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Propylene epoxidation over Ti/MCM-41 catalysts prepared by chemical vapor deposition

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Abstract

Ti-containing mesoporous catalysts were prepared by chemical vapor deposition (CVD) of $TiCl_4$ on silica MCM-41 in the 700–900 °C temperature range. These samples were characterized (with XRD, ICP, nitrogen adsorption, FT-IR, ESCA, and TEM) and evaluated for the epoxidation of propylene with two alkyl hydroperoxides. The increase of CVD temperature resulted in the decrease of titanium content, catalyst hydroxyl population, crystallinity, and surface area. Catalyst selectivity to the desired product – propylene oxide – was highly sensitive to the deposition temperature. The best Ti/MCM-41 catalyst was prepared at the temperature of 800 °C, which had the maximum propylene oxide yield of 94.3%.

Keywords: Propylene Oxide; Ti/MCM-41; Chemical vapor deposition; Epoxidation catalysts; $TiCl_4$

1. Introduction

Propylene oxide (PO) is an important commodity chemical with the present annual world demand of around 5 million tons. It is primarily used in the manufacture of polyurethanes, unsaturated polyesters, and surfactants. Organic hydroperoxide process is currently a leading commercial method for PO production [1,2]. It involves the reaction of propylene with alkyl hydroperoxide ($C_3H_6 + ROOH \rightarrow C_3H_6O + ROH$, where ROOH is either tert-butyl hydroperoxide (TBHP) or ethylbenzene hydroperoxide (EBHP)), catalyzed by homogeneous molybdenum compounds or heterogeneous titanium silica (Ti/SiO_2) catalyst [3]. The commercial Ti/SiO_2 catalyst was prepared by impregnating silica with $TiCl_4$ or an organic titanium compound followed by calcination and silylation [4].

Chemical vapor deposition (CVD) method is a useful method for the preparation of highly dispersed catalysts. It has been defined as the process of deposition using reaction between surface sites such as OH groups and vapors of metal compounds [5]. Recently, Li and Chen [6] used CVD method (reaction of $TiCl_4$ vapor with hydroxyl groups on the surface of silica gel) to prepare Ti/SiO_2 catalysts and found that the catalyst prepared at the deposition temperature of 900 °C had high selectivity in the epoxidation of propylene to propylene oxide [6].

The discovery of MCM-41 mesoporous molecular sieves in 1991 resulted in the availability of a support with very attractive features [7]. This material possesses a uniform arrangement of hexagonally shaped pores with dimensions of 10–150 Å. Titanium ions have been introduced in the MCM-41 by hydrothermal synthesis [8] and by liquid-phase surface grafting [9,10]. The molecular precursors used for preparing the surface-grafted Ti/MCM-41 included Ti-cyclopentadienyl complexes [9] and tris(ter-butoxy)siloxy titanium complexes [10]. Calcination step was necessary to eliminate the organic fraction of the Ti complexes anchored onto the surface of MCM-41.

This paper deals with the use of chemical vapor deposition method to prepare Ti/MCM-41 catalysts in a deposition temperature range of 700–900 °C, and deals with the use of the resulting catalysts for catalyzing the epoxidation of propylene with two alkyl hydroperoxides. We observed the yield of propylene oxide reached a maximum value of 94.3% for the catalyst prepared at the deposition temperature of 800 °C.

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2. Experimental section

Purely siliceous MCM-41 with a mean pore size of 27 Å (obtained from nitrogen adsorption measurements) was synthesized using sodium silicate, tetrapropylammonium bromide and cetyltrimethylammonium bromide according to a method reported before [11,12]. Chemical vapor deposition experiments (deposition of $TiCl_4$ vapor on MCM-41) and propylene epoxidation experiments were carried out following the procedures given elsewhere [6]. Titanium contents of the resulting Ti/MCM-41 samples were determined with an inductively coupled plasma-atomic emission (ICP-AES) spectrometer (Kontron, Model S-35) after HF acid digestion of the solid. N_2 adsorption/desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2020 apparatus. Catalyst crystalline structure was examined by X-ray diffraction (XRD) crystallography on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) observations were made using JEOL JEM-2010. The X-ray photoelectron spectroscopy (XPS) data were acquired on a VG Microtech MT-500 spectrometer using Al Kα X-ray radiation (1486.6 eV).

