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Synthesis of Ti containing molecular sieves using a diethoxysiloxane-ethyltitanate polymer

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Ti-MCM-41 and SiO_2–TiO_2-xerogel were prepared using a double alkoxide precursor, diethoxysiloxane-ethyltitanate (DESET, 93.75 mol Si : 6.25 mol Ti). Characterization of the materials prepared was carried out using XRD, N_2 and water adsorption isotherm, SEM/EDS, TEM analysis, UV–Vis and FT-IR spectroscopies. Catalytic activity was measured for cyclohexene epoxidation using H_2O_2 as an oxidant. High titanium amounts in tetrahedral coordination in DESET resulted in Ti-MCM-41 with high catalytic activity accompanied by enhanced H_2O_2 selectivity. It was also possible to prepare TS-1 with MFI structure using DESET as a precursor, but titanium species in the sample were highly unstable and mostly came out from the framework to form large TiO_2 clusters upon calcination.

KEY WORDS: TS-1; Ti–MCM-41; SiO_2–TiO_2-xerogel; diethoxysiloxane-ethyltitanate.

1. Introduction

Titanium silicalite-1 (TS-1) prepared by Enichem [1] in the middle of 1980's has been proven to be an excellent catalyst for selective oxidation of relatively small organic molecules in the presence of H_2O_2. Larger pore Ti-Beta was synthesized afterwards, but its application was still limited to molecules smaller than 7 Å. Soon after the Mobil [2] discovery of M41S materials eventually came the Ti-MCM-41 with regular pore sizes greater than 35 Å. Investigations of these titanium incorporated epoxidation catalysts support the general consensus that the most active and selective sites are isolated, mononuclear, 4-coordinate Ti(IV) centers. Attachment of a titanocene-derived catalyst precursor to the pore walls of MCM-41 by post-synthetic grafting was reported to be an effective means to generate such active sites [3]. At the same time, several attempts were made to increase the titanium loading in the mesoporous silica materials either by utilizing a complexing agent to titanium species to harmonize the hydrolysis activity of the resulting precursor mixtures or by using a more stable titanium precursor such as Ti-bis(ethyl acetoacetato) diisopropoxide or titanylacetylacetonate [4,5]. Formation of nanosized TiO_2, however, was inescapable at higher Ti loadings. Interestingly, it was claimed earlier by Miller *et al.* [6] that Ti in titania–silica aerogels prepared by using diethoxysiloxane-ethyltitanate (DESET) copolymer (6.25 mol% Ti) is primarily tetracoordinated. This claim was supported by the finding that their aerogel was inactive for 1-butene isomerization due to lack of Bronsted acid sites, which are known to form by charge imbalance created by mismatches between the coordination numbers and valencies of heteroatoms [7]. In addition, there have been reports claiming that Ti can substitute isostructually for Si and remain tetrahedrally coordinated up to a titania loading of ca. 8.3 mol% in mixed oxides [8,9]. These reports prompted us to investigate the potential of using the double alkoxide as a precursor for a series of other Ti-containing molecular sieve catalysts, which is promising on two accounts; in-built tetrahedral coordination in Ti–O–Si and the substantially high Ti-loading in the precursor chemical composition in DESET. In this work, we present the results of the physicochemical properties of titania–silica xerogel, Ti-MCM-41, and TS-1 prepared using the DESET copolymer. Cyclohexene epoxidation using H_2O_2 as an oxidant was used as a model probe reaction for their catalytic activities. It is noteworthy that, recently, the same approach was employed by Tilley group [10,11] by preparing a titania–silica material using tris(tert-butoxy)siloxy complex, $Ti[OSi(O^tBu)_3]_4$.

