

The dispersion effect of TiO_2 loaded over ZSM-5 zeolite

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Received 25 October 1996; revised 3 July 1997; accepted 21 July 1997

Abstract

The low-loading titanium dioxide was prepared on the surface of ZSM-5 zeolite by means of the impregnation method. Based on the results of XPS, ESR and photoluminescence measurements, an interaction between ZSM-5 zeolite and TiO_2 was clarified. ESR spectra of trapped species for photo-induced electrons were compatible with those of bulk TiO_2 powder. The influence of NO on the TiO_2 particles (Ti/ZSM-5) shows that Ti^{3+} serves as active site during photo-decomposition of NO. © 1998 Elsevier Science B.V.

Keywords: TiO_2 ; ZSM-5; Zeolite; NO; Photocatalysis

1. Introduction

Recently, TiO_2 has been widely investigated for the photocatalytic abatement of gaseous environmental pollutants. The dimensions of solid photocatalyst need to be the form of powder or film to satisfy the practical Photoreaction. Dispersed TiO_2 on various supports has a unique character that can promote the photocatalytic reaction. Anpo et al. reported their results loading TiO_2 on glass and mixing TiO_2 with SiO_2 or Al_2O_3 as binary oxide [1–3]. In every case, the highly dispersed TiO_2 exhibited the higher photocatalytic activity in the photohydrogenation or the isomerization of propylene and propyne.

Yoneyama et al. prepared the size quantized TiO_2 in clay interlayers and Nafion films, their

higher activities for decomposition of carboxylate were observed [4,5]. The size effect of photocatalysis has been reviewed [6,7]. Due to the low concentration of pollutants in the air, the porous materials such as active carbon was used to support the TiO_2 powder as photocatalyst [8]. Since zeolite has a vast internal space as a reactive field, the Ti-inserted zeolite has attracted much attention to improve the photocatalytic activity. As for the action of zeolite in the titanium modified zeolite photocatalysts, Yoneyama et al. used the adsorption constant to explain the decomposition activity of gaseous propionaldehyde over the mixture of TiO_2 and various supports such as zeolite A, mordenite, and ferrierite [9]. They suggested that the zeolite can serve as adsorbent to condense the substrate around the loaded TiO_2 .

Xu and Langford noticed that at low (< 2%) loading of titanium oxide on ZSM-5 zeolite the

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maximal photocatalytic activity was observed for the decomposition of chlorophenol [10]. Based on the measurements by XRD, BET, FT-IR, and Raman spectroscopy, they suggested that adsorption and zeolite structure are factors which may be responsible for enhancement of photocatalytic activity of supported TiO_2 .

We have investigated titanium modified zeolites by using an ion exchange method to insert the titanium into the pore of X and Y zeolites [11] and by a high temperature reaction method to replace the titanium ion for the aluminum ion of ZSM-5 zeolite [12]. By using these modified zeolites, photocatalytic reactions have been conducted for the decomposition of NO, which is regarded as a very uneasily abated pollutant in the preservation of the global environment. In this report, we focused TiO_2 loading on the ZSM-5 zeolite, and the interaction between zeolite and TiO_2 . Properties of photoexcitation and deactivation will be discussed based on the measurements of XPS, ESR, and photoluminescence.

2. Experimental details

2.1. Preparation of photocatalysts

HZSM-5 (Nissan Girdler Catalysts) was dried and impregnated with cyclohexane solution of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (Nacalai Tesqu) for 15 h. After the cyclohexane solvent was completely vaporized at 313 K, the zeolite was dried at 393 K for 6 h, and calcined in the air in three different steps; 473 K for 1 h, 623 K for 1 h, and then 723 K for 4 h. By the calcination in the air, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was oxidized into TiO_2 on the zeolite surface. The formation of TiO_2 was confirmed from the absorption spectra [12] and the loss of the Ti reagent in the preparation was ignored. The modified zeolite is abbreviated as Ti/ZSM-5. In order to specify the content, the amount of titanium in wt% was given in the parentheses following the symbols. The TiO_2 powder (P-25) and mixture of TiO_2 powder and ZSM-5 (ab-

breivated as $\text{TiO}_2/\text{ZSM-5}$) were also used for comparison.

