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Solvent-free Mukaiyama-aldol condensation catalyzed by Ce–Al–MCM-41 mesoporous materials

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ABSTRACT

MCM-41 samples containing Ce^{4+} and Al^{3+} in the network, designated as Ce_x–Al–MCM-41 ($x = 0.0$–0.04), were synthesized and characterized systematically. These samples exhibited higher catalytic activity for Mukaiyama-aldol condensations to produce β-hydroxy carbonyl compounds under the solvent free conditions, compared to the samples containing either of the two cations. The product yield was found to depend on the electron donating/withdrawing characteristics of reactant molecules being responsible for the observed trend. Series of solvents were also investigated but considerably high yield of aldol products (~95%) could be achieved without using any solvents. In all the cases, the selectivity was found to be 100%, typical of such Mukaiyama-aldol condensations. The higher catalytic activity of Ce_x–Al–MCM-41 is explained on the basis of certain new acid sites generated due to co-incorporation of Ce and Al cations.

1. Introduction

The development of an efficient and non-polluting route for the carbon–carbon bond formation reactions via aldol condensation using a selective solid acid catalyst is a thrust area of research at the interface of catalysis and organic transformations [1–3]. The Mukaiyama-aldol [4,5] reactions of silyl ketene acetal/silyl enol ethers and aldehyde is a facile method for the Lewis acid-catalyzed C–C bond formation under the homogeneous conditions and at sub-ambient temperatures. These reactions have been investigated in heterogeneous mode also and the solid Lewis acid catalysts, such as clays, Naffion-117, acid-polymers, amorphous silica-alumina and zeolites are found to serve as promising catalysts [6–11]. Solid bases, such as zeolites substituted with alkali or alkaline earth metals, alkaline earth oxides, hydrotalcites and AlPOs have been utilized for the nucleophilic reactions, e.g. Michael, Aldol, and Knoevenagel type condensation reactions involving carbonyl compounds [12].

The Mukaiyama-type Aldol and Michael reactions of silyl ketene acetal with aldehydes and α,β-unsaturated carbonyl compounds have been reported using microporous molecular sieves [13–15], tin incorporated mesoporous materials [16,17] and Ti–MCM-41 [18]. It has been reported in our earlier studies that the Ce_x–Al_y–MCM-41 catalysts, with different values of x and y, exhibit acidic properties that are different from Ce–MCM-41 or Al–MCM-41 samples individually [19–22]. We have employed *in situ* FT-IR spectroscopy to demonstrate that certain new Lewis and Brönsted acid sites were generated as a result of the simultaneous incorporation of Ce and Al in MCM-41 network, leading thereby to overall increased acidity (both density and strength) of these materials [22].

In the present study, we now report the catalytic properties of Ce-substituted Al–MCM-41 samples for the Mukaiyama-aldol carbon–carbon bond formation reactions mentioned above. In order to monitor the solvent effect on the reaction progress, the experiments were carried out in presence of different organic solvents as well as under solvent free conditions, while keeping all other reaction conditions the same. The effects of catalyst amount, temperature and addition of aldehydes and silyl enol ethers on the catalytic activity have also been investigated in detail.

2. Experimental

2.1. Materials and synthesis

The hydrothermal synthesis of Al–MCM-41, Ce–MCM-41 and various compositions of Ce-containing Al–MCM-41 samples with different Si/Ce ratios was carried out in a teflon-lined autoclave at 383 K for 24–36 h. Whereas fumed silica (Sigma Aldrich, USA), NaOH (Merck, India), sodium aluminate ($NaAlO_2$, 42.0%, Al_2O_3, 39.0%, Na_2O and 19.0% H_2O; Loba Chemie, India), and $Ce(SO_4)_2 \cdot 4H_2O$ were employed as precursor material, cetyltrimeth-

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ylammonium bromide (CTMABr; Loba Chemie, India) was used as a structure directing agent. The molar gel composition of Ce-containing Al–MCM-41 samples was: $1SiO_2:xCeO_2:.04Al_2O_3:0.32NaOH:0.25CTMABr:125H_2O$, where *x* varied in the range of 0.0–0.04. After hydrothermal synthesis, the samples recovered on filtration were washed thoroughly, first with distilled water and then with acetone, followed by drying (353 K) and calcination (775 K, 8 h) in flowing air. The samples thus obtained were treated with 0.5 M ammonium acetate solution followed by filtration, drying and calcination at 775 K for 7 h, in order to get the H-form of different samples. The synthesis gel and the final products obtained after calcination were analyzed by atomic absorption spectroscopy (AAS) for chemical composition. These results are given in Table 1.

