Transesterifications over titanosilicate molecular sieves

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Abstract

Titanosilicate molecular sieves (TS-1, Ti-MCM-41 and amorphous TiO_2–SiO_2) catalyze transesterification reactions. Acidity measurements (pyridine adsorption-IR and NH_3-TPD) reveal the presence of only weak Lewis acid sites. Catalytic activity parallels the acid strength and increases in the order: TS-1 < Ti-MCM-41 < amorphous TiO_2–SiO_2. TS-1 efficiently catalyzes the transesterification of only linear esters (ethylacetoacetate and diethylmalonate), but fails for cyclic esters like propylene carbonate. Ti-MCM-41 and amorphous TiO_2–SiO_2 are superior for the latter. The catalysts could be recycled without any loss in activity/selectivity.
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1. Introduction

Acids and bases are known to accelerate the rate of trans-esterifications (Eq. (1)) [1]. Transesterification is a crucial step in several industrial processes such as (i) production of higher acrylates from methylmethacrylate (for applications in resins and paints), (ii) polyethylene terephthalate (PET) from dimethyl terephthalate (DMT) and ethylene glycol (in polyester manufacturing), (iii) intramolecular transesterifications leading to lactones and macrocycles, (iv) alkoxy esters (biodiesel) from vegetable oils, and (v) co-synthesis of dimethyl carbonate (DMC) (an alkylating agent, octane booster and precursor for polycarbonates) and ethylene glycol from ethylene carbonate and methanol [2]. Other than mineral acids and bases, compounds like metal alkoxides (aluminum isopropoxide, tetraalkoxytitanium, $(RO)Cu(PPh_3)_n$, $PdMe(OCHCF_3Ph(dpe))$, organotin alkoxides, etc.), non-ionic bases (amines, dimethylaminopyridine, guanidines, etc.) and lipase enzymes also catalyze these transformations [1]:

$$RCOOR_1 + R_1OH \rightleftharpoons RCOOR_2 + R_1OH \qquad (1)$$

Tatsumi et al. [3] have reported the synthesis of dimethyl carbonates from ethylene carbonate and methanol using K-TS-1 as a solid base catalyst. The transesterification of dimethyl oxalate with phenol has also been reported recently [4]. Titanosilicates have been widely investigated, over more than two decades, as selective oxidation catalysts [5]. We now report the application of TS-1, Ti-MCM-41 and amorphous TiO_2–SiO_2 in the transesterifications of a monoester—ethylacetoacetate (EAA), a diester—diethylmalonate (DEM) and a cyclic ester—propylene carbonate (PC) with several alcohols.

2. Experimental

2.1. Catalyst preparation

TS-1 was synthesized according to the procedure of Thangaraj et al. [6] (Si/Ti = 33; S_{BET} = 485 m^2/g).

Ti-MCM-41 was synthesized from the gel of molar composition: TEOS:0.25 CTMABr:0.3 TMAOH:0.0303 TBOT:40 H_2O:5 CH_3OH. In a typical synthesis, 10.9 g of tetramethylammonium hydroxide (25 wt.% TMAOH, 99% Aldrich) was taken in 72 g of distilled water. To that, 8.75 g of cetyltrimethylammonium bromide (CTMABr, S. D. Fine Chem. Ltd., India) was added. Then, 20.8 g of tetraethylorthosilicate (TEOS, Aldrich) in 16 g of methanol was added dropwise over a period of 20 min. To the resultant

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solution, 1.03 g of titanium tetrabutoxide (TBOT, Aldrich) in 10 ml of isopropanol was added over a period of 10 min. The resultant gel was stirred for further 4 h at 298 K and then transferred into a teflon-lined stainless steel 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 (Si/Ti = 35; S_{BET} = 1055 m^2/g; pore volume = 0.77 cm^3; average pore diameter = 29.4 Å).

