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Photocatalytic property of titanium silicate zeolite

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Abstract

Titanium silicate zeolite was prepared by treating a dealuminated ZSM-5 zeolite with the vapor of titanium tetrachloride, and characterized by means of XRD, FT-IR, XPS, UV-Vis and photoluminescence spectroscopies. By the introduction of titanium, the zeolite had a unique absorption phenomenon and an emission band and became sensitive to UV irradiation. The obtained titanium silicate zeolites showed catalytic activity for abatement of NO at room temperature under UV irradiation.

Keywords: Titanium silicate; Photocatalysis; Decomposition; NO

1. Introduction

Titanium silicate zeolite has been found to be able to catalyze the oxidation of aromatics, olefins and alcohols with hydrogen peroxide [1]. In each reaction, the titanium shows different physico-chemical properties. Sometimes the framework titanium can catalyze the oxidation of alkane, and sometimes it in nanophase titanium oxide plays a role in oxidation of phenol or nitrous [2]. The other titanium modified catalysts, in which titanium was coated on porous Vycor glass, [3] encapsulated in copolymer, [4,5] or mixed with silicon as binary oxide powder [6] or glass [7], have been thoroughly investigated.

In this report, the photoluminescence and light absorption were measured on the titanium silicate zeolite. From the viewpoint of photocatalysis, photocatalytic decomposition of NO was examined. The effects of the titanium on photocatalytic properties in the decomposition of NO were discussed.

2. Experimental

The Pentasil zeolite (ZSM-5) was kindly supplied from Nissan Girdler Catalysts Co Ltd. Titanium silicate zeolite was prepared by a high temperature displacement method consisting of two steps. First step is dealumination. The parent HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$) zeolite was treated with 1 M HCl at 353 K, washed with deionized water thoroughly, dried at 393 K for 2 h, and finally calcined at 773 K for 4 h. In the secondary step, the dealuminated zeolite was treated at 723 K with the vapor of titanium tetrachloride saturated in nitrogen carrier. The modified zeolite was abbreviated to Ti-ZSM-5. For comparison, the catalysts represented with $\text{TiO}_2/\text{ZSM-5}$ were prepared by mechanical mixing of the parent HZSM-5 with TiO_2 powder. In order to prepare the catalysts on which external surface was covered with TiO_2 , $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in the cyclohexane solvent was impregnated into HZSM-5 powder and oxidized to TiO_2 by the calcination in air at 723

K. This modified zeolite is represented as Ti/ZSM-5.

The titanium silicate zeolite was characterized by XRD, FT-IR, UV-Vis and XPS spectroscopies. The X-ray diffraction chart was obtained with a Rigaku RAD 3A goniometer. For FT-IR measurement, catalysts were ground with potassium bromide powder and then pressed into disks. Transmission spectra of the disks were measured with a JASCO FT-IR-5A. UV-Vis diffuse reflectance spectra were obtained at 298 K on 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 sample contained in a Sprasil cell was immersed in liquid nitrogen in a Dewar vessel with quartz windows.

The photocatalytic reductions of NO was evaluated with a flow fix-bed microreactor system. In a reactor made of quartz, a rod of glass was installed to make the bed of the catalyst in the form of blank cartridge. This reactor system provides a large surface area of bed which can be irradiated with a high pressure mercury lamp. The reactant gas consisted of 0.34% NO and 99.66% He. The weight of catalyst packed in the reactor was 1.5 g.

The decomposition of NO 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 .

