Catalytic epoxidation of α-pinene over bifunctional mesoporous molecular sieves

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Bifunctional titanium-mesoporous molecular sieves containing different trivalent ions, e.g. B^{3+}, Al^{3+} or Fe^{3+}, were synthesized and characterized. These catalysts, which contain both acid and oxidizing catalytic sites, are very active in epoxidation of bulky olefins and highly selective in diol formation. A reasonably good stability and re-usability are also observed.

Keywords: MCM-41, HMS, bifunctional materials, epoxidation, bulky olefins, α-pinene and diol

1. Introduction

The discovery of hexagonal mesoporous (pore sizes ranging from 15 to more than 100 Å) molecular sieves, designated as MCM-41 [1,2] and HMS [3] provided new opportunities for the synthesis of original catalysts based on isomorphous substitution of Si^{4+} by foreign cations in order to generate catalytic activity. Various elements such as Ti, V, Al, B, Mn, Fe, and Ga [1–10] were incorporated into the network of [SiO_4] units of siliceous mesoporous molecular sieves using a direct synthesis route or grafted in a post-synthesis sequence using, for example, dichlorotitanicene in the case of titanium [8]. The acidity, catalytic properties and applications of these modified materials mainly depend on the characteristics and concentration of the framework cations. Ti- [3,4,8] and V-containing [6] MCM-41 and HMS materials are known to exhibit high activities for bulky olefins epoxidation. On the other hand, incorporation of Al and B in Ti-MCM-41 is expected to modify the catalytic properties of these materials by introducing only weak acid sites, even weaker than those in B-ZSM-5 [5,7].

Even though the simultaneous incorporation of trivalent metal ion (e.g. B^{3+}, Al^{3+}, Ga^{3+} or Fe^{3+}) along with Ti^{4+} has been reported for the zeolitic [9,10] and amorphous [11] silica materials, little information is available concerning the bifunctional mesoporous molecular sieves and their catalytic performance in the epoxidation of bulkier olefins. Due to the relatively limited pore size of zeolites, there are steric restrictions to the diffusion and reaction of the bulkier reactants. Thus, as a consequence of their higher surface area and larger channel apertures, bifunctional mesoporous molecular sieves were thought to be potential highly selective catalysts for both the oxidation and acid-catalysed reactions.

In the present communication, we report the direct synthesis and characterization of mesoporous silicas (e.g., MCM-41 and HMS) simultaneously incorporated with titanium and a trivalent ion (e.g., B^{3+}, Al^{3+} or Fe^{3+}). The influence of the nature of the trivalent ion on the activity in epoxidation of α-pinene and selectivity towards formation of the corresponding diol is also discussed.

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2. Experimental

2.1. Catalyst preparation

Titanium mesoporous silicas with B^{3+}, Al^{3+} or Fe^{3+} were prepared from tetraethyl orthosilicate (TEOS), tetra-isopropoxide titanate (TPOT), H_3BO_3, $Al(NO_3)_3$ and $Fe(NO_3)_2$ as the sources of Si, Ti, B, Al and Fe, respectively. Gels with the following molar chemical composition were prepared: SiO_2:0.02TiO_2 - 0.015M_2O_3 - 0.13$(C_{16}TMA)_2O$ - 0.13 $(TMA)_2O$ - 0.13$(NH_4)_2O$ - 55H_2O (M = B, Al or Fe). A typical synthesis of titanium MCM-41 was performed as follows: Solution A was prepared by adding a solution of 20 g of TMAOH (25 wt%) in 80 g of water to 41.5 g of TEOS at constant rate for ca. 30 min with constant stirring and then 1.14 g of TPOT in 10 ml of 2-propanol was slowly injected with constant stirring. Solution B was prepared by mixing 6.5 g NH_4OH (29 wt%) to 19.5 g $C_{16}TMABr$ (98 wt%) in 30 ml of ethanol and 100 ml of water to bypass the exchange procedure. Solutions A and B were mixed and gently stirred at room temperature for 2 h. The pH was adjusted with dilute sulfuric acid to 11.5, and the homogeneous mixture was then transferred into a Teflon-lined autoclave and heated to 373 K for 72 h. The solid product was filtered, washed with distilled water, dried at 353 K and finally calcined at 813 K for 6 h under continuous air flow (with heating rate of 1 K/min). The Ti-MCM-41 containing B^{3+}, Al^{3+}, Fe^{3+} and pure silica

