

# Functionalization of Silica Gel and MCM-41 via Gas Phase Adsorption – For Metal Removal

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## Introduction

Porous silica materials are attractive for a broad range of applications. Among the advantages of these materials are the numerous possibilities of shaping (powders, beads, membranes, cylindrical monoliths or tubes) as well as the adjustable pore width and pore volume. Furthermore, these materials are easy to functionalize, chemically inert, photochemically and thermally stable. Via the Si-OH-groups on the surface different functionalities can be covalently attached. This possibility is the basis for the development of regenerable and selective adsorbents, e.g., for heavy metals or CO<sub>2</sub>.

Commonly used methods for the functionalization of silica materials are performed in the liquid phase by the use of different organic solvents such as toluene or DMF. Another rarely described method is the gas phase adsorption of silanes onto porous silicas. This method was applied by Wikström et al. [1] who functionalized porous silica gels with aminosilanes resulting in very well distributed layers of silane functionalities on the surface [2]. In contrast to the functionalization in the liquid phase, the polycondensation of the silanes is reduced [3] and a multilayer formation can be prevented. This is of special importance for the functionalization of materials with smaller mesopores as present, e.g., in MCM-41. Thus, the “blocking” of the pores is avoided.

The present contribution describes the silylation of silica gel and MCM-41-type silicas [2] with mercaptopropyltrimethoxysilane (MPTMS) via gas phase adsorption. After functionalization the adsorption of palladium on the surface was studied via static adsorption experiments and flow experiments in a packed column.

## Materials and Methodes

- Silica gel with pore size of 15 nm, surface area of 290 m<sup>2</sup> g<sup>-1</sup> and 1 cm<sup>3</sup> g<sup>-1</sup> pore volume and MCM-41-material (MCM-pore volume of 0.49 and 0.83 cm<sup>3</sup> g<sup>-1</sup>) was used as starting material for functionalization.
- Certain amounts of MPTMS (Tab. 1) were added to a mixture of MeOH/ H<sub>2</sub>O for liquid phase reaction at 70°C in a teflon bottle.
- Gas phase functionalization were performed at 120°C, MPTMS were added to a reservoir whereupon it can evaporate and interact with the silica sample.
- Breakthrough curve, 500 mg silica-material, 1 ml min<sup>-1</sup> flow rate, 0,5 M l<sup>-1</sup> PdCl<sub>2</sub>-solution.
- Determination of concentration by UV-Vis measurement at 451 nm wave length.

