Controlling the Selectivity of Competitive Nitroaldol Condensation by Using a Bifunctionalized Mesoporous Silica Nanosphere-Based Catalytic System

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Recent progress in functionalization of MCM and SBA types of mesoporous silicas with catalytically active groups has highlighted the potential of utilizing these structurally uniform materials as a new generation of heterogeneous catalysts with high selectivity. Several previous studies[1] involved immobilization of single-site catalysts, such as transition metal complexes and Lewis or Brønsted acids and bases, onto the mesopore surfaces. However, in contrast to zeolite-based catalysts, which utilize the "shape/size selective cavity effect",[2] the selectivity of mesoporous silica-based systems was mainly controlled by the intrinsic coordination environment of the heterogenized catalytic group. The mesoporous silica itself served only as an inert supporting matrix with large surface area, whose chemical and geometric properties were often not utilized.[1a,c,3]

We recently reported a new synthetic method based on co-condensation, which allowed us to functionalize mesoporous silica materials with multiple organic groups.[4] By using this method, not only the loading of functional groups but also the particle size and shape of the resulting mesoporous silicas could be controlled.[4] Herein we apply the same principle to synthesize a class of bifunctionalized mesoporous silica nanosphere (MSN) materials, where one common functional group (primary group) served as a catalyst and the other functionality (secondary group) provided different noncovalent interactions to reactants and thereby controlled the reaction selectivity. By varying the secondary group in these bifunctionalized MSN catalysts, we investigated the selectivity of a nitroaldol (Henry) reaction of two competing benzaldehydes reacting with nitromethane by measuring the molar ratio of the nitroalkene products as depicted in Figure 1. To the best of our knowledge, this is the first demonstration of utilizing multifunctionalized mesoporous silicas as heterogeneous catalysts to control the selectivity of a competitive organic reaction.

The bifunctionalized MSN materials with a common 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) group and three different secondary groups, ureidopropyl (UDP), mercaptopropyl (MP), and allyl (AL) functionalities, were synthesized by introducing equal amounts of AEP-trimethoxysilane with UDP-, MP-, or AL-trialkoxysilane precursors to our co-condensation reaction.[4a,b] A monofunctionalized MSN with only AEP group incorporated inside the mesoporous silica framework was also synthesized via the same method.[4a] Despite a variation in the particle sizes, all of the organically functionalized MSNs exhibited the same spherical particle shape (Figure 2). The XRD measurements showed large (100) peaks and broad higher diffraction patterns in all samples, typical of disordered porous structure.[5] The observed d_{100} values ranged between 38.4 Å for sample AEP/AL-MSN and 41.7 Å for sample AEP/UDP-MSN. The TEM study of these materials further confirmed their disordered channel structure (Figure 2e).[5]

The N_2 surface sorption analyses of these mono- and bifunctionalized MSNs showed typical type IV BET isotherms.[5] The measured BET surface areas of AEP-MSN, AEP/UDP-MSN, AEP/MP-MSN, and AEP/AL-MSN are 805.8, 759.6, 778.7, and 703.5
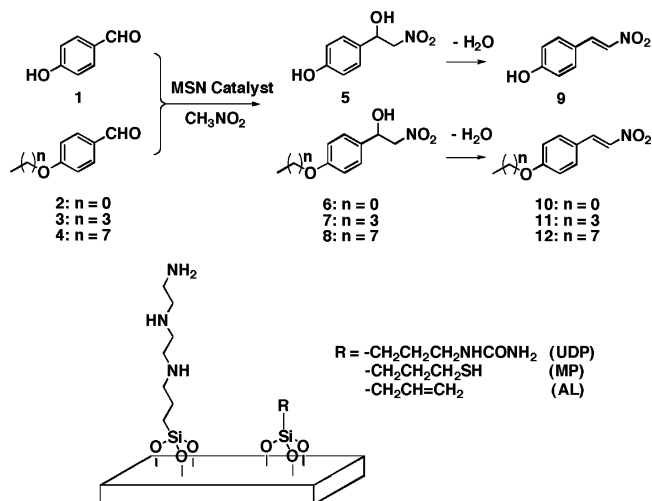

