

Metal Phosphides and Zeolite-like Mesoporous Materials as Catalysts

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Abstract: Two new classes of materials, which we developed and use in our catalytic research, are described. Metal phosphides are studied for their use as model compounds for hydrodenitrogenation catalysis. M41S type materials contain mesopores, which enhance diffusion and, thus, the effectiveness of zeolitic materials in liquid-phase reactions. After grafting with sulfonic acid groups, they are used as wide-pore solid acids.

Keywords: Catalysis · Grafting · Hydrodenitrogenation · MCM-41 · Metal phosphides

Introduction

The improvement of existing catalysts and the invention of new ones goes hand-in-hand with research on catalytic materials. In this contribution, two classes of materials will be described. Metal phosphides are model systems for hydrodenitrogenation; the removal of nitrogen atoms from nitrogen-containing molecules, such as pyridine and quinoline, from oil fractions. Zeolites belong to an industrially very important class of compounds, which are used especially as detergents and as catalytic cracking catalysts. Their use in liquid-phase reactions is hampered by the slow diffusion through the narrow micropores. The creation of materials with well-defined mesopores will be introduced as well as the grafting of sulfonic acid groups on the walls of the mesopores.

Transition-Metal Phosphides as Hydrodenitrogenation Catalysts

The catalytic removal of nitrogen (hydrodenitrogenation) and sulfur (hydrodesulfurization) from crude oil is an increasingly important process and is

used in refineries worldwide. Sulfur- and nitrogen-containing compounds are not only extremely poisonous for noble metal catalysts used in the refineries, but also cause environmentally harmful emissions (NO_x , SO_2). Catalysts based on molybdenum disulfide have been successfully used in these processes for many years. However, significant improvements are necessary to meet the requirements of future environmental legislation. For this reason our research focuses on the development of more active catalysts.

During the hydrodenitrogenation and hydrodesulfurization processes, nitrogen- and sulfur-containing compounds are converted by H_2 to hydrocarbons and to NH_3 and H_2S , respectively. In industry, Co- or Ni-promoted MoS_2 -type phases, supported on $\gamma\text{-Al}_2\text{O}_3$, are used as the catalyst [1]. Apart from these promoted MoS_2 -type phases, transition-metal carbides and nitrides have also been tested and proved to be catalytically active as well [2]. Compared with sulfidic HDN catalysts, molybdenum nitrides behave more like metals, resulting in a higher selectivity to hydrogenolysis products. In contrast to the extent of research into nitrides and carbides, only few studies have been carried out on transition-metal phosphides. Phosphides or mixed phosphide sulfides have been considered in a few cases only as HDN or HDS catalysts, such as Ni_2P in the HDN of quinoline and NiPS_3 in the HDS of thiophene.

Transition-metal phosphides have a wide range of interesting chemical and

physical properties and show a variety of structural types [3]. The local coordination environment of the metal centers ranges from trigonal prismatic in MoP (Fig. 1) to triply capped trigonal prismatic in NiMoP (Fig. 2). Phosphides may be classified in various ways, the usual being based on the stoichiometry, *i.e.* metal-rich phosphides ($M/P > 1$), monophosphides ($M/P = 1$), and phosphorus-rich phosphides ($M/P < 1$). Due to the thermal and chemical instability of phosphorus-rich phosphides, better applicability is expected for phosphides with a ratio of $M/P \geq 1$. Metal-rich phosphides and, similarly, monophosphides are usually hard, brittle substances with a relatively high thermal and electrical conductivity and thermal stability. Since the hydrodenitrogenation reaction is performed at high temperatures and high pressures of H_2 , the stability of these compounds is particularly favourable. To investigate the hydrodenitrogenation of *o*-propylaniline (Scheme 1), we prepared and characterized Co_2P , Ni_2P , MoP , WP , CoMoP and NiMoP .

The general procedure that we used for preparing transition metal phosphides is as follows: Di-ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ is dissolved in deionized water. Then a solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, ammonium metatungstate $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ ($x = 18$), nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, or cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is added. In the case of the two ternary phosphides, first a solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7$

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$O_{24} \cdot 4H_2O$ followed by a solution of nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ or cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ are added to the phosphate solution. After evaporation of the water, the obtained solid is calcined in air at 773 K for 5 h and then reduced in a stream of H_2 at 823 K (Co_2P , Ni_2P), 923 K (MoP, WP, $NiMoP$), and 1023 K ($CoMoP$). Finally, the surface of the phosphides is passivated in a flow of 0.5% O_2/He at room temperature, so that the samples can be handled in air [4].