Amorphous TiO_2–SiO_2 was prepared from the gel of molar composition: TEOS:0.55 CTMABr:0.33 TMAOH:0.0303 TBOT:60 H_2O. In a typical synthesis, 12.0 g (25 wt.%) of TMAOH was taken in 108 g of distilled water. To it, 20 g of CTMABr was added. Then, to this solution, 20.8 g of TEOS was added dropwise over a period of 20 min. Subsequently, 1.03 g of TBOT dissolved in 10 ml isopropanol was added in 10 min. The resultant gel was stirred for 2 h at 298 K and then transferred to a teflon-lined stainless steel autoclave and heated to 383 K for 5 days. The solid product was filtered, washed with distilled water, dried at 353 K and finally calcined at 813 K for 6 h. The minor changes in the synthetic procedure from that of Ti-MCM-41 have resulted in an amorphous TiO_2–SiO_2 solid (Si/Ti = 37; S_{BET} = 273 m^2/g).

2.2. Physicochemical properties

The physicochemical properties of the catalysts were characterized as reported earlier [6].

2.3. Acidity measurements

2.3.1. Pyridine adsorption-IR

IR spectral measurements were performed on a Shimadzu SSU 8000 DRIFT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector. Samples were activated at 698 K for 2 h under nitrogen flow. Then they were cooled to 323 K and pyridine (30 μl) was adsorbed. The sample temperature was raised to a desired value and held at that temperature for 30 min and then the spectrum was recorded.

In some measurements, the samples were initially hydrated by keeping them overnight in a desiccator containing water. Then they were subjected to IR measurements by adsorbing pyridine at 298 K.
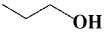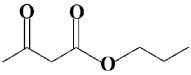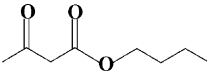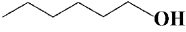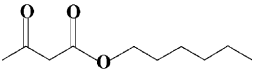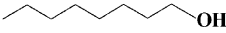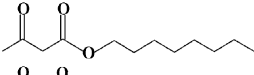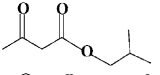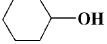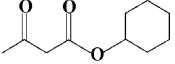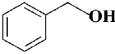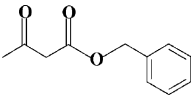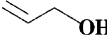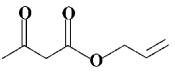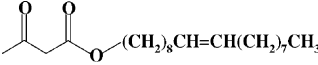
2.3.2. NH_3-TPD

Temperature programmed desorption (TPD) measurements were performed on a Micromeritics Autochem 2910 instrument. The sample (500 mg) was initially activated at 773 K for 2 h in He flow (20 ml/min). It was then cooled to 353 K and 10% NH_3 in He was adsorbed for 30 min. The sample was flushed with He (30 ml/min) for 1 h at 373 K and the desorption was monitored by increasing temperature from 373 to 723 K at a ramp rate of 10 K/min.

2.3.3. Reaction procedure

All the transesterifications were performed in glass batch reactor placed in a temperature controlled oil bath and fit-

Table 1
Transesterification of ethylacetoacetate (EAA) with various alcohols (ROH) over TS-1[a]

Entry	ROH	Transester product	Conversion (EAA, mol%)	Product yield (%)
1			95.6	92.9
2			100	87.1
3			97.6	90.7
4			99.2	85.0
5			96.2	84.3
6			96.4	95.3
7			86.4	69.5
8			83.1	66.9
9	$CH_3(CH_2)_7CH=CH(CH_2)_7CH_2OH$			87.6[b]

[a] Reaction conditions: catalyst (TS-1; Si/Ti = 33), 130 mg; EAA, 5 mmol; ROH, 15 mmol; temperature = 383 K, run time = 4 h.
[b] Isolated yield.

Table 2
Transesterification of diethylmalonate (DEM) with various alcohols (ROH) over TS-1[a]

ROH	DEM conversion (mol%)	Total transester selectivity (%)	Products distribution (%)	
			Mono	Di
n-Propanol	97.5	98.4	26.6	73.4
n-Butanol	99.3	97.0	16.0	84.0
n-Butanol[b]	95.8	100	46.4	53.6
n-Butanol (recycle I)[b]	95.0	100	45.9	54.1
n-Butanol (recycle II)[b]	94.4	100	46.6	53.4
n-Hexanol	99.7	100	10.9	89.1
n-Octanol	100	100	82.6	17.4
iso-Butanol	95.6	96.3	58.0	42.0
Cyclohexanol	100	100	34.4	65.6
Benzyl alcohol	84.2	88.8	39.0	61.0

[a] Reaction conditions: catalyst (TS-1; Si/Ti = 33), 130 mg; DEM, 5 mmol (0.8 g); ROH, 15 mmol; temperature = 383 K, run time = 12 h.
[b] Reaction conditions: same as in "a" except temperature = 353 K.

