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In situ characterization of highly dispersed catalysts included within zeolite cavities and their photocatalytic reactivities (*)

M. ANPO (**)
Department of Applied Chemistry, Osaka Prefecture University - Sakai, Osaka 599, Japan

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Summary. — A detailed characterization of catalysts prepared within zeolite cavities and their photocatalytic reactivities have been investigated using *in situ* photoluminescence, diffuse reflectance absorption, XAFS (XANES and FT-EXAFS) and ESR techniques. With the Ag^+/ZSM-5 catalyst, it was found that Ag^+ ions are highly dispersed in an isolated state within the zeolite cavities. UV irradiation of the Ag^+/ZSM-5 catalyst in the presence of NO leads to the decomposition of NO into N_2, O_2 and N_2O at 275 K. Dynamic studies show that the electron transfer from the excited state of the Ag^+ ions ($4d^9 5s^1$) plays a significant role in initiating the decomposition of NO. Titanium oxide catalysts prepared within the Y-zeolite cavities via an ion-exchange method exhibit high and unique photocatalytic reactivities for the decomposition of NO into N_2 and O_2 as well as the reduction of CO_2 with H_2O showing a high selectivity for the formation of CH_3OH. It was also found that the charge transfer excited state of the titanium oxide species, $(T^{3+}\text{-}O^-)^*$, plays a vital role in these unique photocatalytic reactions.

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1. – Introduction

The design of highly efficient and selective photocatalytic systems for the useful application of photocatalysts especially in the reduction/elimination of toxic elements in the environment is of vital concern. In particular, our research into environmentally friendly photocatalysts which successfully and efficiently decompose NO into N_2 and O_2 as well as carries out the reduction of CO_2 with H_2O will contribute greatly to the development of such applicable systems. The use of zeolite cavity spaces to design such efficient and selective photocatalytic systems is significant because zeolites offer unique nano-scaled pore reaction fields, an unusual internal surface topology, and

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(**) E-mail: anpo@chem.osakofu-u.ac.jp

ion-exchange capacities [1-3]. Furthermore, the ion-exchangeable sites are well separated from each other within the cavities, making the design of photocatalysts by ion-exchange with metal ions an ideal approach. In view of these developments, meticulous characterizations of the specific properties and effects of both the metal cations and metal oxides encapsulated within the zeolite cavities at the molecular level will facilitate the design of such useful photocatalysts [1-11].

In the present study, highly dispersed Ag^+ ions as well as titanium oxides included within zeolite cavities were prepared via an ion-exchange method and used as photocatalysts for the decomposition of NO as well as for the reduction of CO_2 with H_2O. The characterization of these catalysts by means of *in situ* photoluminescence, diffuse reflectance absorption, XAFS (XANES and FT-EXAFS), FT-IR and ESR measurements have been carried out to clarify the mechanisms involved in the photocatalytic reactions. Special attention has been focused on the relationship between the local structure of the catalysts and the selectivity of the photocatalytic reactions [3-5].

2. – Experimental

The Ag^+/ZSM-5 ($SiO_2:Al_2O_3 = 23:1$) catalysts were prepared by ion-exchange with an aqueous $Ag(NH_3)^{2+}$ solution. After washing with water and drying in air, the silver loadings of the samples were determined to be 6.7 wt% as metal. Prior to spectroscopic and photocatalytic measurements, the catalysts were degassed at 295 K for 1 h, calcined at 675 K in the presence of O_2 for 1 h, then degassed at 475 K for 1 h [5,6].

The Ti-oxide/Y-zeolite ($SiO_2/Al_2O_3 = 5.5$) catalyst was prepared via an ion-exchange method with an aqueous titanium ammonium oxalate solution (1.1 wt% as TiO_2 and referred to as the ex-Ti-oxide/Y-zeolite). Furthermore, two types of Ti-oxide/Y-zeolite catalysts having different Ti contents (1.0 wt% and 10 wt% as TiO_2) were prepared by an impregnation method (referred to as the imp-Ti-oxide/Y-zeolite) [7]. TiO_2 powdered catalysts (JRC-TIO-4: anatase 92 %, rutile 8 %) were supplied as standard reference catalysts by the Catalysis Society of Japan.

Photocatalytic reactions were carried out at 298 K using a high-pressure mercury lamp, color filters, and a water filter. The reaction products were analyzed by gas chromatography and mass spectrometry. EXAFS measurements were obtained at the Photon Factory of the National Laboratory for High-Energy Physics, Tsukuba. The ESR spectra were recorded at 77 K using a JES-RE2X spectrometer (X-band). The photoluminescence spectra were recorded with a Shimadzu RF-5000 spectrofluorophotometer at 77 K.