2. Experimental

To synthesize an SiO_2–TiO_2-xerogel, we mixed the following two solutions prepared in a glove-box purged with nitrogen; one containing 10 mL of DESET (Gelest, 93.75 mol Si : 6.25 mol Ti) in 10 mL of methanol and the other containing 1.18 mL of deionized water and 10 mL of methanol. The mixture was stirred for 10 min, and then removed from the glove box, whereupon 1 mL of teterapropylammonium hydroxide (TPAOH, 1 M) was added. A clear gel formed in ca. 10 min after stirring the solution continuously by a magnetic bar.

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The gel was aged for 1 h and dried in a convection oven maintained at 363 K overnight and finally calcined at 823 K for 5 h.

To prepare Ti-MCM-41, cetyltrimethylammonium bromide (CTMABr) was added to NH_4OH solution in de-ionized water. This mixture was stirred at 343 K. After the mixture became clear, DESET was added to the mixture, and kept at 363 K for 4 days. The composition of the substrate was 1.0DESET: 0.12CTMABr: $8NH_4OH$: $114H_2O$. The solid product obtained was filtered and surfactant was extracted from Ti-MCM-41 using ethanol at room temperature. After drying, it was calcined at 823 K.

TS-1 was hydrothermally prepared following the procedures of the Enichem patent [1] using DESET as a combined silica and titanium source. Calculated amount of DESET was introduced drop by drop to TPAOH diluted in de-ionized water in N_2 atmosphere under vigorous stirring. The composition of the gel mixture was 1.0DESET: $0.46TPA^+$: $35H_2O$. Hydrolysis was performed at room temperature for 4–5 h and ethyl alcohol produced was removed by evaporation. The solution was transferred to a Teflon-lined stainless-steal bomb and heated to 348 K in a convection oven for 3 days. After filtering and washing with copious amount of distilled water, the solid product was dried overnight and was calcined in air at 823 K for 5 h.

The powder X-ray patterns of the samples were measured on a Rigaku D/MAX-III diffractometer using CuK_α radiation. The morphology of the samples was examined by SEM (Hitachi, S-4200) and TEM (Philips, CM 220). The specific surface areas and average pore diameters were measured by N_2 adsorption using a Micromeritics ASAP 2000. UV–Vis diffuse reflectance spectroscopy of the samples was performed under ambient conditions using dehydrated MgO as a reference in the range of 190–600 nm on a Varian CARY 3E double beam spectrometer. Water vapor adsorption on samples was measured using Quantachrome Autosorb Automated Gas Sorption System. Samples were degassed at 473 K for 4 h and the sorption measurement was conducted at 300 K. The catalytic activities of these samples were measured for cyclohexene epoxidation using H_2O_2 as an oxidant. It was carried out at 333 K for 3 h using 33 mmol substrate, 10 mmol H_2O_2, 20 mL methanol (solvent), and 200 mg catalyst under vigorous stirring in a two-neck pyrex round bottom reactor equipped with a condenser and a thermometer. The products were analyzed by using a HP5890 series II GC equipped with a Supelco Nukol™ fused silica capillary column and a FID. H_2O_2 remained after reaction was determined by cerium sulfate titration with ferroin indicator.

3. Results and discussion

A promising approach to make solid-state materials with novel and superior properties in many cases involves the use of building blocks derived from molecular precursors, which offer well-defined compositions and desirable structural features. Furthermore, using a heterometallic alkoxide precursor can alleviate difficulty encountered in preparing a homogeneous multi-component oxide. DESET has desirable property of high titanium loading in-built in tetrahedral coordination.

