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Ti-Si DOUBLE ALKOXIDE AS A SYNTHESIS PRECURSOR OF MOLECULAR SIEVE CATALYSTS FOR LIQUID PHASE EPOXIDATION

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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 synthesis of Ti-MCM-41 with regular pore sizes greater than 35 Å. Investigations of titanium incorporated epoxidation catalysts support the general consensus that the most active and selective sites are isolated, mononuclear, 4-coordinate Ti(IV) centers. 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 harmonize the hydrolysis activity of the resulting precursors or by using a more stable titanium precursor such as Ti-bis(ethyl acetoacetato) diisopropoxide or titanylacetylacetonate. However, formation of nanosized TiO_2 was inescapable at higher Ti loadings. Interestingly, it was claimed sometime ago by Miller et al [3] that Ti in titania-silica aerogels prepared by them using diethoxysiloxane-ethyltitanate inorganic oxide copolymer (6.25 mol % Ti) is primarily tetra-coordinated. 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 [4]. This report prompted us to further investigate the potential of using the Ti-Si double alkoxide as a precursor for a series of other Ti-containing silica catalysts, which is promising on two accounts; one being the in-built tetrahedral coordination in Ti-O-Si, the other being the substantially high Ti-loading in the precursor chemical composition. In this work, we will present the results on the physicochemical properties of titania-silica xerogel, Ti-MCM-41, and TS-1 prepared using the diethoxysiloxane-ethyltitanate copolymer. Cyclohexene epoxidation using H_2O_2 as an oxidant was used as a model probe reaction for their catalytic activities.

2. Experiment

To synthesize an SiO_2 - TiO_2 -xerogel, we mixed two solutions prepared in a glove-box purged with nitrogen, one containing 10 ml of diethoxysiloxane-ethyltitanate (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, following the synthetic protocol of Miller et al [3]. The mixture was stirred for 10 min, and then removed from the glove-box, whereupon 1 ml of TPAOH (1 M) was added. A clear gel formed in ca. 10 min after the solution being stirred continuously by a magnetic stir bar. The gel was aged for 1 h and dried in a convection oven maintained at 363 K for overnight and finally calcined at 823K for 5h.

To prepare a Ti-MCM-41, CTMABr was added in deionized water and NH_4OH solution. This

mixture was stirred at 343 K. After mixture became clear, diethoxysiloxane-ethyltitanate was added to the mixture, and kept 363 K for 4 days. The composition of the substrate was 1.0DESET: 0.12CTMABr: 8NH₄-OH: 114H₂O. 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 synthesis protocol of the Enichem patent [1] using diethoxysiloxane-ethyltitanate (DESET) as a combined silica and titanium source. Calculated amount of DESET was introduced dropwise to TPAOH diluted in deionized water in N₂ atmosphere under vigorous stirring. The composition of the gel mixture was 1.0DESET: 0.46TPA⁺: 35H₂O. 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-steel 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.

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 N₂ adsorption using a Micromeritics ASAP 2000. UV-Vis diffuse reflectance spectroscopy of the titanium grafted 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. The catalytic activities of these samples were measured for cyclohexene epoxidation using H₂O₂ as an oxidant. It was carried out at 333K for 3h using 33mmol substrate, 10mmol H₂O₂, 20ml methanol (solvent), and 200mg catalyst under vigorous stirring in a two-neck pyrex round bottom reactor equipped with a condenser and a thermometer. The products were analysed by using a HP5890 series II GC equipped with a Supelco NukolTM fused silica capillary column and a FID.

3. Results and Discussion

Figure 1 shows the XRD patterns of TS-1(a) and Ti-MCM-41(b), respectively. Diffractogram (a) shows peaks corresponding to the characteristic of zeolite MFI structure 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 titanium [5]. SiO₂-TiO₂-xerogel prepared was XRD amorphous, as expected.