2.2. Spectral measurements

UV–vis diffuse reflectance spectra were obtained at 298 K on a JASCO UNIDEC model 660 spectrometer equipped with an integrating sphere, where an Al_2O_3 plate was used for the reference. ESR measurements were taken at 77 K on a JEOL RE2X instrument equipped with a liquid–nitrogen Dewar. After drying at 393 K for about 2 h the sample was put into a quartz tube of 5 mm diameter, then the tube was evacuated and sealed at the pressure of 0.66–1.33 Pa. The sealed tube was then installed in the cavity, and irradiated with a 500 W high pressure Hg lamp through a glass filter (Hoya U360). Photoluminescence spectra were measured at 77 K with a HITACHI model 850 spectrofluorometer. A Sprasil flat cell containing the sample powder was immersed in liquid nitrogen filled in a Dewar vessel with quartz windows.

3. Results and discussion

3.1. Photoluminescence and XPS results

Fig. 1 shows the photoluminescence spectra of Ti/ZSM-5 zeolites and TiO_2 powder. The

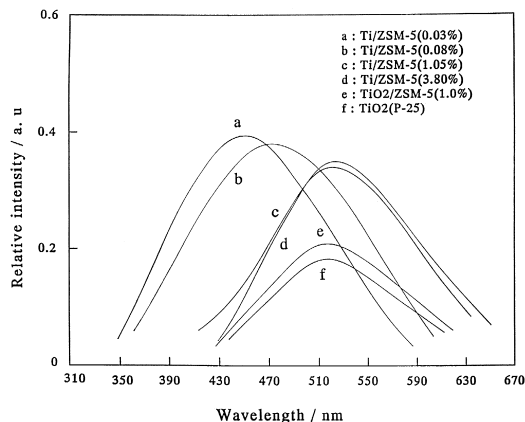


Fig. 1. Photoluminescence spectra of Ti/ZSM-5 zeolite, $\text{TiO}_2/\text{ZSM-5}$ zeolite, and TiO_2 powder measured at 77 K with the excitation at 270 nm.

Table 1
Optical and XPS properties of Ti-loaded ZSM-5

	Ti content (wt%)	Bandgap (eV)	Absorption threshold (nm)	Luminescence peaks (nm)	Binding energy ^a (eV)
Ti/ZSM-5	0.03	—	—	450	—
Ti/ZSM-5	0.08	3.63	341	470	462.2 ^b
Ti/ZSM-5	1.02	3.53	351	520	462.0
Ti/ZSM-5	3.80	3.45	359	530	461.6
TiO ₂ /ZSM-5	1.00	3.33	372	520	461.6
TiO ₂	100	3.32	373	520	—

^aBinding energy of Ti-2p electrons. Referenced with C-1s of 288.0 eV.

^bMeasured for 0.35 wt% of Ti.

wavelength at maximum luminescence intensity was listed in Table 1, where the threshold wavelength of the absorption spectra was also shown. The photoluminescence wavelength shifts from 520 to 450 nm, as the amount of loading titanium decreases from 1.02% to 0.03%. The longest wavelength of 520 nm for Ti/ZSM-5 is the same as the wavelength for TiO₂/ZSM-5 (1.0%) and TiO₂ powder, even though the reported wavelengths of the photoluminescence peak for TiO₂ powder sometimes differ from each other in literature. Anpo et al. observed that the maximum value of TiO₂ locates at around 400 or 500 nm according to the different preparation procedure [1,13].

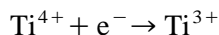
As shown in Table 1, with increasing amount of loading titanium on Ti/ZSM-5 the luminescence wavelength increases. Meanwhile the band gap energy calculated with the absorption threshold decreases. The binding energy of the 2p-electron of the titanium atom of Ti/ZSM-5 and TiO₂/ZSM-5, which was compensated with reference carbon, tend to decrease with the loading titanium. This result suggests that when the amount of titanium becomes smaller, the interaction between titanium and ZSM-5 zeolite increases. This interaction is reflected by the change of coordination environment of titanium. When the amount of titanium reached above 1.02%, no more differences from bulk TiO₂ in the binding energy were observed when TiO₂ was just mechanically mixed with ZSM-5 zeolite. This suggests that titanium oxide highly loaded on ZSM-5 zeolite behaves similarly as

does TiO₂ powder. The change in the binding energy of titanium-containing Ti/ZSM-5 is mainly caused by the interaction between titania and zeolite, because it is already known that the change is to be caused by the interaction rather than the different size of TiO₂ dispersed on SiO₂ support [14].