Catalytic measurements of the hydrodenitrogenation of *o*-propylaniline were done in the presence and in absence of H_2S by determining the activity before, during, and after addition of H_2S to the feed. All our phosphides are active in the hydrodenitrogenation of *o*-propylaniline. The cobalt compounds, Co_2P and $CoMoP$, are the least active catalysts. Ni_2P and $NiMoP$ perform much better, but Ni_2P loses some of its activity in the presence of H_2S . MoP and WP are the most active catalysts, with MoP having the highest activity. Moreover, MoP is the only sample which is activated by H_2S , *i.e.* its activity is significantly higher after the treatment with H_2S than before (Fig. 3) [4]. An estimation of the intrinsic activity of the MoP catalyst (Fig. 1) showed that this catalyst, although unsupported, is approximately six times more active than an MoS_2/Al_2O_3 catalyst [5].

Preparation of the binary and ternary phosphides on high-surface area carriers and the final tuning of the catalytic activity will be the next step in our research.

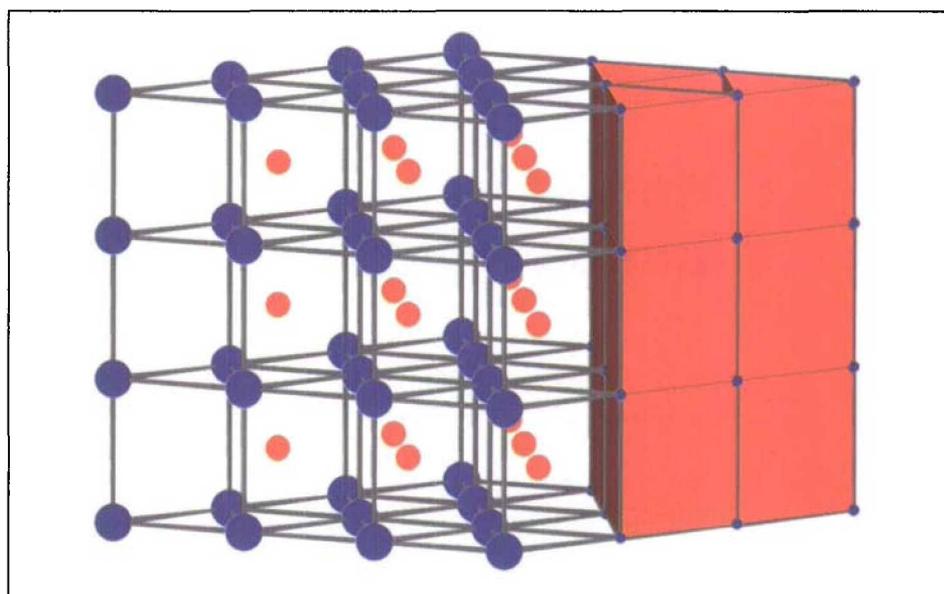


Fig. 1. Structure of MoP

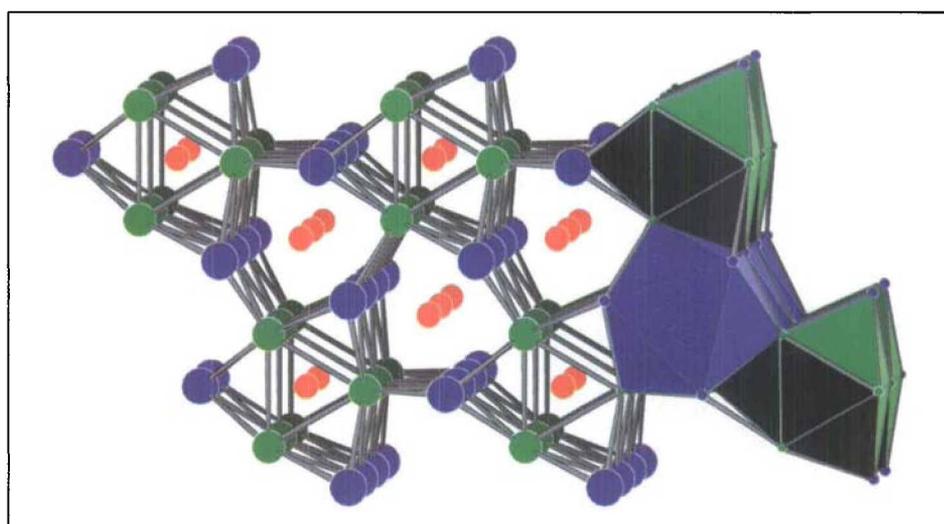
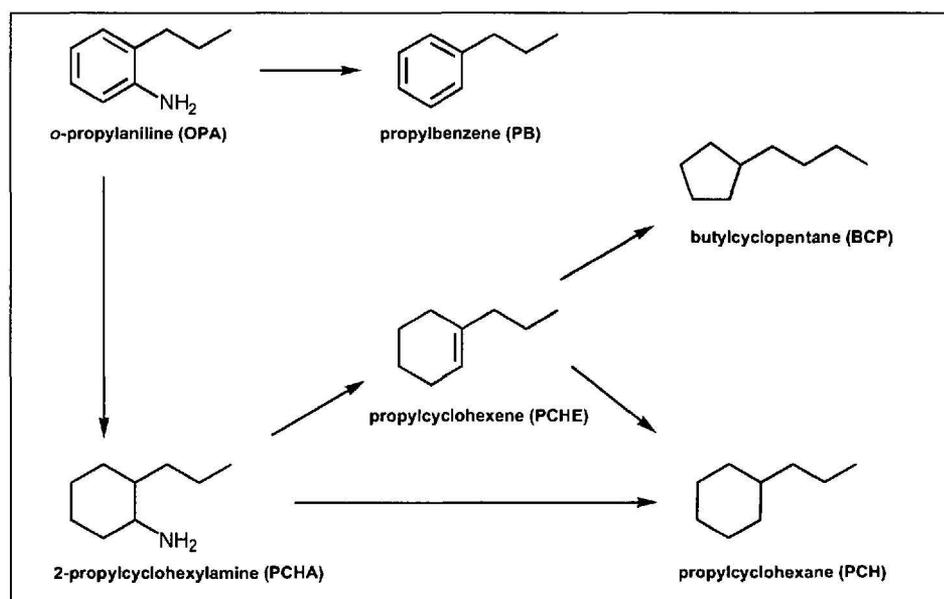


Fig. 2. Structure of NiMoP

Grafted Mesoporous M41S Materials as Acid Catalysts

Zeolites (microporous aluminosilicates) have two outstanding properties: (i) They have regular pores of defined size and can, thus, geometrically discriminate between molecules according to their size and steric arrangement. (ii) Due to their ion exchange capacity, which is given by the aluminum content, protons (Brønsted acid sites) or other cations (*e.g.* alkali-metal or transition-metal cations) can be introduced into the zeolite pores. The cations serve to change the sorption properties of the material, or they can be used as catalytic sites for a wide variety of chemical reactions. Owing to these properties zeolites have found widespread application as sorbents and catalysts. As catalysts, they are used mainly in the petroleum industry, especially zeolite Y, which is used as a fluid

