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Selective formation of CH_3OH in the photocatalytic reduction of CO_2 with H_2O on titanium oxides highly dispersed within zeolites and mesoporous molecular sieves

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Abstract

Highly dispersed titanium oxide catalysts have been prepared within zeolite cavities as well as in the zeolite framework and utilized as photocatalysts for the reduction of CO_2 with H_2O to produce CH_4 and CH_3OH at 328 K. In situ photoluminescence, ESR, diffuse reflectance absorption and XAFS investigations indicate that the titanium oxide species are highly dispersed within the zeolite cavities and framework and exist in tetrahedral coordination. The charge transfer excited state of the highly dispersed titanium oxide species play a significant role in the reduction of CO_2 with H_2O with a high selectivity for the formation of CH_3OH, while the catalysts involving the aggregated octahedrally coordinated titanium oxide species show a high selectivity to produce CH_4, being similar to reactions on the powdered TiO_2 catalysts. Ti-mesoporous molecular sieves exhibit high photocatalytic reactivity for the formation of CH_3OH, its reactivity being much higher than the powdered TiO_2 catalysts. The addition of Pt onto the highly dispersed titanium oxide catalysts promotes the charge separation which leads to an increase in the formation of CH_4 in place of CH_3OH formation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalyst; Photocatalytic NO decomposition; Titanium oxide; Zeolite; Mesoporous molecular sieve

1. Introduction

The large-scale emission of carbon dioxide into the atmosphere is one of the most serious problems upon the earth, especially with regard to the devastating consequences of the greenhouse effect. The reduction and/or fixation of carbon dioxide can be said to be one of the most important areas of research in chemistry today, not only for solving the many urgent problems resulting from the pollution of the global environment but also for finding ways to maintain vital carbon resources which are being depleted by the burning of fossil fuels as well as making the design of an artificial photosynthesis reaction system possible. The design of highly efficient and selective photocatalytic systems for the reduction of CO_2 with H_2O is of vital interest [1–9]. Although pioneering works on the photoreduction of CO_2 on semiconductors in aqueous suspension systems were summarized by Halmann [1] and recent work in solid–gas systems were reviewed by Anpo and Yamashita [2], the efficiency of CO_2 reduction was low when water was used as the reductant. Recently, it has been found that the photocatalytic reduction of CO_2 with gaseous H_2O proceeded on

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powdered TiO_2 at 328 K [2,4,7]. The highly dispersed titanium oxide (Ti-oxide) catalyst anchored on porous Vycor glass exhibited a high and characteristic photocatalytic reactivity compared to bulk TiO_2 powder [2,3,7].

The utilization of the zeolite cavity spaces is also vital to the design and application of highly efficient and selective photocatalytic systems because zeolites offer unique nano-scaled pore reaction fields, an unusual internal surface topology, and ion-exchange capacities. Unique photocatalytic properties which cannot be realized in normal catalytic systems have been observed recently in such modified reaction spaces [8–12]. The Ti-oxide species prepared within the zeolite cavities or the zeolite framework have been revealed a unique local structure as well as a high photocatalytic reactivity for the decomposition of NO_x into N_2 and O_2 [12]. However, the true chemical nature of these Ti-oxide species as photocatalysts are yet little known, especially the photocatalytic reactivity for the reduction of CO_2 with H_2O.

In the present study, highly dispersed Ti-oxides included within the zeolite cavities and framework were prepared using an ion-exchange method and hydrothermal synthesis and utilized as photocatalysts for the reduction of CO_2 with H_2O at 328 K. Special attention has been focused on the relationship between the structure of the Ti-oxide species and the reaction selectivity in the photocatalytic reduction of CO_2 with H_2O to form CH_3OH. The effect of size and structure of zeolite cavities on the photocatalytic reactivity were also investigated using Ti-mesoporous zeolite catalysts. In addition, the effects of the addition of Pt on the photocatalytic properties has been studied in order to obtain useful and important information required for the design and application of highly active and selective photocatalytic systems.

