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Photocatalytic reduction of CO_2 with H_2O on Ti-MCM-41 and Ti-MCM-48 mesoporous zeolite catalysts

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Abstract

Titanium oxide species included within the framework of mesoporous zeolites (Ti-MCM-41 and Ti-MCM-48) prepared by a hydrothermal synthesis exhibited high and unique photocatalytic reactivity for the reduction of CO_2 with H_2O at 328 K to produce CH_4 and CH_3OH in the gas phase. In situ photoluminescence, diffuse reflectance absorption, ESR and XAFS investigations indicated that the titanium oxide species are highly dispersed within the zeolite framework and exist in tetrahedral coordination. The charge transfer excited state of the highly dispersed titanium oxide species played a significant role in the reduction of CO_2 with H_2O exhibiting a high selectivity for the formation of CH_3OH.

Keywords: Photocatalytic reduction of CO_2 with H_2O; Ti-mesoporous zeolite; Ti-MCM-48; Ti-MCM-41; Selective CH_3OH formation

1. Introduction

The utilization of the zeolite cavity and framework is attractive to the design and application of highly efficient and selective photocatalytic systems, because zeolites provide unique micropore reaction fields, an unusual internal surface topology, and an ion-exchange capacity as well as molecular condensation effect [1,2]. Recently, zeolites involving transition metal ions within the zeolite framework have opened new possibilities in many research areas not only for catalysis but also for various photochemical processes [3–6]. The titanium oxide species prepared within the zeolite cavities and framework have revealed a unique local structure as well as a high selectivity in the oxidation of organic substances with hydrogen peroxide [7,8]. However, the true chemical nature and reactivities of these titanium oxide species as a photocatalyst are yet little known, especially the photocatalytic reactivity of the Ti-containing mesoporous zeolites.

The efficient photocatalytic reduction of CO_2 with H_2O is one of the most desirable and challenging goals in the research of environmentally friendly catalysts [9–16]. Although pioneering works on the photoreduction of CO_2 on semiconductors in aqueous suspension systems were summarized by Halmann [9] and

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recent work in solid–gas systems were reviewed by Anpo and Yamashita [10], the efficiency of CO_2 reduction was low when water was used as the reductant. Recently, several researchers have reported that the photocatalytic reduction of CO_2 with gaseous H_2O proceeded on powdered TiO_2 at room temperature to form small amounts of CH_4 [10–16]. It was also found that the highly dispersed titanium oxide catalysts anchored on Vycor glass and Y-zeolite exhibit a high and characteristic photocatalytic reactivity compared to bulk TiO_2 powder [11,14].

In the present study, highly dispersed titanium oxides included within the zeolite framework were prepared using a hydrothermal synthesis to be used as photocatalysts for the reduction of CO_2 with H_2O at 328 K. The characterization of these catalysts by means of in situ photoluminescence, diffuse reflectance absorption, XAFS (XANES and FT–EXAFS), and ESR measurements have been carried out to clarify the characteristics of the photocatalytic reduction of CO_2 with H_2O at 328 K. Special attention has been focused on the relationship between the local structure of the titanium oxide species and the reaction selectivity in the photocatalytic reduction of CO_2 with H_2O to form CH_3OH. The effects of pore size and geometry of zeolite cavities on the photocatalytic efficiency have also been clarified by comparing the results obtained with Ti-containing mesoporous zeolites (Ti-MCM-41, Ti-MCM-48) and Ti-microporous (TS-1) zeolite.

2. Experimental

Ti-MCM-41 (Si/Ti=100), Ti-MCM-48 (Si/Ti=80) and TS-1 (Si/Ti=85) were hydrothermally synthesized according to procedures reported previously [15]. The Pt-loaded Ti-MCM-48 (0.1 and 1.0 wt% Pt) were prepared by impregnating with an aqueous solution of H_2PtCl_6. TiO_2 powdered catalysts (JRC-TIO-4: anatase 92%, rutile 8%) were supplied by the Catalysis Society of Japan.

The photocatalytic reduction of CO_2 with H_2O was carried out with the catalysts in a quartz cell with a flat bottom connected to a conventional vacuum system (10^{-6} Torr range) [15,17]. Prior to photoreactions and spectroscopic measurements, the catalysts were heated in O_2 at 725 K for 2 h and then evacuated at 475 K for 1 h. In the case of Pt-loaded catalysts, the pretreated catalyst was heated in H_2 at 475 K for 2 h and evacuated at 475 K for 1 h. UV irradiation of the catalysts in the presence of CO_2 (24 μmol) and gaseous H_2O (120 μmol) was carried out using a high-pressure Hg lamp (λ>280 nm) at 328 K. The reaction products collected in the gas phase were analyzed by gas chromatography.

