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Surface and texture properties of mesoporous silica materials modified by silicon-organic compounds containing quaternary amino groups for their application in base-catalyzed reactions

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ABSTRACT

The synthesis of organic–inorganic composite materials (OICM) was performed by the surface modification of mesoporous silica material (MM) type MCM-41 by *N*-((trimethoxysilyl)propyl)-*N*,*N*,*N*-trimethylammonium chloride (TMTMAC). The application of diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, X-ray diffraction (XRD), N_2 adsorption/desorption and thermogravimetric analysis (TGA) showed that the distribution of grafted TMTMAC strongly depended on polarity and nature of solvent used for grafting. For water a clustering of TMTMAC resulted in a pore blockage. Methanol was identified to be the most suitable solvent to obtain a low loading and more homogeneous distribution of aminosilanes. Thermogravimetric analysis showed the composites were thermally stable up to 180 °C.

1. Introduction

Organic–inorganic composites attract significant interest as polyfunctional materials. The combination of properties of various materials increases the efficiency of material usages. Change of structural characteristics at nanolevel and use of more ordered structures allows to make processes more purposeful with fewer expenses.

In 1990, Kuroda and co-workers first reported the preparation of mesoporous silica with uniform pore size distribution. These materials were named FSM-16 [1,2]. Beck et al. reported materials having large uniform pore structures, high specific surface area, specific pore volume and hexagonal geometry (MCM-41) [3]. The ordered mesoporous materials MCM-41 are of particular interest as inorganic matrices. The pore system of MCM-41 consists of parallel tubes having a hexagonal structure of mesopores with a size of about 40 Å [3]. In addition, they have high surface area, enabling access of organofunctional groups during the modification. The functionalization of solid-state nanoporous materials with organic amino guests has opened wide perspectives for application of these materials in various fields of science and technology, such as adsorption [4–6], chromatography [7,8], sensors [9] and electrochemistry [10,11]. Since their discovery [3], mesoporous materials have been used as appropriate host materials for various organic functional groups [12–15] due to their tunable, highly ordered pore structures, high surface areas and pore volumes [3]. Several authors reported successful grafting of inorganic backbones by aminoorganosilanes [16–19], while others reported similar compounds could be obtained by sol–gel synthesis [10,20–22]. Both methods allow tailor-made creation of basic surface properties. Although the development of one-pot synthesis of functionalized mesoporous silica is still progressing, the postsynthetic grafting of initial silica matrix continues to be of great interest because, in most cases the mesostructure of the initial silica is retained and there is a possibility to control the pore size and periodicity. However, in postsynthetic grafting, there is a problem of non-homogeneous distribution of organic groups. The reaction occurs mostly at the pore openings, which impedes the diffusion of organosilanes into the center of the pores [23] and should be controlled.

The homogeneity of grafting is influenced by: (1) the presence of water trace in solvent used for grafting; (2) the nature of proposed aminosilane – monoalkoxy-, dialkoxy-, trialkoxysilanes; (3) the polarity of solvent. In this work the focus has been done on the polarity of solvent, used during the grafting of MM.

Some researchers have already published papers discussing functionalization of silica with primary [24,25] and quaternary

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[9,20] amine groups. The reaction of surface silanol groups with aminosilanes was usually conducted by refluxing in toluene [14,25–34]. By applying such a surface modification almost all free silanol groups participated in the reaction, which leads to obtaining the organic–inorganic hybrids with a high percentage of pores filled with organic moieties. In some cases, dichloromethane can be used for these purposes [9,35]. The decrease of both surface area and pore volume follows a high density of functional groups [36] that, in the application of such materials as catalysts, can result in hindering the diffusion of both reactant and products, i.e., deactivation of a catalyst material. Brüwiler et al. [25] also found the influence of the polarity of used solvent (toluene and THF) on the distribution of aminogroups. The polar-protic (isopropanol, ethanol, methanol, formamide), dipolar-aprotic (THF, acetone, DMF, acetonitrile, DMSO) and nonpolar solvents (toluene, chloroform, ethyl acetate) were also investigated as the media for grafting reaction [37]. Polar-protic solvents solvate the reactants better than nonpolar, which provide negligible solvation of silanol groups. Grafting in such type of solvent resulted in a lower number of immobilized organic groups compared to grafting in toluene; it produced materials with better structures and properties, including higher surface area and possibly more site-isolated organocatalytic sites. Although, there are some publications devoted to the synthesis procedure of mesoporous materials, modified by primary aminosilanes with homogeneous filling of organic moieties [36,37], to the best of our knowledge the work about obtaining the mesoporous materials with grafted quaternary aminosilanes has not been reported.

The aim of this work was the synthesis of composite materials with quaternary amino groups by chemical surface modification of mesoporous material and their application as base catalysts for Knoevenagel condensation. Special emphasis was placed on homogeneous distribution of functional groups in the pore space while maintaining the characteristic ordered pore structure.