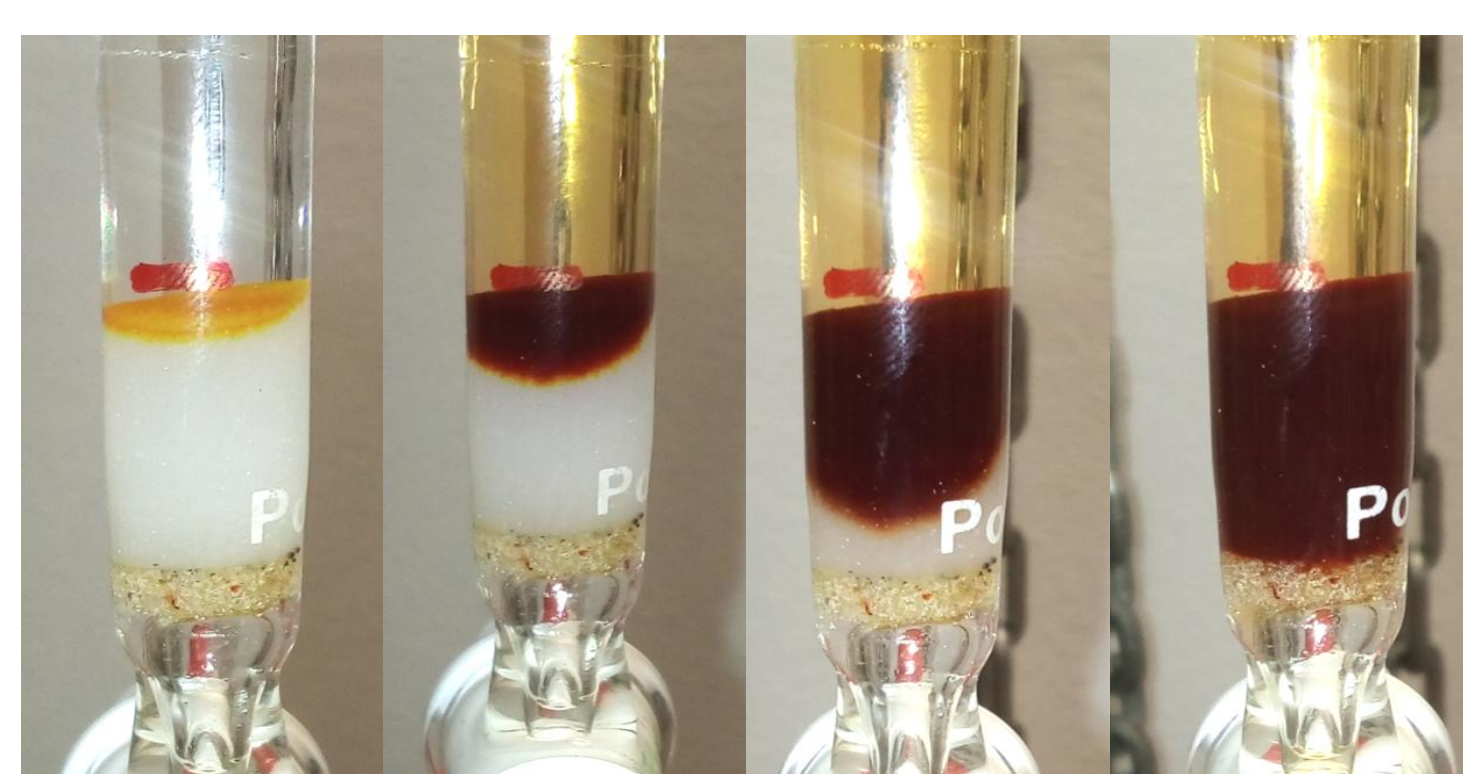


Fig. 1 Column for breakthrough measurements with 0,5 M l<sup>-1</sup> PdCl<sub>2</sub>-solution