Figure 1. Competitive nitroaldol reaction. Reaction condition: 50 mg MSN catalyst, 10 mL CH_3NO_2, 5.0 mmol aldehydes, 363 K for 24 h.
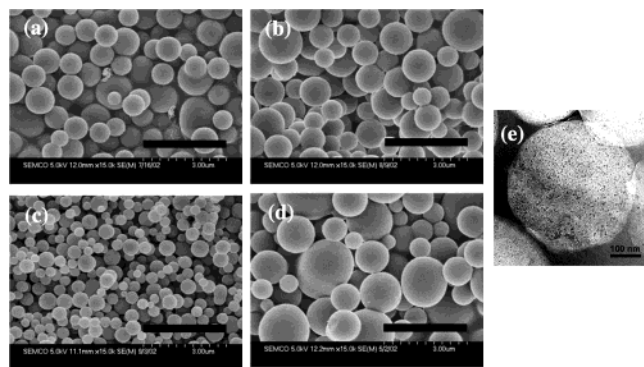

Figure 2. FE-SEM images of (a) AEP/UDP-MSN (0.7−1.3 μm), (b) AEP/MP-MSN (0.7−1.6 μm), (c) AEP/AL-MSN (0.2−0.7 μm), and (d) AEP-MSN (0.8−2.1 μm). TEM micrograph of the ultramicrotomed sample (60−90 nm thickness) of AEP/AL-MSN (e). Scale bar is 3 μm for the (a−d) micrographs and 100 nm for the (e) micrograph.

m^2/g, respectively. Interestingly, the BJH pore distributions of the MSNs functionalized with hydrophilic organic groups, i.e., AEP-MSN and AEP/UDP-MSN, displayed average pore diameters of 26.0 and 22.9 Å, respectively, whereas functionalization with the hydrophobic functional groups (AEP/MP-MSN and AEP/AL-MSN) resulted in smaller mean pore diameters of ca. 15 Å, as evidenced by the TEM images.[5]

The structures of organic functional groups in the mesopores, their relative concentrations, and the overall surface coverages were scrutinized by ^{29}Si MAS, ^{29}Si CPMAS, and ^{13}C CPMAS solid-state NMR spectroscopy.[5] The ^{29}Si and ^{13}C NMR spectra confirmed the successful functionalization of MSNs. The resulting materials were surfactant-free. The ^{29}Si resonances were observed at positions typical of silicon groups Q^n ($(\equiv SiO)_n Si(OH)_{4-n}$, where n is 2, 3,
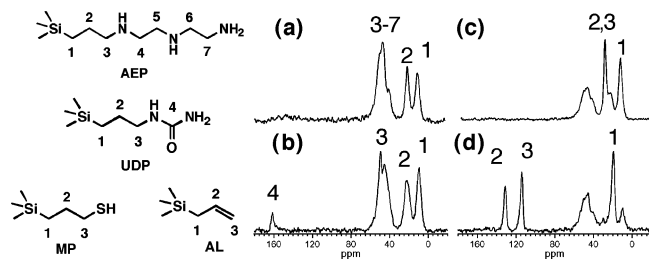
Figure 3. ¹³C CPMAS spectra of (a) AEP, (b) AEP/UDP, (c) AEP/MP, (d) AEP/AL-MSN. Only the resonances due to secondary groups are marked in spectra (b−d).

or 4) and T^n ($(\equiv SiO)_n Si(OH)_{4-n}R$, where n is 2 or 3).[5,6] The ¹³C peaks (Figure 3) were assigned on the basis of the solution spectra of the corresponding precursors and on our earlier study of AEP-, AL-, and UDP-MSN's.[4a] Also detailed in the Supporting Information are the quantitative ¹³C and ²⁹Si measurements, which showed that all MSNs contained approximately equal total amounts of organic functional groups (1.0 mmol/g in AEP/UDP-MSN, 1.4 mmol/g in AEP/MP-MSN, and 1.3 mmol/g in AEP/AL-MSN). This corresponded to 15, 25, and 23%, respectively, of surface silicon atoms being involved in Si−C bonds. Furthermore, the relative molar concentrations between AEP and the secondary groups were very similar (1.17, 1.04, and 1.13 for AEP/UDP-MSN, AEP/MP-MSN, and AEP/AL-MSN).[5]