2. Experimental

The Ti-oxide/Y-zeolite (1.1 wt% as TiO_2) was prepared by ion-exchange with an aqueous titanium ammonium oxalate solution using Y-zeolite samples (SiO_2/Al_2O_3=5.5) (ex-Ti-oxide/Y-zeolite). Ti-oxide/Y-zeolites having different Ti contents (1.0 and 10 wt% as TiO_2) were prepared by impregnating the Y-zeolite with an aqueous solution of titanium ammonium oxalate (imp-Ti-oxide/Y-zeolite). TS-1 (Si/Ti=85), Ti-MCM-41 (Si/Ti=100) and Ti-MCM-48 (Si/Ti=80) were hydrothermally synthesized according to procedures reported previously [9,12]. The features of mesoporous molecular sieves are: the pore volume (ml g^{-1}): 0.79 (Ti-MCM-41), 1.1 (Ti-MCM-48); the pore size (Å): 27 (Ti-MCM-41), 25 (Ti-MCM-48); the unit cell size a_0 (Å): 44.3 (Ti-MCM-41), 87.2 (Ti-MCM-48) [12]. The Pt-loaded ex-Ti-oxide/Y-zeolite and Pt-loaded Ti-MCM-48 (1.0 wt% as 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 as standard reference by the Catalysis Society of Japan.

The photocatalytic reduction of CO_2 with H_2O was carried out with the catalysts (150 mg of the catalyst involving zeolite) in a quartz cell with a flat bottom (88 ml) connected to a conventional vacuum system (10^{-6} Torr range). 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 spectra (XANES and EXAFS) were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba.

3. Results and discussion

3.1. Ti-oxide/Y-zeolite prepared by the ion-exchange method

UV irradiation of powdered TiO_2 and Ti-oxide/Y-zeolite catalysts prepared by ion-exchange or impreg-

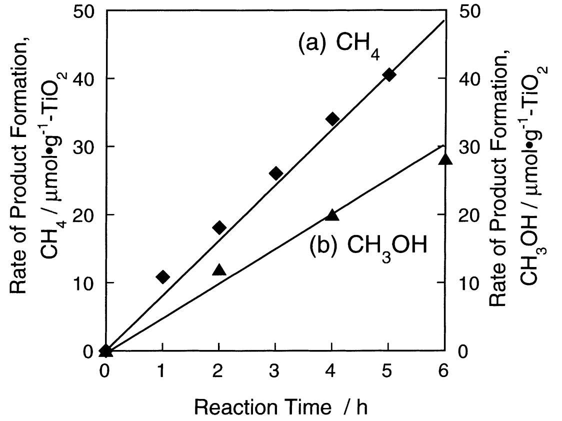

Fig. 1. The reaction time profiles of the photocatalytic reduction of CO_2 with H_2O to produce CH_4 (a) and CH_3OH (b) on the ex-Ti-oxide/Y-zeolite catalyst.

nation methods 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. As shown in Fig. 1, the yields of these photoformed products increase linearly against the UV irradiation time and the reaction immediately ceases when irradiation is discontinued, indicating the photocatalytic reduction of CO_2 with H_2O on the catalysts. The specific photocatalytic reactivities for the formation of CH_4 and CH_3OH are shown in Fig. 2. 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-oxide/Y-zeolite catalysts which have been normalized by unit gram of Ti in the catalysts are much higher than bulk TiO_2. The ex-Ti-oxide/Y-zeolite exhibits a high reactivity and a high selectivity for the formation of CH_3OH while the formation of CH_4 was found to be the major reaction on bulk TiO_2 as well as on the imp-Ti-oxide/Y-zeolite.

The absorption spectra of the Ti-oxide/Y-zeolite and bulk TiO_2 catalysts were measured by the UV diffuse reflectance method. A significant shift to shorter wavelengths in the absorption band was observed with the ex-Ti-oxide/Y-zeolite, clearly suggesting that the dispersion of the Ti-oxide species on this catalyst was higher than on catalysts prepared by impregnation methods. Thus, a clear relationship can be seen between the reactivity for the photocatalytic reduction of CO_2 with H_2O, especially to form CH_3OH, and the magnitude of the shift toward the shorter wavelength of these catalysts.

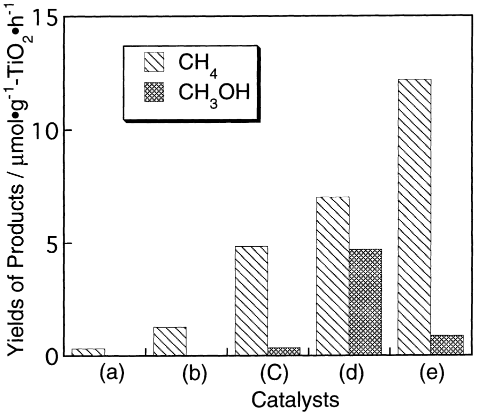

Fig. 2. The product distribution of the photocatalytic reduction of CO_2 with H_2O on anatase TiO_2 powder (a), the imp-Ti-oxide/Y-zeolite (10.0 wt% as TiO_2) (b), the imp-Ti-oxide/Y-zeolite (1.0 wt% as TiO_2) (c), the ex-Ti-oxide/Y-zeolite (1.1 wt% as TiO_2) (d), the Pt-loaded ex-Ti-oxide/Y-zeolite (e) catalysts.

