Multiphasic acetalization and alkylation on organically modified MSU-X silica

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Mesoporous silicas were functionalized with phenyl groups and were used as solid acid catalysts in acetalization of aldehydes and ketones with ethylene glycol or methanol. It was shown that cyclohexanone as well as aromatic and linear aldehydes could be converted to the corresponding dimethylacetals in high conversion and selectivity over the catalyst. They also performed well in the isopropylation reactions of naphthalene with isopropanol.

KEY WORDS: acetals; catalysis; functionalized mesoporous silica

1. Introduction

Since the development of M41S materials by Mobil Oil researchers in 1992 [1,2], many different mesoporous inorganic materials have been prepared and applied in catalysis, separation and purification technology [3–6]. They have been also extensively used as catalyst or catalytic supports for synthesis of fine chemicals in multiphasic reactant systems. However, although reasonably good stability and re-usability are observed in the metal incorporated mesoporous materials (such as Al-MCM-41), the leaching of the transition metal from the silicate framework through local hydrolysis or reaction with the substrate is still a matter of question. Functionalized mesoporous silicas, such as grafted or hybrid MCM and HMS type materials, have been recently reported by researchers [7,8]. These materials have stood for the extension of applications of zeolites to the conversion of large bulky molecules due to their unique textural characteristics and surface active sites. Researchers developed the covalent attachment of the alkylsulfonic acid groups to the surface of MCM and HMS molecular sieves, via secondary synthesis or direct one-step synthesis. The resulting materials were good solid-acid catalysts in some reactions [9,10]. But the above process would lead to low surface area and pore volume of the derivatives (*e.g.,* 399 m^2/g and 0.19 ml/g, respectively), which limited the conversion of reactants. As an alternative, we prepared the phenyl sulfonic acid functionalized MSU-X (denoted PSA-MSU-X) based further sulfonation of the phenyl-modified mesoporous materials [11]. In this work, emphasis is placed on the use as catalyst in reactions for acetalization of aldehydes and ketones as well as alkylation of naphthalene.

2. Experimental

2.1. Synthesis of PSA-MSU-X

The improved procedure developed by Pinnavaia and co-workers [12] for synthesis of MSU-X was used to synthesize phenyl–MSU-1 (Ph-MSU-1), and then the phenyl-functionalized MSU-1 was sulfonated to form phenyl sulfonic acid–MSU-1 (PSA-MSU-1):

(1) *Synthesis of Ph-MSU-1.* In this work, the non-ionic alkylpolyethylene oxide surfactant ($C_{11–15}H_{23–31}$–$(CH_2CH_2O)_9H$, denoted as AEO_9) was used as the template. Typically, a mixture of tetraethoxysilane (TEOS) and phenyltriethoxysilane (PhTES) was added into aqueous AEO_9 solution under stirring at ambient temperature. After stirring for about 1 h, KF was added and then the final molar gel composition is 0.9 TEOS : 0.1 PhTES : 0.34 AEO_9 : 0.12KF : $490H_2O$. Finally, the solution was stirred for 2 h and maintained at 50 °C for 72 h (or transferred into an autoclave at 100 °C for 72 h). The resultant samples were filtered, rinsed with distilled water and dried at 50 °C. The surfactant extraction was performed by Soxhlet extraction over ethanol for 48 h, the solid was filtered, washed with distilled water and dried at 100 °C in air.

(2) *Sulfonation of Ph-MSU-1.* The phenyl groups of the Ph-MSU-1 were sulfonated to the corresponding phenylsulfonated acid derivatives by the reaction with concentrated H_2SO_4. Typically, after heating at $\sim$100 °C under a vacuum of less than 10^{-5} Torr for 6 h, the extracted Ph-MSU-1 sample was carefully treated by the concentrated H_2SO_4 (98 wt%) under controlled heat for more than 48 h at 70 °C. During the sulfonation, the reactor was open in order to remove the trace water in the mix-

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ture. The sample turned light red gradually and finally it was washed with water to neutrality and then dioxane to remove residual sulfuric acid.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a D/MAX-rA diffractometer with Cu Kα radiation 30 kV/30 mA. Nitrogen adsorption isotherms were obtained at −196 °C on an ASAP 2000 surface analyzer. Typically, a sample was degassed at 150 °C for 6 h prior to the analysis. ^{29}Si MAS NMR spectra were obtained on a Bruker MSL-400 spectrometer at 79.46 MHz. ^{13}C MAS NMR spectra were obtained on a Bruker DRX-400NMR spectrometer at 100.62 MHz. UV-Raman spectra were performed on a Raman spectroscope, which involved an UV cw laser, a spex 1877 D triplemate spectrograph, a CCD detector, and an optical collection system.