MCM-41 were prepared in a similar manner. 0.38 g of H_3BO_3, 2.25 g of $Al(NO_3)_3{\cdot}9H_2O$ and 2.42 g of $Fe(NO_3)_3{\cdot}9H_2O$ were added to the gels to obtain B–Ti-MCM-41, Al–Ti-MCM-41 and Fe–Ti-MCM-41 samples respectively. For comparison, the Ti-HMS and B–Ti-HMS samples were also prepared according to ref. [3], except that the boron source was added for the preparation of B–Ti-HMS.

2.2. Characterization

Powder X-ray diffraction patterns of the sample were recorded on a Rigaku D-MAX II VC X-ray diffractometer using nickel filtered Cu Kα ($\lambda = 1.5406$ Å). Nitrogen adsorption/desorption isotherms were carried out at 77 K using an Omnisorp-100. The volume of adsorbed nitrogen was normalized to standard temperature and pressure (STP). The specific surface area was determined from the linear part of the BET plot ($p/p_0 = 0.05$–0.30). Mesopore size distribution (PSD) was calculated using the desorption branches of the nitrogen adsorption/desorption isotherm and the Barrett–Joyner–Halenda (BJH) formula [14,15].

The specific BET surface areas and average pore size were determined by N_2 adsorption–desorption isotherms at 77 K using an Omnisorp-100. Diffuse reflectance UV–vis spectroscopy was performed using a Perkin-Elmer Lambda 5 spectrophotometer and using pure silica MCM-41 as a standard, except in the case of Fe–Ti-MCM-41 where Fe-MCM-41with the same Fe content was used as a standard. The ^{27}Al and ^{11}B MAS-NMR spectra were recorded on a Bruker ASX 300 spectrometer at room temperature.

2.3. Reaction

Catalytic epoxidation reactions were carried out batchwise in a glass reactor under stirring and reflux. The reaction temperature was maintained at 328 K using a temperature controlled water bath. In a typical reaction procedure, the calculated amount of α-pinene (0.037 mol) in chloroform (98%, 0.134 mol), 0.1 g of catalyst and tert-butyl hydroperoxide, TBHP (0.011 mol, 50% in chlorobenzene/water) were mixed. To check the stability and re-usability, the catalysts were recovered after the 24 h of reaction. The catalysts were filtered off, dried and again calcined for 4 h at 813 K. The recovered catalysts were again used for the epoxidation reaction under similar reaction conditions.

In an other set of reaction procedures in catalysts evaluation using H_2O_2 as an oxidizing agent, a mixture of α-pinene (0.037 mol), 0.1 g of catalyst and H_2O_2 (0.0441 mol, 30% in aqueous solution) was stirred at 328 K for 5 h.

The special experiment was designed to evaluate the peroxide decomposition under the similar reaction conditions over pure silica gel and pure silica MCM-41 (surface area = 740 and 1280 $m^2\,g^{-1}$ respectively).

Conversion and selectivity were determined by gas chromatography (HP 5890 A) using a capillary column (DB-Wax). Product identification was achieved from the retention time of the pure compounds.

