Characterization of Titanium Oxide Encapsulated Zeolites and Its Photocatalytic Application for NO Decomposition

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Titanium oxide-encapsulated X and Y zeolites were prepared by ion exchange with $(NH_4)_2TiO(C_2O_4)_2$. The obtained zeolites were characterized by means of XRD, FT-IR, XPS, UV-vis and photoluminescence spectroscopies. By the introduction of TiO^{2+} ions, the zeolites exhibited adsorption and photoluminescence bands and became sensitive to UV irradiation. A high catalytic activity of NO decomposition was obtained at room temperature under UV irradiation. The major products in the presence of oxygen were N_2 and N_2O. In reference experiments of TiO_2 powder significant production of NO_2 was observed.

1 INTRODUCTION

For the preservation of the global environment, some zeolite catalysts modified by Cu, Ga, Pt and Ce have been studied for decomposition of NO_X under thermal conditions and in the presence of reductants[1-4]. For photocatalytic decomposition of NO, Anpo et al. reported the experimental results obtained by using Cu-Y and Cu-ZSM-5 catalysts under irradiation of a high pressure mercury lamp[5]. They suggested that monovalent copper ions play a significant role in initiation of the NO decomposition. Furthermore, photocatalytic decomposition of N_2O into N_2 and O_2 on degassed Cu-ZSM-5 zeolite or on TiO_2-dispersed glass has been reported by Ebitani[6] and Cant[7]. Since zeolite has the well-defined crystalline structure with the internal pore and cage, semiconductors such as TiO_2, CdS and ZnS could be encapsulated in it. These modified zeolites subsequently exhibited photocatalytic properties[8-11]. The other titanium oxide catalysts reported so far were placed on porous vycor glass[12], encapsulated in copolymer[13], and mixed with silicon as binary oxide powder[14] or glass[15]. However, there were no reports on the photocatalytic decomposition of NO over these catalysts.

In this report, titanium was introduced into the internal pores of X and Y zeolites by an ion-exchange method. The photocatalytic decomposition of NO over the modified zeolites was examined. Effect of the modification on the photocatalytic activity and selectivity are discussed.

2 EXPERIMENTAL

Na-X and Na-Y zeolites were kindly supplied from Mizusawa Chemical Engineering Co. Ltd. In order to introduce titanium into the zeolite pores, ion-exchange method was carried out by using $(NH_4)_2TiO(C_2O_4)_2$ as followed. A solution of 100 ml (18.0 mmol/dm^3) of $(NH_4)_2TiO(C_2O_4)_2$ was used for treating 3.0 g of zeolite at 303 to 313 K for about 15 hours. The treated zeolites were washed with deionized water and dried at 393 K for overnight. After repeated the ion-exchange treatment, the zeolites were calcined at 793 K for 6 hours. The obtained zeolites were denoted as Ti-X and Ti-Y. The contents of titanium in the Ti-X and Ti-Y zeolites were 0.67 wt% and 0.63 wt%, respectively.

The zeolite catalysts were characterized by means of XRD, FT-IR, UV-vis and XPS spectroscopies. The X-ray diffraction measurements were performed with a Rigaku RAD 3A goniometer. For FT-IR measurements, catalysts were ground with potassium bromide and then pressed into disks. The transmission IR spectra of the disks were measured with a JASCO FT-IR-5A. UV-vis diffuse reflectance spectra were taken at 298 K

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with a JASCO UNIDEC model 660 spectrometer equipped with an integrating sphere. An Al_2O_3 plate was used for the reference. Photoluminescence was measured at 77 K with a HITACHI model 850 instrument. The samples contained in Sprasil cell were immersed in liquid nitrogen in a Dewar vessel with quartz windows.

The photocatalytic reaction of NO was evaluated with a fix-bed flow reactor system. In the quartz reactor, a glass rod was installed to make the bed of the catalyst in the form of blank cartridge. This method increased the surface area of the bed which was irradiated with a high pressure mercury lamp. The reactant gas having 1.2% NO, 1.0% air and 97.8% of He was used. The flow rate of the reactant gas was 4 ml/min. The weight of the catalyst packed in the reactor was 0.8 g.

The NO decomposition was analyzed by a gas chromatography (Gasukuro Kogyo, model 370) using a molecular sieve 5A column for O_2, N_2 and NO, and a Porapak Q column for the separation of N_2O.