Scheme 1. HDN reaction network of *o*-propylaniline

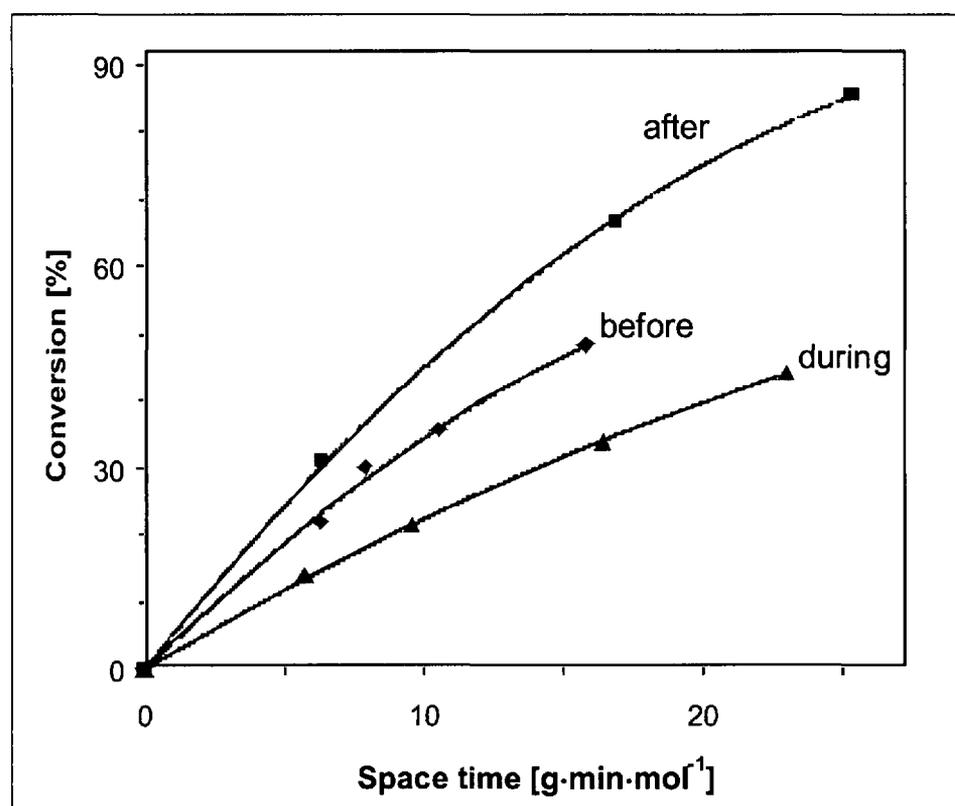


Fig. 3. HDN conversion of *o*-propylaniline over MoP before, during, and after treatment with H₂S

catalytic cracking catalyst. New fields of applications are emerging, however, in environmental and fine chemistry. Transition-metal exchanged zeolites have attracted much interest for the removal of NO_x from exhaust streams and for the destruction of chlorinated volatile organic compounds. In fine chemistry, there is a tendency to heterogenize homogeneously catalyzed reactions in order to facilitate the recovery of the catalyst from the solution. Much effort has been made, for example, to replace liquid acids by zeolites.

For many fine chemistry applications, however, the zeolite pores are too small. When bulkier organic molecules have to be converted, their diffusion to the active sites in the zeolite pores can be strongly restricted or even completely prohibited. In such cases, mesoporous materials like MCM-41 come into play. These materials have tunable pore sizes ranging from 20 to 35 Å. By adapting the synthesis procedure, even larger pore sizes of up to 80 Å are attainable [6]. These materials (M41S) have less regular pores than MCM-41 and a broader size distribution. The major disadvantages of MCM-41 and M41S are that, unlike zeolites, they have amorphous pore walls and, thus, only weak Brønsted acidity. Their main use is as support materials for catalytically active sites, which can be anchored to the MCM-41 surface by grafting. The