3. Results and discussion

Table 1 gives the chemical compositions and textural properties of the various samples. The samples MCM-41 and HMS show quite narrow pore size radius distributions centered around 19 and 22 Å respectively. The surface areas obtained which are around 1000 and 1200 m^2/g for MCM-41 and HMS materials respectively, are comparable to the ones previously reported for these materials [1–7]. The adsorption/desorption isotherms for all samples exhibit sharp inflection at $p/p_0 > 0.3$, which is characteristic of capillary condensation within uniform mesopores (not shown). The hysteresis loop in the isotherms is characteristic of pore structure. However, for the metal-substituted materials the hysteresis loop at high partial pressure ($p/p_0 > 0.9$) was observed, indicating the presence of some amorphous phase in these samples. The X-ray diffraction patterns of calcined MCM-41 samples shown in figure 1 are typical of MCM-41 as described by Beck et al. [1,2]. However, the relative peaks for the metal-substituted materials (figures 1a–1d) were weaker and broader than that of the pure silica analogue (figure 1e). Moreover, a very small amorphous hump in the 20–30's 2θ range was also observed for the metal-substituted materials. This probably indicates the reduction of the long-range order of the mesopores after incorporation of metal cations, such as Ti^{4+} or Al^{3+}, into the silica framework without damaging the essentially mesoporous nature of the material [4,7].

The UV–vis spectra of the calcined Ti-MCM-41, Ti-MCM-41 containing different trivalent ions (figure 2)

Table 1
Chemical composition (atomic ratios) and textural properties of the mesoporous molecular sieves

Catalyst	Si/Ti	Si/M [a]	Pore size radius (Å)	BET surface area ($m^2\,g^{-1}$)
MCM-41 pure	–	–	18.5	1280
Ti-MCM-41	48	–	19.0	1230
B–Ti-MCM-41	46	34	19.5	1250
Al–Ti-MCM-41	51	32	18.5	850
Fe–Ti-MCM-41	52	38	18.0	1050
Ti-HMS	47	–	21.5	1300
Ti–B-HMS	52	35	22.0	1380
Ti-MCM-41 recycled [b]	–	–	20.0	950
Al–Ti-MCM-41 recycled	–	–	19.5	630

[a] M = B, Al or Fe as per catalyst designation.
[b] Catalyst recycled after 24 h of reaction.

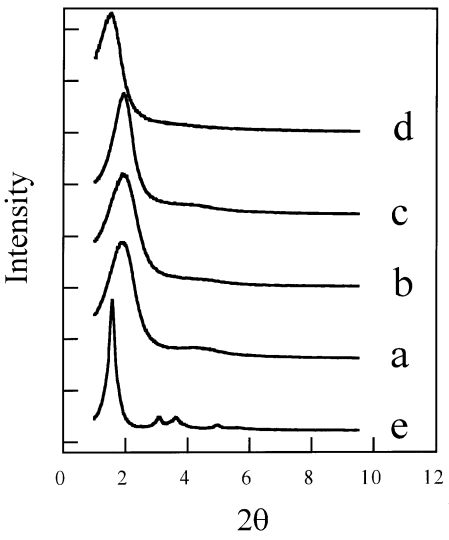


Figure 1. X-ray diffraction patterns of calcined mesoporous molecular sieves MCM-41 samples. (a) Ti-MCM-41, (b) Al–Ti-MCM-41, (c) B–Ti-MCM-41, (d) Fe–Ti-MCM-41, (e) pure silica MCM-41.

and Ti-HMS samples (not shown) exhibit a strong band at ca. 230 nm, which has been assigned to isolated tetrahedral Ti atoms in the framework [4]. No band at ca. 330 nm characteristic of anatase was observed. Morever, the Ti K-edge (XANES) spectra (not shown) of the dehydrated Ti-MCM-41 and Ti-HMS (table 1) also confirm that titanium is only present as tetrahedral [TiO_4] units. The ^{27}Al MAS-NMR spectrum of calcined Al–Ti-MCM-41 shows a main peak at around 50 ppm exhibiting most of the Al atoms in a tetrahedral environment. The ^{11}B MAS-NMR spectra of calcined B–Ti-MCM-41 and B–Ti-HMS show the simultaneous presence of both tetrahedral and trigonal framework boron [5]. Finally, mild acid sites (Brønsted and Lewis) in the Al-MCM-41 and B-MCM-41 samples (weak compared to those in boron silicalite) were identified by adsorption–desorption of pyridine [5,7].