The conversion of NO and the yield of N_2 or N_2O were defined by the following relations:

Conversion of NO = $(M^o_{NO} - M_{NO})/ M^o_{NO}$

Yield of N_2 or N_2O = $2M_{N_2} / M^o_{NO}$

or $2M_{N_2O} / M^o_{NO}$

where M and M^o are the mole flow rates of the component indicated by the subscript at the outlet and inlet of photocatalytic reactor, respectively.

3 RESULTS AND DISCUSSION

3.1 Characterization of titanium - encapsulated zeolites

The X-ray diffraction patterns of Ti-modified zeolites showed that the zeolites did not contain a detectable TiO_2 phase. The crystallinity of the obtained zeolites was not affected by the ion exchange of TiO^{2+} and the calcination at elevated temperature.

Figure 1 shows IR spectra of Y zeolite (Na-Y) and Ti-modified one (Ti-Y). After ion exchange with TiO^{2+}, the Ti-Y zeolite has a peak at 910 cm^{-1} in the spectrum. It was reported by Liu et al. that this is due to the introduction of TiO^{2+} ions[11]. A strong absorption band appeared near 1000 cm^{-1} is characteristic for zeolite framework. The shift of this band to the higher wavenumber side indicates that the TiO^{2+} ions were introduced into the internal pores of zeolite. For Na-X and Ti-X zeolites, their IR spectra are shown in Figure 2. The overlap of a broad peak in 550 -

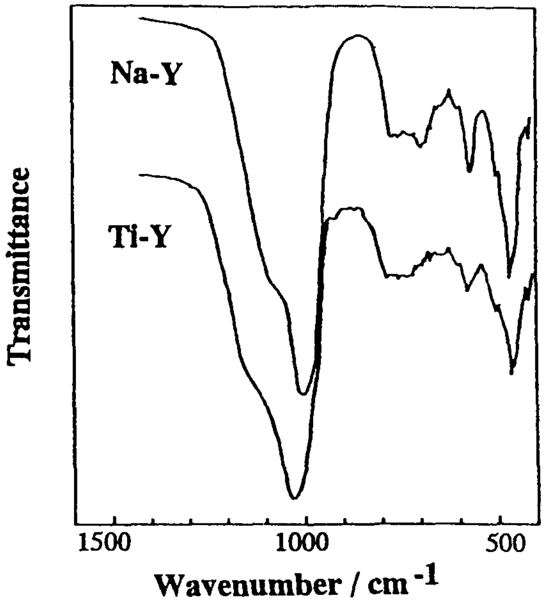

Fig. 1 FT-IR spectra of Na-Y and titanium exchanged Ti-Y zeolites.

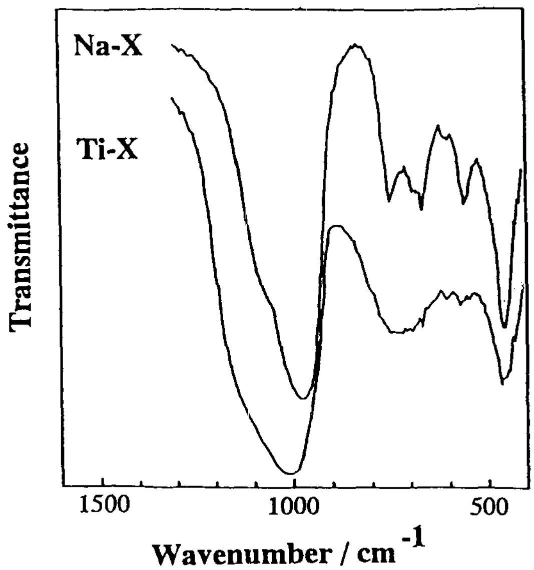

Fig. 2 FT-IR spectra of Na-X and titanium exchanged Ti-X zeolites.

800 cm^{-1} region and the shift of the peak at 1000 cm^{-1} indicates a large interaction of Ti species with zeolites.

Figure 3 shows UV-vis reflectance spectra of the obtained zeolites and TiO_2 powder (74% anatase and 26% rutile). By the introduction of TiO^{2+} into the zeolite pores, the Ti-X and Ti-Y zeolites exhibited absorption with threshold wavelengths at 390 and 360 nm, respectively. On the other hand, the absorption intensities of Na-X and Na-Y were small even in the wavelength region shorter than 300 nm. The absorption intensity of Ti-X is higher than that of Ti-Y. The results of XPS experiments indicated that the titanium content on the surface of Ti-X zeolite was about 2.2 times as much as Ti-Y zeolite. This observation was consistent with the large absorbance in the UV spectra of Ti-X. However, by comparing with TiO_2 powder, the absorption for Ti-X and Ti-Y zeolites was smaller in the intensity and shorter in the threshold wavelength. This result indicates that the different circumstances in the zeolites affect the UV absorption with different interaction. The above observation in UV spectra was similar to that reported for the titanium-dispersed titanium silicate zeolite[16)].