The conversion was defined as the percentage of hydroperoxide in the feed that had reacted. Propylene oxide yield was defined as the moles of propylene oxide formed per mole of hydroperoxide in the feed. Propylene oxide selectivity was defined as the percentage of hydroperoxide reacted to propylene oxide (i.e., propylene oxide selectivity = propylene oxide yield/hydroperoxide conversion).

3. Results and discussion

3.1. Propylene epoxidation

Five Ti/MCM-41 catalysts were prepared by deposition of $TiCl_4$ vapor on MCM-41 at the temperatures of 700, 750, 800, 850, and 900 °C. These CVD-prepared samples were used to study the reaction between propylene and two alkyl hydroperoxides (TBHP and EBHP). The experimental results are presented in Fig. 1, in which the conversion of hydroperoxides (curve "a " is for TBHP and curve "c" is for EBHP) and the yield of propylene oxide (curve "b" is for TBHP and curve "d" is for EBHP) are plotted as a function of the $TiCl_4$ deposition temperature. All of the conversions shown in curves (a) and (c) are above 90%, which indicate that the catalyst activity is not sensitive to the change of the deposition temperature. However, the yield of propylene oxide (i.e., the catalyst selectivity to the desired product – propylene oxide) is very sensitive to the change of deposition temperature. Each of curves (b) and (d) exhibits volcano shape with a maximum propylene oxide yield, which occurs at the deposition temperature of around 800 °C. For the catalyst prepared at the deposition temperature of 700 °C, the PO yields were only 76.4% (the epoxide selectivity was 80%) and 75.4% (the epoxide selectivity was 83%) respectively, with the use of TBHP and EBHP as the oxidants. With the increase of CVD temperature, the propylene oxide yield increased rapidly and reached the maximum value for the catalyst prepared at the deposition temperature of 800 °C. The maximum propylene oxide yields obtained were 90% (the epoxide selectivity was 91.8%) and 94.3% (the epoxide selectivity was 97.3%) respectively, with the use of TBHP and EBHP as the oxidants. Further increase of the deposition temperature ($T > 800$ °C) resulted in the decrease of propylene oxide yield and selectivity. Additional epoxidation results were obtained (PO yield = 65% with a TBHP conversion of 95%) using a catalyst prepared at the CVD temperature of 600 °C. The epoxidation data and Fig. 1 indicate that the catalyst selectivity increase with the increase of the deposition temperature in the CVD temperature range ≤ 800 °C.

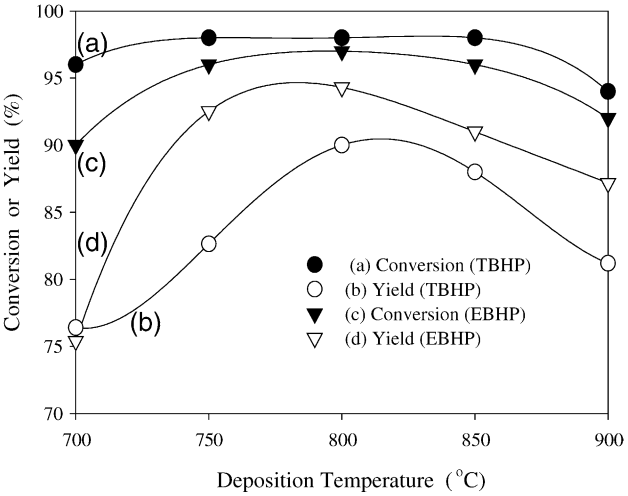

Fig. 1. Influence of $TiCl_4$ deposition temperature on hydroperoxide conversion and propylene oxide yield.

Table 1 compares the yields of propylene oxide obtained with Ti/MCM-41 catalysts and Ti/SiO_2 catalysts, which were prepared at the CVD temperatures of 700 and 800 °C. Under identical CVD temperature, Table 1 shows that Ti/MCM-41 produces slightly more propylene oxide than Ti/SiO_2 studied before [6]. This might be due to the fact that Ti/MCM-41 has much higher surface area than Ti/SiO_2.