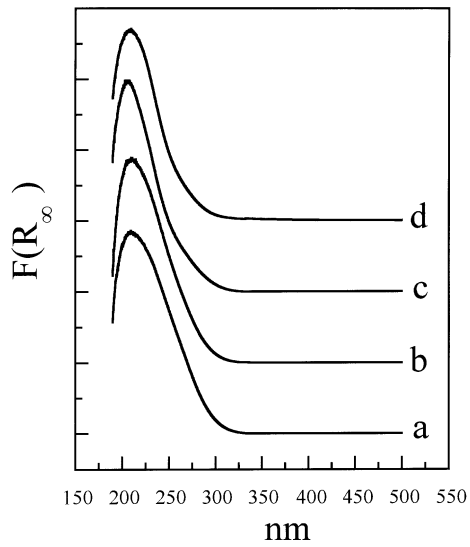


Figure 2. Diffuse reflectance UV–vis spectra of calcined mesoporous molecular sieves MCM-41 samples (pure silica MCM-41 used as a standard and Fe-MCM-41with the same Fe content used as a standard for Fe–Ti-MCM-41). (a) Ti-MCM-41, (b) Al–Ti-MCM-41, (c) B–Ti-MCM-41, (d) Fe–Ti-MCM-41.

To demonstrate the usefulness of these bifunctional catalysts, titanium-mesoporous molecular sieves containing the different trivalent cations were used as catalysts in the epoxidation of a large organic molecule, namely α-pinene, by diluted *t*-butyl hydroperoxide (TBHP). The results for the epoxidation of α-pinene with TBHP over Ti-MCM-41 are summarized in table 2. 11% conversion of α-pinene with 100% selectivity to α-pinene oxide was achieved after 5 h of reaction. The TBHP conversion was satisfactory with maximum 95% selectivity. Under the same reaction conditions, the B–Ti-MCM-41, Al–Ti-MCM-41, and Fe–Ti-MCM-41 were also found to be very active in epoxidation of α-pinene and highly selective in diol formation. The catalytic conversion of α-pinene and the selectivity to secondary products over all the bifunctional catalysts, however, depend on the nature of the trivalent cation (scheme 1). The amount of water present in the reaction system is sufficient to allow the hydrolysis reaction and to open the epoxy ring to the 1,2 diol. Compared to B–Ti and Al–Ti, Fe–Ti mesoporous molecular sieve exhibits a lower conversion. The α-pinene conversion follows the order: Ti-MCM-41 > B–Ti-MCM-41 > Al–Ti-MCM-41> Fe–Ti-MCM-41. The TBHP selectivity and conversion also follow similar trends. However, the additional weak acidic sites due to the framework incorporated trivalent cation, affect significantly the product distribution (table 2). The selectivity of diol formation is in the order Al–Ti-MCM-41 > B–Ti-MCM-41 > Fe–Ti-MCM-41. Thus, the framework titanium is catalytically active in epoxidations and the trivalent cation in the titanium-silica framework favors the diol formation. Morever, for the Al–Ti-MCM-41, the selectivity of diol is higher compared to that obtained over B–Ti and Fe–Ti mesoporous molecular sieves. This is probably associated to the relatively stronger acidity in Al–Ti-MCM-41 than in B–Ti-MCM-41 and Fe–Ti-MCM-41.

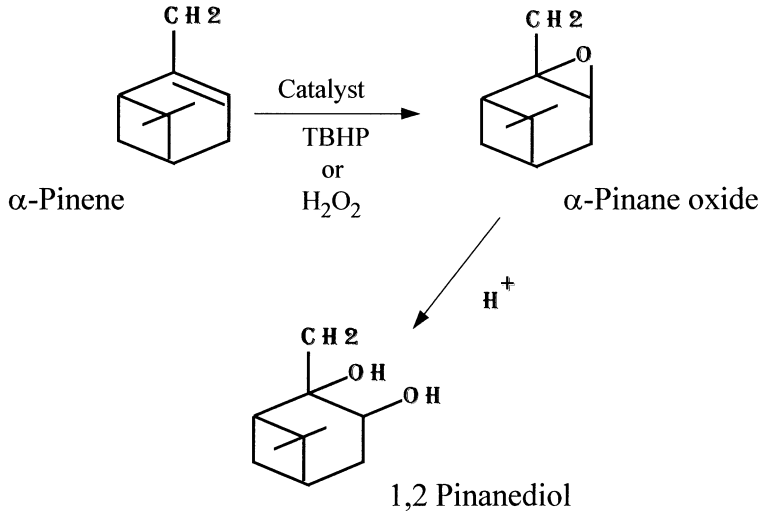
The epoxidation of α-pinene with TBHP was also performed over Ti-incorporated mesoporous molecular sieve HMS [3]. As seen in table 2, the Ti-HMS and B–Ti-HMS exhibit comparatively lower activity and selectivity than Ti-MCM-41 and bifunctional Ti-MCM-41, while the TBHP conversion and selectivity remain unchanged.