FT-IR spectra were recorded on FTS-25PC IR analyzer. Bulk mesoporous materials were probed by transmission electron microscope (TEM, Hitachi 9000) operating at a voltage of 100 keV. Thermogravimetric analysis (TGA) was carried out on a TGA-92 (STEARAM) thermal analyzer and the sample was heated from 25 to 700 °C at 10 °C/min under air.

2.3. Catalytic activities of PSA-MSU-X for acetalization and alkylation reactions

Carbonyl compounds of 10.0 mmol were reacted on phenyl sulfonic acid–MSU-1 catalyst in 7 ml of toluene (reaction parameters shown in table 1). All of the acetalization reactions were performed in a magnetically stirred flask at 70 °C. The reagents used here were of commercially available, non-anhydrous grade and used without further dehydration treatment. The so-produced catalyst was maintained at ambient condition just before use in the reaction but used without any drying. The products were identified by GC-MS spectroscopy and periodically analyzed by GC.

Isopropylation reactions of naphthalene with isopropanol were performed in an autoclave at 250 °C for 4 h. Decalin was used as solvent and the ratio of isopropanol/naphthalene was 2/1. The so-produced catalyst was used without any drying with 5 wt% naphthalene. In this work, the reactor was flushed with N_2 flow for 30 min and then heated to 250 °C at a rate of 5 °C/min.

Table 1
Acetalization of aldehydes and ketones with EG or MeOH on PSA-MSU-1.

Entry	Substrate 1	Substrate 2	Catalyst (mg)	Time (h)	Temp. (°C)	Conv. (%)
1	HEX	EG	20	9	70	100
2	HEX	EG	30	6	70	97.0
3	HEX	EG	40	7	70	100
4	Benzaldehyde	EG	20	11	50	74.3
5	Benzaldehyde	Methanol	20	5	70	76.4
6	Valeraldehyde	EG	30	7	60	100
7	Valeraldehyde	Methanol	30	2	60	95.0

The reaction products were analyzed on a gas chromatograph with SE-54 glass capillary column (50 m × 0.2 mm id). FID was used as detector.

3. Results and discussion

3.1. Properties of the catalysts

The structure of Ph-MSU-1 and PSA-MSU-1 was confirmed by the appearance of one peak in the X-ray diffraction pattern, which was similar to that in siliceous MSU-X. ^{13}C CP-MAS NMR of Ph-MSU-1 showed two strong resonances that can be assigned to the phenyl group at 128 and 134 ppm. Figure 1 shows the ^{29}Si CP-MAS NMR spectra for extracted, pure-silica MSU-1 and the organic functionalized MSU-1. It is clear from the spectrum of the hybrid material that the phenyl group is covalently linked to the framework silicon atom (peaks at −69 and −79 ppm, assigned to T^2 [phenyl$(SiO)_2$Si–OH] and T^3 [phenyl$(SiO)_3$Si], respectively). The presence of phenyl was further confirmed by FT-IR identified as below: aromatic C=C, 1431 cm^{-1}; C–H, 3000–3100 cm^{-1}; finger region of aromatic ring, 797, 740 and 700 cm^{-1}. Subsequent sulfonation of the phenyl rings produced intrapore sulfonic acid sites that performed acid catalytic activity. The characterization and their use in organic reaction can be seen in our previous reports [11,13]. Figure 2 shows the^{13}C CP-MAS NMR spectrum of

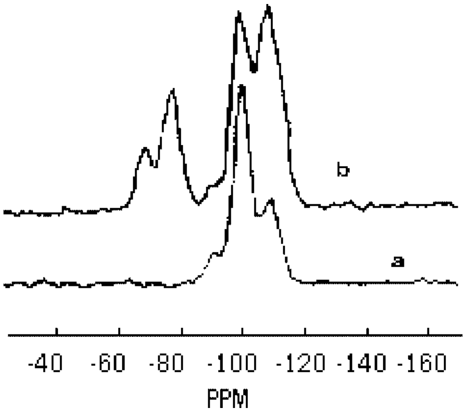

Figure 1. ^{29}Si MAS NMR spectra of (a) pure-silica MSU-1 and (b) Ph-MSU-1. Spectra are from extracted samples.