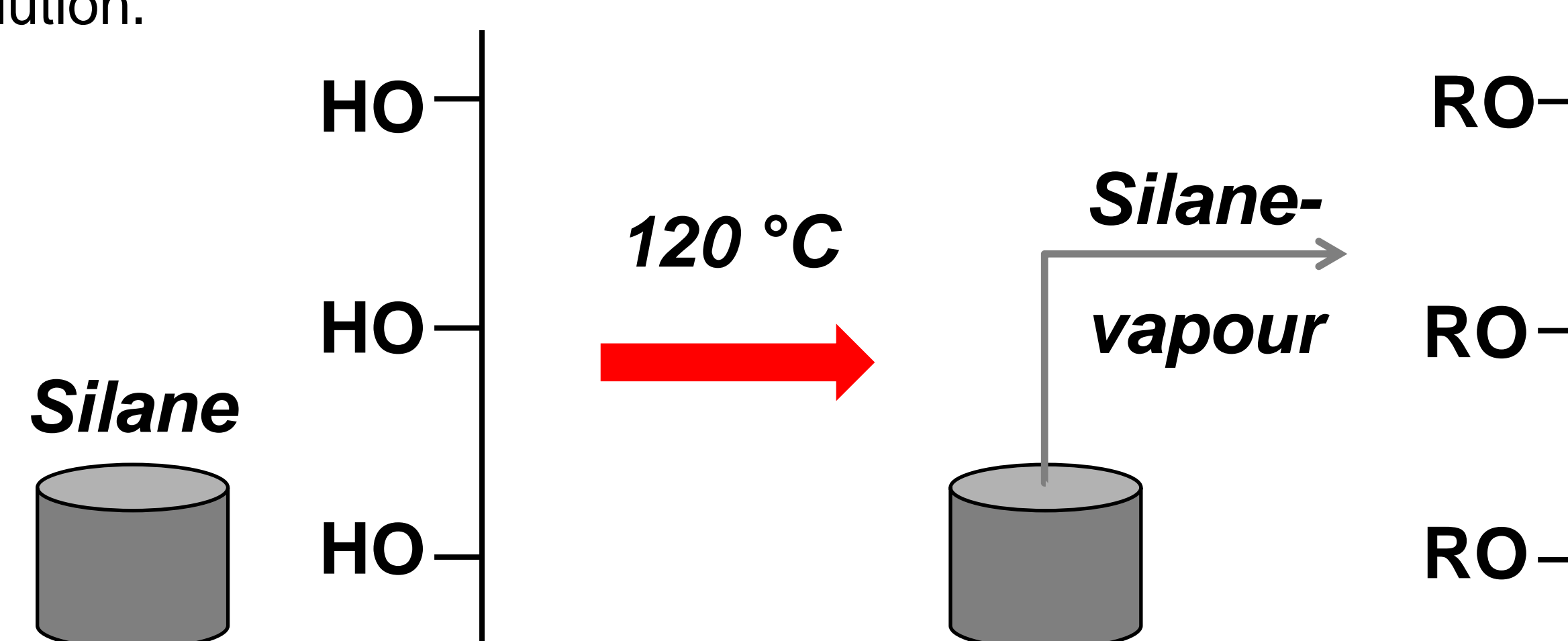


Fig. 2 Scheme of gas phase reaction of silane with hydroxyl terminated surface of the porous silica.

## Results

- 2 silica-gel samples functionalized in liquid phase (LP-250 and LP-180).
- 2 samples of silica-gel and 2 samples of MCM-41 (50% and 100%) functionalized in gas phase (GP).
- Considerable differences between adsorption capacity of materials functionalized in gas phase reaction and such materials functionalized in liquid phase (Fig. 4 and Tab. 2) based on the amount of silane.
- Homogeneously distributed layers of mercaptopropyl-groups via gas phase reaction on show higher effective adsorption capacities.
- Polymerisation occurring during the liquid phase reaction and thereby triggered steric hindrance could be the reason for reduced adsorption capacities.

Tab. 1 Comparison of textural data from starting material and functionalized materials

Sample name	A <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>	V <sub>mesopore</sub> / cm <sup>3</sup> g <sup>-1</sup>	V <sub>MCM-41</sub> / cm <sup>3</sup> g <sup>-1</sup>	d <sub>P Mesopore</sub> / nm*	d <sub>P MCM-41</sub> / nm*
Silica gel	290	1,10	-	15,0	-
GP-90	266	0,96	-	13,9	-
GP-180	240	0,86	-	13,9	-
50MCM-41	650	0,49	0,49	23,7	4,1
GP-50MCM-41	500	0,4	0,32	23,7	3,8
100MCM41	1040	0,11	0,83	24,6	4,1
GP-100MCM-41	911	0,13	0,47	-	3,5

\*From nitrogen sorption measurement

Tab. 2 Comparison of used materials with sulfur content and adsorption capacity

Sample name	Amount MPTMS / μl g <sup>-1</sup>	S-content / wt.-% <sup>1)</sup>	M <sub>Ads Pd</sub> / mmol g <sup>-1 2)</sup>	n <sub>Pd</sub> / n <sub>S</sub> ratio
Silica gel	0	0	0	0
LP-250	250	3,8	0,58	0,48
LP-500	500	4,9	0,73	0,47
GP-90	90	1,5	0,46	0,98
GP-180	180	2,7	0,76	0,90
GP-50MCM-41	180	2,7	0,69	0,81
GP-100MCM-41	300	4,1	0,99	0,77