Also, when 30% H_2O_2 was used as the oxidant instead of TBHP, the selectivity was considerably reduced. The catalytic results of the epoxidation of α-pinene using H_2O_2 over Ti and B–Ti mesoporous materials (table 3) illustrate the relatively lower potential of the use of H_2O_2. In similar static conditions, a conversion of 6.0%

Table 2
Epoxidation of α-pinene by *t*-butyl hydroperoxide over titanium containing mesoporous molecular sieves with different trivalent ions [a]

Sample	Reaction time (h)	α-pinene conversion (%)	*t*-butyl hydroperoxide		Product selectivity (%)	
			conversion (%)	selectivity (%)	α-pinane oxide	1,2-pinane diol
Ti-MCM-41	1	4.2	15.5	90.5	100	0
	3	7.2	26.0	91.5	100	0
	5	11.0	38.5	94.5	100	0
B–Ti-MCM-41	1	3.6	14.5	80.5	70.5	29.5
	3	6.4	24.5	85.5	57.0	43.0
	5	9.9	36.0	90.0	36.5	63.5
Al–Ti-MCM-41	1	3.3	13.0	83.5	80.5	19.5
	3	6.1	23.5	85.0	58.5	41.5
	5	8.8	33.5	87.0	28.0	72.0
Fe–Ti-MCM-41	1	1.4	8.0	56.5	95.5	4.5
	3	4.9	22.5	71.5	84.0	16.0
	5	7.9	34.0	76.5	56.5	43.5
Ti-HMS	1	2.6	9.5	92.4	100	0
	3	5.5	19.5	92.5	100	0
	5	9.2	32.0	95.5	100	0
Ti–B-HMS	1	2.5	10.5	79.0	73.5	26.5
	3	5.0	19.5	85.0	67.0	33.0
	5	8.2	30.0	90.5	45.0	55.0
Ti–MCM-41 recycled	1	3.6	17.9	86.8	100	0
	3	6.1	29.6	89.2	100	0
	5	9.3	43.7	91.0	100	0
Al–Ti-MCM-41 recycled	1	2.8	16.6	74.7	86.1	13.9
	3	5.2	26.2	75.9	65.8	34.2
	5	7.9	40.9	78.1	37.9	62.1

[a] Reaction conditions: catalyst = 0.10 g, α-pinene = 0.037 mol, TBHP (50% solution in chlorobenzene/water) = 0.011 mol, solvent (chloroform, 98%) = 0.134 mol, reaction temperature = 328 K, reaction duration = 5 h.



Scheme 1.

Table 3
Epoxidation of α-pinene by hydrogen peroxide (H_2O_2) over titanium containing mesoporous molecular sieves with different trivalent ions [a]

Sample	Reaction time (h)	α-pinene conversion (%)	Hydrogen peroxide		Product selectivity (%)	
			conversion (%)	selectivity (%)	α-pinane oxide	1,2-pinane diol
Ti-MCM-41	1	1.6	29.0	5.0	100	0
	3	3.9	38.0	9.5	100	0
	5	6.0	46.0	11.5	100	0
B–Ti-MCM-41	1	1.1	33.5	3.5	63.0	38.0
	3	2.6	43.0	8.0	49.5	50.5
	5	4.9	57.5	9.5	32.0	68.0
Ti-HMS	1	1.6	22.5	5.0	100	0
	3	3.7	34.5	10.5	100	0
	5	5.8	43.0	13.0	100	0
B–Ti-HMS	1	1.0	24.5	4.0	70.0	30.0
	3	2.3	36.0	9.0	52.0	48.0
	5	4.2	40.5	10.5	38.0	62.0
pure silica [b] MCM-41	1	–	18.6	–	–	–
	3	–	27.9	–	–	–
	5	–	38.1	–	–	–
pure silica gel [b]	1	–	5.3	–	–	–
	3	–	8.5	–	–	–
	5	–	12.2	–	–	–