Figure 1 shows the XRD patterns of TS-1(a) and Ti-MCM-41(b), respectively, all prepared by using DESET as a starting material. Diffractogram (a) shows peaks corresponding to the characteristic of zeolite MFI structure of TS-1 with almost identical peak intensities. Diffractogram (b) shows single intense peak in low angle region corresponding to (100) of MCM-41 structure at $2\theta = 2.1$, whereas two minor characteristic peaks in $2\theta = 3.4$–4.6 region are rather smeared out reflecting the diminished long range order caused by the presence of

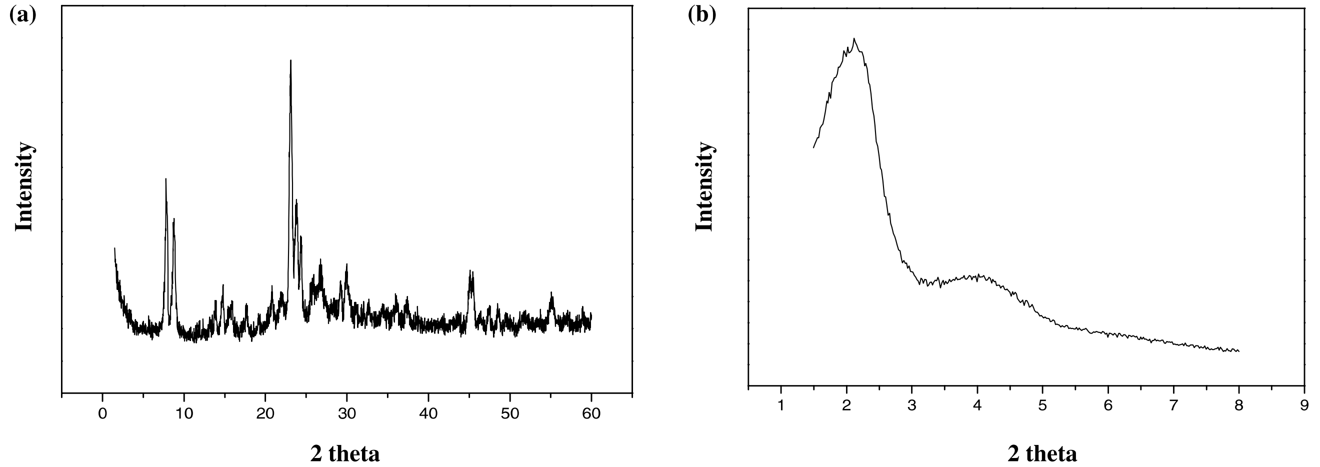

Figure 1. XRD spectra of (a) TS-1 and (b) Ti-MCM-41 prepared using DESET.

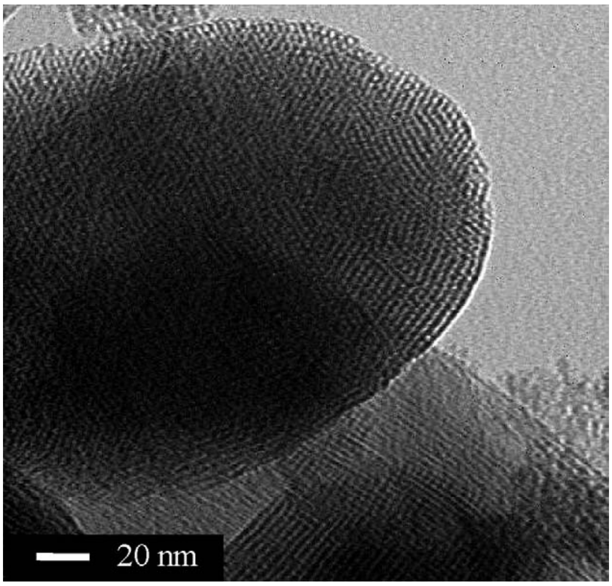

Figure 2. TEM image of Ti-MCM-41 prepared using DESET.

titanium [12]. SiO_2–TiO_2-xerogel prepared was XRD amorphous, as expected.