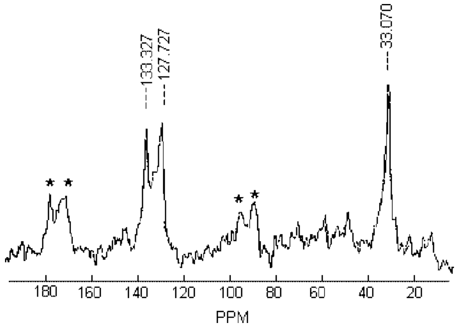

Figure 2. ^{13}C CP-MAS NMR spectrum of APS-MSU-1; ∗ denotes spinning bands.

PSA-MSU-1. There are two strong resonances at 127 and 133 ppm assigned to the phenyl group after sulfonation, and resonances below 70 ppm correspond to the carbons of the solvent. In the UV-Raman spectrum of PSA-MSU-1, the bands at 1110 and 1212 cm^{-1} should be contributable to the SO_3 sym. and unsym. stretch, respectively. The loss of the phenyl group by TGA was mainly in the range of 400–550 °C for both Ph-MSU-1 and PSA-MSU-1. Upon sulfonation, a new weight loss is evident in the range of 150–200 °C, attributable to the addition of SO_3 to the phenyl rings of phenyl. The acid content of so-produced PSA-MSU-1 is $\sim$0.15 mmol-$\mathrm{H}^+\,\mathrm{g}^{-1}$ by titration with aqueous NaOH solution [14]. A large number of "worm-like" pore channels were apparent from transmission electron micrographs (TEM). The N_2 adsorption–desorption and BET measurements gave a pore diameter of 3.43 nm and a surface area of 791 $\mathrm{m}^2\,\mathrm{g}^{-1}$ for PSA-MSU-1 (figure 3), which were larger than that in Ph-MSU-1 (3.18 nm and 700 $\mathrm{m}^2\,\mathrm{g}^{-1}$) due to the sulfonation of the phenyl group. The surface area and pore volume of phenyl-functionalized MSU-1 was larger than that in HSO_3-MCM-type materials obtained *via* oxidation of the HS-MCM-41 [6]. During the initial process, MSU-type materials have several advantages over M41S from a synthetic viewpoint: the use of cheap biodegradable nontoxic neutral surfactant as the structure-directing agent; easy removal of the template and no hydrothermal reaction.

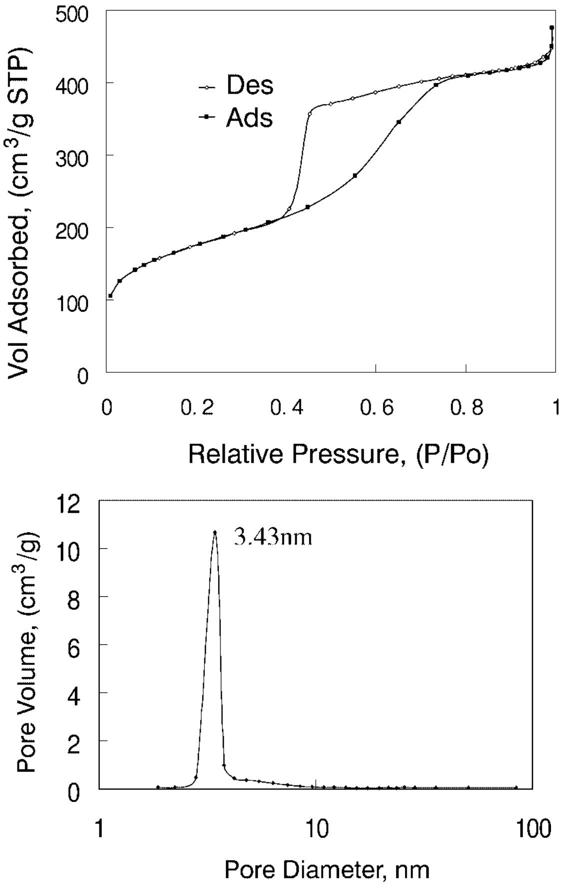

Figure 3. PSA-MSU-1 N_2 adsorption–desorption isotherms and BJH pore distribution.