[a] Reaction conditions: catalyst = 0.10 g, α-pinene = 0.037 mol, H_2O_2 (30% aqueous solution) = 0.0441 mol, reaction temperature = 328 K, reaction duration = 5 h.
[b] Pure silica gel (Alfa Davision) and pure silica MCM-41 with surface area of 697 and 1280 $m^2\ g^{-1}$ respectively.

with an epoxide selectivity of 100% is found over Ti-MCM-41. The H_2O_2 conversion was about 45.9% with very low selectivity 11.6% after 5 h of reaction. The B–Ti-MCM-41 shows comparatively lower conversion than Ti-MCM-41, but they are highly selective in diol formation (68.1%). Again, the H_2O_2 conversion was high enough (57.6%) with very low selectivity 9.71% (table 3).

In separate experiments, we have also shown that both Ti-HMS and Ti–B-HMS catalysts exhibit comparatively lower conversion and selectivity for 1,2 diol than Ti-MCM-41 and Ti–B-MCM-41 respectively. The H_2O_2 conversion was also lower while the selectivity of H_2O_2 was slightly improved. NMR studies reveal that MCM-41 is rich in silanol groups even after the template molecules have been removed [2,16]. These silanols are expected to act as functional groups in catalytic reactions [17]. The results of a special experiment conducted demonstrated a three times higher H_2O_2 decomposition on pure silica MCM-41 compared to silica gel under identical reaction conditions (table 3). Mechanistically, in epoxidation of α-pinene with TBHP and H_2O_2, it is proposed that the high concentration of hydroxyl groups present on the wall surface is responsible for the higher decomposition of H_2O_2 as compared to TBHP. Indeed, it should be noted that the TBHP-catalyst, under the given reaction conditions, gave little decomposition with a selectivity higher than 90% (table 2).

Finally, the results of the epoxidation of α-pinene with TBHP catalysed by the recycled catalysts (table 2) illustrate that these mesoporous materials are essentially structurally stable catalysts, which provides a simple and general procedure for the synthesis of epoxides and corresponding 1,2 diols. The catalytic data reveal that these mesoporous materials still display a considerable activity even after 24 h of reaction. The catalytic conversion of α-pinene was relatively lowered (9.3%) on the recycled catalyst as compared to the fresh catalyst (11.0%). This is associated with the observed decrease in surface area (table 1) and small increase in pore size. Both effects are induced by a minor collapse of the structure which corresponds to an increased surface concentration of hydroxyl groups [12,13]. Obviously this more defective structure leads to a reduction in the selectivity of TBHP reaction to epoxide, even though its conversion is increased. This suggests that surface OH's promote the decomposition of TBHP.

The comparison between fresh and recycled Al–Ti-MCM-41 catalysts shows the same trends. In addition the lower selectivity of 1,2 diol reflects the decreased rate of its formation due to a decreased production of α-pinane oxide by the primary reaction.

4. Conclusion

Our study demonstrates that bifunctional titanium-mesoporous molecular sieves can catalyze the epoxidation of bulky olefins, being highly selective for diol formation. Their acidity is low enough to open the epoxy ring while preventing secondary reactions of oxidation products. The selectivity of the peroxide use in epoxidation is considerably lower when H_2O_2 is used as the oxidant instead of TBHP. These mesoporous materials were found to be reasonably stable and reusable for the epoxidation reaction. Hence, they have a real potential as catalysts in the fine-chemical industry. Work is in progress to gain further insight into the mechanistic aspects of this process.

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