Short communication

Tuning component enrichment in amino acid functionalized (organo)silicas

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ABSTRACT

A straightforward procedure to synthesize cysteine functionalized materials with tailored support properties has been developed. It allows tuning the hydrophobicity of the material via the incorporation of aliphatics, aromatics or silica in the framework structure. The aldol condensation of 4-nitrobenzaldehyde and acetone, as a probe reaction for the catalytic activity of the produced materials, exhibited a remarkable interplay between the reactant, solvent, traces of water and support hydrophobicity. A selective enrichment in the catalyst pores of specific bulk phase molecules is believed to be the key to achieve the targeted catalyst performance.

1. Introduction

Since the development of mesoporous silica materials, such as the MCM and SBA families [1,2], research on these materials has ever been increasing. They are characterized by large pore sizes, i.e., between 2 and 50 nm and large surface areas, often exceeding 1000 m^2/g. Moreover, the functionality of silica materials can easily be manipulated by incorporation of active sites in the walls (co-condensation) or by anchoring active species on the surface (post-functionalization). As a result, mesoporous silica materials exhibit promising performances in many applications including adsorption [3,4], chromatography [5,6], electronics [7,8], drug delivery [9,10] and catalysis [11,12]. In the framework of catalysis, an interesting research field is situated in the use of aminated silica materials to catalyze carbon-carbon coupling reactions [13–22]. These reactions are widely used in the pharmaceutical industry and fine chemicals production [23]. Moreover, a bright future in the valorization of biomass-based resources has been forecasted for these reactions [24,25]. However, mesoporous silica materials exhibit a limited hydrothermal stability, which is often related to the hydrolysis of Si-O-Si bonds [26,27]. Hence, the water tolerance of these materials should be enhanced in order to further broaden their scope of application.

In 1999, three research groups, independent from one another, incorporated organic groups in the pore walls through the condensation of bridged organobissilanes, with the general formula $(R'O)_3$-Si-R-Si-$(OR')_3$, in the presence of a surfactant [28–30]. The presence of the organic moieties specifically results in periodic mesoporous organosilicas (PMOs), which have a more hydrophobic character compared to the original silica materials. It turns the PMOs into materials which are comparatively more robust in an aqueous environment [31]. Originally, only a limited number of organobissilanes (methane, ethane, ethene and benzene bissilanes) were used. Nowadays, a wide variety is available, providing opportunities to tune the hydrophobicity of the organosilica materials. Moreover, these organobissilanes allow the incorporation of a more extended range of functional groups in the materials, either by the direct introduction via the organobissilanes or by the post-modification of the organic moieties incorporated in the pore walls [32].

In this work, the wide variety of organo(bis)silanes is used to probe the selective enrichment of reactant molecules in amino acid functionalized catalysts and, consequently, optimize the catalytic performance in different environments. A catalyst library comprising different cysteine functionalized materials is prepared and the effect of the incorporation of different organic moieties is investigated in the aldol reaction of acetone with 4-nitrobenzaldehyde. Additionally, the ability of the materials to cope with traces of water in the reaction mixture is studied.

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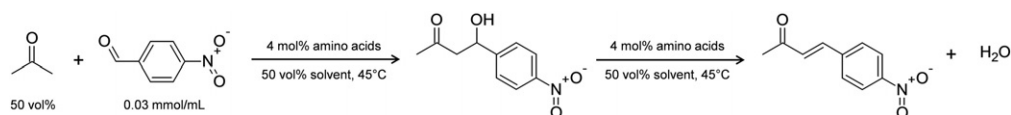
Scheme 1. Aldol condensation of acetone and 4-nitrobenzaldehyde towards the primary aldol product, 4-hydroxy-4-(4-nitrophenyl)-3-buten-2-one, and the secondary ketone product, 4-(4-nitrophenyl)-3-buten-2-one.

2. Experimental procedures

2.1. Catalyst synthesis

Three catalysts have been synthesized in the present work. Two had hydrophobic organosilica supports, i.e., catalyst E, which was synthesized using 1,2-bis(triethoxysilyl)ethane (BTEE, 97%, ABCR) and catalyst B synthesized using 1,4-bis(triethoxysilyl)benzene (BTEB, 95%, ABCR). The third one had a hydrophilic silica support, i.e., catalyst S synthesized using tetraethyl orthosilicate (TEOS, 98%, ABCR). 1 to 10 mol% vinyltriethoxysilane (VTES, 98% ABCR) was also included during the synthesis to allow post-functionalization with cysteine. A final amino acid site density in the range between 0.06 and 0.07 mmol/g was aimed at because at higher site densities intermolecular interactions between amino acids on different linkers may lead to a significant decrease of the turnover frequency (TOF) [33].