3.2. Catalyst characterization

The relationships between catalyst titanium loading (obtained from ICP measurements) and CVD temperature are presented in Table 2, which shows that Ti content decreased continuously with the increase of CVD tempera-

Table 1
Comparisons of propylene oxide yield obtained with Ti/MCM-41 catalysts and Ti/SiO_2 catalysts (TBHP as the oxidant)

CVD temperature (°C)	700	800
Ti/MCM-41 catalyst (%)	76.4	90
Ti/SiO_2 catalyst (%)	73.1	89

Table 2
Effect of CVD temperature on titanium loading and surface area of Ti/MCM-41 catalysts

CVD temperature (°C)	700	750	800	850	900
Ti content (wt.%)	2.13	1.93	1.81	1.43	1.25
Surface area (m^2/g)	808	768	558	356	177

ture. The decrease of Ti content should be due to the fact that the surface Si–OH groups available for reaction with $TiCl_4$ vapor (Si–OH + $TiCl_4$ → Si–O–$TiCl_3$ + HCl) decreased with the increase of CVD temperature.

Table 2 also shows that the Ti/MCM-41 catalyst surface area decreased continuously with the increase of the CVD temperature. The decrease of the catalyst surface area might be due to the condensation of OH groups belonging to different primary particles followed by siloxanone – bridge formation (i.e., Si–OH + Si–OH = Si–O–Si + H_2O) [13].

Fig. 2 shows the Ti 2p XPS spectrum recorded from the Ti/MCM-41 catalyst prepared at the deposition temperature of 800 °C. The spectrum intensity was quite weak due to the low concentration (1.8 wt.%) of titanium in the sample. The spectrum shows two spin-orbit doublet ($2p_{1/2}$ and $2p_{3/2}$) peaks. The binding energy for the Ti($2p_{3/2}$) was 456 eV, and the binding energy for the Ti($2p_{1/2}$) was 462 eV. The difference in the binding energy between Ti($2p_{3/2}$) peak and Ti($2p_{1/2}$) peak was 6 eV, which was similar to that reported in the literature [14]. For bulk Ti metal, the $2p_{3/2}$ binding energy was 453.8 eV, and the difference in the binding energy between $2p_{3/2}$ peak and $2p_{1/2}$ peak was 6.15 eV [14].

Sandell et al. [15] studied the adsorption and decomposition of $TiCl_4$ on W(1 1 0). They reported that the Ti($2p_{3/2}$) peak binding energy was 458.3 eV for $TiCl_4$. In addition, the Ti($2p_{3/2}$) peak binding energy for TiO was reported to be 454.7 eV [14]. Therefore, the Ti($2p_{3/2}$) binding energy (= 456 eV) observed in Fig. 2 suggests that the species in Ti/MCM-41 catalyst might be $SiOTiCl_3$, which was formed from the reaction of $TiCl_4$ with a silanol group (Si–OH + $TiCl_4$ → Si–O–$TiCl_3$ +HCl) [16].

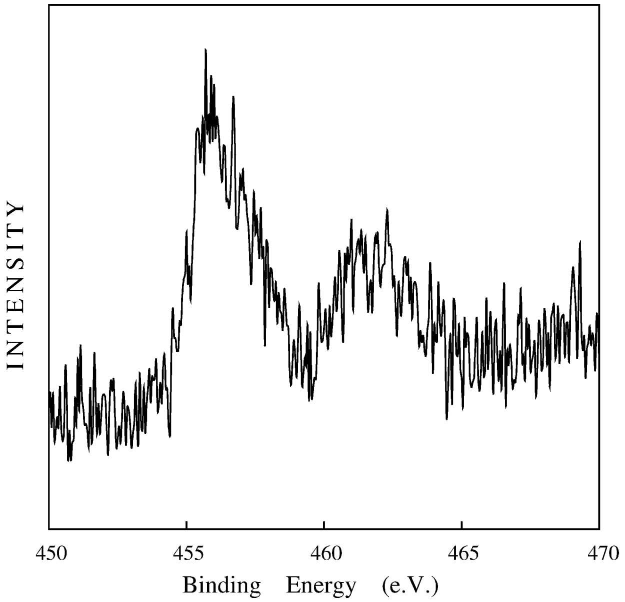

Fig. 2. Ti 2p XPS spectrum obtained for the Ti/MCM-41 sample prepared at 800 °C.