3. Results and discussion

3.1. Characterization of titanium silicate

Fig. 1 shows the IR spectra of the titanium silicate, parent HZSM-5 and dealuminated HZSM-5. On the titanium silicate, an absorption peak at 970 cm^{-1} is observed. On the other hand, for both the dealuminated HZSM-5 and the parent HZSM-5, no peaks were seen in this area. When the parent HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 78$) and HZSM-5

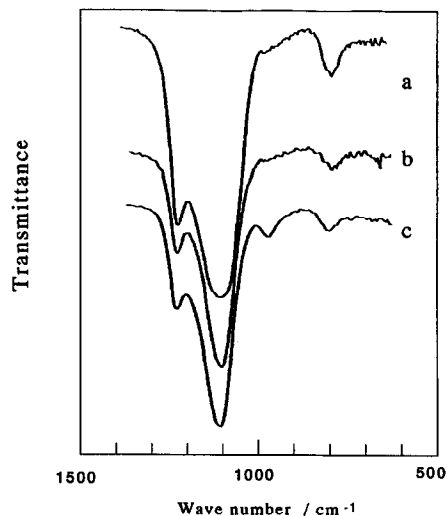


Fig. 1. FT-IR spectra of (a) HZSM-5, (b) after dealumination, (c) Ti-ZSM-5.

($\text{SiO}_2/\text{Al}_2\text{O}_3 = 215$) zeolites were modified under the same condition as HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$), the modified zeolites showed different intensities in the absorption peak at 970 cm^{-1} . The peak intensity increased in the order of Ti-ZSM-5 (28), Ti-ZSM-5 (78) and Ti-ZSM-5 (215). According to the work of Taramasso et al., this absorption peak is characteristic of titanium silicates [8]. With the treatment of hydrochloric acid, aluminum ions could be abstracted from the framework of HZSM-5 and then produced the lattice vacancies, and by the reaction with vapor of titanium tetrachloride, titanium was able to be inserted into the vacancies of zeolite framework. The number of vacancies depended on the aluminum ratio of HZSM-5 zeolites. Thus the amount of the titanium reflects the different intensities in the IR spectra.

From the experimental observations of X-ray diffraction measurements, it was clear that no detectable titanium dioxide was found in the titanium silicate zeolite.

3.2. Reflectance and photoluminescence

Fig. 2 shows the UV-Vis reflectance spectra of Ti-ZSM-5, $\text{TiO}_2/\text{ZSM-5}$ and TiO_2 powder. The absorbance increased in the order of Ti-ZSM-5, $\text{TiO}_2/\text{ZSM-5}$ and TiO_2 . Although the titanium

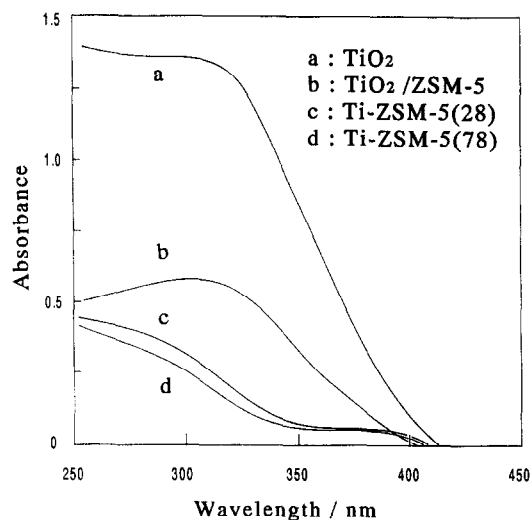


Fig. 2. UV-Vis reflectance spectra of titanium modified zeolites and TiO_2 .

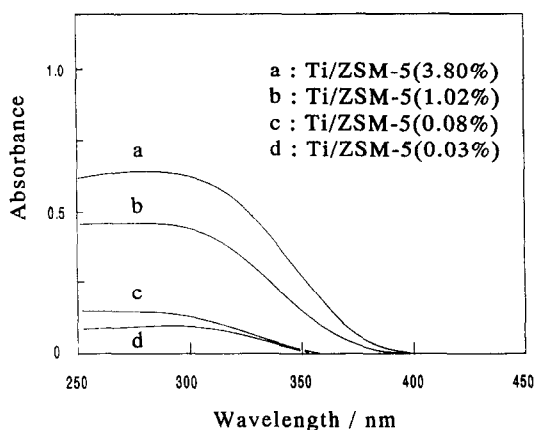


Fig. 3. UV-Vis reflectance spectra of modified zeolites.