As demonstrated in recent literature reports,[7] MCM-41 silicas grafted with amines or polyamines could effectively catalyze nitroaldol reactions to produce nitroalkenes in high yields, whereas the pure inorganic MCM-41 silica gave rise to only small amounts of β-nitro alcohol intermediates. To investigate how the secondary functional groups of our bifunctionalized MSN catalysts could influence the reaction selectivity, three series of competitive nitroaldol reactions were performed by introducing equal molar concentrations of 4-hydroxybenzaldehyde (**1**) and one of the three different alkoxybenzaldehydes (**2**, **3**, and **4**) to nitromethane solutions of a chosen bifunctional MSN. By analyzing the molar ratios between products (**10/9**, **11/9**, and **12/9**), we observed that the monofunctionalized AEP-MSN and the hydrophilic bifunctionalized AEP/UDP-MSN catalysts did not show any reaction selectivity for all three combinations of the reactants as shown in Figure 4 and the Supporting Information. However, an increase of reaction selectivity toward the nonpolar and more hydrophobic alkoxybenzaldehyde reactants (**2**, **3**, and **4**) was clearly observed in the cases of AEP/MP-MSN and AEP/AL-MSN catalysts, where the catalytic AEP groups are situated in mesopores decorated with hydrophobic groups. The hydrophobic nature of MP and AL is corroborated by the low dielectric constants of 1-propanethiol (5.94) and propene (2.14).[5] The AEP/AL-MSN displayed the highest reactant selectivity toward alkoxybenzaldehydes. For example, a molar product ratio (**12/9**) of 2.58 (Figure 4) was reached when 4-*n*-octyloxybenzaldehyde (**4**) was used in competition with 4-hydroxybenzaldehyde (**1**) indicating the high selectivity of AEP/AL-MSN catalyst toward the nonpolar reactant. The results suggested that the hydrophobic secondary groups (MP and AL) played a significant role in preferentially allowing the more hydrophobic reactants to penetrate into the mesopores and react with the AEP functionality. To demonstrate this hydrophobic solvation effect, 1 mmol of reactants **1** and
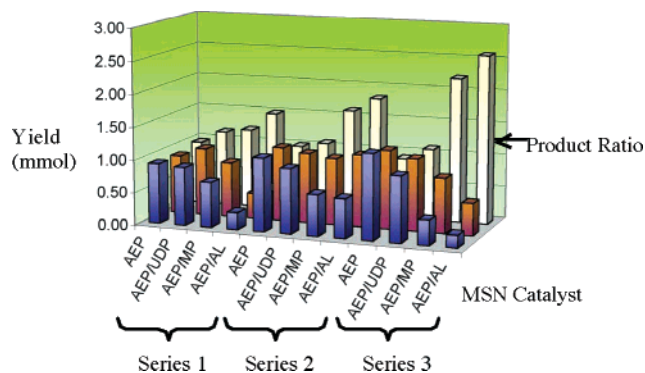

Figure 4. Histogram of the competitive nitroaldol reactions. Blue bars: yield of **9** (mmol); red bars: yield of **10**, **11**, or **12** (mmol); white bars: molar ratio of products (**10/9**, **11/9**, or **12/9**). Series 1, 2, and 3 are experiments conducted with reactants **1** and **2**, **1** and **3**, and **1** and **4**, respectively.

4 were introduced to 1 mL of 1-propanethiol to simulate the penetration/dissolution of these substituted benzaldehydes with different polarities[5] into the mercaptopropyl-functionalized mesopores. The fact that the more polar reactant **1** was insoluble in 1-propanethiol, whereas compound **4** was completely miscible with 1-propanethiol, indicated that the selectivity of our catalysts most likely originated from the variation of the physicochemical properties of the bifunctionalized mesopores, i.e., polarity and hydrophobicity.

Supporting Information Available: Syntheses and spectroscopic characterizations of the bifunctional MSN materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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