Fig. 3 shows the XANES spectra of the Ti-oxide/Y-zeolite catalysts. The XANES spectra of the Ti-oxide catalyst at the Ti K-edge show several well-defined pre-edge peaks which are related to the local structures surrounding the Ti atom. The ex-Ti-oxide/Y-zeolite exhibits an intense single pre-edge peak, indicating that the Ti-oxide species in this catalyst have a tetrahedral coordination [9]. On the other hand, the imp-Ti-oxide/Y-zeolite exhibits three characteristic weak pre-edge peaks attributed to crystalline anatase TiO_2. Fig. 3 also shows the FT-EXAFS spectra of the catalysts and all data are given without corrections for phase shifts. The ex-Ti-oxide/Y-zeolite exhibits peak only at around 1.6 Å assigned to the neighboring oxygen atoms (Ti–O) indicating the presence of isolated Ti-oxide species in this catalyst. From the curve-fitting analysis of the EXAFS spectra, it was found that the ex-Ti-oxide/Y-zeolite catalyst consists of 4-coordinate titanium ions with a coordination number (N) of 3.7 and an atomic distance (R) of 1.78 Å. On the other hand, the imp-Ti-oxide/Y-zeolite catalysts exhibit an intense peak at around 2.7 Å assigned to the neighboring titanium atoms behind the oxygen (Ti–O–Ti), indicating the aggregation of the Ti-oxide species in these catalysts.

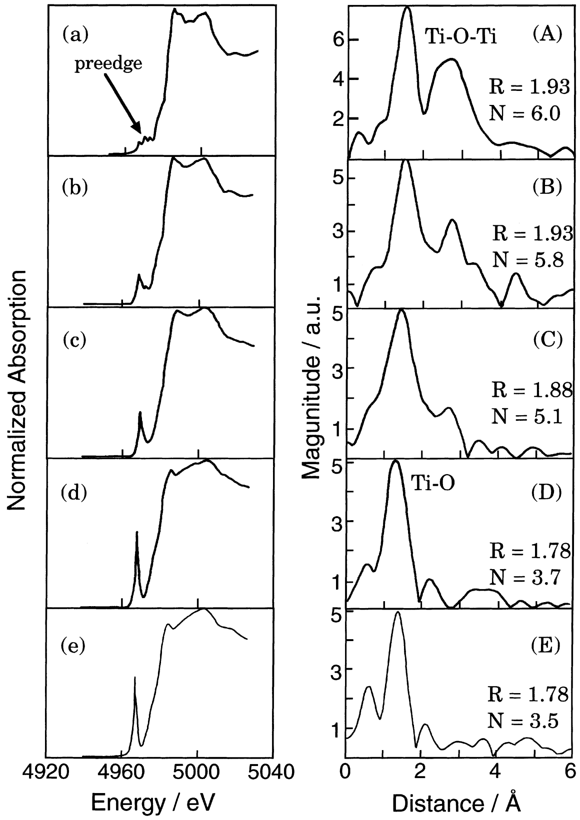

Fig. 3. The XANES (a–d) and FT-EXAFS (A–D) spectra of anatase TiO_2 powder (a, A), the imp-Ti-oxide/Y-zeolite (10.0 wt% as TiO_2) (b, B), the imp-Ti-oxide/Y-zeolite (1.0 wt% as TiO_2) (c, C), the ex-Ti-oxide/Y-zeolite (d, D), and the Pt-loaded ex-Ti-oxide/Y-zeolite (e, E) catalysts.

Fig. 4 shows that the ex-Ti-oxide/Y-zeolite catalyst exhibits a photoluminescence spectrum at around 490 nm by excitation at around 290 nm at 77 K. The observed photoluminescence and absorption bands are in good agreement with those previously observed with the highly dispersed tetrahedrally coordinated Ti-oxides prepared in silica matrices [3,12]. We can therefore conclude that the observed photoluminescence spectrum is attributed to the radiative decay process from the charge transfer excited state to the ground state of the highly dispersed Ti-oxide species in tetrahedral coordination as shown in Scheme 1. On the other hand, the imp-Ti-oxide/Y-zeolite catalysts did not exhibit any photoluminescence spectrum. Thus, these results clearly indicate that the ex-Ti-oxide/Y-zeolite catalyst consists of highly dispersed isolated tetrahedral Ti-oxide species, while the imp-Ti-oxide/Y-zeolite catalysts involve the aggregated octahedral Ti-oxide species which do not exhibit any photoluminescence spectrum.

