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Efficient functionalization of mesoporous MCM-41 with aromatic organo-lithium reagents

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ABSTRACT

The mesoporous framework of MCM-41 can be modified with various metal-organic reagents, enabling the introduction of functional groups to the surface of the silica material. We demonstrate the direct organic functionalization of mesoporous silica with easily accessible lithiated aromatic compounds. Detailed ^{13}C solid-state NMR studies revealed that the choice of the lithiation agent is of key importance for the organo-functionalization; the lithiation of 4-bromo arenes with *tert*-butyllithium is highly favorable compared to the lithiation with n-butyllithium. Based on the availability of numerous reagents, remarkably reduced cost for the synthesis, and the unique features of these novel functionalized inorganic–organic hybrid materials, lithiated aromatic compounds are promising candidates for the post-synthesis modification of mesoporous silica materials. We describe the synthesis and immobilization of heteroatom-bearing compounds such as esters, ethers and a heteroarene (e.g., 4-bromoanisole, 4-bromobenzaldehyde dimethylacetal and 2-bromothiophene). The high specific surface areas, the well-defined pore size distribution and the typical 2D hexagonal array of the porous channels were retained during the synthesis of the inorganic–organic hybrid materials. Additionally, we achieved a high loading of organic moieties in these novel mesoporous hosts.

1. Introduction

Ever since the development of MCM-41 by Beck et al. [1,2] in 1992 there has been an increasing interest in the field of mesoporous silica materials. Their scope of applications has grown in the last two decades, ranging from solid supports for catalysts [3–5], gas sensors [6] and host materials for gas adsorption [7,8] to nanocarriers for advanced drug delivery applications [9–11]. Mesoporous materials offer the possibility to tune particle morphology, pore size and pore topology according to the needs of the application, and it is possible to modify their internal and external surfaces via molecular functionalization [12–17]. Among the numerous mesoporous silica materials that are known today, MCM-41 has been widely used as a promising solid support for organic catalysts: For example, Das et al. [18] attached a Jacobsen catalyst onto MCM-41 and Yang et al. immobilized dicyano functionalized arenes together with palladium(0) for Heck-reactions in the mesoporous network [19]. Various pathways enabling the introduction of molecular functionalities into mesoporous frameworks are known [20]. Specifically, post-synthesis grafting and co-condensation represent two important approaches for introducing molecular functionality. However, it is of interest to incorporate complex structures and a broad variety of functionalities into the mesoporous framework of silica materials at affordable costs. Whereas the availability of appropriate organo-silane reagents is limited, numerous bromo-functionalized aliphatic and aromatic compounds are readily available or can be easily synthesized with standard methods of organic chemistry. If a pathway could be opened that would ultimately replace the bromine atom in brominated organic molecules with a surface silicon atom in mesoporous silica, a wealth of organic moieties could be immobilized in these hosts. This would offer the unique possibility to design promising catalysts directly and to incorporate them into the mesoporous framework of the solid support. Sailor and coworkers showed the successful modification of nanocrystalline silicon with aryl lithium species [21]. The approach of employing metal-organic compounds for the direct organic modification of mesoporous silica materials was developed independently by Lim et al. and by some of us [22,23]. We found a synthetic method that offers a broad spectrum of functionalities for the modification of the solid support [23]. Initially, the synthesis was based on Grignard

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reactants, followed by the reaction of lithiated arene compounds with the silica framework [24]. Very low temperatures are employed during the synthesis, which can be an advantage when grafting sensitive organic moieties. The functionalization with metal-organic reagents offers the possibility to introduce multiple functionalities into the mesoporous framework of silica materials. The procedure developed by Angloher et al. has already been employed to generate promising catalysts for Michael-additions [25,26]. In the above-cited publications, nitrogen-containing arene compounds were immobilized on the solid support. Here we focus on the immobilization of oxygen- and sulfur-containing molecules that offer interesting possibilities for further functionalization. Moreover, we further improved the synthesis procedure by using *tert*-butyllithium (tBuLi) as lithiating agent instead of n-butyllithium (nBuLi) to prevent unwanted by-products.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS, Fluka, >98%), cetyltrimethylammonium bromide (CTAB, Aldrich, 95%), aqueous ammonia (25 wt.%, Fluka), n-butyllithium (nBuLi, Aldrich, obtained as 1.7 M solution in pentane), *tert*-butyllithium (tBuLi, Aldrich, obtained as 1.7 M solution in pentane), 1-bromo-4-(chloromethyl) benzene (Br-ArCH$_2$Cl, Aldrich, >97%), 4-bromobenzaldehyde dimethylacetal (Br-BDMA, Aldrich, 98%), 2-bromothiophene (Aldrich, 98%), 4-bromoanisole (Br-ArOMe, Aldrich, >99%), 4-bromo-N,N-dimethylaniline (Br-ArNMe$_2$, Aldrich, 97%), sodium azide (Aldrich, 99%), methanol (MeOH, Fluka, >99%), diethyl ether (Et$_2$O), dichloromethane (Acros, >99%), absolute ethanol (EtOH, Aldrich, >99.5%), n-hexane (anhydrous, Sigma, >95%). Unless otherwise noted, all reagents were used without further purification. Bi-distilled water from a Millipore system (Milli-Q Academic A10) was used for syntheses and purification steps.