The photoluminescence spectra were measured at 77 K using a Shimadzu RF-5000 spectrophotofluorometer. The diffuse reflectance absorption spectra were recorded with a Shimadzu UV-2200A spectrometer at 295 K. The ESR spectra were recorded at 77 K using a JEOL JES-RE2X spectrometer in the X-band mode. The XAFS (XANES and EXAFS) spectra were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. The Ti K-edge absorption spectra were recorded in the transmission mode or fluorescence mode at 295 K. The normalized spectra were obtained by a procedure described in previous literature [18] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 3–10 $Å^{-1}$. The curve-fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method and the empirical backscattering parameter sets extracted from the shell features of titanium compounds.

3. Results and discussion

3.1. Characterization of zeolite catalysts

Fig. 1 shows the absorption spectra of the Ti-containing zeolites and bulk TiO_2 powder measured by the UV diffuse reflectance method. The Ti-containing zeolites exhibit absorption bands in the wavelength regions of 220–280 nm, shifting into shorter wavelength regions as compared to the bulk TiO_2 catalyst. Such a shift to the shorter wavelength in the absorption band of titanium oxides can be attributed to the presence of titanium oxide species having a tetrahedral coordination [14,19].

Fig. 2 shows the XANES spectra of the titanium oxide catalysts. The XANES spectra of the titanium oxide catalysts at the Ti K-edge show several well-defined preedge peaks which are related to the local

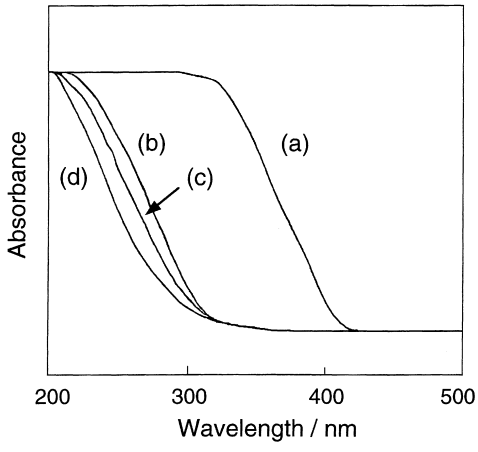

Fig. 1. The diffuse reflectance absorption spectra of TiO_2 powder (a), Ti-MCM-48 (b), Ti-MCM-41 (c), and TS-1 (d) zeolite catalysts.

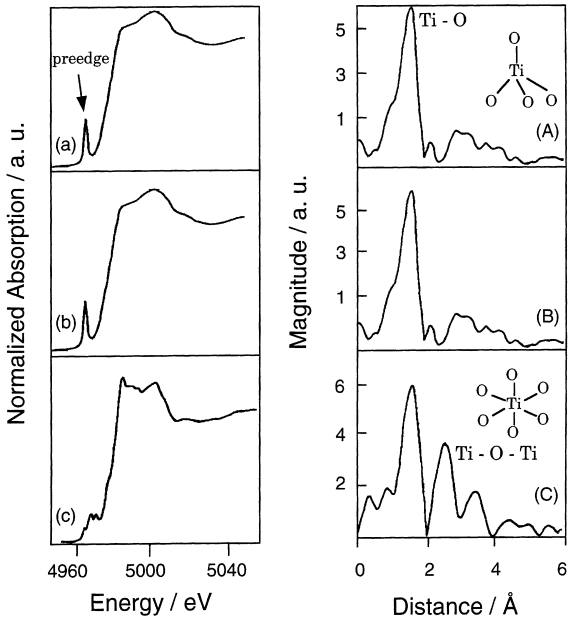

Fig. 2. The XANES (a)–(c) and FT–EXAFS (A)–(C) spectra of Ti-MCM-41 (a, A) and Ti-MCM-48 (b, B) zeolite catalysts and TiO_2 powder (c, C).

structures surrounding the Ti atom. These relative intensities of the preedge peaks provide useful information on the coordination number surrounding the Ti atom [14,18,19]. As shown in Fig. 2(a) and (b), the Ti-mesoporous zeolites exhibit an intense single preedge peak which is similar to that of TS-1, while the bulk TiO_2 powder exhibits three characteristic weak pre-edge peaks attributed to the transitions from the 1s core level of Ti to three different kinds of molecular orbitals ($1t_{1g}$, $2t_{2g}$, and $3e_g$) of anatase TiO_2. Because tetrahedrally coordinated Ti such as $Ti(OPr^i)_4$ was found to exhibit an intense single preedge peak due to the lack of an inversion center in the regular tetrahedron structure, the observation of this intense single preedge peak indicates that the titanium oxide species included within the framework of mesoporous zeolites have a tetrahedral coordination.