3.2. Photo-induced ESR spectra

In order to investigate the surface trapped states of photo-induced electrons and holes, we measured the ESR spectra of Ti/ZSM-5 zeolite under light-irradiation at 77 K. The obtained spectra were shown in Fig. 2. For comparison, a photo-induced ESR spectrum was also measured on TiO₂ (P-25) treated under the same condition as Ti/ZSM-5. Without titanium, ZSM-5 zeolite does not show an ESR signal, indicating that the signal originates from the Ti atom and/or the vicinity of the Ti atom.

Fig. 2 shows that the signals at *g* values of 2.017, 2.004, and 1.982 are observed on the Ti/ZSM-5 (2.45%) zeolite. For bulk TiO₂ powder, a *g* value of 2.028 is observed beside *g* values at 2.017, 2.004, and 1.982. Concerning the photo-irradiated electron and hole on TiO₂, some people have reported their results. The principal *g* values are listed in Table 2. The signal having a *g* value of 1.982 could be assigned to the trapped-electron species as Ti³⁺ that was produced as follows.



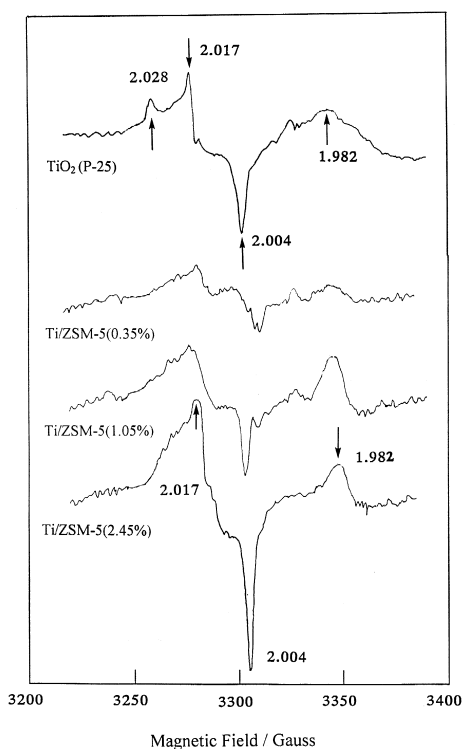


Fig. 2. Photo-induced ESR spectra of Ti/ZSM-5 and TiO_2 measured at 77 K.

Since this peak shows the broad feature, it may locate in some asymmetric environment, or exist on the surface of TiO_2 particles [17].

In contrast to the fact that the trapped electrons are assigned to Ti^{3+} ions, the chemical species of trapped holes are not unique at present. Howe and Graetzel considered that the trapped hole species are lattice oxide ions immediately below the surface [15]. Anpo suggested that this species may be surface OH

radicals from the comparison of the photoluminescence spectra [13]. Micic et al. assigned this species to an oxygen surface anion radical covalently bound to a titanium atom [16]. From the similarity of the trapped-hole signals with reported g values, the chemical structure of trapped hole on Ti/ZSM-5 in this work may be of $\text{Ti}-\dot{\text{O}}-\text{Ti}$, that is, oxygen radical coordinates to two Ti atoms. On the other hand, that observed on TiO_2 may be attributable to oxygen radicals bonding to one Ti atom [16]. As mentioned in the XPS results shown in Table 1, when the amount of titanium dioxide loading on the zeolite surface is small, the coordination of titanium is different from that of bulk TiO_2 . The difference in the ESR spectra is probably induced by the difference in the Ti coordination but not by the size of TiO_2 . This observation is consistent with the report that the same ESR signals were observed for TiO_2 particles of diameters ranging from 25 to 300 Å [16].