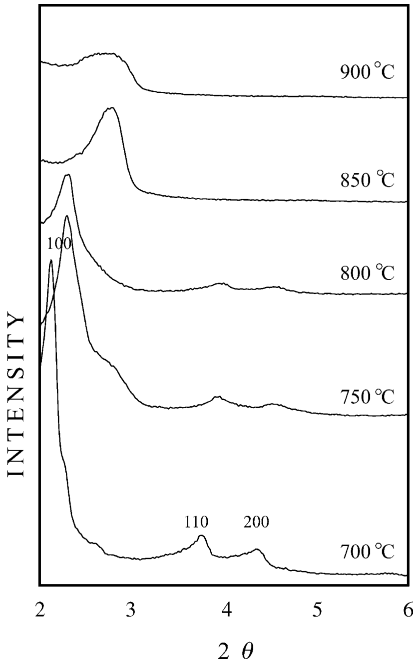

Fig. 3. X-ray diffraction patterns of the Ti/MCM-41 samples prepared at the deposition temperature of 700–900 °C.

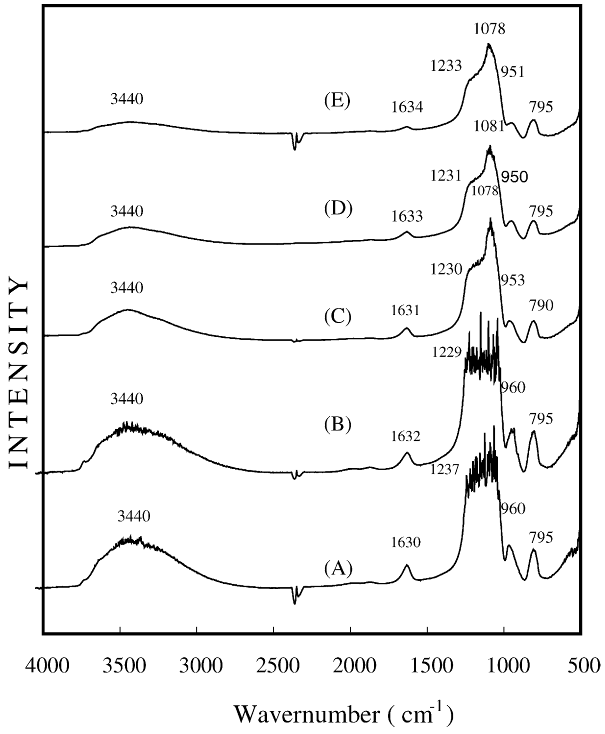

Fig. 4. Infrared spectrum of Ti/MCM-41 samples prepared at the deposition temperature of 700–900 °C. (A) 700 °C, (B) 750 °C, (C) 800 °C, (D) 850 °C, and (E) 900 °C.