Fig. 2 also shows the FT–EXAFS spectra of the catalysts and all data are given without corrections for phase shifts. All of the catalysts investigated in the present study exhibit a strong peak at around 1.6 Å (uncorrected for the phase shift) which can be assigned to the neighboring oxygen atoms (a Ti–O bond). The Ti-MCM-41 (Fig. 2(A)) and Ti-MCM-48 (Fig. 2(B)) as well as TS-1 exhibit only Ti–O peaks indicating the presence of the isolated titanium oxide species on these catalysts. From the results obtained by the curve-fitting analysis of the EXAFS spectra, as shown in Fig. 2, it was found that the Ti-mesoporous zeolites consist of 4-coordinate titanium ions with an atomic distance of 1.86 Å for Ti-MCM-41 and 1.88 Å for Ti-MCM-48. These atomic distances are a little longer than those observed with tetrahedrally coordinated titanium oxide included within the framework of silicalite zeolite (TS-2), 1.81 Å [5,20], but much shorter than that of the bulk TiO_2, 1.96 Å [18]. These XANES and FT–EXAFS investigations indicate that the dispersion level of the titanium oxide species is high in the present Ti-containing zeolites and the tetrahedral titanium oxide species are included within the zeolite framework.

Ti-containing zeolites exhibited a photoluminescence spectrum at around 450–600 nm by an excitation at around 260–290 nm at 77 K. Fig. 3 shows the typical photoluminescence observed on Ti-MCM-48 by the excitation with UV light. The observed photoluminescence and absorption bands are in good agreement with those previously observed with the highly dispersed tetrahedrally coordinated titanium oxides prepared in silica matrices, where the absorption of UV light at around 280 nm brings about an electron transfer from the lattice oxygen (O_l^{2-}) to the titanium ion (Ti^{4+}) to form a charge transfer excited state

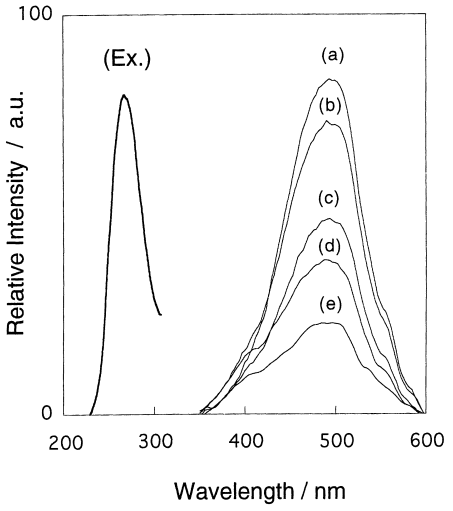

Fig. 3. Photoluminescence spectrum of the Ti-MCM-48 zeolite catalyst (a) and the effects of the addition of H_2O (b)–(e) on the spectrum. Measured at 77 K, excitation at 270 nm, pressure of H_2O: (b) 0.1, (c) 0.5, (d) 1.0 and (e) 5.0 Torr.

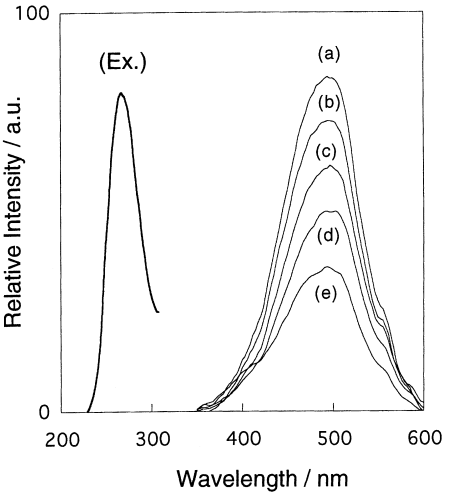

Fig. 4. Photoluminescence spectrum of the Ti-MCM-48 zeolite catalyst (a) and the effects of the addition of CO_2 (b)–(e) on the spectrum. Measured at 77 K, excitation at 270 nm, pressure of CO_2: (b) 0.1, (c) 0.5, (d) 2.0 and (e) 10.0 Torr.