TEM micrograph of Ti–MCM-41 prepared was shown in figure 2, which clearly shows the highly uniform mesopore structure of the material. N_2-adsorption/desorption isotherms for three different types of the Ti containing catalysts and summary of their textual properties are shown in figure 3 and table 1, respectively. BET surface area and pore volume of SiO_2–TiO-xerogel were 872 m^2/g and 0.71 g/cm^3, respectively, and average pore diameter by BJH method (desorption) gave ca. 3.5 nm with narrow pore size distribution, whereas, for Ti-MCM-41, surface area and pore volume were 790 m^2/g and 0.83 g/cm^3, respectively. Interparticle textual mesoporocity was observed in N_2-adsorption isotherm for Ti-MCM-41, which resulted in the larger average pore diameter of Ti-MCM-41 (4.0 nm) than the SiO_2–TiO_2-xerogel. When the textual mesoporocity was excluded, the pore diameter of the highest population was ca. 2.8 nm for Ti-MCM-41and 4.0 nm for the xerogel, respectively. SEM-EDS analysis indicated Ti/Si mol ratio of 6.7(xerogel) and 6.4 mol% (MCM-41), which closely match the Ti mol percentage in DESET. TS-1 after removing the template, TPAOH, by calcinations produced BET surface area of 335 m^2/g. However, N_2-adsorption isotherm showed serious departure from the type I expected of the microporous zeolite and Ti content by EDS gave abnormally high value. Thus, serious relocation of titanium from the TS-1 framework to the the surface is suspected forming large TiO_2 clusters.

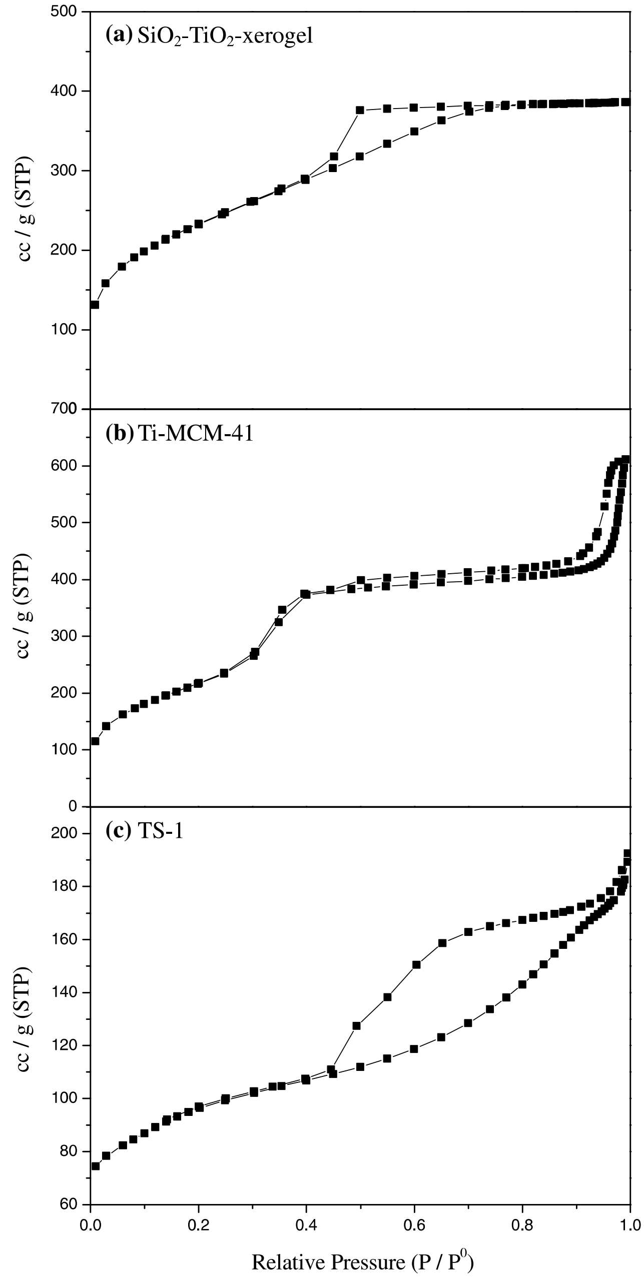

Figure 3. N_2 adsorption–desorption isotherm plot of (a) SiO_2–TiO_2-xerogel, (b) Ti-MCM-41, (c) TS-1 prepared using DESET.