3. – Results and discussion

3˙1. *The photocatalytic decomposition of* NO *on the* Ag^+/ZSM-5 *photocatalyst*. – As shown in fig. 1, UV irradiation of the Ag^+/ZSM-5 catalyst in the presence of NO at 295 K leads to the formation of N_2, O_2, N_2O, and NO_2($N_2:N_2O:NO_2 = 1.0:0.38:0.10$). Formation of these products can be found only under UV irradiation and the yields of these products increase with a good linearity against the irradiation time. The value of the photo-formed N_2 molecules per total number of Ag^+ ions included in the catalyst exceeds 1.0 with 6500 min of UV irradiation, and even after this time the decomposition of NO proceeds linearly with the UV irradiation time, indicating that the reaction takes

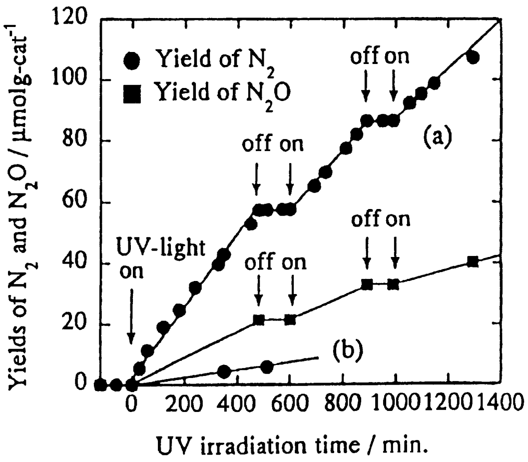

Fig. 1. – Time profiles of the photocatalytic decomposition of NO into N_2 and O_2 on the Ag^+/ZSM-5 catalyst (a) and Cu^+/ZSM-5 catalyst at 298 K (b).

place photocatalytically. The rate of N_2 formation per one Ag^+ on the Ag^+/ZSM-5 catalyst is about 20 times faster than for the Cu^+/ZSM-5 catalyst [2, 5, 6], indicating that the photocatalytic decomposition of NO proceeds more quickly on the Ag^+ ions than on the Cu^+ ions. For the Ag^+/ZSM-5 catalyst, it was found that the UV-light effective for NO decomposition lies in the wavelength region of 220 nm to 250 nm.

The FT-EXAFS spectrum of the catalyst exhibits a well-defined peak due to the neighboring oxygen atoms (Ag-O) only at around 1.8 Å. Bulk Ag_2O exhibits a peak at around 3.5 Å which can be attributed to the Ag-O-Ag bonding, while FT-EXAFS of the

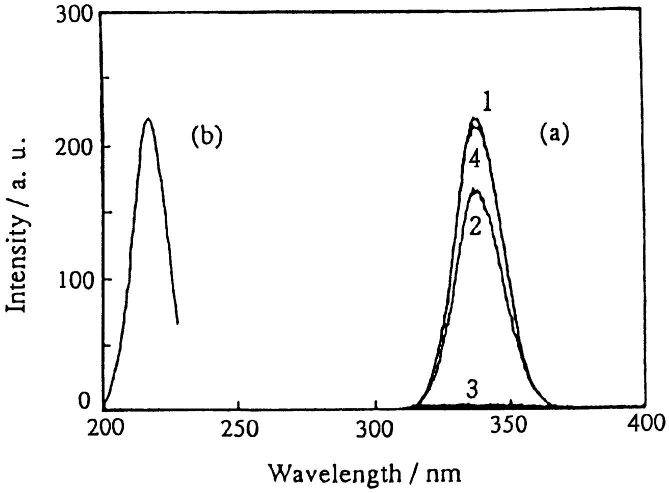

Fig. 2. – Photoluminescence spectrum (a-1) and its excitation spectrum (b) of Ag^+/ZSM-5 catalyst, and the effect of the addition of NO on the photoluminescence spectrum (2 and 3) and after evacuation of NO at 298 K (4).

Ag foil exhibits a peak at around 2.5 Å due to the Ag-Ag bonding. These results suggest that silver ions on the Ag^+/ZSM-5 catalyst are anchored within the micropores of the zeolite in an isolated state forming neither clusters nor Ag metal or oxide crystals.