Table 3
Comparative activity of TS-1, Ti-MCM-41 and amorphous TiO_2–SiO_2 in transesterification of (a) ethylacetoacetate with benzyl alcohol and allylalcohol and (b) diethylmalonate with *n*-butanol[a]

Catalyst	Benzyl alcohol		Allylalcohol	
	Ester conversion (mol%)	Transester yield (%)	Ester conversion (mol%)	Transester yield (%)
(a) Ester—ethylacetoacetate (run time = 4 h)				
TS-1	86.4	69.5	83.1	69.8
Ti-MCM-41	93.7	90.2	85.2	84.5
Amorphous TiO_2–SiO_2	95.2	91.9	87.3	86.1
Catalyst	Ester conversion (mol%)	Transester yield (%)	Monotransester selectivity (%)	Ditransester selectivity (%)
(b) Ester—diethylmalonate (run time = 12 h); alcohol—*n*-butanol				
TS-1	58.2	57.4	59.0	41.0
Ti-MCM-41	66.5	65.6	87.2	12.8
Amorphous TiO_2–SiO_2	68.6	66.7	89.2	10.8

[a] Reaction conditions: Ester, 5 mmol; alcohol, 15 mmol; catalyst, 130 mg; temperature, 383 K.

ted with a water-cooled condenser. In a typical reaction, a known quantity of the reactants and catalyst (see Tables 1–4 for compositions) were taken and the reaction was conducted at a desired temperature (298–423 K) for a specific period. At the end of the reaction, the catalyst was separated and the liquid portion was analyzed by gas chromatography (Varian 3400; CP-SIL8CB column; 30 m long, and 0.53 mm i.d.). The products were identified by GC-MS (Shimadzu QP-5000; 30 m long, 0.25 mm i.d., and 0.25 μm thick capillary column DB-1), GC-IR (Perkin Elmer 2000; BP-1 column; 25 m long, and 0.32 mm i.d.) and ^{1}H NMR (Bruker AC 200). In some cases, the product was isolated by column chromatography (silica gel (60–80 mesh); petroleum ether:ethylacetate = 80:20 v/v eluent).

Table 4
Transesterification of cyclic propylene carbonate (PC) with different alcohols and phenol (ROH) over titanosilicates

Titanosilicate	ROH	Reaction time (h)	Conversion of PC (mol%)	Selectivity of transester product (mol%)[c]
TS-1[a]	Methanol	2	Nil	–
TiMCM-41[a]	Methanol	2	5.1	
	Phenol	8	58.9	24.4
Amorphous TiO_2–SiO_2[b]	Methanol	4	71.4	48.2
		8	86.0	51.2
	Ethanol	8	73.0	61.8
	Propanol	12	86.3	69.4
	n-Butanol	12	85.0	73.4
	n-Hexanol	12	49.0	61.5

[a] Reaction conditions: catalyst (TS-1 or TiMCM-41), 400 mg; propylene carbonate, 1.36 g, ROH (methanol, 3.2 g; phenol, 4.7 g); temperature, 393 K.
[b] Reaction conditions: catalyst (amorphous titanosilicate), 400 mg; propylene carbonate, 1.02 g (0.01 mol); ROH, 0.1 mol; temperature, 423 K.
[c] Balance is the corresponding ether.
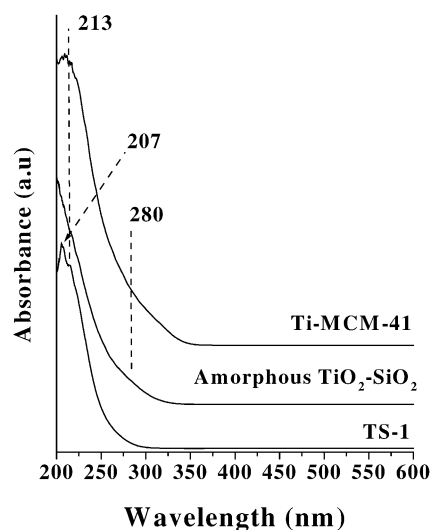
Fig. 1. Diffuse reflectance UV–vis spectra of TS-1, Ti-MCM-41 and amorphous TiO_2–SiO_2.