TEM micrograph of Ti-MCM-41 prepared was shown in Figure 2, which clearly shows the uniform mesopore structure of the material. BET surface area and pore volume of SiO₂-TiO₂-xerogel were 872 m²/g and 0.71 g/cm³, respectively, and average pore diameter by BJH method (desorption) gave ca 3.5nm with narrow distribution, whereas, for Ti-MCM-41, surface area and pore volume were 790 m²/g and 0.83 g/cm³, respectively. Textual mesoporosity was observed in N₂-adsorption isotherm for Ti-MCM-41, which resulted in the larger average pore diameter of Ti-MCM-41(4.0 nm) than xerogel. If the textual mesoporosity is ignored, the pore diameter of the highest population was ca 2.8 nm for Ti-MCM-41 and 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 of the DESET precursor. TS-1 after removing the template, TPAOH, by calcinations produced BET surface area of 335 m²/g. However, N₂-adsorption isotherm showed serious departure from the type 1 expected of the microporous zeolite and Ti content by EDS gave abnormally high value. Thus, serious relocation of titanium from the TS-1 interior to the external surface is suspected to form a large TiO₂ cluster.

FT-IR analysis of samples (TS-1, Ti-MCM-41, SiO₂-TiO₂-xerogel) all showed the characteristic absorption band at 960 cm⁻¹ corresponding to Si-O-Ti linkage [6]. UV-Vis spectra of the corresponding samples are shown in Figure 3., which showed a broad absorption band at 220 nm and at 280 nm. The characteristic absorption band at ca. 220 nm corresponds to titanium species in tetrahedral coordination [7], whilst the peak at ca. 270 nm is known to indicate octahedrally-coordinated TiO₂ clusters. TS-1 before calcinations showed a single 220 nm peak, but massively red-shifted almost

overlapping with the xerogel. As shown in Fig.3, Ti-MCM-41 showed a minor contribution of 280 nm peak than in the SiO₂-TiO₂-xerogel.

Catalytic property of the SiO₂-TiO₂-xerogel and Ti-MCM-41 were tested by cyclohexene epoxidation using H₂O₂ as a oxidant, and experimental results are summarized in Table 1. The catalytic activities of Ti-MCM-41 and SiO₂-TiO₂-xerogel were found to be very close; Ti-MCM-41 (26.1 % conversion) and SiO₂-TiO₂-xerogel (25.4 %). However, H₂O₂ selectivity of Ti-MCM-41 compared with SiO₂-TiO₂-xerogel was very high close to 85 % indicating that unproductive H₂O₂ decomposition is substantially reduced. Absence of octahedrally coordinated TiO₂ can contribute to the high H₂O₂ selectivity by avoiding the formation of Bronsted acid sites known to be harmful inducing H₂O₂ decomposition. For microporous TS-1, 1-hexene epoxidation was attempted, but only 1.4 % conversion was observed compared with 15.1 % by commercial TS-1 with 2 mol % Ti loading. Apparently, the massive UV-Vis spectral shift indication the escape of titanium from the zeolite framework is responsible for this low activity.