Figure 2 shows the photoluminescence spectra when the absorption band of the Ag^+ ion on the catalyst is excited by beams of around 220 nm. The photoluminescence spectrum at around 340 nm is attributed to the presence of an isolated Ag^+ ion, *i.e.* to the radiative deactivation due to the $(4d^9 5s^1 \rightarrow 4d^{10})$ electronic transition of the Ag^+ ion. Figure 2 also shows the effect of the addition of NO on the photoluminescence. The addition of NO onto the catalyst leads to the efficient quenching of the photoluminescence which can be attributed to the isolated Ag^+ ions. As shown in fig. 2, after the complete quenching, the evacuation of the system leads to the recovery of the photoluminescence to its original intensity level. These results clearly indicate that the interaction of NO with the Ag^+ ion is weak and that the added NO easily interacts with the Ag^+ species in the ground as well as excited states [5, 6].

The most effective UV wavelengths for the photocatalytic decomposition of NO were found to lie in the same wavelength regions as the absorption and excitation bands. The results also indicate that the decomposition of NO proceeds photocatalytically on the Ag^+ ions. Furthermore, EPR investigations show that the addition of O_2 or NO at high pressures did not lead to the oxidation of Ag^+ to Ag^{2+} in the Ag^+/ZSM-5 catalyst, in clear contrast to the easy oxidation of Cu^+ to Cu^{2+} in the Cu^+/ZSM-5 catalyst [3, 5, 6]. Since Ag^+ ions are chemically stable even in an oxidative atmosphere, the Ag^+/ZSM-5 catalyst can clearly be considered a potential photocatalyst for the direct decomposition of NO at ambient temperatures.

From these various findings, we can see that the photo-excited electronic state of highly dispersed Ag^+ ions $(4d^9 5s^1)$ plays a significant role in the photocatalytic decomposition of NO, while an electron transfer from the photo-excited Ag^+ into the π anti-bonding molecular orbital of NO leads to the weakening of the N-O bond and initiates the decomposition of the NO. The remarkably high photocatalytic reactivity of the Ag^+/ZSM-5 catalyst can be attributed to the high chemical stability of the Ag^+ ion and the efficient interaction of the excited electronic state of the Ag^+ ion with NO [5, 6].

3·2. *Photocatalytic reactions on the* Ti-*oxide/*Y-*zeolite photocatalysts.* – UV irradiation of the Ti-oxide/Y-zeolite catalysts as well as the powdered TiO_2 in the presence of NO was found to lead to the formation of N_2, O_2 and N_2O at 275 K with different yields and product selectivities [7].

As shown in fig. 3, the yields of photo-formed N_2, O_2 and N_2O increased linearly to the irradiation time and the reaction immediately ceased when irradiation was discontinued. These reaction products were not detected in dark conditions nor in UV-irradiation of the zeolite without titanium oxides. After prolonged UV irradiation, the number of photo-formed N_2 per total number of Ti ions included within the catalyst exceeded 1.0 [7,10].

The photocatalytic reactivities of various titanium oxide catalysts for the direct decomposition of NO are shown in table I. The specific photocatalytic reactivities of the Ti-oxide/Y-zeolite catalysts which have been normalized for the unit amount of TiO_2 in the catalysts are much higher than the bulk TiO_2 catalysts. Table I also shows the yields of the photo-formed N_2 and N_2O (efficiency) and their distribution (selectivity) in the photocatalytic decomposition of NO. It is clear that the efficiency and selectivity for the formation of N_2 strongly depend on the type of catalyst. The ex-Ti-oxide/Y-zeolite

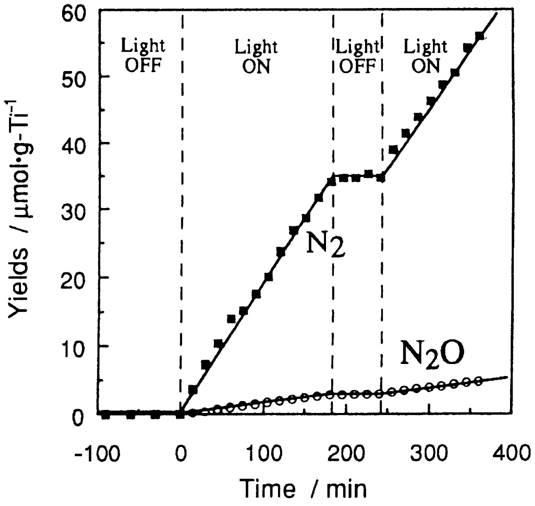

Fig. 3. – Time profiles of the photocatalytic decomposition of NO into N_2 and O_2 on the Ti-oxide/ZSM-5 catalyst prepared by an ion-exchange method.

catalyst exhibits a high reactivity as well as a high selectivity for the formation of N_2, while the formation of N_2O was found to be the major reaction on the bulk TiO_2 catalyst as well as on the imp-Ti-oxide/Y-zeolite catalyst.

