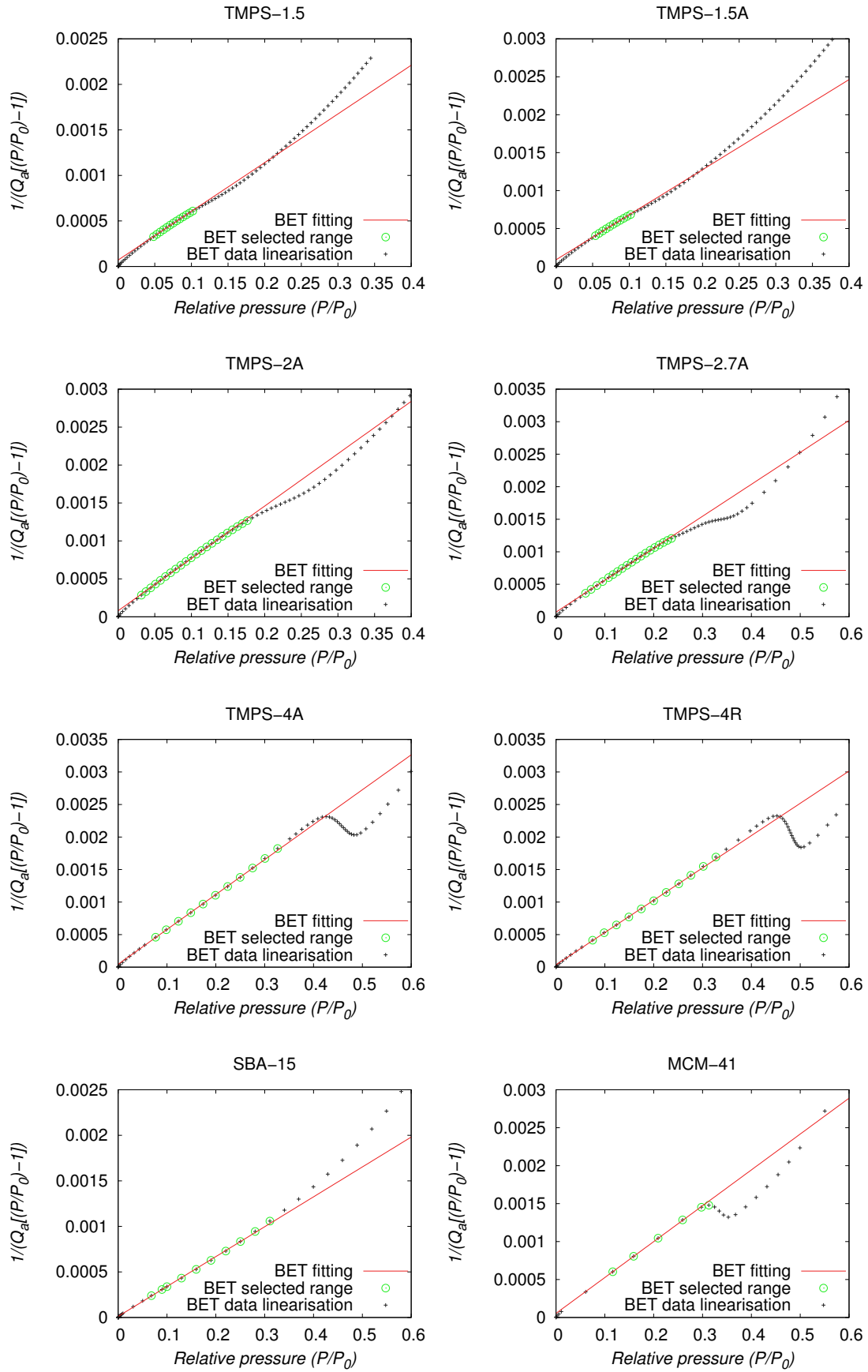


FIGURE A.2: BET analysis on the TMPS materials and regular mesoporous silica SBA-15 and MCM-41