3.3. Effects of NO

Fig. 3 shows the quenching of the photoluminescence of Ti/ZSM-5 (2.45%) zeolite by NO molecules. The photoluminescence is quenched when it contacts with NO gas, suggesting that titanium in the Ti/ZSM-5 tends easily to react with NO gas. The quenched luminescence intensity can increase by evacuating NO at room temperature. However, the intensity did not completely recover to the state as that before contacting with NO. It can be completely recov-

Table 2
ESR parameters of paramagnetic species in TiO_2

	Trapped holes			Trapped electrons		Remarks	
	assignment	g_1	g_2	g_3	g_{\perp}		g_{\parallel}
TiO_2	$\text{Ti}-\dot{\text{O}}-\text{Ti}$	2.016	2.012	2.002	1.990	1.960	Howe and Graetzel [15]
TiO_2	($\dot{\text{O}}\text{H}$)	2.0146	2.0146	2.003	1.998	1.988	Anpo et al. [13]
TiO_2	$\text{Ti}-\text{O}-\text{Ti}-\dot{\text{O}}$	2.027	2.019	2.007	1.987	1.928	Micic et al. [16]
Ti/ZSM-5 (2.45%)		2.017	2.011	2.004	1.982	1.93	this work
TiO_2 (P-25)		2.028	2.017	2.014	1.982	1.934	this work

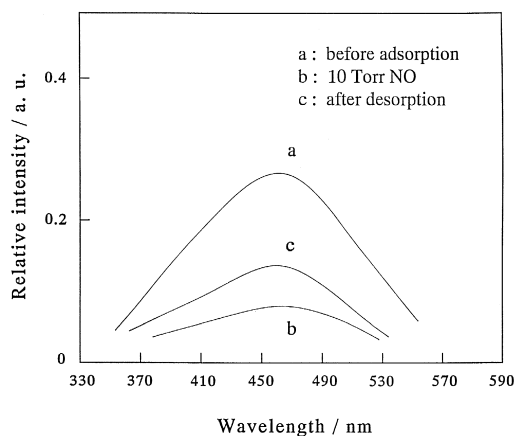


Fig. 3. Photoluminescence spectra of Ti/ZSM-5 and the effect of the addition of NO gas: Measured at 77 K with the excitation at 270 nm.

ered when the sample was evacuated at 473 K. This observation suggests that the chemical adsorption of NO takes place on Ti/ZSM-5 and the titanium in Ti/ZSM-5 has the potential ability serving as photo-induced active site to catalyze NO reaction.

Fig. 4 shows the change in ESR signal for Ti/ZSM-5 zeolites observed after the contact with 10 Torr of NO. Compared with Fig. 2, the signals of the trapped electron species decrease

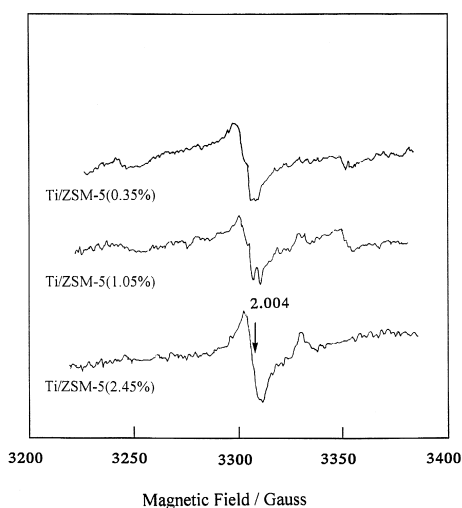


Fig. 4. Photoinduced ESR spectra of Ti/ZSM-5(0.035%) zeolites and the effect of the addition of NO gas measured at 77 K.

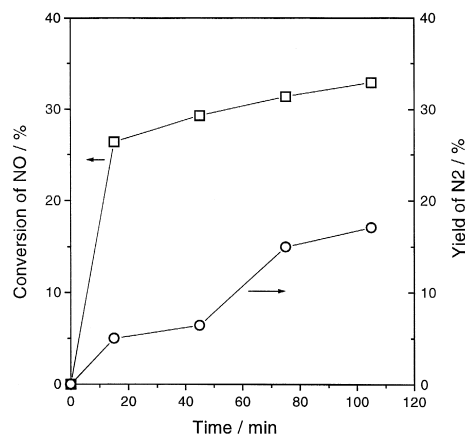
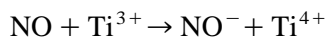


Fig. 5. Photo-decomposition of NO on Ti/ZSM-5 under irradiation with the UV light at room temperature.

with the adsorption of NO for the samples examined. This observation shows the existence of the following process in which NO could easily accept an electron from trapped electrons Ti^{3+} .