The Ti-oxide/Y-zeolite catalyst prepared by ion-exchange exhibits an absorption band in the wavelength region of 280–330 nm, which is a shift into shorter wavelength regions as compared to the bulk TiO_2. Such a significant blue shift in the absorption band observed with the ex-Ti-oxide/Y-zeolite catalyst clearly suggests that the dispersion of the Ti-oxide species on the catalyst is higher than on catalysts prepared by the impregnation method. Thus, a clear relationship can be seen between the reactivity for the photocatalytic decomposition of NO and the magnitude in the blue shift of these catalysts [7,10].

As shown in fig. 4, the Ti-oxide/Y-zeolite catalyst exhibits an intense single preedge peak in its XANES spectrum, indicating that the titanium oxide species has a

TABLE I. – *Comparisons of yields of* N_2 *and* N_2O *and their selectivities in the direct photocatalytic decomposition of* NO *at* 275 K *on various types of the* Ti *oxide/zeolite catalysts and the powdered bulk* TiO_2 *catalyst.*

Catalysts	Ti content (wt % of as TiO_2)	Yields (μmol/g-catal h)			Selectivity (%)	
		N_2	N_2O	total	N_2	N_2O
ex-Ti oxide/Y-zeolite	1.1	14	1	15	91	9
imp-Ti oxide/Y-zeolite	1.0	7	10	17	41	59
imp-Ti oxide/Y-zeolite	10	5	22	27	19	81
powdered TiO_2	100	2	6	8	25	75

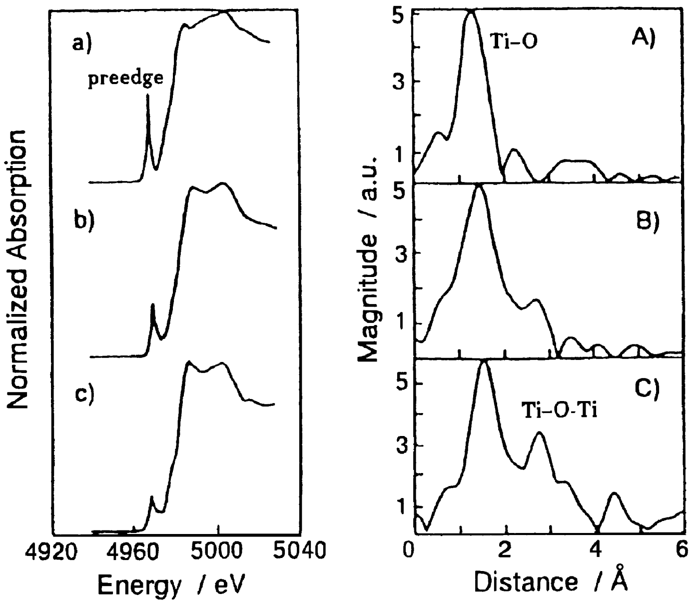

Fig. 4. – XANES (a) and FT-EXAFS (A) spectrum of the ex-Ti-oxide/Y-zeolite catalyst, and the imp-Ti-oxide/Y-zeolite catalyst with a Ti content of 1.0 (b, B) and 10 wt% as TiO_2 (c, C).

tetrahedral coordination. For the imp-Ti-oxide/Y-zeolite catalyst having a small Ti content, the single characteristic preedge peak is rather weak, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated titanium oxide species while the imp-Ti-oxide/Y-zeolite catalyst having a high Ti content exhibits three characteristic weak preedge peaks due to the crystalline anatase TiO_2. Figure 4 also shows the FT-EXAFS spectra of the catalysts. The ex-Ti-oxide/Y-zeolite catalyst exhibits only Ti-O peaks indicating the presence of an isolated titanium oxide species. A curve-fitting analysis of the EXAFS spectrum shows that the ex-Ti-oxide/Y-zeolite consists of 4-coordinate titanium ions, while the imp-Ti-oxide/Y-zeolite exhibits an intense peak at around 2.7 Å assigned to the neighboring titanium atoms (Ti-O-Ti) as well as to the Ti-O peak, indicating the presence of an aggregated octahedral titanium oxide species. The ESR spectrum of the Ti^{3+} ions formed by the photoreduction of the ex-Ti-oxide/Y-zeolite catalyst with H_2 at 77 K showed only one type of Ti^{3+} signal indicating the presence of a Ti^{3+} species having a tetrahedral coordination [7, 9-11].