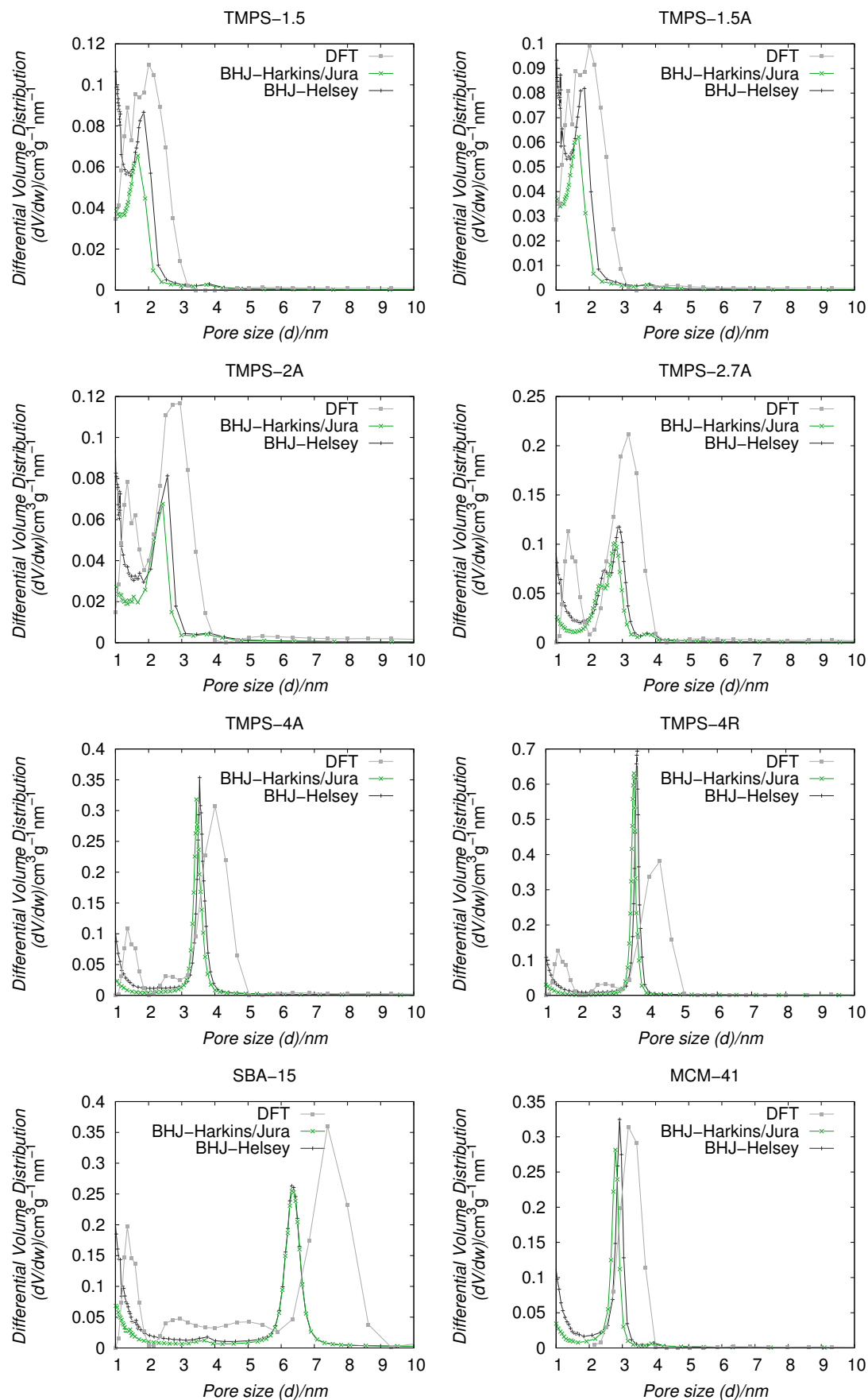


FIGURE A.3: Pore size distribution the TMPS materials and regular mesoporous silica SBA-15 and MCM-41