3. Results and discussion

3.1. Catalyst characterization

The crystallinity and phase purity of TS-1 and Ti-MCM-41 were confirmed from their XRD patterns [7]. Amorphous TiO_2–SiO_2 (prepared with template CTABr) showed weakly intense signals indicating mesoporous short-range ordering (broad (1 0 0) reflection; barely seen higher 2θ reflections). However, the XRD pattern (not shown here) and peak intensity revealed that this material was mainly amorphous in nature.

The tetrahedral coordination of Ti in our samples is confirmed by diffuse reflectance UV–vis spectroscopy (Fig. 1) wherein the characteristic oxygen to metal charge trans-

fer band occurred at 207–213 nm. The band at 207 nm in TS-1 and 213 nm in Ti-MCM-41 indicate variations in the tetrahedral structural geometry of Ti in these silicates. This observation is in agreement with the X-ray absorption spectroscopic results wherein a tripodal structure $Ti(OH)(OSi)_3$ in Ti-MCM-41 and both tripodal and tetrapodal structures $(Ti(OH)(OSi)_3$ and $Ti(OSi)_4)$, respectively, in TS-1 (the latter being more preponderant than the former) were determined [8,9]. Amorphous TiO_2–SiO_2 also shows a similar charge transfer transition (Fig. 1). Spectral deconvolutions revealed an additional, weak band at 280 nm in Ti-MCM-41 and amorphous TiO_2–SiO_2 due to small amounts of penta/hexacoordinated Ti species. Absence of 330 nm band indicates that the samples contain no anatase TiO_2.

3.2. Acidity measurements

The acidic properties of the samples were investigated by pyridine adsorption-IR (Fig. 2) and NH_3-TPD (Fig. 3). Pyridine adsorptions were performed on both dehydrated and hydrated surfaces. It is known that upon hydration Ti ions in titanosilicates expand their coordination from 4 to 5 or 6 (8). Studies were also performed on titanium-free silicalites (Si-MCM-41, for example).

Peaks around 1595 and 1445 cm^{-1} due to hydrogen-bonded pyridine and 1580 and 1485 cm^{-1} due to pyridine-coordinated to weak Lewis acid sites are observed. The absence of peaks at 1623 and 1455 cm^{-1} indicates absence of strong Lewis acid sites. Brönsted sites in both dehydrated and hydrated samples are absent (absence of peaks at 1639 and 1546 cm^{-1}) (see Fig. 2). The IR bands are relatively more intense in Ti-MCM-41 and amorphous TiO_2–SiO_2 than in TS-1 consistent with the easy accessibility of the Ti sites in the former two titanosilicalites than in the latter. Titanium-free silicalite samples (Si-MCM-41) showed the

Fig. 2. FT-IR spectra of pyridine adsorbed on dehydrated (a) TS-1, (b) Ti-MCM-41 and (c) amorphous TiO_2–SiO_2 at different temperatures.

Scheme 1. Transesterification of ethylacetoacetate (EAA) with *n*-butanol.