2.2. General procedure for Mukaiyama-aldol condensation

The catalytic reaction was performed in liquid-phase using a two-necked continuously stirred round bottom flask, equipped with a water condenser. The catalyst was pre-activated at 393 K in a vacuum oven and the reactions were carried out under N_2 atmosphere. In a typical procedure, the methyl trimethylsilyl dimethylketene acetal (10 mmol) in dry dichloromethane (DCM) was added to a pre-activated catalyst (0.21 g), followed by addition of benzaldehyde (10 mmol) to reaction vessel. The products were analyzed by gas chromatography (Varian model CP-3800) equipped with capillary column and flame ionization detector (FID), as well as by thin layer chromatography (TLC). After completion of the reaction, the catalyst was filtered out and the filtrate was diluted with DCM and then washed with 1 N HCl and finally washed with water. The organic layer was separated and dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporator and the product was purified through column chromatography using silica gel (100–200 mesh) as a stationary phase and petroleum ether + ethyl acetate (3:1) as eluent. The final products were identified with the help of GC, GC–MS, ^{1}H NMR, ^{13}C NMR. White powder; M.P. 66–67 (petroleum ether: ethyl acetate = 3:1), ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.17 (s, 3H), 3.29 (d, 1H), 3.72 (s, 3H), 4.91 (d, 1H), 7.22–7.44 (m, 5H). ^{13}C NMR (200 MHz, $CDCl_3$) δ 19.0, 23.2, 47.7, 52.5, 78.4, 127.6, 139.9, 178.2.

2.3. Characterization techniques

The powders X-ray diffractogram of as-synthesized and calcined samples were recorded on a Rigaku Miniflex diffractometer (Cu-K_α radiation, $\lambda = 1.54054$ Å) in 2θ range of 1.5–10° at a scanning rate of 1° min^{-1}. The specific surface area (S_{BET}) and mesoporosity were checked by N_2 sorption at 77 K using NOVA 1200 Quantachrome equipment. The samples were evacuated at 573 K before N_2 sorption. The surface area was calculated from linear part of BET (Brunauer–Emmet–Teller) equation and the method of Barret–Joyner–Halenda (BJH) was employed to determine the pore-size distribution (PSD). The coordination of the metal ions was monitored by using diffuse reflectance UV–Vis spectroscopy. A Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment was employed for this purpose using $BaSO_4$ as reference.

The concentration and strength of acid sites in different samples were monitored with the help of IR spectroscopy of adsorbed pyridine molecules. A Thermo Nicolet (model-Nexus 870) FT-IR was employed for recording of IR spectra in transmission mode. The details of stainless-steel cell used in these studies and the experimental procedure adopted have been described earlier [22,23]. A self-supporting wafer (~50 mg) of 25 mm diameter, placed in a sample holder block, was heated *in situ* for 8–10 h at 550–575 K under vacuum (~1 × 10^{-3} Torr). For acidity measurements, samples were exposed at 420 K to multiple doses of pyridine (~9.5 μmol each) to achieve saturation coverage. A gas mixture of pyridine vapor + - dry nitrogen was used for this purpose. IR spectra were then plotted after cooling the sample to room temperature followed by evacuation for ~10 min. Scans (300) were co-added for plotting of each spectrum at a resolution of 4 cm^{-1}. The strength of the acid sites was evaluated by recording the temperature programmed desorption of ammonia (TPD-NH_3) with the help of a Micromeritics Autochem 2910 instrument. For this purpose, 200 mg of a sample was taken in a U-shaped quartz tube and was activated for 2 h at 775 K under helium flow (20 ml/min). After exposure to ammonia vapor at room temperature the sample was flushed with He and its temperature was subsequently raised to 775 K at a ramp of 10 K min^{-1}.

The XPS analyses were conducted on a Perkin–Elmer model 5300 X-ray photoelectron spectrometer equipped with MgK_α radiation.

3. Results and discussion

3.1. Powder X-ray diffraction

The powder XRD patterns of Si–MCM-41, Al–MCM-41, Ce–MCM-41, and Ce–Al–MCM-41 are given in curves a–d, respectively, of Fig. 1. The presences of (1 0 0) line along with weak reflections (1 1 0), (2 0 0) and (2 1 0) in Fig. 1(a–d) are the characteristic features of MCM-41. Although a small decrease in the intensity of XRD lines was observed in the case of Ce–Al–MCM-41 samples with higher Ce-contents, the hexagonal order was retained as can be seen by hkl (1 0 0) reflection. No free CeO_2 phase was observed in all our Ce–Al–MCM-41 samples. This is confirmed by comparing the XRD pattern of Ce–Al–MCM-41 (curve d, inset) with that of a physical mixture of CeO_2 (2.5%) and Al–MCM-41 (curve e, inset) and pure CeO_2 (curve f, inset). The d_{100} values of different MCM-41 samples along with the values of corresponding unit cell parameter (a_o) are recorded in Table 1. The unit cell parameter a_o was calculated for hkl (1 0 0) reflection using the equation

Table 1
Physicochemical characteristics of Ce-substituted Al–MCM-41 samples.

Sample	Catalyst	Mole ratio		S_{BET} (m^2/g)	d_{100} (Å)	a_o[a] (Å)	Pore diameter (Å)	Total acidity (μmol NH_3 g^{-1})
		Si/Ce	Si/Al					
A	Si–MCM-41	0	0	1165	37.90	43.76	27.6	–
B	Al–MCM-41	0	30	1104	37.88	43.74	27.9	334.5
C	Ce–MCM-41	30	0	850	37.63	43.57	27.1	160.6
D	Ce–Al–MCM-41	108	32	995	38.45	44.39	28.9	338.6
E	Ce–Al–MCM-41	80	32	989	38.44	44.38	29.5	365.7
F	Ce–Al–MCM-41	59	33	971	38.43	44.37	30.85	419.7
G	Ce–Al–MCM-41	38	34	940	38.41	44.35	31.14	468.3

[a] a_o, Unit cell parameter = $2d_{100}/\sqrt{3}$.