3.2. Catalytic performance in reactions

Acetalization of cyclohexanone (HEX) with ethylene glycol (EG) was first measured to illustrate the catalytic activity of the sulfonated phenyl-functionalized MSU-1. The PSA-MSU-1 was an active catalyst for the formation of 2,2-pentamethylene-1,3-dioxolane (cyclic ketal) from ethylene glycol and cyclohexanone (HEX), see table 1 (entries 1–3). The conversion of cyclohexanone reached over 80% within 40 min due to the reaction equilibrium, but HEX was finally converted into cyclic ketal to almost 100% within 6–7 h. Increasing the amount of catalyst improved the conversion. No product other than acetal was detected by careful GC-MS analyses of the reaction mixture. Pure siliceous MSU-1 treated with the same sulfonation procedure in the above manner, showed almost no production of cyclic ketal after 9 h reaction. In addition, the filtrate obtained from a 7 h stirred mixture of the PSA-MSU and toluene and EG showed no catalytic activity at all. This ruled out the possibility that some components eluted from the phenyl-MSU solid. It follows that the acetalization was indeed catalyzed by the PSA-MSU-1 and this activity was due to the phenyl–sulfonic acid groups covalently linked to the MSU framework.

Two other kinds of carbonyl compounds in addition to cyclohexanone were also investigated. Table 1 shows the results of reactions for benzaldehyde and valeraldehyde with ethylene glycol or methanol, respectively (entries 4 and 5). The reaction of benzaldehyde with EG or methanol gave the corresponding acetals at the predetermined time. But the conversion was lower than that in HEX (entries 1–3). On the other hand, valeraldehyde could be converted in excellent yields at the given temperature. It should be noted that the conversion in the reaction of benzaldehyde was relative due to the different reaction conditions. The results obtained for entries 4–7 were comparable to those observed for a Ce-mont catalyst and MCM-41 [15], while the excellent results in entries 1–3 have never been reported, to the best of our knowledge.

In fact, aluminosilicate MCM-41 showed catalytic activities for aldol condensation, Friedel–Crafts acylation and Diels–Alder reaction. Here the Friedel–Crafts reaction of naphthalene isopropylation in addition to cyclohexanone was next investigated. These reactions produce valuable products such as 2,6- or 2,7-alkylnaphthalene as the main products. The naphthalene methylation reaction, a model reaction, has been studied in detail. In this work, the reaction proceeded well although the conversion of naphthalene is lower (57%) than on metal-supported MCM materials (see table 2). But it can be seen from the GC analysis that the selectivity for the mono- and diisopropylnaphthalene products was high due to the small amount of tri- and multi-substituted products. The activity of the catalyst reflects the surface properties, which depends on the sulfonation procedure during the synthesis. The results suggest that the Friedel–Crafts reaction, *e.g.*, isopropylation of naphthalene, needs much stronger acidic density than in aldol condensation. The improvement of the materials for the alkyla-

Table 2
Catalytic performances for isopropylation of naphthalene over PSA-MSU-1[a] mesoporous molecular sieves.

No.	Sulphonating temp. (°C)	Conv. (%)	MIPN (%)	DIPN (%) 2,6-	2,7-	Others	TIPN + others	2-IPN/ 1-IPN	2,6-/ 2,7-
1[b]	70*	0	0	0	0	0	0	0	0
2	70*	56.49	63.38	12.55	55.0	32.46	5.73	0.53	0.23
3	50	33.54	75.74	13.39	54.93	31.68	2.71	0.47	0.24

[a] Reaction temperature, 250 °C; the ratio of isopropanol/naphthalene is 2; MINP – monoisopropylnaphthalene, DIPN – diisopropylnaphthalene, TIPN – triisopropylnaphthalene, IPN – isopropylnaphthalene.

tion of naphthalene is being under way and will be reported in a future contribution.

4. Conclusion

Acetalization has widely been used to protect the carbonyl group of aldehydes and ketones. The organic-functionalized MSU-X materials described here provide new opportunities for solid catalysts for the acetalization of carbonyl compounds including linear aldehydes. No strict anhydrous condition, *e.g.*, use of dehydrated regent or drying the catalyst *in vacuo*, was required to achieve good yields. The easiness of removing the catalyst from the reaction mixture would also be convenient for chemists wanting to protect carbonyl groups by using acetalization. In principle, any functional group that catalyses homogeneous reactions could be "tailor-made" into an intrachannel of porous materials and their texture could also be controlled by varying the synthesis system with the requirement of its use. Thus far, we have placed numerous functional groups into mesoporous structures (especially MSU-X type materials), for example phenyl, vinyl, methyl and ureidopropyl. Thus, organic-functionalized mesoporous materials should provide new catalytic applications especially for large bulk molecules.

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