FIGURE A.4: FTIR analysis of the TMPS materials and regular mesoporous silica SBA-15 and MCM-41

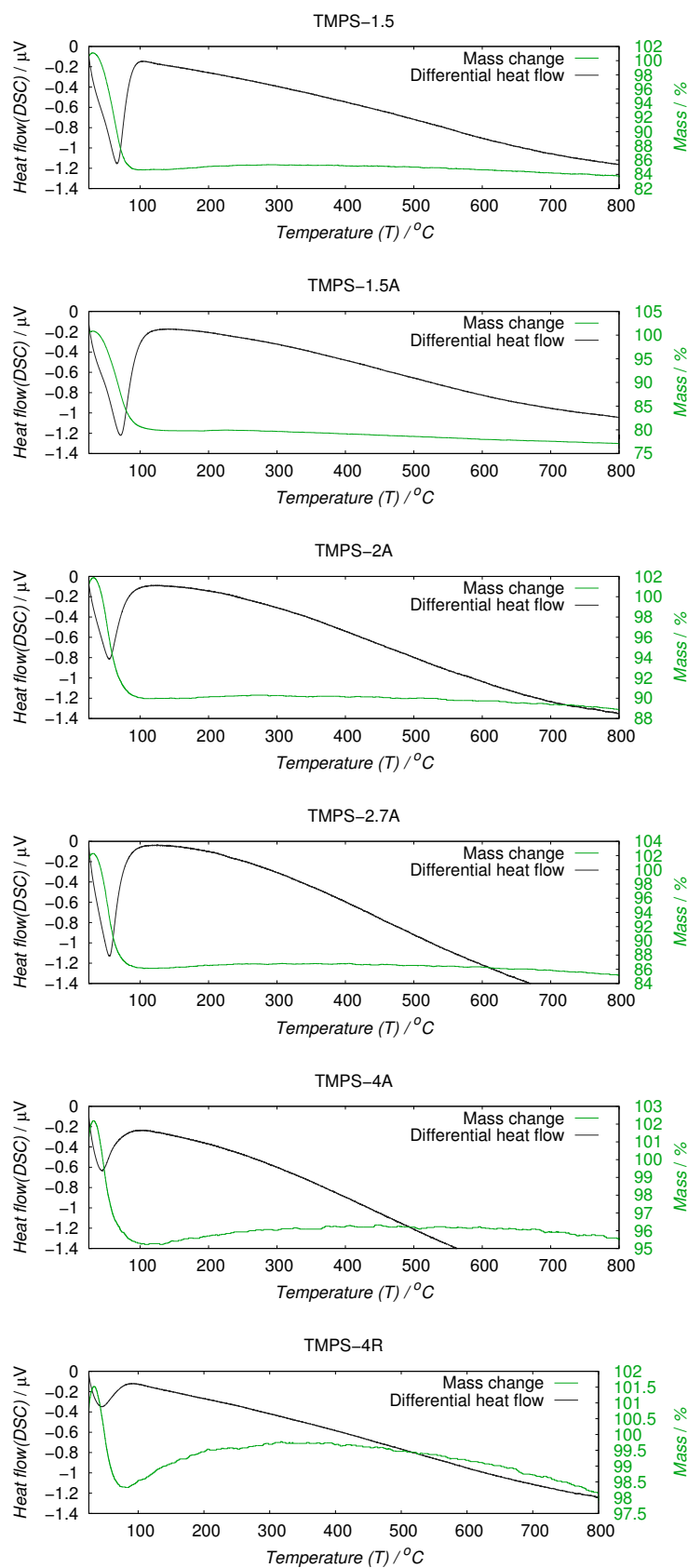


FIGURE A.5: Thermogravimetical analysis of the TMPS materials. Material stabilized in humid environment prior to measurement

Appendix B

Additional results on
adsorption-desorption kinetics on
TMPS and mesoporous silica
materials in finite volume
experiment

