Characterization and photocatalytic reduction of CO_2 with H_2O on Ti/FSM-16 synthesized by various preparation methods

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Ti/FSM-16 photocatalysts were prepared by various methods and their reactivity for the photocatalytic reduction of CO_2 with H_2O at 323 K was investigated. UV irradiation of Ti/FSM-16 in the presence of CO_2 and H_2O led to the formation of CH_4 and CH_3OH. The photocatalytic reactivity and selectivity differed remarkably by variations in the preparation method. Analyses of the UV-Vis absorption and XAFS spectra showed that the dispersion and local structure of the Ti-oxide species greatly depended on the preparation method. The formation of CH_3OH was found to be related to the local structure of the Ti-oxide species while the yield of the photoluminescence was attributed to the charge transfer excited state of the highly dispersed tetrahedrally coordinated Ti-oxide species. Methanol formation was found to be more efficient on Ti/FSM-16 having such highly dispersed tetrahedrally coordinated Ti-oxide species.

Keywords: Photocatalysis, Ti-oxide, CO_2 Reduction, CH_3OH synthesis, XAFS

1. Introduction

The fixation and/or reduction of CO_2 with H_2O using a photocatalytic method is one of the most important and challenging issues not only to reduce the concentration of CO_2 in the atmosphere, the "greenhouse effect", but also to develop ways to recycle vital carbon resources. Recently, we have reported that the photocatalytic reduction of CO_2 with H_2O on TiO_2 powder at 323 K led to the formation of small amounts of CH_4 (Anpo *et al*., 1997). On the other hand, the highly dispersed Ti-oxide catalyst anchored on Vycor glass exhibited high and distinctive photocatalytic reactivity as compared to the bulk TiO_2 powder (Anpo & Chiba, 1992). However, more detailed information on the relationship between the local structure of the Ti-oxide species and the reactivity and selectivity is necessary to achieve a higher efficiency.

In the present study, Ti/FSM-16 photocatalyts were prepared by various preparation methods and used for the reduction of CO_2 with H_2O. Using XAFS, diffuse reflectance UV-Vis absorption, photoluminescence measurements the local structure of the Ti-oxide species on these photocatalysts were investigated.

2. Experimental Section

2.1. Catalysts. The FSM-16 mesoporous molecular sieve was supplied by Toyota Central R&D Lab. Ti/FSM-16 photocatalysts (Ti contents: 1wt%) were synthesized by four different preparation methods. (1) The TiO_2/FSM-16 photocatalyst was prepared by a physical mixture of FSM-16 with Degussa P-25 TiO_2 powder. (2) The imp-Ti/FSM-16 photocatalyst was prepared by impregnating FSM-16 with an aqueous solution of titanium ammonium oxalate. (3) The anc-Ti/FSM-16 photocatalyst was prepared by an anchoring method utilizing the reaction of tetraisopropyl orthotitanate (TPOT) with the surface hydroxyl groups of FSM-16. The FSM-16 and TPOT mixture solution was diluted in ethanol stirred and heated at 343 K for 1h. (4) The Ti-FSM-16 photocatalyst containing Ti-oxide species in the framework of FSM-16 was prepared by a pre-synthetic procedure; previously reported (Inagaki *et al*., 1996). The sodium silicate powder (Kishida Chemical, Japan) as a starting material, was impregnated with TPOT diluted in ethanol and the resulting products were calcined at 973 K for the formation of the precursor Ti-kanemite. All four samples were calcined at 823 K for 6 h in air before use.

2.2. *Photocatalytic Reactions.* The photocatalytic reduction of CO_2 with H_2O was carried out with the catalysts (50 mg) in a quartz cell with a flat bottom (88 ml) connected to a conventional vacuum system (10^{-4} Pa range). Prior to photoreactions and spectroscopic measurements, the catalysts were degassed at 723 K for 2 h, heated in O_2 at the same temperature for 6 h, and finally evacuated at 473 K for 2 h. UV irradiation of the catalysts in the presence of CO_2 (36 μmol) and gaseous H_2O (180 μmol) was carried out using a 100 W high-pressure Hg lamp at 323 K. The reaction products collected in the gas phase were analyzed by gas chromatography.

2.3. *Characterization.* The XRD patterns were recorded with a RIGAKU RINT 2500 using Cu Kα radiation. The diffuse reflectance absorption spectra were recorded with a Shimazu UV-2200A photospectrometer. The XAFS spectra (XANES and EXAFS) were measured at the BL-9A facility (Nomura *et al*., 1999) of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. The Ti K-edge absorption spectra were recorded in the fluorescence mode at room temperature. The photoluminescence spectra of the catalysts were measured at 77 K using a SPEX FLUOROLOG-3 spectrophotofluorometer.

3. Results and Discussion

The XRD patterns of the Ti/FSM-16 photocatalysts suggested the presence of a typical hexagonal structure, in agreement with those of FSM-16 shown in previous literature (Inagaki *et al*., 1996).