with *n*-butanol (Scheme 1) at 383 and 298 K. TS-1 exhibits high activity in the transesterification reaction. About 70% EAA conversion, with 94% transester selectivity (theoretical) were achieved in the initial 1 h itself. Comp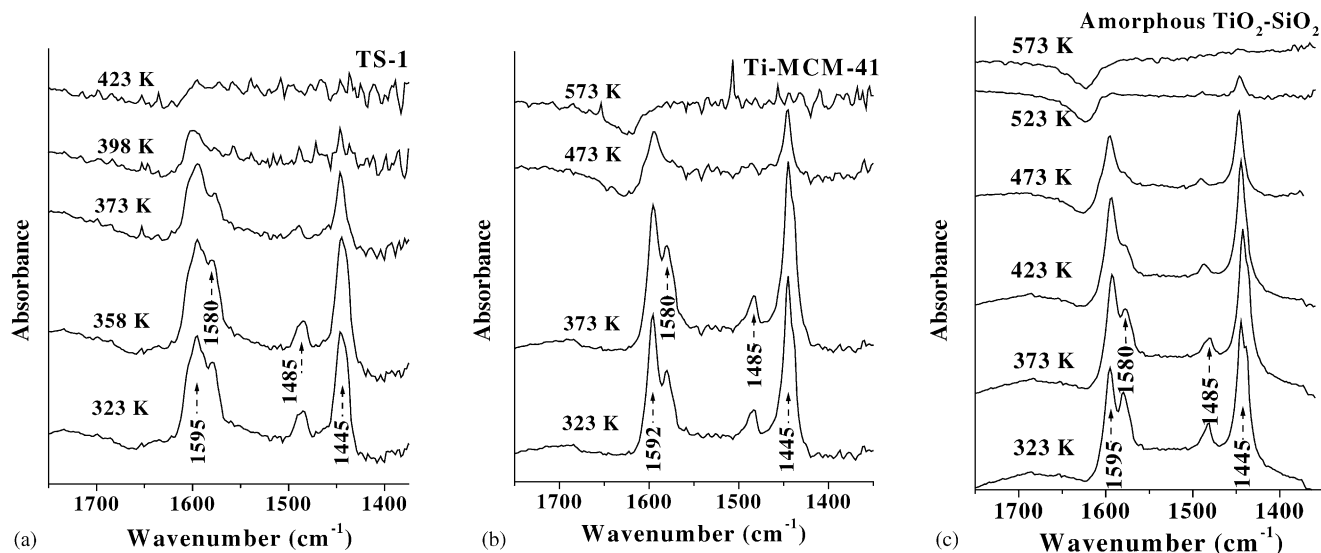lete conversion of EAA was obtained at the end of 4 h. However, the transester selectivity decreased to about 84%. The reaction can be performed even at 298 K (EAA conversion = 47% and transester selectivity = 100% at 1 h). Complete EAA conversions were obtained at longer hours (~12 h) at 298 K instead of 4 h at 383 K. Table 1 shows that the transesterification of EAA can be performed with various alcohols with high efficiency over TS-1. Allylic acetoacetates are difficult to prepare because of facile decarboxylated rearrangement (Carrol rearrangement). TS-1 shows good activity for this reaction also (Table 1; entry 8).

3.3.2. Transesterification of diester—diethylmalonate

TS-1 exhibits high activity in the reactions of DEM with various alcohols (Scheme 2). With DEM and *n*-butanol reactants, about 85% DEM conversion could be achieved in the initial 3 h over TS-1; mono to diester selectivity was 70:30. When the reaction was continued for 12 h, complete conversion of DEM and diester selectivity of 90% were achieved (Fig. 4(ii)). Entries 4 and 5 in Table 2 show that the catalyst can be separated and reused. No loss in activity and product selectivity was observed. Transesterifications were performed with various alcohols. Complete conversion of DEM was achieved in 12 h but the product selectivity (monoester/diester) depended on the alcohol group. The conversion was lower (84%) with benzyl alcohol (Table 2, entry 10), probably due to diffusional limitations in microporous TS-1. In the TS-1 samples calcined at different temperatures (723–923 K) activity (DEM conversion) varies with the acidity of the TS-1 catalysts (Fig. 4(iii)).

Table 3 demonstrates the influence of catalyst structure/acidity on the transesterification of (a) EAA with benzyl alcohol and allylalcohol and (b) DEM with *n*-butanol. The efficiency and transester yield increase with the acidity and catalyst structure in the order: TS-1 < Ti-MCM-41 < amorphous TiO_2–SiO_2.

3.3.3. Transesterification of cyclic esters—propylene carbonate

Transesterification of cyclic carbonates especially with methanol is important because the transester, DMC is a

Fig. 3. Temperature programmed desorption of NH_3 (NH_3-TPD) profiles of TS-1, Ti-MCM-41 and amorphous TiO_2–SiO_2.