Figure 4 shows the photoluminescence spectra of Ti-X and Ti-Y zeolites at 77 K. For the Ti-X zeolite, a peak in the emission spectrum appeared at 510 nm, while for the Ti-Y, it appeared at a shorter wavelength of 490 nm. The dispersion degree on the whole Ti-Y zeolite particle might be relatively larger than that on Ti-X zeolite, because the titanium content on the external surface layer of the Ti-Y zeolite was smaller than that of Ti-X zeolite and the total amount of titanium atoms was almost equal for both zeolites. The high dispersion may cause strong interaction of the titanium atom with the zeolite framework and may explain the shorter peak wavelength in the emission spectra and the smaller absorbance in the UV spectra. The same phenomenon was also observed in titanium-silicon binary oxide catalysts[14)], where the photoluminescence of the binary oxide containing 0.3% titanium showed a smaller intensity and appeared at shorter wavelength compared with that containing 1.0% titanium. As shown by the broken line in Figure 4, the photoluminescence of Ti-X and Ti-Y is somewhat quenched on the contact with 20 kPa oxygen. Comparing with TiO_2 powder, the quenching phenomenon of the Ti-X and Ti-Y zeolites was similar to that observed for the titanium-silicon oxides[14)] and the titanium

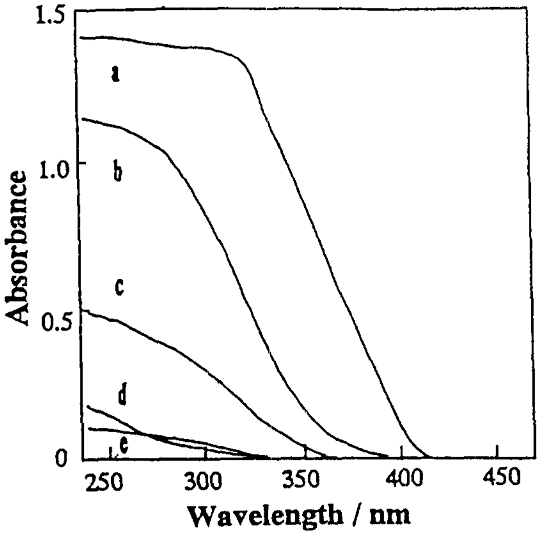

Fig. 3 UV-vis reflectance spectra of bulk TiO_2 and zeolites.
(a) TiO_2 (b) Ti-X (c) Ti-Y (d) Na-X
(d) Na-Y

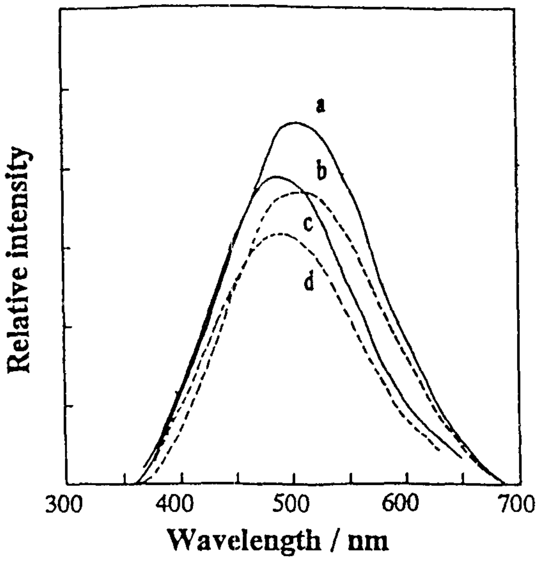

Fig. 4 Photoluminescence of titanium exchanged zeolites and the effects of adding O_2 on zeolites.
(a) Ti-X (b) Ti-X (O_2: 20 kPa)
(c) Ti-Y (d) Ti-Y (O_2: 20 kPa)
measurement: 77K, excitation: 240 nm

coated porous vycor glass[15].

The different degree of the titanium dispersion might be caused by the difference of the ion exchange site in the X and Y zeolites and by the condensation of TiO^{2+} ions during the calcination[11]. In order to avoid the colloidal formation in the ion exchange procedure, $(NH_4)_2TiO(C_2O_4)_2$ salt was used to introduce the TiO^{2+} ions into the zeolites. However, it was not clear that on which site in faujusite the TiO^{2+} ions located.