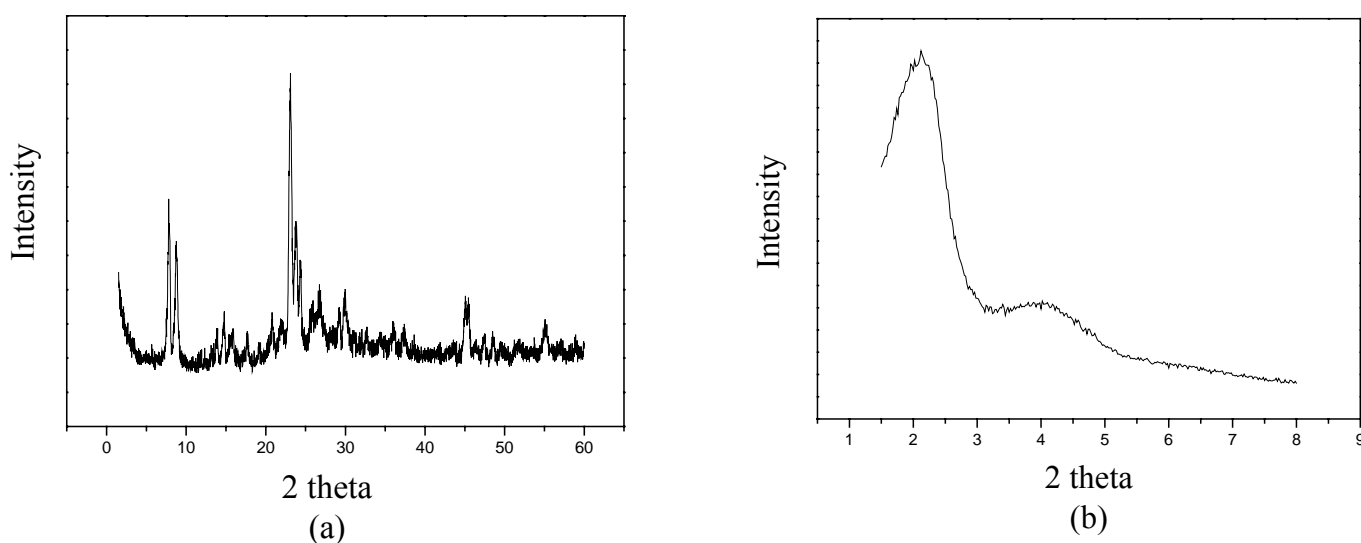


Figure 1. . XRD spectra of (a) TS-1, (b) Ti-MCM-41

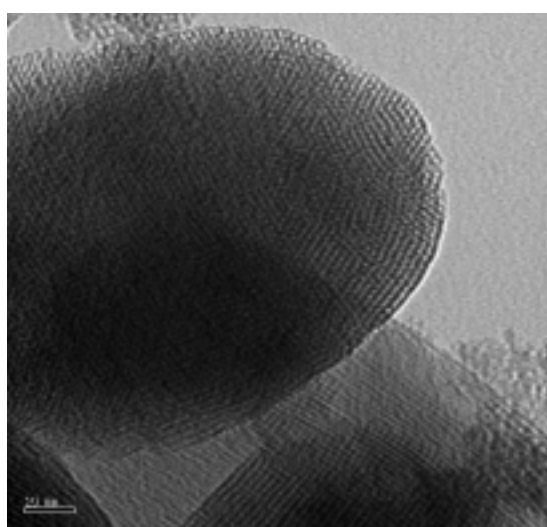


Figure 2. TEM images of Ti-MCM-41

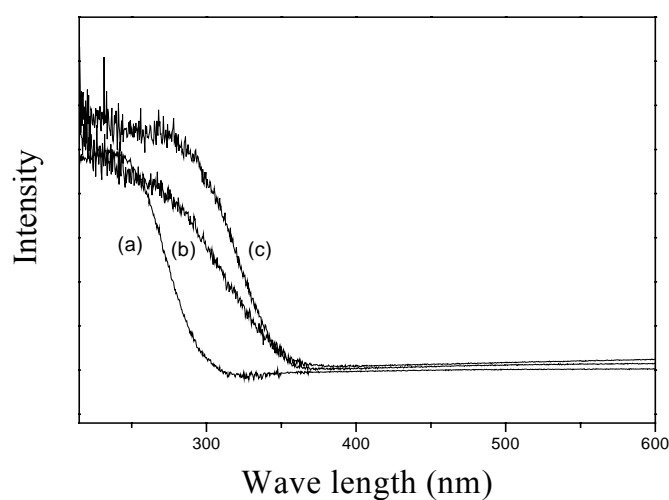


Figure 3. UV-Vis spectra of (a) TS-1, (b) Ti-MCM-41, (c) SiO₂-TiO₂-xerogel

Table 1. Cyclohexene epoxidation

Sample	Cyclohexene conversion	H ₂ O ₂ conversion	H ₂ O ₂ selectivity
Ti-MCM-41	26.1 %	46.2 %	84.7 %
SiO ₂ -TiO ₂ -xerogel	25.4 %	68.8 %	55.4 %

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

4. Conclusions

TS-1, Ti-MCM-41, and SiO₂-TiO₂-xerogel were successfully prepared using a double alkoxide precursor, diethoxysiloxane-ethyltitanate(DESET). This double alkoxide precursor contains high titanium amount with mostly in tetrahedral coordination, which can lead to improved performance in liquid phase oxidation reactions. Both substantially higher catalytic activity accompanied by high H₂O₂ selectivity was obtained with Ti-MCM-41 prepared in this work in cyclohexene epoxidation compared to Ti-MCM-41 with low titanium contents reported earlier. Evolution of TS-1 structure using DESET as a precursor was rather unexpected due to its bulkiness and high titanium content. However, titanium in the sample was in a highly unstable state and mostly came out from the framework forming large TiO₂ clusters upon calcinations.

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