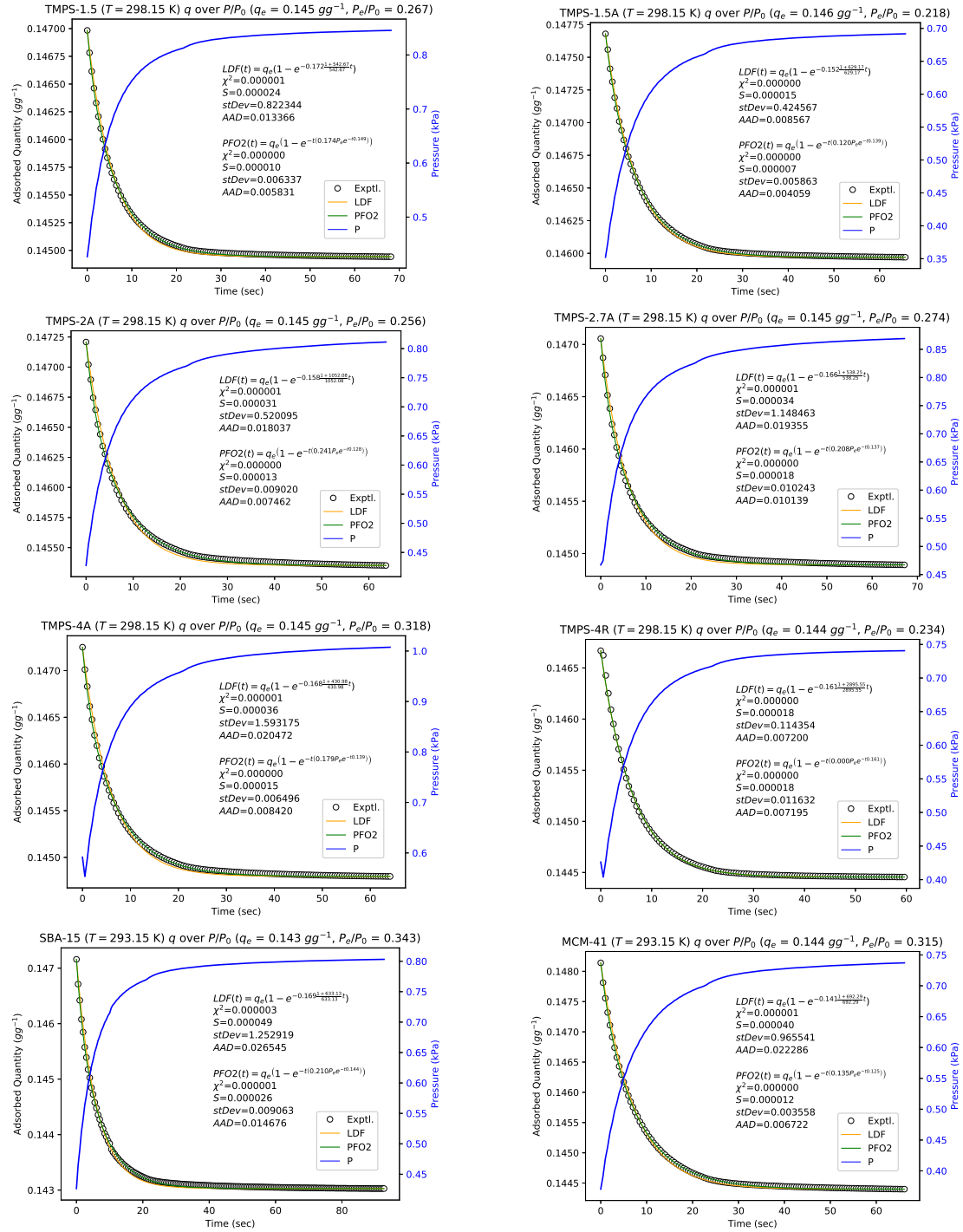