The diffuse reflectance absorption spectra of the variously prepared Ti/FSM-16 were also measured. For Ti-FSM-16 and anc-Ti/FSM-16, an absorption band centered at around 210 nm could be observed and this was attributed to the ligand-to-metal charge-transfer transition (LMCT) involving an electron transfer from the oxygen ligand to the Ti cation (Marchese *et al*., 1997). These results indicated that the Ti-oxides species are highly dispersed Ti-oxides having tetrahedral coordination. On the other hand, imp-Ti/FSM-16 and TiO_2/FSM-16 exhibited on absorption band at around 300 nm, indicating the presence of aggregated Ti-oxides or small TiO_2 particles.

Figure 1 shows the XAFS spectra of the various Ti/FSM-16 catalyst. The XANES spectra of the Ti-oxide photocatalysts at

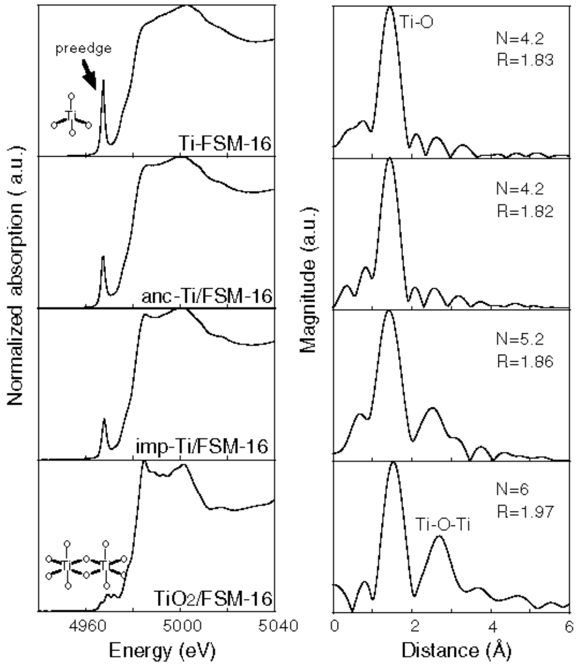

Figure 1
XAFS spectra of the Ti/FSM-16 photocatalysts prepared by various methods. Ti content : 1 wt%. N: Coordination number R: Ti-O bond distances (Å)

the Ti K-edge shows several well-defined preedge peaks which are related to the local structure surrounding the Ti atom. The relative intensities of the preedge peaks provide useful information on the coordination number surrounding the Ti atom. Ti-FSM-16 and anc-Ti/FSM-16 exhibited an intense single preedge peak which indicates that the Ti-oxides species of these photocatalysts exists in tetrahedral coordination (Zhang *et al*., 1997). On the other hand, the imp-Ti/FSM-16 and TiO_2/FSM-16 exhibited a weak preedge peak. This indicates the presence of aggregated octahedrally coordinated Ti-oxides on these photocatalysts.

Figure 1 also shows the Fourier transforms of EXAFS (FT-EXAFS) spectra of the photocatalysts shown without corrections for errors in the phase shift. All of the catalysts exhibited a strong peak at around 1.6 Å which can be assigned to the neighboring oxygen atoms (Ti-O bond). Ti-FSM-16 and anc-Ti/FSM-16 exhibited only Ti-O peaks, indicating the presence of the isolated Ti-oxides species on these photocatalysts. From the curve-fitting analysis of the EXAFS spectra, it was found that the tetrahedrally coordinated Ti-oxide species of Ti-FSM-16 and anc-Ti/FSM-16 consists of four Ti-O bonds having an atomic distance of 1.83 Å for Ti-FSM-16 and 1.82 Å for anc-Ti/FSM-16, in agreement with the results observed with the tetrahedral coordinated Ti-oxides incorporated within the zeolite framework (Liu *et al*., 1994; Yamashita *et al*., 1996). On the other hand, imp-Ti/FSM-16 and TiO_2/FSM-16 exhibited an intense peak at around 2.7 Å as well as the Ti-O peak. This peak can be assigned to the neighboring Ti atoms (Ti-O-Ti), indicating the aggregation of the Ti-oxide species on these photocatalysts. These results indicate that the Ti-oxide species of Ti-FSM-16 and anc-Ti/FSM-16 is isolated in tetrahedral coordination, while imp-Ti/FSM-16 and TiO_2/FSM-16 involve an aggregated octahedral Ti-oxide species. These findings are in good agreement with the results obtained from the diffuse absorption investigations.