IR peaks (spectra not shown here) due to hydrogen-bonded pyridine only. Absence of infrared bands at 1580 and 1485 cm^{-1} in Si-MCM-41 confirms that these bands in the titanosilicate samples arise from pyridine attached to Ti sites.

The IR peaks due to pyridine disappeared completely above 398 K on TS-1 and 523 K on Ti-MCM-41 and amorphous TiO_2–SiO_2 (Fig. 2) suggesting that the strength of the Lewis acid sites on Ti-MCM-41 and amorphous TiO_2–SiO_2 is higher than on TS-1. The easy accessibility of the Ti sites in Ti-MCM-41 with open tetrahedral Ti(OH)(OSi)$_3$ structure form stabler Ti–pyridine complexes than the Ti in TS-1 possessing closed tetrahedral Ti(OSi)$_4$ structure.

NH_3-TPD studies showed a desorption peak at 448 K (Fig. 3). This band in Ti-MCM-41 and amorphous TiO_2–SiO_2 is more intense and asymmetric indicating that the strength of the Lewis acid sites in different titanosilicates increases in the order: TS-1 (NH_3 desorbed = 2.01 mmol/g) < Ti-MCM-41 (2.57 mmol/g) ≤ amorphous TiO_2–SiO_2 (2.75 mmol/g) in broad agreement with the IR spectra for adsorbed pyridine (Fig. 2). NH_3-TPD measurements were also performed on TS-1 samples (Si/Ti = 33) calcined at different temperatures (723–923 K). The amount of NH_3 desorbed increased up to 823 K and then decreased (calcination temperature, ammonia desorbed: (723 K, 1.65 mmol/g); (773 K, 1.79 mmol/g); (823 K, 2.01 mmol/g); (923 K, 1.86 mmol/g)).

3.3. Transesterifications—catalytic activity

3.3.1. Transesterification of monoester—ethylacetoacetate

Reaction did not take place (at our experimental conditions) in the absence of TS-1 or with Ti-free silicalite samples indicating that the acid sites associated with substituted Ti are the active sites in the reactions. Fig. 4(i) shows the catalytic activity of TS-1 in the transesterification of EAA

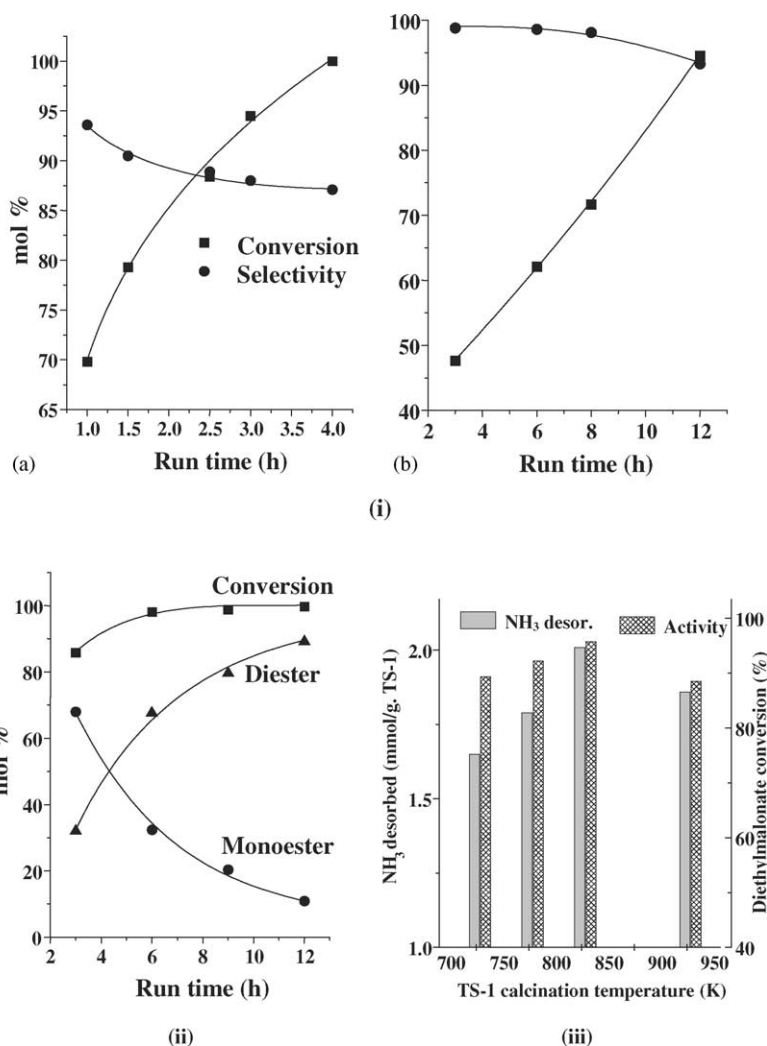Scheme 2. Transesterification of diethylmalonate (DEM) with alcohols.