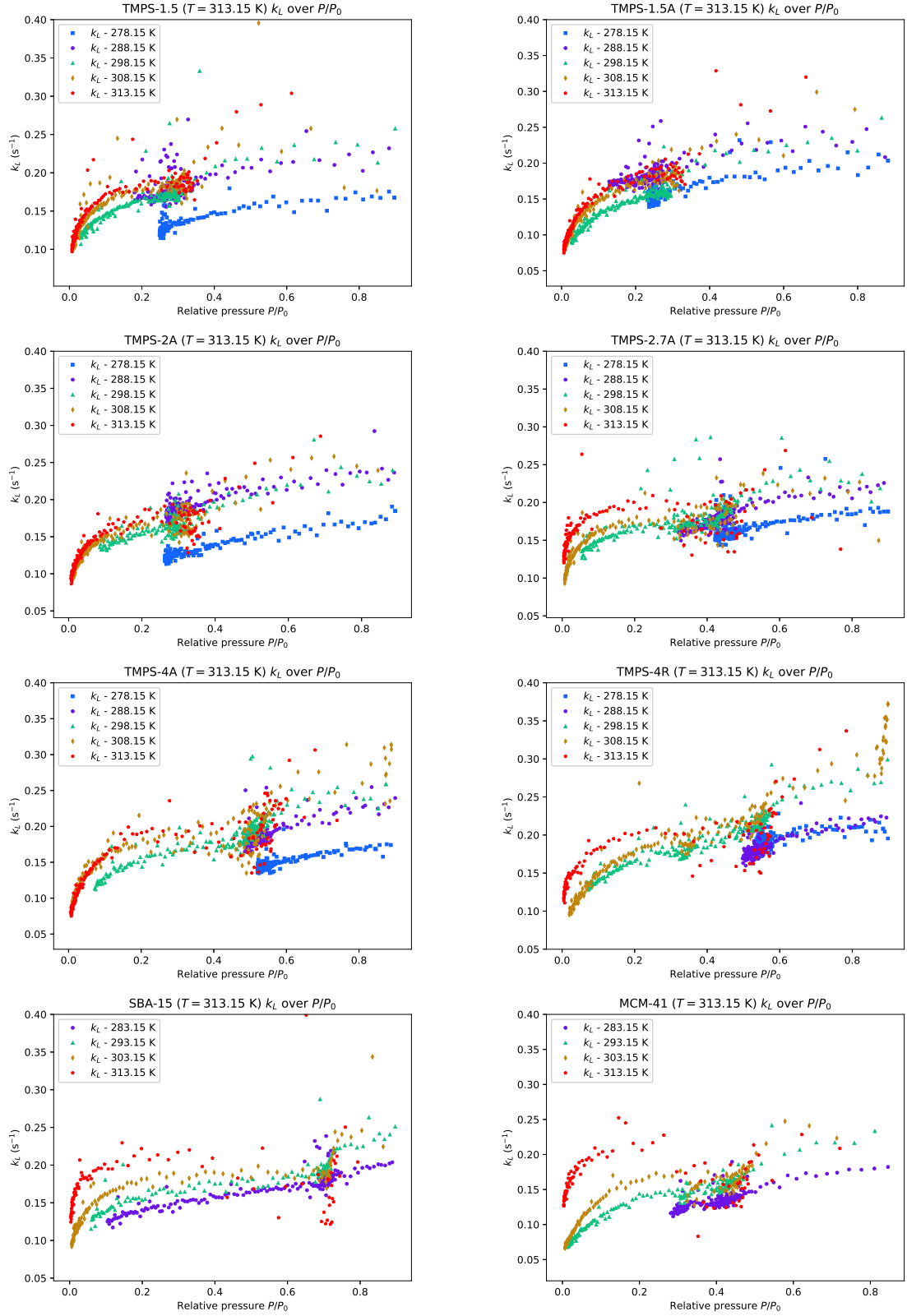