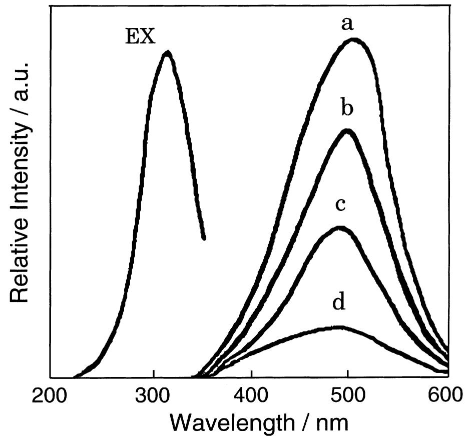

Fig. 4. Photoluminescence spectrum of the ex-Ti-oxide/Y-zeolite catalyst (a), its excitation spectrum (EX), and the effects of the addition of CO_2 and H_2O (b, c) and the loading of Pt (d) on the photoluminescence spectrum. Measured at 77 K, excitation at 290 nm, emission monitored at 490 nm, amounts of added CO_2: (b) 8.5, and H_2O; (c) 2.9 μmol g^{-1}.

As shown in Fig. 4, the addition of H_2O or CO_2 molecules onto the ex-Ti-oxide/Y-zeolite catalyst leads to an efficient quenching of the photoluminescence. 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 gases. Such an efficient quenching of the photoluminescence with CO_2 or H_2O suggests not only that tetrahedrally coordinated Ti-oxide species locate at positions accessible to the added CO_2 or H_2O but also that added CO_2 or H_2O interacts and/or reacts with the Ti-oxide species in both its ground and excited states.

UV irradiation of the anchored Ti-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 [7,8]. From these results the reaction mechanism in the photocatalytic reduc-

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

Scheme 1.

tion of CO_2 with H_2O on the highly dispersed Ti-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 $OH^•$ 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.

3.2. *Ti-mesoporous molecular sieves prepared by the hydrothermal synthesis*

In situ photoluminescence, ESR, diffuse reflectance absorption and XAFS investigations indicate that the Ti-oxide species in the Ti-mesoporous molecular sieves (Ti-MCM-41 and Ti-MCM-48) and the TS-1 zeolite are highly dispersed within their framework and exist in a tetrahedral coordination. Upon excitation with UV light at around 260–290 nm, these catalysts exhibit photoluminescence spectra at around 450–650 nm, as shown in Fig. 5. The addition of CO_2 or H_2O onto these catalysts results in a significant quenching of these photoluminescence spectra, suggesting the excellent accessibility of the Ti-oxide species to CO_2 and H_2O. In addition, quenching with H_2O is much more effective than with CO_2 reflecting the stronger interaction of H_2O with the Ti-oxide species.

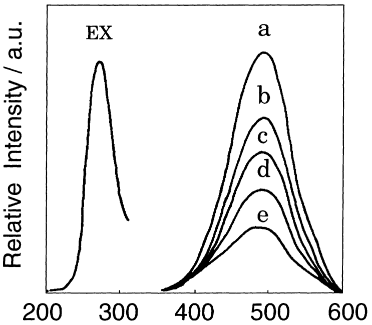

Fig. 5. Photoluminescence spectrum of the Ti-MCM-48 catalyst (a), its excitation spectrum (EX), and the effects of the addition of CO_2 and H_2O on the photoluminescence spectrum. Measured at 77 K, excitation at 290 nm, emission monitored at 480 nm, amounts of added CO_2: (b) 2.7, (d) 54 and H_2O: (c) 2.7, and (e) 27 µmol g^{-1}.

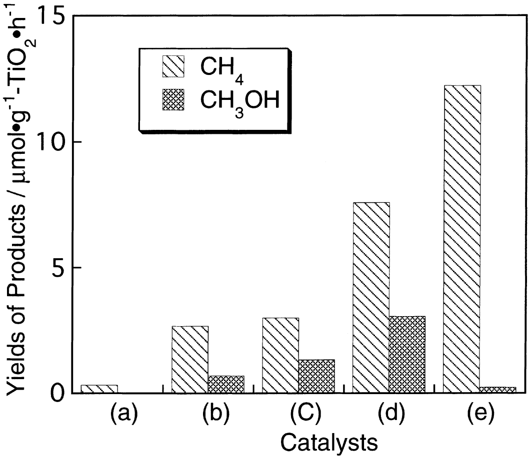

Fig. 6. The yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O on TiO_2 powder (a), TS-1 (b), Ti-MCM-41 (c), Ti-MCM-48 (d), and the Pt-loaded Ti-MCM-48 (e) catalysts.