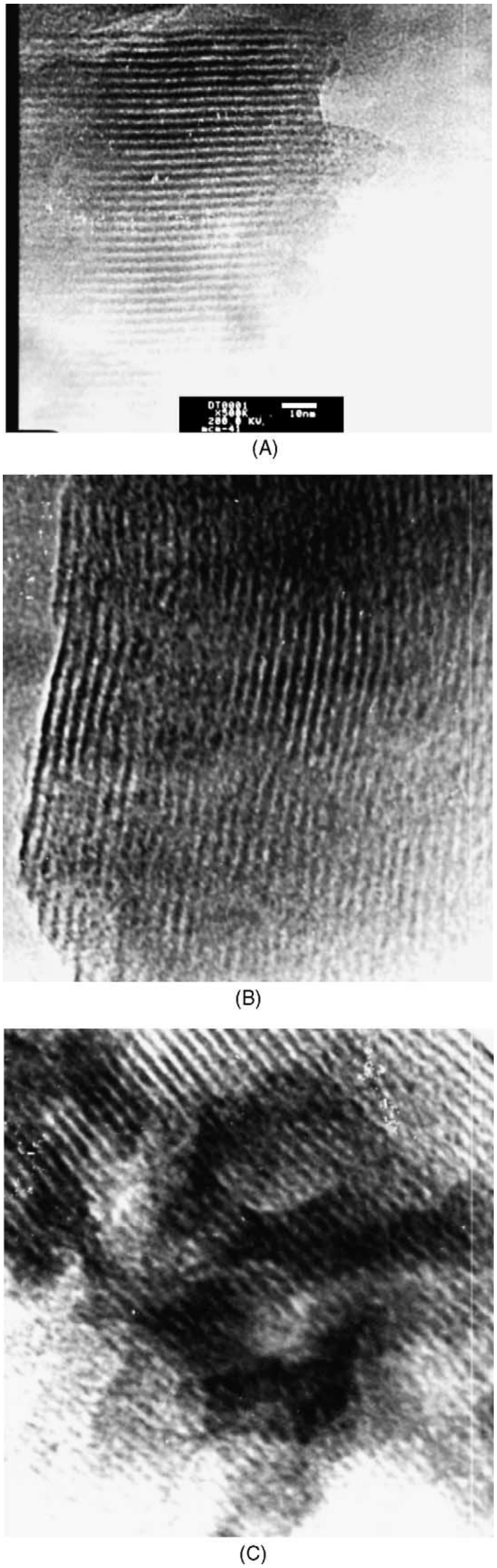

Fig. 5. Transmission electron micrographs of (A) Si-MCM-41, (B) Ti/MCM-41 prepared at 700 °C, and (C) Ti/MCM-41 prepared at 800 °C.

Fig. 3 displays the X-ray diffraction (XRD) spectra of Ti/MCM-41 samples prepared at the deposition temperature range of 700–900 °C. For the samples prepared at the deposition temperature $\leq$800 °C, their XRD patterns had well-defined (1 0 0), (1 1 0), and (2 0 0) reflections. But the peak intensity decreased with the increase of the deposition temperature, indicating that the catalyst crystallinity decreased with the increase of deposition temperature.

Fig. 4 shows the infrared spectra of Ti/MCM-41 samples prepared at five different CVD temperatures: (A) 700 °C, (B) 750 °C, (C) 800 °C, (D) 850 °C, and (E) 900 °C. The band due to the stretching vibration of SiO units bound to Ti atoms [17] is observed at the wavenumber of around 960 cm^{-1} in the IR spectra, which indicates that Si–O–Ti bond existed in the Ti/MCM-41 catalysts. The peak area of the Si–O–Ti band decreases with the increase of CVD temperature, which is consistent with the ICP data reported in Table 1 (i.e., the titanium content decreased with the increase of the deposition temperature).

In Fig. 4, the very broad band in the region of around 3440 cm^{-1} is due to the silanol (Si–OH) groups, which may behave as Bronsted acid sites ($\text{Si–OH} + \text{B} = \text{SiO}^- + \text{HB}^+$) [18]. These Bronsted acid sites can catalyze the decomposition of hydroperoxides (an undesired reaction) and decrease the selectivity to epoxide [6]. With the increase of deposition temperature, the number of surface silanol groups decreased due to dehydration, which can be clearly seen from the decrease of the OH peak area in Fig. 4. This decrease of the Bronsted acid sites should be responsible for the better epoxide selectivity observed for the Ti/MCM-41 catalysts prepared at the deposition temperature of 800 °C (shown in Fig. 1).

Fig. 5 shows the transmission electron micrographs (TEM) of (A) Si-MCM-41 before chemical vapor deposition, (B) Ti/MCM-41 prepared at 700 °C, and (C) Ti/MCM-41 prepared at 800 °C. These graphs illustrate the regular hexagonal array of mesoporous channels. The channels in graph (B) are similar to those in graph (A), indicating that the pore structure remains unchanged at the deposition temperature of 700 °C. However, the darker areas in graph (C) indicate that some of the inner channels collapse at the deposition temperature of 800 °C. The TEM results are in agreement with those obtained from XRD data, which indicated that the catalyst crystallinity decreased for the sample prepared at the deposition temperature of 800 °C.

4. Conclusions

Ti/MCM-41 epoxidation catalysts with a variety of titanium contents were prepared with a chemical vapor deposition (CVD) method. The change of CVD temperature had much stronger effect on the catalyst selectivity than on the catalyst activity. Catalyst selectivity to propylene oxide increased rapidly with the increase of the deposition temperature, and reached the maximum value at 800 °C.

Based on the FTIR spectra, the increase of catalyst selectivity to propylene oxide was explained in terms of the decrease of silanol groups, which exhibited the undesired Bronsted acid properties. Catalyst selectivity decreased at temperature ≥850 °C, which might be due to the destruction of the MCM-41 structure, as indicated by the XRD data. X-ray photoelectron spectroscopic study suggested that $SOTiCl_3$ was the active species for catalyzing propylene epoxidation to propylene oxide.

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