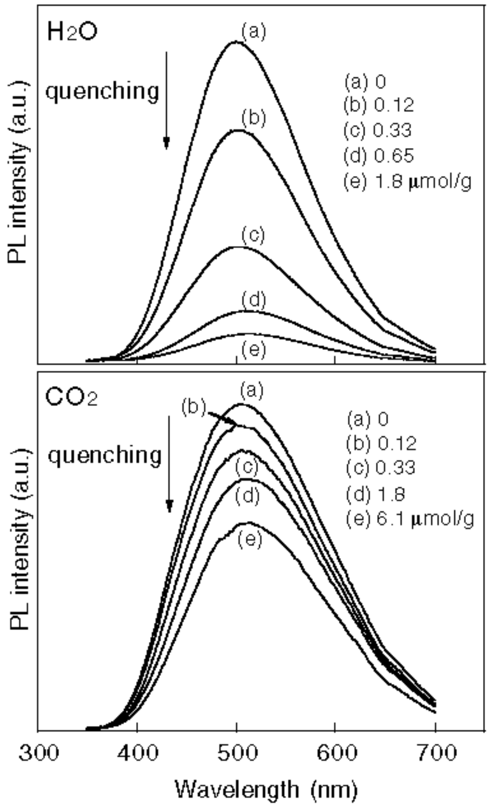

Figure 2
The effects of addition of H_2O and CO_2 on photoluminescence spectrum of Ti-FSM16 photocatalyst measured at 77 K. (Excitation at 260 nm)

Ti-FSM-16 exhibits a photoluminescence spectrum at around 500 nm by excitation at around 260 nm at 77 K, as shown in Fig. 2. The observed absorption and photoluminescence are attributed to the charge transfer absorption process on the tetrahedrally coordinated Ti-oxide species and the reverse radiative decay process from the charge transfer excited state to the ground state of the highly dispersed Ti-oxide species having a tetrahedral coordination, as shown in the scheme below (1) (Yamashita *et al*., 1996; Anpo *et al*., 1998). A similar photoluminescence spectrum could be observed for anc-Ti/FSM-16.

$$(\mathrm{Ti}^{4+} - \mathrm{O}^{2-}) \underset{h\nu'(\text{photoluminescence})}{\overset{h\nu(\text{absorption})}{\rightleftharpoons}} (\mathrm{Ti}^{3+} - \mathrm{O}^{-})^{*} \qquad (1)$$

On the other hand, the photoluminescence spectra of the imp-Ti/FSM-16 and TiO_2/FSM-16 having an aggregated octahedral Ti-oxide species could scarcely be observed.

As shown in Fig. 2, the addition of H_2O and CO_2 molecules onto Ti-FSM-16 led to an efficient quenching of the photoluminescence. Such an efficient quenching with CO_2 and H_2O additions suggests that these molecules interact the charge transfer excited state of the tetrahedrally coordinated Ti-oxide species.

UV irradiation of the Ti/FSM-16 photocatalysts in the presence of CO_2 and H_2O led to the formation of CH_3OH and CH_4 as the main products. Figure 3 shows the relationship between the yields of CH_4 and CH_3OH and the photoluminescence yield of the Ti-oxide species. It was found that anc-Ti/FSM-16 and Ti-FSM-16, with their higher photoluminescence yields, exhibit higher reactivity and selectivity for the formation of CH_3OH than imp-Ti/FSM-16 and TiO_2/FSM-16. These results suggest that the highly dispersed tetrahedrally coordinated Ti-oxide species exhibit higher reactivity and selectivity for CH_3OH formation and the charge transfer excited state of the highly dispersed tetrahedrally coordinated Ti-oxide species is important for the formation of CH_3OH on the Ti/FSM-16 photocatalysts.

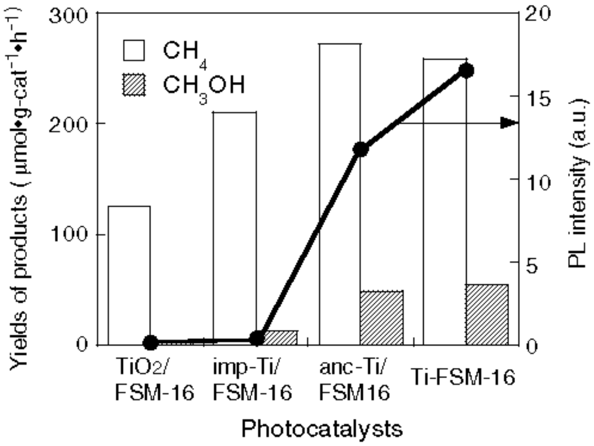

Figure 3

Yields of the products formed in the photocatalytic reduction of CO_2 with H_2O and pholuminescence of various Ti/FSM-16 photocatalysts.

4. Conclusions

It was found that the dispersion state and the local structure of the Ti-oxide species on the Ti/FSM-16 photocatalysts depending on the preparation methods. UV irradiation of the Ti/FSM-16 photocatalysts in the presence of CO_2 and H_2O led to the formation of CH_4 and CH_3OH. Anc-Ti/FSM-16 and Ti-FSM-16, with the presence of a highly dispersed tetrahedrally coordinated Ti-oxide species, exhibited high photocatalytic reactivity and a remarkably high yield of CH_3OH formation. The formation of CH_3OH was closely related to the yield of the photoluminescence attributed to the charge transfer excited state of the highly dispersed tetrahedrally coordinated Ti-oxide species $(Ti^{3+}\text{-} O^{-})^{*}$.

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