2. Experimental

2.1. Materials

Mesoporous silica material (MM), synthesized by Süd Chemie (Germany) was used as an inorganic matrix for the synthesis of composites. The synthesis was carried out according to the literature [3]. The modifier *N*-((trimethoxysilyl)propyl)-*N*,*N*,*N*-trimethylammonium chloride (TMTMAC), 50% concentration in methanol, was purchased through the ABCR Company (Germany). Toluene and methanol were obtained from Sigma Aldrich (Germany). Before use the solvents were dried with zeolite over 24 h. Water was purified by distillation.

2.2. Surface modification of MM with quaternary aminogroups

Quaternary aminofunctionalized MM samples were prepared by the addition of TMTMAC to a suspension of calcined MM and corresponding solvent (Table 1). Prior to the modification, MM was pretreated by activation at 130 °C over 12 h in a flow of nitrogen. In a typical reaction, 1 g of dry MM was added to 50 ml of solvent, followed by the addition of 1 ml of TMTMAC. The solution was mixed at room temperature for 4 h. Then the products were washed with 100 ml of corresponding solvent and 100 ml of n-hexane and dried at 60 °C for 4 h. The surface modification was carried out in water, toluene and methanol in order to compare the influence of specific solvent on the properties of the materials. Modified materials were denoted below as MNW – modification in water, MNT – in toluene and MNM – in methanol. An amount of TMTMAC of $\nu = 1.8–3.6$ mmol/g was applied to study the influence of concentration on the degree of grafting (Table 1).

Table 1
Quantities of TMTMAC used for grafting in different solvents.

Sample	Solvent	$\nu_{\text{mod, mmol}}$[a]
MNM1	Methanol	3.6
MNM2	Methanol	1.8
MNT	Toluene	1.8
MNW	Water	1.8

[a] $\nu_{\text{mod, mmol}}$ – applied amount of TMTMAC per gram of MM.

2.3. Characterization of modified MM samples

Nitrogen adsorption/desorption isotherms were obtained at 77 K and relative pressure range $p/p_0 = 0.10–0.99$ using Quadrasorb-SI MP (Quantachrome, USA). Prior to each measurement the samples were degassed at 65 °C for 20 h in a vacuum. Surface area was determined from adsorption branches of the isotherm according to the Brunauer–Emmett–Teller (BET) method [38]. The pore size and its distribution were calculated by applying the Barrett–Joyner–Halenda (BJH) model. Solid-state ^{29}Si NMR-spectra were obtained at 79.5 MHz on a Bruker 400 NMR spectrometer. Pulse delay was 1s and the 4 mm probe was spun with a frequency of 10 kHz. Powder X-ray diffraction (XRD) patterns were recorded with a ARL XTRA diffractometer using Cu Kα radiation ($\lambda = 1.54056$ Å). DRIFT spectra were recorded on a Bruker Equinox 55 for a wavenumber range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Samples were prepared by mixing the test sample with KBr (Merck, Germany) at a ratio of 1:4. The «Harricks cell» attachment for *in situ* heating was used to remove adsorbed water from the samples, as well as to detect structural changes of the sample during the heating. Nitrogen was passed through the sample at a flow rate of approximately 60 ml/min, removing the products of desorption and decomposition. IR spectra were recorded for the samples after being held for 90 min at 25 °C. This procedure was repeated at temperatures of 150 and 250 °C, respectively. Determination of thermal stability was carried out using thermoanalyser TGA/SDTA 851e (Mettler-Toledo GmbH, Germany). Thermogravimetric analysis (TGA) was made in an atmosphere of nitrogen, using a maximum heating rate of 5 °C/min in a temperature range of 25–700 °C.

3. Results and discussion

3.1. Nitrogen adsorption/desorption measurements

The influence of solvent on the functionalization of MM with TMTMAC was investigated by nitrogen adsorption/desorption measurements. Figs.1 and 2 provide the nitrogen adsorption/desorption isotherms for the parent and modified MM samples. The data curves refer to the type IV isotherms according to IUPAC classification, which are characteristic for mesoporous materials. Filling of mesopores took place at $p/p_0 = 0.2–0.4$. For the samples treated in toluene and methanol, a change in the type of adsorption isotherms was not observed, suggesting retention of the hysteresis in a relative pressure range of $p/p_0 = 0.4–0.6$. For samples modified both in toluene (MNT) and water (MNW), respectively, drastic decreases in the amount of adsorbed nitrogen were observed. The isotherms after modification in toluene and water, could indicate a high percentage of filled pores with the modifying agent [36], which resulted in a significant reduction in adsorption capacity of samples, in relation to nitrogen and, additionally, in the decrease of calculated surface area and pore volume. From the first approach the data curve for MNW can be referred to type I isotherm. However, it is not completely correct. We suppose that