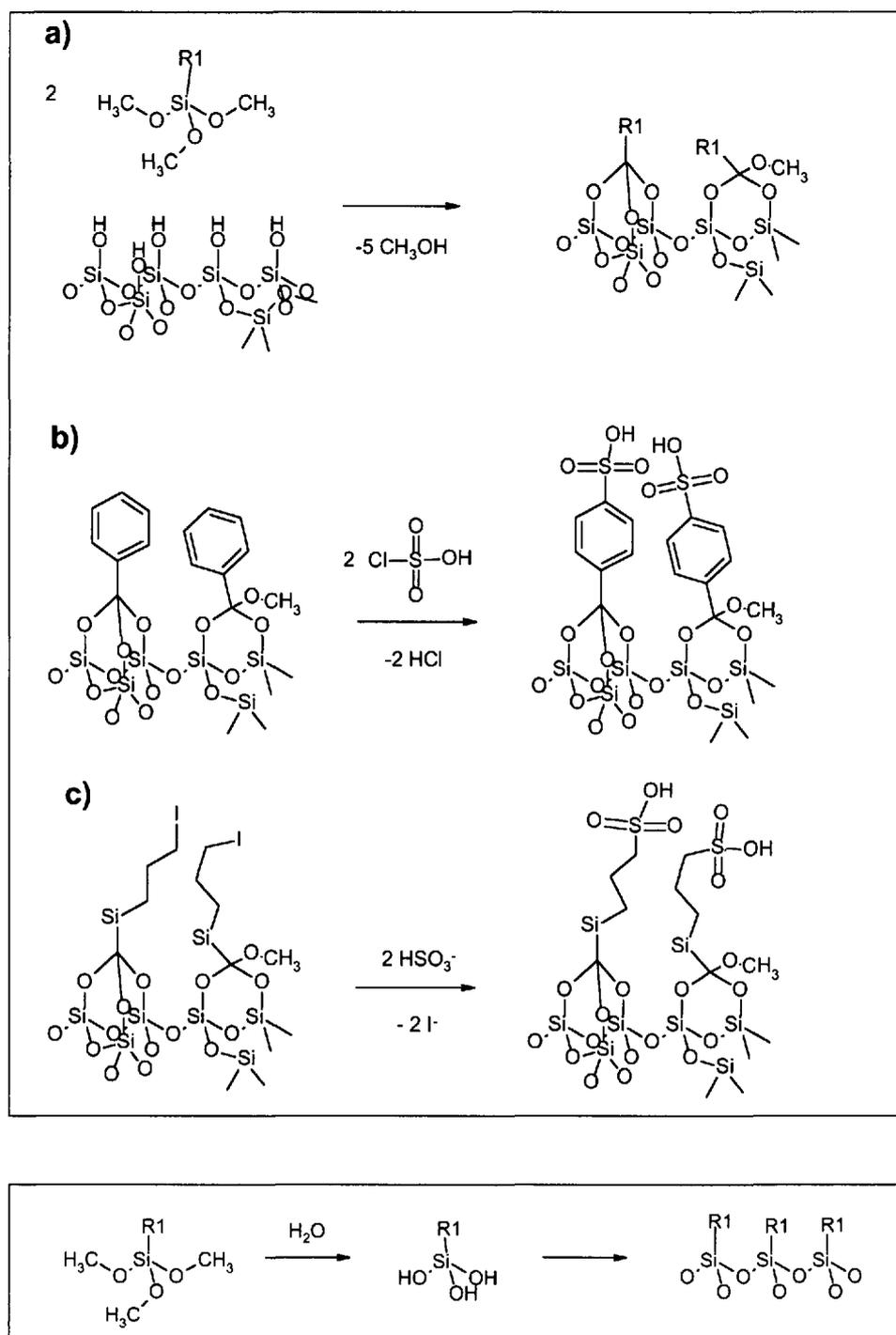
surface area of MCM-41 is very large, about 1000 m²/g, and the material has a high density of silanol groups, making it very suitable for grafting. Several metal-organic oxidation catalysts have been successfully heterogenized by grafting onto MCM-41, with little loss of activity [7].

Research in our group focuses on the introduction of strong acidity into MCM-41, so that it can be used as a zeolite-analogue with larger pores (see Scheme 2). First, a layer of phenyl (or halogenoalkyl) moieties is grafted onto MCM-41 (M41S). Then, -SO₃H groups are introduced by a substitution reaction (S_E on phenyl, S_N on halogenoalkyl). The immobilized sulfonic acid provides the desired strong Brønsted acidity.

We have put much effort into trying to optimize the first of the two steps, *i.e.* the grafting of organic moieties onto MCM-41 (M41S). As expected, we found that a high density of silanol groups in the starting material is crucial for obtaining a high coverage of the grafted species. The density of the silanol groups strongly depends on the post-synthesis treatment of MCM-41. MCM-41 (M41S) is synthesized using surfactant molecules (*e.g.* cetyltrimethylammonium bromide) as a template. They form a micelle, around which the silica pore wall is assembled. In order to remove the template from the pores, the material must be calcined at

high temperatures. During this high-temperature treatment, many silanol groups on the surface condense. They can be restored, however, by boiling the calcined MCM-41 (M41S) in water. This leads to the opening of tense and, thus, weak Si-O-Si bonds, formed during the calcination of the parent material. The water, which remains adsorbed on the material after the hydroxylation, can, however, affect the following grafting step. Too much water can hydrolyze the Si-OR bonds of the grafting agent and lead to an internal condensation of the siloxane (see Scheme 3) instead of a condensation with the surface silanol groups. Therefore, in the original procedure [8], some of the water was removed by azeotropic distillation before the grafting. This, of course, leads to recondensation of some of the silanol groups. Our results show that the concerns about internal condensation of the grafting agent are unfounded, and that the best grafting results are achieved when the hydroxylated MCM-41 is used as such.