Table 1
Textual properties of the catalysts prepared

Catalyst (calcined)	Ti content (mol%) (EDS analysis)	Surface area (m^2/g)	Average pore diameter (nm)
SiO2–TiO2-xerogel	6.7	872	3.8
Ti-MCM-41	6.4	790	4.1
TS-1	14.4	335	–

FT-IR spectra (not shown) of all three samples exhibited the characteristic absorption band at 960 cm^{-1} corresponding to Si–O–Ti linkage [13]. UV–Vis spectra of the corresponding samples are compared in figure 4, which showed a broad absorption band at 220 nm and a shoulder at 280 nm. The characteristic absorption band at ca. 220 nm corresponds to titanium species in

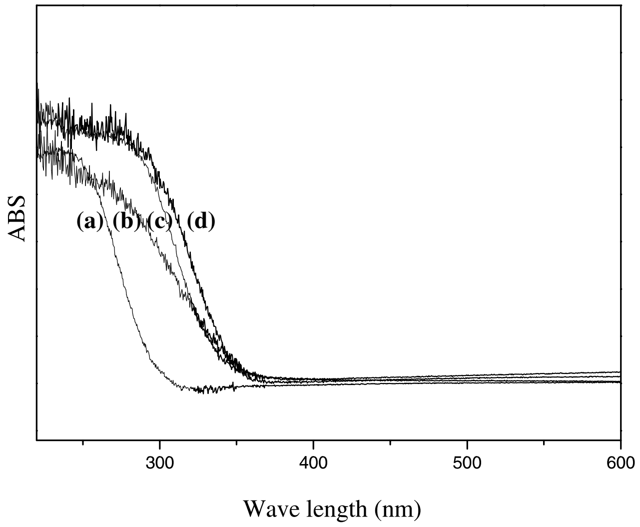

Figure 4. UV–Vis spectra of (a) TS-1 (as-synthesized), (b) Ti-MCM-41, (c) TS-1 (calcined), (d) SiO_2–TiO_2-xerogel.

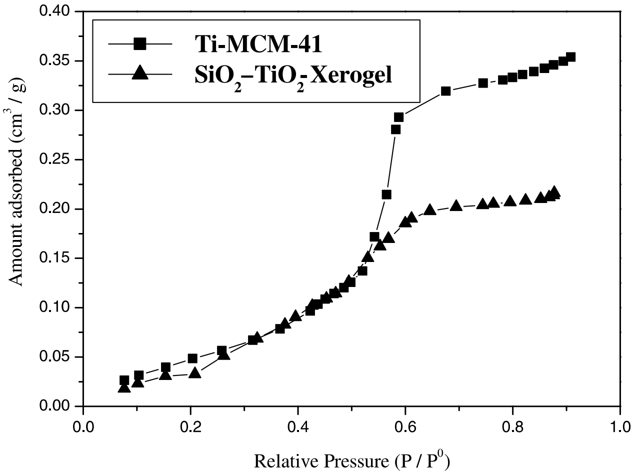

Figure 5. Water adsorption isotherms of the samples prepared using DESET.

tetrahedral coordination [14], whilst the peak at ca. 280 nm is known to indicate octahedrally coordinated TiO_2 nano clusters. TS-1 before calcination showed a single 220 nm peak. But, massively red-shifted after calcination almost overlapping with the spectra of the SiO_2–TiO_2-xerogel. Ti-MCM-41 showed a relatively minor contribution of 280 nm peak than in the SiO_2–TiO_2-xerogel.