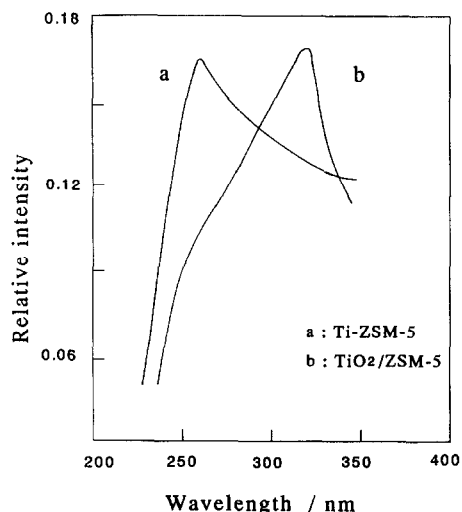


Fig. 4. Excitation spectra of modified zeolites.

content in Ti-ZSM-5 is almost the same as that in $\text{TiO}_2/\text{ZSM-5}$, the absorbance of Ti-ZSM-5 was smaller than that of $\text{TiO}_2/\text{ZSM-5}$. This observation suggests that the absorption relates with the state of titanium. Since the shape of absorption curve of $\text{TiO}_2/\text{ZSM-5}$ is similar to that of TiO_2 , the situation of titanium atoms in $\text{TiO}_2/\text{ZSM-5}$ was expected to be of TiO_2 crystalline. By considering onset wavelength of Ti-ZSM-5 (28) and Ti-ZSM-5 (78), their absorbance remained at a constant level. However, at the wavelength shorter than 350 nm, the absorbance increased with decreasing the wavelength. So a unique absorption phenomenon that is different from the others was observed on Ti-ZSM-5. Since the amount of titanium in Ti-ZSM-5 (28) was larger than that in Ti-ZSM-5 (78), the absorption intensity of Ti-ZSM-5 (28) was larger than Ti-ZSM-5 (78) in the whole wavelength range measured.

In order to explain the distinctive feature of UV reflectance on Ti-ZSM-5, the Ti/ZSM-5 catalysts abbreviated as Ti/ZSM-5 (0.03 Ti wt%), Ti/ZSM-5 (0.08 Ti wt%), Ti/ZSM-5 (1.02 Ti wt%) and Ti-ZSM-5 (3.8 Ti wt%) were used to compare with Ti-ZSM-5. Fig. 3 shows that their absorbance intensities distinctly increased with the titanium content. Apart from the Ti/ZSM-5 (0.03) and Ti/ZSM-5 (0.08), both the onset and turning wavelength on Ti/ZSM-5 (1.02) and Ti/ZSM-5 (3.8) were very similar to that of $\text{TiO}_2/\text{ZSM-5}$ catalyst. The absorbance change with the titanium content was also similar in the dependence. These observations indicate that the titanium atoms in Ti/ZSM-5 catalyst exist in TiO_2 cluster phase like $\text{TiO}_2/\text{ZSM-5}$.

Fig. 4 shows the photoluminescence excitation spectra of Ti-ZSM-5 and $\text{TiO}_2/\text{ZSM-5}$. Because the titanium in the Ti-ZSM-5 was dispersed into the framework of zeolite, the interaction between titanium and oxygen is larger than that of titanium dioxide. Then the peak in the excitation spectrum shifted toward shorter wavelength comparing with $\text{TiO}_2/\text{ZSM-5}$. This observation agrees with the works of Anpo et al. [3,6] for titanium silicon binary oxide.