As shown in Fig. 4, besides the decrease of trapped electron species, the trapped hole species also show differences, only the signal at $g = 2.004$ can be observed. We supposed that it is caused by interaction between NO and the titanium atom which locates close to the trapped electron species.

Fig. 5 shows the results of photo-induced decomposition of NO. After the start of the irradiation, the conversion of NO becomes 26.4% and tends to slowly increase with the reaction time. The yield of N₂ gradually increases with the reaction time. Because at the beginning of the reaction, mainly N₂O can be detected, these results suggest that N₂ is probably produced from N₂O which directly comes from NO.

In conclusion, by using the impregnation method, low-loading titanium dioxide can be prepared on the surface of ZSM-5 zeolite. With decreasing the amount of loading titanium, the absorption threshold and photoluminescence

maximum shift to higher energy. From the XPS observation and photoluminescence measurement, the interaction was suggested between the highly dispersed titanium and support zeolite. Based on the ESR measurement, ESR spectra of trapped holes indicate the existence of interaction with the support, while the photo-induced trapped electrons are similar to those observed for bulk TiO_2 powder. NO molecules can easily receive electrons from photo-induced Ti^{3+} on the surface of Ti/ZSM-5. The chemical adsorption and the photo-induced decomposition of NO prove the existence of interaction between photo-irradiated Ti/ZSM-5 and NO molecules, and the trapped electron species Ti^{3+} actually acts as reactive site for the decomposition of NO.

Acknowledgements

The authors wish to give thanks to Dr. Y. Nakaoka for his help in the ESR measurement, and also to Professor Y. Inoue, Dr. K. Sato, and Dr. M. Kohno of the analysis center of our university for their support in the experiments.

References

- [1] M. Anpo, H. Nakaya, S. Kodama, Y. Kubokawa, K. Domen, T. Onishi, *J. Phys. Chem.* 90 (1986) 1633.
- [2] M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, E. Giamello, *J. Phys. Chem.* 89 (1985) 5017.
- [3] M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, E. Giamello, *J. Phys. Chem.* 89 (1985) 5689.
- [4] H. Yoneyama, S. Haga, S. Yamanaka, *J. Phys. Chem.* 93 (1989) 4833.
- [5] H. Miyoshi, S. Nippa, H. Uchida, H. Mori, H. Yoneyama, *Bull. Chem. Soc. Jpn.* 63 (1990) 3380.
- [6] H. Yoneyama, *Crit. Rev. Solid State Mater. Sci.* 18 (1993) 69.
- [7] Y. Nosaka, *Shokubai* 36 (1994) 507.
- [8] S. Nishikata, K. Shinkai, M. Miyamoto, T. Takahashi, T. Ibusuki, K. Takeuchi, *Shokubai* 36 (1994) 134.
- [9] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, *J. Phys. Chem.* 99 (1995) 9986.
- [10] Y. Xu, C.H. Langford, *J. Phys. Chem.* 99 (1995) 11501.
- [11] S. Zhang, T. Kobayashi, Y. Nosaka, N. Fujii, *Denki Kagaku* 63 (1995) 927.
- [12] S. Zhang, T. Kobayashi, Y. Nosaka, N. Fujii, *J. Mol. Catal. A: Chem.* 106 (1996) 119.
- [13] M. Anpo, T. Shima, Y. Kubokawa, *Chem. Lett.*, (1985) 1799.
- [14] G. Lassaletta, A. Fernandez, J.P. Espinos, A.R. Gonzalez-Elipe, *J. Phys. Chem.* 99 (1995) 1484.
- [15] R.F. Howe, M. Graetzel, *J. Phys. Chem.* 91 (1987) 3906.
- [16] O.I. Micic, Y. Zhang, K.R. Chromic, A.D. Trifunac, M.C. Thurnauer, *J. Phys. Chem.* 97 (1993) 7277.
- [17] T. Rajh, A.E. Ostafin, O.I. Micic, D.M. Tiede, M.C. Thurnauer, *J. Phys. Chem.* 100 (1996) 4538.