UV irradiation of the Ti-mesoporous zeolites and the TS-1 zeolite in the presence of CO_2 and H_2O also led to the formation of CH_3OH and CH_4 as the main products. The yields of CH_4 and CH_3OH per unit weight of the Ti-based catalysts are shown in Fig. 6. It can be seen that Ti-MCM-48 exhibits much higher reactivity than either TS-1 or Ti-MCM-41. Besides the higher dispersion state of the Ti-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 one-dimensional channel structure; Ti-MCM-48 has both a large pore size (>20 Å) and three-dimensional channels [13,14]. 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 Ti-oxide species and large pore size having a three-dimensional channel structure. Although the detailed reaction mechanisms behind the present reaction deserves further investigation, the present results strongly indicate that mesoporous zeolites with highly dispersed Ti-oxide species in their framework are promising candidates to serve as effective photocatalysts for the photoreduction of CO_2 with H_2O.

3.3. *Effect of Pt-loading*

The effect of Pt-loading on the photocatalytic reactivity of Ti-containing zeolite and molecular sieve has also been investigated and the changes in the yields of CH_4 and CH_3OH formation are shown in Figs. 2 and 6. Although the addition of Pt onto the Ti-containing catalysts is effective in an increase in the photocatalytic reactivity, only the formation of CH_4 is promoted, accompanied by a decrease in the CH_3OH yields. The absorption spectra of the Pt-loaded catalysts were the same as those observed with original Ti-containing catalyst without Pt-loading. As shown in Fig. 5, the Pt-loaded catalyst also exhibits the same pre-edge peak in the XANES spectra and the same Ti–O bonding peak in the FT-EXAFS spectra as those of original Ti-containing catalyst. Furthermore, as shown in Fig. 4, Pt-loading onto the Ti-containing catalyst leads to an efficient quenching of the photoluminescence, accompanied by the shortening of its lifetime. Because the results obtained by XAFS and absorption measurements indicate that the local structure of the Ti-oxide species dispersed in the catalyst was not altered by the Pt loading, the effective quenching of the photoluminescence can be attributed to the electron transfer from the photo-excited Ti-oxide species to Pt metals which exist in the neighborhood of the Ti-oxide species. The electrons are easily transferred from the charge transfer excited state of Ti-oxide species, electron–hole pair state of $(Ti^{3+}–O^{-})^{*}$, to the Pt moieties while the holes remain in Ti-oxide species, resulting in the charge separation of electrons and holes from the photo-formed electron–hole pair states. As a result, on Pt-loaded Ti-containing zeolite catalyst, photocatalytic reactions which proceed in the same manner as on bulk TiO_2 catalysts become predominant, and the reduction reaction by electrons and the oxidation reaction by holes occur separately from each other on different sites, leading to the selective formation of CH_4.

4. Conclusions

An efficient photocatalytic reactivity and selectivity for the formation of CH_3OH in the photocatalytic reduction of CO_2 with H_2O was achieved with the ex-Ti-oxide/Y-zeolite catalyst having highly dispersed tetrahedral Ti-oxide species, while the formation of CH_4 in the photocatalytic reduction of CO_2 with H_2O was found to proceed on the bulk TiO_2 catalysts and on the imp-Ti-oxide/Y-zeolite catalysts involving aggregated octahedrally coordinated Ti-oxide species. On the tetrahedral Ti-oxide species, the charge transfer excited complexes of the oxides, $(Ti^{3+}–O^{-})^{*}$, formed under UV irradiation play a significant role in the formation of CH_3OH. On the other hand, with the aggregated or bulk TiO_2 and Pt-loaded catalysts, the photo-formed holes and electrons rapidly separate from each other with large spaces between the holes and electrons, thus preventing the reaction between the carbon radicals and $OH^{\cdot}$ radicals on the same active sites, resulting in the formation of CH_4 due to the reaction between the H atoms and carbon radicals formed at the electron trapped center. Furthermore, Ti-mesoporous molecular sieves exhibit high photocatalytic reactivity for the formation of CH_3OH, its reactivity being much higher than the powdered TiO_2 catalysts.

The present study clearly demonstrates that zeolite and molecular sieve catalysts involving Ti-oxide species highly dispersed in their cavities and framework are promising candidates as new and efficient photocatalysts for the photoreduction of CO_2 with H_2O and the control of the charge separation is important in developing highly efficient and selective photocatalysts.

Acknowledgements

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