The aim of grafting alkyl (aryl) alkoxy-silanes is to achieve a homogeneous, fully condensed layer of silane on the surface, which completely covers the silanol groups. In order to obtain tight anchoring, a reaction of all three hydroxyl groups of RSi(OH)₃ with the surface is the preferred binding mode. Surface coverage and the binding mode can be deter-



Scheme 2. Schematic representation of (a) the grafting of alkyl(aryl) trimethoxysilanes onto MCM-41 (M41S), (b) the sulfonation of grafted phenylsilane with chlorosulfonic acid, and (c) the sulfonation of grafted iodopropylsilane with sulfite.

Scheme 3. Schematic representation of the internal condensation of alkyl(aryl)siloxanes, catalyzed by water.

mined by thermogravimetric analysis (TGA) and by ^{29}Si NMR spectroscopy. In TGA, the grafted MCM-41 is slowly heated in a stream of N_2 , which leads to the removal of the organic moieties at higher temperatures. The surface coverage can be calculated from the loss of weight and the molecular weight of the grafted molecule.

^{29}Si NMR, on the other hand, gives more detailed information on the binding mode with the surface. Depending on the type and number of neighbors, *i.e.* $-\text{OSi}$, $-\text{OH}$, $-\text{R}$, the ^{29}Si nuclei give different NMR signals. One can differentiate between Q_n atoms in the pore wall, with

$\text{Si}(\text{OSi})_n(\text{OH})_{4-n}$ coordination, and the T_n atoms of the silane, with $\text{SiR}(\text{OSi})_n(\text{OH})_{3-n}$ coordination (see Fig. 4). The higher the n , the higher the shielding, and the signals appear at higher fields. T_n atoms generally appear at less negative δ -values than Q_n -atoms.

The real power of NMR is, however, that it can differentiate between surface species in co-grafting experiments. Co-grafting of halogenoalkylsilanes with alkylsilanes is used to regulate the concentration of functional groups, which can be obtained by substitution of the halogen (see Scheme 2c), and to dilute them on the surface. For example, the co-grafting

of propyltrimethoxysilane and iodopropyltrimethoxysilane was studied. By integration of the ^1H NMR signals characteristic of C_3H_7 and $\text{C}_3\text{H}_6\text{I}$, we proved that the ratio of C_3H_7 and $\text{C}_3\text{H}_6\text{I}$ on the surface is the same as that used in the grafting solution (Fig. 5).

However, the second step of the reaction, the introduction of the sulfonic acid group, has not yet been performed successfully. While the reaction $\text{R-I} + \text{HSO}_3^- \rightarrow \text{R-SO}_3\text{H} + \text{I}^-$ proceeds smoothly in quantitative yield in aqueous solution, nucleophilic substitution was rarely observed in M41S. A unimolecular substitution reaction ($\text{S}_{\text{N}}1$) is prevented, be-

Fig. 4. ^{29}Si NMR spectra of a) water-treated M41S, b) phenyl-trimethoxysilane grafted M41S, and c) phenyl-trimethoxysilane.