<sup>1)</sup> From ICP-OES; <sup>2)</sup> From breakthrough experiments

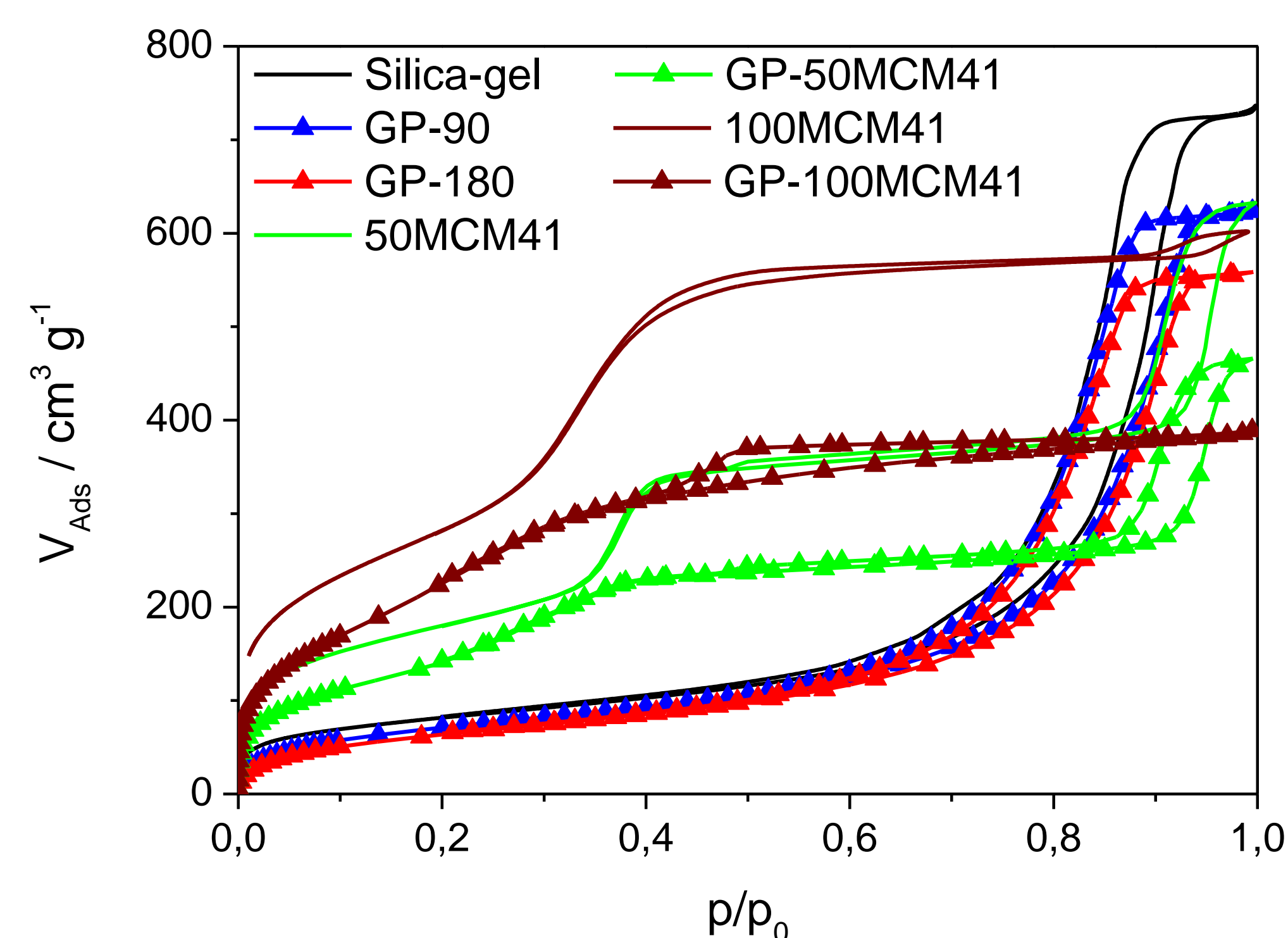


Fig. 3 Nitrogen sorption isotherms of the different starting materials and functionalized products