3.2 Photocatalytic activity for NO decomposition

The experimental results of NO decomposition over the Ti-X, Ti-Y and TiO_2 catalysts are shown in Figure 5. The main products of the photocatalytic decomposition of NO were N_2, N_2O and O_2. The conversions of NO for Ti-X and Ti-Y zeolites were higher than that for TiO_2. The yields of N_2O observed for the Ti-X and Ti-Y zeolites tend to increase with the reaction time. The amount of NO_2 formed was very small over Ti-X and Ti-Y. However, the formation of NO_2 was found three times as much as the formation of N_2O over TiO_2. On both modified zeolites and TiO_2, a little amount of O_2 was produced. For unmodified Na-X and Na-Y zeolites, no formation of N_2 and N_2O was found under the UV irradiation.

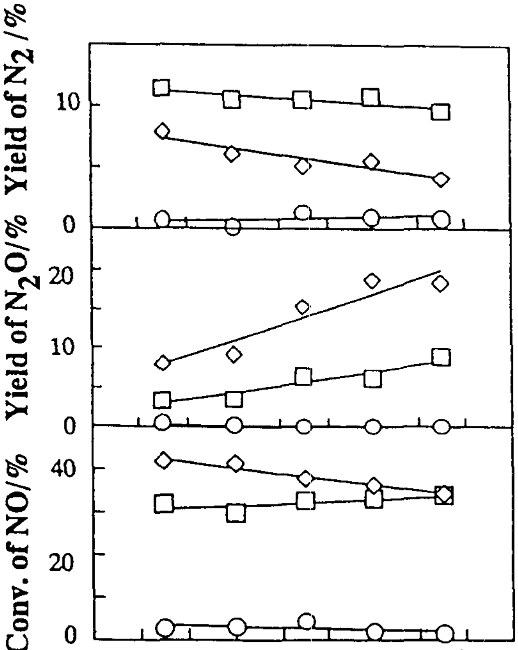

Fig. 5 Time profiles of the photocatalytic decomposition of NO on Ti-X (□), Ti-Y(◇) and TiO_2 (○) catalysts under UV irradiation at 298 K in the fixed-bed flow reactor.

As shown in Figure 5, the zeolites encapsulated by titanium have high photocatalytic reactivity compared with that of the bulk TiO_2. From the product components, it seems that the titanium-encapsulated zeolites mainly catalyze the reduction of NO, but the bulk TiO_2 catalyzes the oxidation of NO under the present experimental conditions.

The high reactivity on the modified zeolite could be explained by that the coordinative unsaturated titanium atoms were highly dispersed onto zeolites. According to the results of XPS, UV-vis absorption and photoluminescence measurements, the surface content of titanium on the Ti-X zeolite was larger than that on the Ti-Y zeolite. Since the efficiencies of the NO decomposition were almost same in the two types of zeolites, the decomposition reaction might occur not only on the external surface of zeolite, but also on the internal surface. On the other hand, the different selectivity in the photocatalytic decomposition was observed. The yield of N_2O was larger on Ti-Y, while that of N_2 was larger on Ti-X. In addition, it is noted that the high reactivity for the Ti-X and Ti-Y zeolites was observed even in the presence of oxygen. The photoluminescence intensity shown in Figure 4 was not completely quenched even though they contacted with 20 kPa of oxygen. It is probable that, under the irradiation condition, the encapsulated titanium gives its electron to the anti-bonding π orbital of NO and assists the decomposition. Meanwhile, it is suggested that the produced oxygen species, such as O^- and OH, were not effective to react continuously with NO on the Ti-X and Ti-Y zeolites. On the other hand, the reactivity for NO decomposition over TiO_2 powder was not so high as expected. Because the active oxygen species O^{2-}, O^- and OH could be easily generated on the irradiated TiO_2 surface, NO tended to be oxidized to NO_2 and nitrate[17].

In conclusion, the ion exchange treatment with $(NH_4)_2TiO(C_2O_4)_2$ allowed titanium to disperse into the X and Y zeolites. Characterization by means of XRD, FT-IR and other spectroscopies proved that titanium was introduced into the zeolites. The introduction of titanium caused the UV light absorption and photoluminescence. The modified zeolites had a high activity for the decomposition of NO compared with that of TiO_2 powder at room temperature under the irradiation with UV light. The N_2, N_2O and O_2 were produced from NO on the modified zeolites. The present results suggest that the titanium modified zeolites have a possibility serving as a new type of material for NO photodecomposition.

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