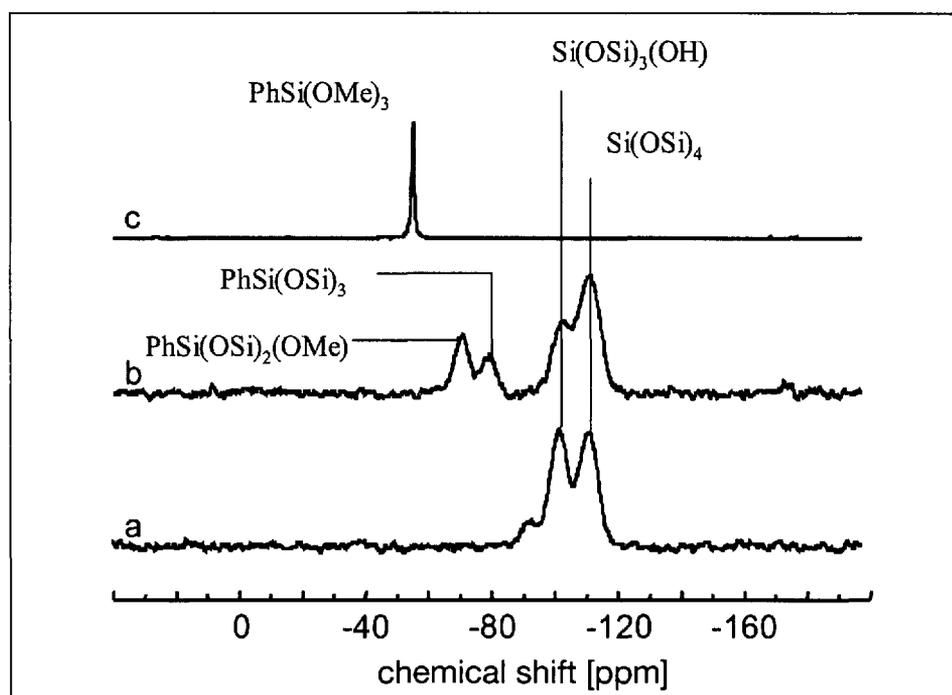
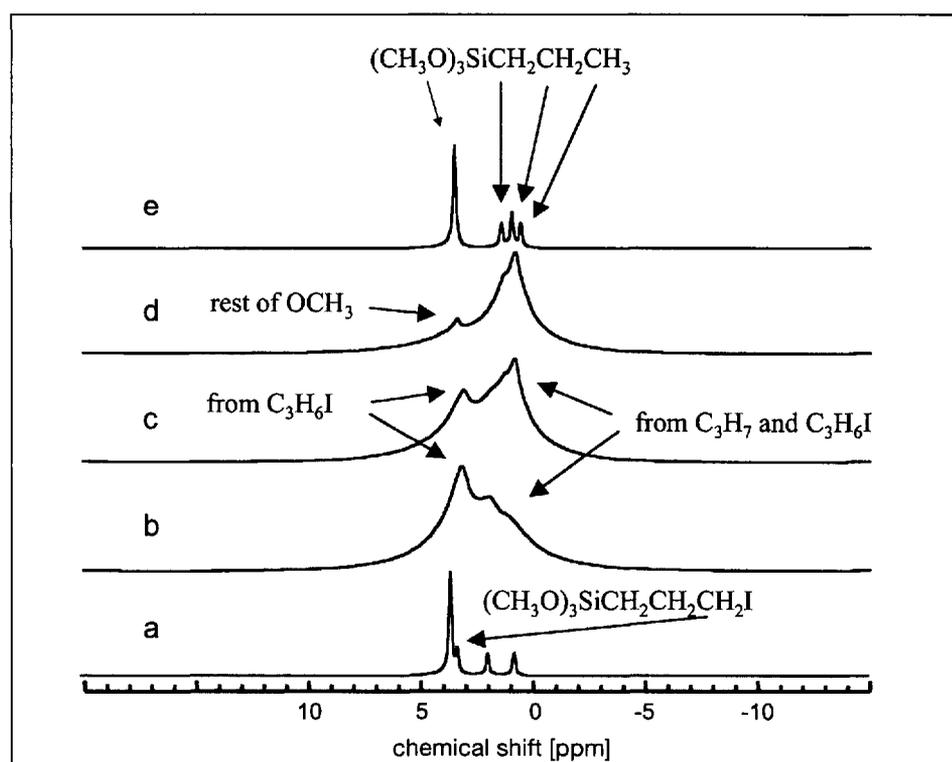


Fig. 5. ^1H NMR spectra of a) iodopropyl-trimethoxysilane (IPr-TMS), b) IPr-TMS grafted on M41S, c) a 1:1 mixture of IPr-TMS and propyltrimethoxysilane (Pr-TMS) grafted on M41S, d) Pr-TMS grafted on M41S, and e) Pr-TMS.



cause the hydrophobic M41S pores can only be moistened by a rather apolar solvent, which does not stabilize the ionic intermediates of the $\text{S}_{\text{N}}1$ mechanism. A bimolecular substitution reaction ($\text{S}_{\text{N}}2$), on the other hand, is hindered because the dense arrangement of the propyl-chains on the surface does not enable iodine to attack from the back side. This shows that classical chemistry cannot always be applied for reactions on surfaces. New solutions must be found.

The aim of this overview is to illustrate the possibilities that the grafting of M41S materials offer for the synthesis of novel acid catalysts. Many of these possibilities have yet to be explored.

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