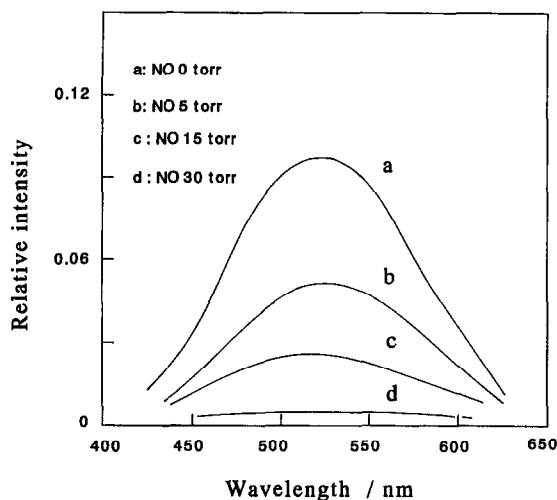


Fig. 5. Photoluminescence of Ti-ZSM-5 zeolite in the presence of various amounts of NO.

Fig. 5 depicts the photoluminescence emission spectra of Ti-ZSM-5. When Ti-ZSM-5 catalyst contacted with NO, the emission was quenched. The extent of the quenching increased with the amount of NO. It is probable that the inserted titanium ions Ti^{4+} could trap electron and become Ti^{3+} under the irradiation condition. The Ti^{3+} then gives its electron to the anti-bonding π orbital of NO molecule and assists the decomposition itself. This suggests that Ti-ZSM-5 zeolite probably has a property showing photocatalytic decomposition of NO, although the coordination state of titanium was not clear at present.

3.3. Photocatalytic activity for NO decomposition

Fig. 6 shows the experimental results of NO decomposition over Ti-ZSM-5 and Ti/ZSM-5 (3.80%) zeolites under irradiation of high pressure mercury lamp at room temperature. The major products of decomposition of NO were N_2 and N_2O for both catalysts. With Ti-ZSM-5 zeolite, its conversion of NO slightly increased with the time, and the main product N_2 also showed the same tendency. On the other hand, with Ti/ZSM-5 zeolite, the conversion of NO showed initially a higher value than Ti-ZSM-5 zeolite and decreased rapidly with time. The yield of N_2 also increased

with the time as Ti-ZSM-5. From the comparison between the experimental results for different modified zeolites, the conversion of NO on Ti/ZSM-5 was higher than Ti-ZSM-5. This could be explained by the higher content of titanium on Ti/ZSM-5 and higher absorption for UV light as shown in Figs. 2 and 3. The relative content of N_2 on Ti-ZSM-5 is higher than Ti/ZSM-5 as shown in Fig. 6. The selectivity of N_2 may relate with the dispersivity of titanium on the internal surface. If the NO molecule diffuses into the pore, any intermediate such as N_2O can be decomposed continually with the aid of titanium. The decomposition of N_2O into N_2 has been already investigated on titanium coated zeolite in our previous work.

In conclusion, by treating dealuminated ZSM-5 zeolite with the vapor of titanium tetrachloride, titanium silicate zeolite could be prepared. Characterization by means of XRD, FT-IR and other spectroscopies showed that titanium atoms are contained in the framework of zeolite. The UV light absorption and photoluminescence were different from that of titanium dioxide itself and ZSM-5 dispersed with titanium at the external surface. The titanium silicate zeolites had a activity for the decomposition of NO at room temperature under the irradiation with UV light and showed a selectivity for N_2 formation than the Ti dispersed ZSM-5. The present results suggest that the titanium silicate zeolite has another property serving as reduction catalyst for the abatement of NO.

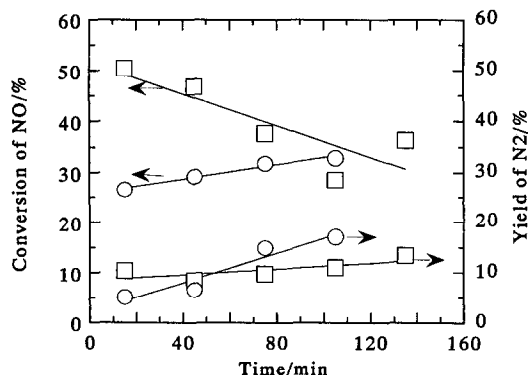


Fig. 6. Time profiles of decomposition of NO on Ti-ZSM-5 (□) and Ti/ZSM-5 (○).

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