FIGURE B.1: Selection of the desorption curves for TMPS materials at $T = 298.15$ K, and for SBA-15 and MCM-41 at $T = 293.15$ K in the step of the equilibrium $q_e \approx 0.145$ $g g^{-1}$

FIGURE B.2: Desorption rates k_L and k_P on the relative pressure P/P_0

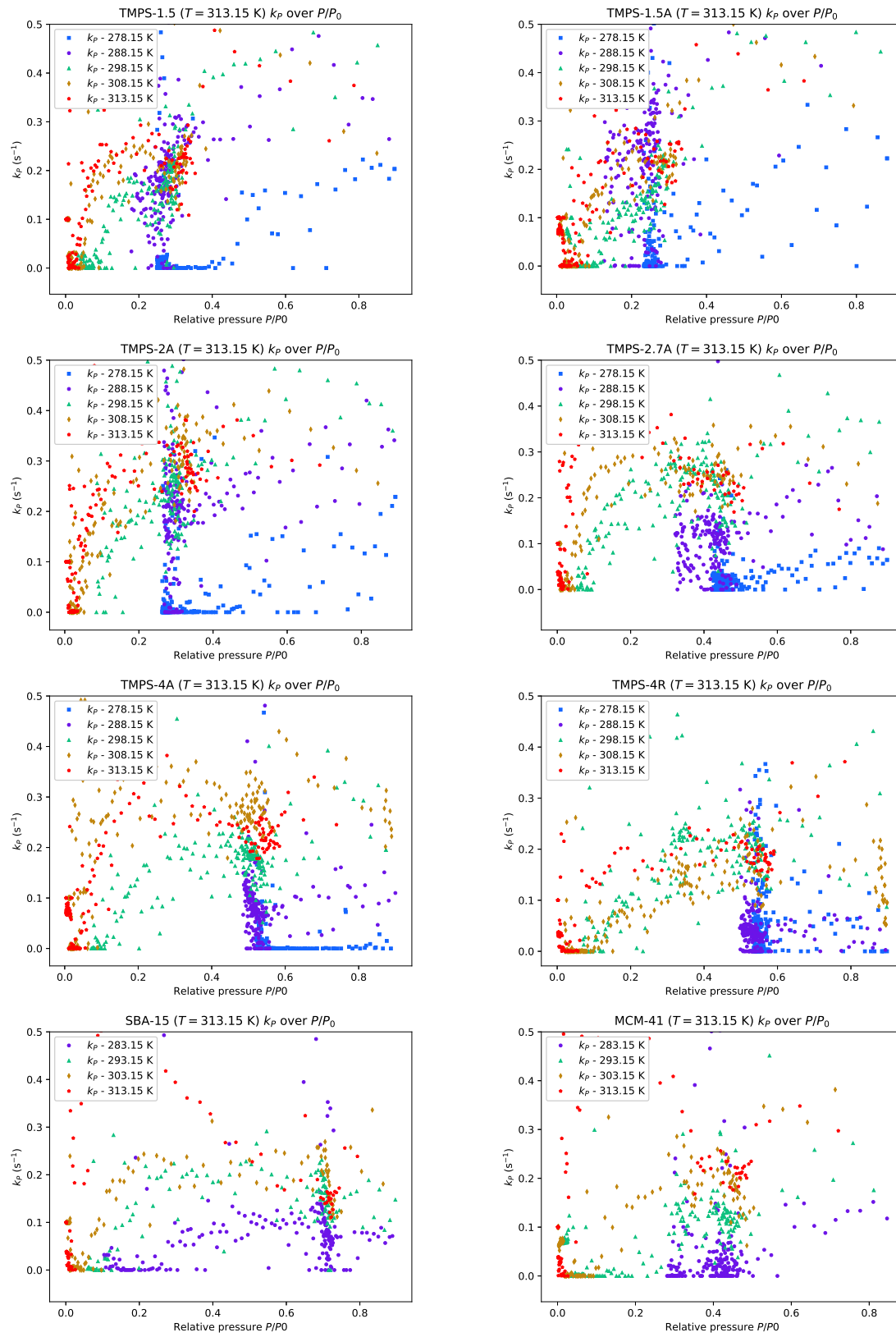


FIGURE B.2: (Continued) Desorption rates k_L and k_P on the relative pressure P/P_0