2.2. Methods

Nitrogen sorption measurements were performed on a Quantachrome Instruments NOVA 4000e. All six samples (15 mg each) were heated to 120 °C for 12 h *in vacuo* (10 mTorr) to outgas the samples before nitrogen sorption was measured at liquid nitrogen temperature. For the calculation of the pore sizes, a non-local density functional theory (NLDFT) equilibrium model of nitrogen on silica was used. A BET model was applied in the range of 0.05–0.20 p/p_0 to evaluate the specific surface area. Cross-polarized ^{13}C and ^{29}Si solid-state NMR (CP-MAS NMR) measurements were performed on a Bruker DSX Avance500 FT spectrometer in a 4 mm ZrO$_2$ rotor. The spinning rate was 10 kHz and a total number of up to 10,000 scans was recorded. Small angle X-ray diffraction was measured at 0.53°–10° on a Bruker D8 Discover diffractometer with Cu K_α-radiation ($\lambda = 1.5406$ Å). Thermogravimetric analysis of the bulk samples was performed on a Netzsch STA 440C TG/DSC with a heating rate of 10 K/min in a stream of synthetic air of about 25 mL/min. The mass was normalized to 100% at 75 °C for all samples and the resulting data are presented in Fig. A12. For transmission electron microscopy the respective samples were investigated with an FEI Titan 80-300 operating at 300 kV with a high-angle annular dark field detector. A droplet of the diluted MCM-41 suspension in absolute ethanol was dried on a carbon-coated copper grid.

2.3. Synthesis of mesoporous MCM-41

MCM-41 was synthesized according to a procedure published by Kumar et al. [27]. We employed the four-fold reaction scale of the original recipe, which is easily scalable. Absolute EtOH (50 g), aqueous ammonia (25 wt.%, 40 mL) and CTAB (9.56 g, 26.3 mmol) were dissolved in water (450 mL) in a 500 mL polypropylene reactor under continuous stirring. Subsequently, tetraethyl orthosilicate (40 g, 192 mmol) was added drop-wise to the stirred template solution. Afterward, the reaction mixture was stirred at room temperature for 2 h at 500 rpm. The white precipitate was filtered off, washed with EtOH until the filtrate was ammonia free (neutral pH-value). The obtained colorless powder was dried at 60 °C in air for 16 h. The template was removed via calcination in air, using a ramping profile with a heating rate of 1 °C min^{-1} up to a temperature of 550 °C. The temperature was kept for 5 h.

2.4. Preparation of MCM-41 for post-synthesis functionalization with lithiated organo compounds

For each reaction, 500 mg template-free MCM-41 was dried in a 50 mL Schlenk-flask at 150 °C *in vacuo* for 6 h. Afterward, the mesoporous material was allowed to cool to ambient temperature before Et$_2$O (anhydrous, 20 mL) was added. The suspension was cooled to −78 °C under continuous stirring.

2.5. Temperature dependent reaction of nBuLi with MCM-41

Three batches of 500 mg dried MCM-41 each were suspended in anhydrous n-hexane (20 mL) cooled to the desired temperature under continuous stirring (−78 °C, −20 °C and ambient temperature). nBuLi (1.6 mL, 2.5 mmol) was added drop-wise to the suspension and the reaction mixture was stirred for 4 h at the given temperature in a 50 mL Schlenk-flask. Afterward, the reaction mixture was quenched with EtOH and water (10 mL each) and filtered off. The obtained white powders were subsequently washed with methanol (30 mL), water (50 mL) and methanol (30 mL) and dried at 60 °C in air.

2.6. Lithiation of 4-bromoanisole (or 4-bromobenzaldehyde dimethylacetal, respectively) with nBuLi and subsequent reaction with MCM-41 (yielding sample MCM-41_ArOMe or MCM-41_BDMA respectively)

The respective 4-bromoarene (4-bromoanisole or 4-bromobenzaldehyde dimethylacetal, respectively – 3.13 mmol, 1 equiv) was dissolved in anhydrous Et$_2$O (10 mL) and cooled to −78 °C under continuous stirring. nBuLi (2.5 mmol, 0.8 equiv) was added drop-wise and the reaction mixture was stirred for 30 min at −78 °C, before it was transferred to the Schlenk-flask (50 mL) containing MCM-41. The *in situ* generated Ar–Li compound was added drop-wise to the stirred suspension of MCM-41 at −78 °C. The resulting reaction mixture was stirred at −78 °C for 10 min and was then allowed to warm to ambient temperature and was stirred for another 4 h. Afterward, the reaction mixture was quenched with water (10 mL) and filtered off. The obtained yellowish powder was subsequently washed with methanol (30 mL), water (50 mL) and methanol (30 mL) and dried at 60 °C in air.

2.7. Lithiation of different 4-bromo arenes with tBuLi (yielding samples MCM-41_Arene)

All reactions were performed according to this synthesis protocol unless otherwise noted.

The respective 4-bromo compound (2.5 mmol, 1 equiv) was dissolved in anhydrous Et$_2$O (10 mL) and cooled to −78 °C under continuous stirring. tBuLi (5 mmol, 2 equiv) was added drop-wise and the reaction mixture was stirred for 10 min at −78 °C before