The supports were synthesized according to the following recipe: about 3 g Brij S10 ($C_{18}H_{37}(OCH_2CH_2)_nOH$, n~10, Sigma-Aldrich) was dissolved in a mixture of 138 mL demineralized water and 10 mL 12.1 M hydrochloric acid (HCl, ACS grade reagent, Sigma-Aldrich). The mixture was stirred for 4 h at 50 °C in order to form micelles. Afterwards, 2.5×10^{-2} mol of Si atoms in the form of TEOS or one of the organobissilanes and VTES was added and the mixture was stirred at 50 °C for 24 h. Subsequently, the magnetic stir bar was removed and the mixture was heated to 90 °C for 24 h. The resulting solid was separated from the mixture by filtration and, subsequently, washed three times by stirring at 80 °C for 24 h in a 98 vol% ethanol (96%, Fiers) – 2 vol% HCl mixture followed by filtration. The material was dried overnight under vacuum at 100 °C.

Afterwards, the supports were functionalized. 2 g L-cysteine (99 + %, Acros) and 1 g 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (98%, Sigma-Aldrich) were dissolved in 50 mL distilled water, 1 g of the solid material was added and the mixture was stirred for 24 h in a Metalight Classic UV reactor (360 nm). The material was recovered by filtration and subsequently washed several times with demineralized water by stirring for 3 h at 40 °C. Finally, the material was dried under vacuum with heating to 100 °C and stored in an inert atmosphere.

2.2. Catalyst characterization

Nitrogen adsorption-desorption measurements were carried out at 77 K using a Micromeritics Tristar II 3020 apparatus. Samples were degassed at 120 °C for 17 h prior to measurement. The specific surface area and pore volume were determined using the Brunauer-Emmett-Teller method. The total pore volumes and pore sizes were calculated using the Broekhoff-de Boer method with the Frenkel-Halsey-Hill modification. The pore ordering of the materials was determined using X-ray diffraction (XRD) patterns which were measured on a Thermo Scientific ARL X'TRA X-ray diffractometer. In order to qualitatively confirm the presence of the functional groups Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy was performed on a Nicolet 6700 spectrometer of Thermo Scientific with a nitrogen cooled MCT-A detector using a Graseby Specac diffuse reactant cell, operating in vacuum at 120 °C. The amino acid site density was determined using elemental (CHNS) analysis. These experiments were performed on a Thermo Flash 2000 elemental analyzer. 4-nitrobenzaldehyde adsorption capacities were determined by adding 0.3 g of support material in 5 mL of acetone (50 vol%), n-hexane (50 vol%) and 4-nitrobenzaldehde (0.003 mmol/mL). The mixture was stirred for 3 h at room temperature after which the decrease in the liquid phase 4-nitrobenzaldehyde concentration was determined via reversed-phase HPLC (Agilent 1100).

2.3. Catalyst performance testing

The activity of each catalyst was assessed in the aldol condensation of acetone (99.6%, Acros) and 4-nitrobenzaldehyde (99%, Acros), see Scheme 1, according to the procedure as published before [33]. The experiments were performed initially in the presence of a nonpolar aprotic solvent, i.e., n-hexane and, subsequently, in the presence of the same solvent including 1 vol% of water. Such an amount significantly exceeds that which can remain in the catalyst pores after synthesis. All data were obtained at differential conditions, meaning that the conversion depended linearly on the batch time and the TOF could be determined from the slope of the observed straight line.

3. Results and discussion

3.1. Catalyst characterization

Three supported amino acid catalysts have been synthesized in the present work, i.e., catalyst E containing ethane bridges, catalyst B containing benzene bridges and a hydrophilic silica material, catalyst S.

The specific BET surface areas, average pore sizes and total pore volumes of the three supports and the corresponding, functionalized catalysts are listed in Table 1. The nitrogen sorption isotherms and the corresponding pore size distributions are reported in the supporting information. All supports are mesoporous with a large specific BET surface area between 870 and 970 m^2/g, an average pore size between 3.1 and 4.1 nm and a total pore volume between 0.70 and 1.08 cm^3/g. Before

Table 1
Catalyst properties determined via nitrogen adsorption-desorption measurements, X-ray diffraction and elemental analysis.

Catalyst	BET surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)	Unit cell width (nm)	Wall thickness (nm)	Amino acid loading (mmol/g)
Aliphatic support	928	3.7	0.94	6.7	3.0	0.00
Catalyst E	783	3.7	0.82	6.8	3.1	0.06
Aromatic support	970	3.1	0.70	6.1	3.0	0.00
Catalyst B	654	3.1	0.46	5.8	2.7	0.07
Silica support	860	4.1	1.08	6.7	2.6	0.00
Catalyst S	690	5.1	0.68	6.7	1.6	0.07