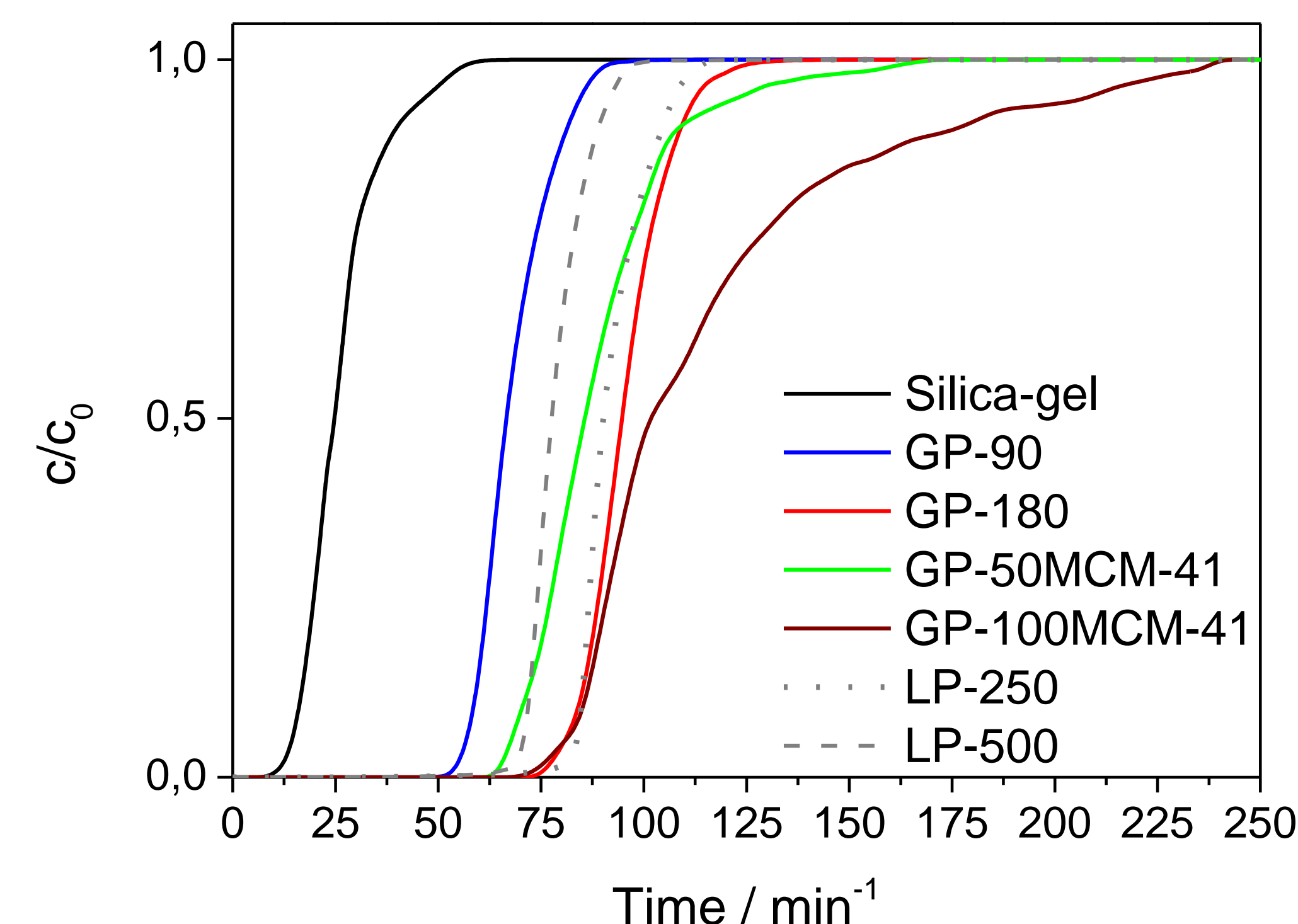


Fig. 4 Breakthrough curve of PdCl<sub>2</sub> from different silica materials functionalized with mercaptopropylsilane

## Conclusions

- Gas phase adsorption is a promising and effective way for functionalization → No solvents are necessary. → green chemistry
- The formation of a monolayer ensures higher adsorption capacities.
- Small pores (MCM-41) results in slower adsorption kinetics.

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