[11,18]. We can therefore conclude that the observed photoluminescence spectrum is attributed to the radiative decay process from the charge transfer excited state formed in this way to the ground state of the highly dispersed titanium oxide species having a tetrahedral coordination as shown in the following scheme:

$$(Ti^{4+}-O^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (Ti^{3+}-O^{-})^*$$

The lifetimes of the charge transfer excited state of the Ti-containing zeolites were determined to be much longer (micro-second order) than that of the TiO_2 powder (nano-second order). Such a long lifetime of the charge transfer excited state is well associated with the presence of highly dispersed tetrahedral titanium oxide species. These results clearly indicate that the Ti-containing zeolites consist of the highly dispersed isolated tetrahedral titanium oxide species in their framework, being in good agreement with results obtained by XAFS investigations.

As shown in Figs. 3 and 4, the addition of H_2O or CO_2 molecules onto the Ti-containing zeolites leads to the efficient quenching of the photoluminescence with different efficiencies. The lifetime of the charge transfer excited state was also found to be shortened by the addition of CO_2 or H_2O, its extent depending on the amount of added gasses. Such an efficient quenching of the photoluminescence with CO_2 or H_2O suggests not only that tetrahedrally coordinated titanium oxide species locate at positions accessible to the added CO_2 or H_2O but also that added CO_2 or H_2O interacts with the titanium oxide species in both its ground and excited states. The addition of CO_2 was less effective for the quenching of the photoluminescence in their intensities and lifetimes than those observed by the addition of H_2O, indicating that the interaction of CO_2 with the titanium oxide species is weaker than that of H_2O.

3.2. *Photocatalytic reduction of CO_2 with H_2O*

UV irradiation of powdered TiO_2 and Ti-containing zeolites in the presence of a mixture of CO_2 and H_2O led to the evolution of CH_4 and CH_3OH in the gas phase at 328 K, as well as trace amounts of CO, C_2H_4 and C_2H_6. The evolution of small amounts of O_2 was also observed. The rates of these photoformed products increased linearly against the UV irradiation time and the reaction immediately ceased when the irradiation was discontinued. The formation of these reaction products were neither detected in dark con-

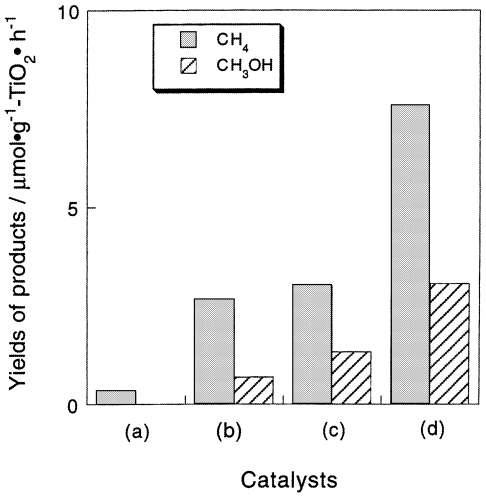

Fig. 5. The yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O on TiO_2 powder (a), TS-1 (b), Ti-MCM-41 (c), and Ti-MCM-48 (d) zeolite catalysts.

ditions nor with UV irradiation of the zeolites without titanium oxides. These results clearly indicate that the presence of both titanium oxides included within the zeolite framework as well as UV irradiation are indispensable for the photocatalytic reduction of CO_2 with H_2O to take place on the catalysts.

The specific photocatalytic reactivities for the formation of CH_4 and CH_3OH are shown in Fig. 5. It is clear that the photocatalytic reaction rate and selectivity for the formation of CH_3OH strongly depend on the type of catalyst. It can be seen that the specific photocatalytic reactivities of the Ti-containing zeolites which have been normalized by a unit gram of TiO_2 in the catalysts are much higher than bulk TiO_2. The Ti-containing zeolites lead to the formation of considerable amount of CH_3OH, while the formation of CH_4 is found to be the major reaction on bulk TiO_2.

Among Ti-containing zeolites, Ti-MCM-48 exhibits much higher reactivity than either TS-1 or Ti-MCM-41. Besides the higher dispersion state of the titanium oxide species, other distinguishing features of these zeolite catalysts are: TS-1 has a smaller pore size (ca. 5.7 Å) and a three-dimensional channel structure; Ti-MCM-41 has a large pore size (>20 Å) but a one-dimensional channel structure; and Ti-MCM-48 has both large pore size (>20 Å) and three-dimensional channels. Thus, the higher reactivity and higher selectivity for the formation of CH_3OH observed with the Ti-MCM-48 zeolite than with any other catalysts used here may be a combined contribution of the high dispersion state of the titanium oxide species and large pore size having a three-dimensional channel structure.