Fig. 4. Catalytic activities of TS-1. (i) Transesterification of ethylacetoacetate (EAA) with *n*-butanol at (a) 383 K and (b) 298 K. Reaction conditions: EAA, 5 mmol; *n*-butanol, 15 mmol; TS-1, 130 mg, reaction time = 4 h. (ii) Transesterification of diethylmalonate (DEM) with *n*-butanol. Reaction conditions: DEM, 5 mmol; *n*-butanol, 15 mmol; TS-1, 130 mg, temperature = 383 K, reaction time = 12 h. (iii) Total NH₃ desorbed in TPD and catalytic activity (DEM conversion) in the transesterification of DEM with *n*-butanol over TS-1 catalysts calcined at different temperatures. Reaction conditions: same as in (ii) except that the temperature = 353 K.

value-added chemical with applications as an efficient methylating agent and precursor for polycarbonates. In addition to acidity, the pore structure of titanosilicates plays an important role in the transesterifications of cyclic esters like propylene carbonate (Scheme 3). TS-1 which exhibited excellent activities for EAA and DEM transesterifications (Tables 1–3), showed no activity for cyclic esters (Table 4). Amorphous TiO₂–SiO₂ exhibited the highest activity (Table 4).
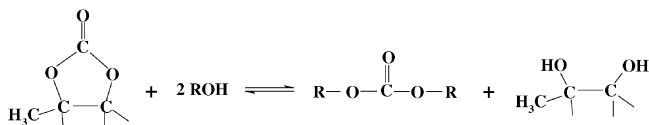
Scheme 3. Transesterification of propylene carbonate (PC) with alcohols.

Propylene carbonate could be transesterified into dialkyl carbonates with various alcohols. However, with lower chain alcohols, the selectivity for the transester product was low. The transester (dialkyl carbonate) participates in a subsequent *O*-alkylation reaction of the diol as suggested by separate experiments of *O*-alkylation reactions of ethylene glycol with methanol or dimethyl carbonate. No alkylation occurred in the absence of the Ti catalyst. With amorphous TiO₂–SiO₂, 30.1% of ethylene glycol was methylated when methanol was the alkylating agent. Complete conversion of ethylene glycol to dimethylated glycol occurred when dimethyl carbonate was the alkylating agent. The alkylating ability of dipropyl and dibutyl carbonates is lower than that of dimethyl or diethyl carbonates and hence their selectivity in the transesterification reaction is higher (Table 4).

4. Conclusions

Titanosilicate molecular sieves (TS-1, Ti-MCM-41 and amorphous TiO_2–SiO_2) exhibit excellent catalytic activity in transesterification reactions. The activity increases with the acidity of the catalysts in the order: TS-1 < Ti-MCM-41 < amorphous TiO_2–SiO_2. Activity of the catalyst depends also on the structure and dimensions of the ester. While high activities are observed for the transesterifications of ethylacetoacetate and diethylmalonate, TS-1 catalysts are inactive in the transesterification of propylene carbonate. Amorphous TiO_2–SiO_2 exhibits superior activity in the latter reaction. The catalyst could be recycled without loss in activity. Pyridine adsorption-IR and NH_3-TPD measurements reveal that the titanosilicates contain only Lewis acid sites. Brönsted sites were not detected even in the hydrated samples.

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