Catalytic property of the SiO_2–TiO_2-xerogel and Ti-MCM-41 were tested by cyclohexene epoxidation using H_2O_2 as an oxidant, and experimental results are summarized in table 2. The catalytic activities of Ti-MCM-41 and SiO_2–TiO_2-xerogel were found to be very close; Ti-MCM-41 (26.1% conversion) and SiO_2–TiO_2-xerogel (25.4%) with similar products distribution. However, H_2O_2 selectivity of Ti-MCM-41 compared with SiO_2–TiO_2-xerogel was very high and was close to 85% indicating that unproductive H_2O_2 decomposition is substantially reduced. Relatively small population of octahedrally coordinated TiO_2 in Ti-MCM-41 must have contributed to the high H_2O_2 selectivity by avoiding the formation of Bronsted acid sites known to be harmful inducing H_2O_2 decomposition.

Hydrophobic titanosilicates favor the adsorption of non-polar hydrocarbons compared with polar molecules such as H_2O or the products of reaction [15]. Hydrophobic catalysts therefore can operate with peroxides in the presence of water with peroxide/water ratio as high as 1 without loss of activity or selectivity [16]. Hydrophobicity of the Ti-MCM-41 and SiO_2–TiO_2-xerogel prepared using DESET were compared by water adsorption experiments and the results are shown in figure 5. Both showed type IV adsorption isotherms with capillary condensation features, and the slopes of adsorption curves at low P/P^0 region showed almost the same values. Difference in the amount of water adsorbed at high P/P^0 region is due to capillary condensation and pore volume differences between the two samples. These adsorption isotherms demonstrate that Ti-MCM-41 and SiO_2–TiO_2-xerogel prepared using DESET have similar surface hydrophobicity.

It has been generally accepted that the upper limit of Ti/(Si + Ti) ratio in TS-1 is ca. 0.025. Thus, considering its bulkiness and high built-in titanium content of 6.25%, it was surprising to obtain microporous TS-1 using DESET as a synthesis precursor. For microporous TS-1, cyclohexene molecules are known too big to enter into the pores, and 1-hexene epoxidation was attempted instead. Only 1.4% conversion was observed with the TS-1 sample prepared using DESET compared with 15.1% by TS-1 standard material with 2 mol% Ti

Table 2
Comparison of catalytic performances in cyclohexene epoxidation

Sample	Cyclohexene conversion	H_2O_2 conversion	H_2O_2 selectivity	Selectivity				
				Cyclohexene oxide	1-ol	1-one	ether	Diol
Ti-MCM-41	26.1%	46.2%	84.7%	4.9%	4.8%	13.9%	59.1%	15.1%
SiO2–TiO2-xerogel	25.4%	68.8%	55.4%	2.5%	5.8%	16.6%	60%	15.1%

Reaction condition: 200 mg catalyst, 2.738 g Cyclohexene, 2.268 g 30%H2O2, 15.72 g Acetonitrile (333 K, reaction duration 3 h).

loading. Apparently, the massive UV–Vis spectral shift mentioned earlier upon calcination indicates the escape of titanium species from the zeolite framework and subsequent formation of TiO_2 clusters, which explains this low activity of the former.

4. Conclusions

TS-1, Ti-MCM-41, and SiO_2–TiO_2-xerogel were prepared using a double alkoxide precursor, DESET. High titanium concentration mostly in tetrahedral coordination in DESET can potentially lead to Ti-containing catalysts with improved performances in liquid phase oxidation reactions. Substantially high catalytic activity accompanied by high H_2O_2 selectivity in cyclohexene epoxidation was obtained with Ti-MCM-41 prepared, extrapolating the catalytic performances of those low (<3%) titanium content Ti-MCM-41 reported earlier in open literatures without sacrificing oxidant efficiency. Microporous TS-1 could also be prepared using DESET as a precursor, which was rather unexpected considering its bulkiness and high built-in titanium content. However, titanium in the TS-1 sample was in a highly unstable state and mostly came out from the framework forming large TiO_2 clusters upon calcination.

Acknowledgments

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