UV irradiation of the anchored titanium oxide catalyst in the presence of CO_2 and H_2O at 77 K led to the appearance of ESR signals due to the Ti^{3+} ions, H atoms, and carbon radicals [11,13]. From these results the reaction mechanism in the photocatalytic reduction of CO_2 with H_2O on the highly dispersed titanium oxide catalyst can be proposed in the following way. CO_2 and H_2O molecules interact with the excited state of the photoinduced $(Ti^{3+}–O^-)^*$ species and the reduction of CO_2 and the decomposition of H_2O proceed competitively. Furthermore, H atoms and $OH^\cdot$ radicals are formed from H_2O and these radicals react with the carbon species formed from CO_2 to produce CH_4 and CH_3OH.

The effect of Pt-loading on the photocatalytic reactivity of Ti-MCM-48 has also been investigated. The changes in the yields of CH_4 and CH_3OH formation with the amount of Pt-loading are shown in Fig. 6. Although the addition of Pt onto the Ti-MCM-48 is effective in increasing the photocatalytic reactivity, only the formation of CH_4 is promoted, accompanied by a decrease in the CH_3OH yields. Pt-loading onto

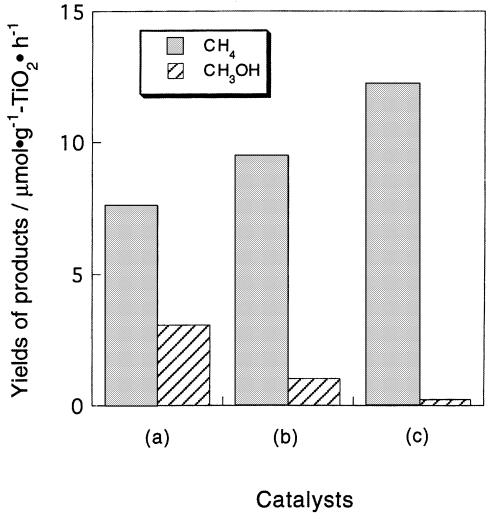

Fig. 6. The effects on Pt-loading on the yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O on the Ti-MCM-48 zeolite catalyst. (a) Ti-MCM-48, (b) Pt-loaded Ti-MCM-48 (0.1 wt% as Pt), and (c) Pt-loaded Ti-MCM-48 (1.0 wt% as Pt).

the Ti-MCM-48 led to an efficient quenching of the photoluminescence, accompanied by the shortening of its lifetime. Because the results obtained by EXAFS and absorption measurements indicated that the local structure of the Ti-oxide species in the Ti-MCM-48 was not altered by the Pt-loading, the effective quenching of the photoluminescence can be attributed to the electron transfer from the photo-excited titanium oxide species to Pt metals. As a result, on the Pt-loaded Ti-MCM-48, photocatalytic reactions which proceed in the same manner as on bulk TiO_2 become predominant, meaning that the reduction reaction by electrons and the oxidation reaction by holes occurring separately from each other on different sites becomes predominant, leading to the selective formation of CH_4.

4. Conclusions

The titanium oxide species included within the zeolite framework have been found to exist as isolated tetrahedral titanium oxide species. These Ti-containing zeolite catalysts exhibited high photocatalytic efficiency and selectivity for the formation of CH_3OH in the photocatalytic reduction of CO_2 with H_2O, while the bulk TiO_2 powdered catalyst led to the formation of CH_4 alone. The present results indicate that the charge transfer excited complexes of the isolated tetrahedral titanium oxides, $(Ti^{3+}–O^{-})^{*}$, formed under UV irradiation play a significant role in the formation of CH_3OH. Especially, Ti-MCM-48 having a large pore size (>20 Å) and three-dimensional channels exhibited a significant high reactivity and selectivity for the formation of CH_3OH, suggesting that the zeolite structure with large pore sizes having a three-dimensional channel structure is suitable not only for achieving the high dispersion state of the titanium oxide species but also for achieving the high efficiency in the photocatalytic reduction of CO_2 with H_2O to produce CH_3OH.

Although the detailed reaction mechanisms behind the present reaction deserves further investigation, the present results strongly indicate that mesoporous zeolites with highly dispersed titanium oxide species in their framework are promising candidates to serve as effective photocatalysts for the photoreduction of CO_2 with H_2O.

Acknowledgements

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