The ex-Ti-oxide/Y-zeolite catalyst exhibits a photoluminescence spectrum at around 490 nm by excitation at around 290 nm at 77 K, as shown in fig. 5. The observed absorption and photoluminescence bands are in good agreement with those of the highly dispersed tetrahedrally coordinated titanium oxides which is attributed to an electron transfer process to form a charge transfer excited state (Ti^{3+}-O^- pair), and the radiative decay process from the excited state to the ground state of the titanium oxide species [7, 8]. On the other hand, the imp-Ti-oxide/Y-zeolite catalysts did not exhibit any photoluminescence spectrum. Thus, these results further support the conclusion that the ex-Ti-oxide/Y-zeolite catalyst consists of an isolated tetrahedral titanium oxide species, while the imp-Ti-oxide/Y-zeolite catalysts involve an

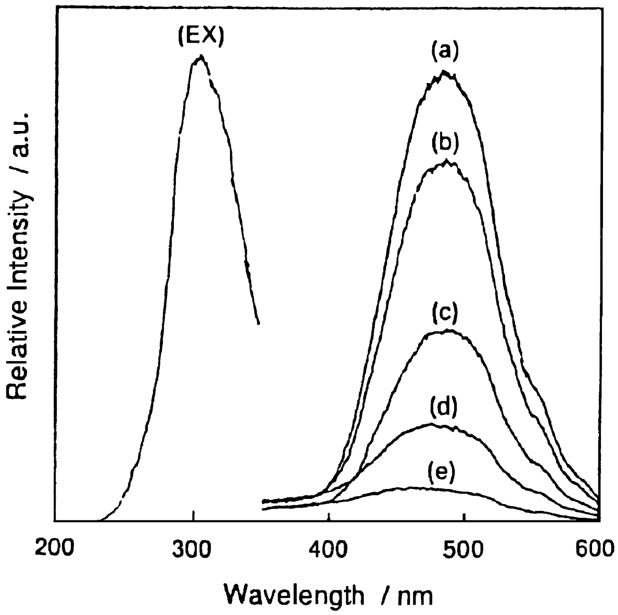

Fig. 5. – Photoluminescence spectrum of the Ti-oxide/Y-zeolite catalyst (a), its excitation spectrum (EX), and the effect of the addition of NO on the photoluminescence spectrum (b-e).

aggregated octahedral titanium oxide species, being in good agreement with results obtained by XAFS investigations.

As shown in fig. 5, the addition of NO onto the ex-Ti-oxide/Y-zeolite catalyst leads to an efficient quenching of the photoluminescence spectrum. The lifetime of the charge transfer excited state was shortened by the addition of NO, its extent depending on the amount of NO added. These findings indicate not only that the tetrahedrally coordinated titanium oxide species locate at positions accessible to NO but also that NO easily interacts with the charge transfer excited state of the species [7, 9-11].

From these results, it can be concluded that a high photocatalytic efficiency and selectivity for the formation of N_2 in the photocatalytic decomposition of NO was achieved with the ex-Ti-oxide/Y-zeolite catalyst having an isolated tetrahedral titanium oxide species, while the formation of N_2O was found to proceed on the bulk TiO_2 catalysts and on the imp-Ti-oxide/Y-zeolite catalysts involving aggregated octahedrally coordinated titanium oxide species. Within the lifetimes of the charge transfer excited complexes, $(Ti^{3+}\text{-}O^{-}\ \text{pair})^*$, of the isolated tetrahedral titanium oxide species, the electron transfer from the Ti^{3+} into the π-antibonding orbital of NO takes place, and simultaneously, the electron transfer from the π-bonding orbital of another NO into the O^- occurs, resulting in the decomposition of two sets of NO into N_2 and O_2 on the Ti-oxide site even at 275 K. On the other hand, with the aggregated or bulk TiO_2 catalysts, the photo-formed holes and electrons rapidly separate from each other with large space distances between the holes and electrons, preventing the simultaneous activation of two NO on the same active sites and resulting in the formation of N_2O and NO_2 in place of N_2 and O_2 [7].

Although the study of the detailed mechanisms involving such local charge separations observed on highly dispersed titanium oxide catalysts will be the subject of our future work, the present study clearly demonstrates that the tetrahedrally coordinated titanium oxide species prepared within zeolite cavities can be considered ideal candidates for new and applicable photocatalytic systems for the reduction of toxic elements such as NO_x as well as for the reduction of CO_2 with H_2O [10, 11].

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