Photocatalytic Reduction of CO_2 with H_2O on Ti-MCM-41 and Ti-MCM-48 Mesoporous Zeolites at 328 K

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Ti-MCM-41 and Ti-MCM-48 mesoporous zeolites were prepared and investigations into the unprecedented use of these catalysts for the photocatalytic reduction of CO_2 with H_2O at 328 K were carried out. Ti-mesoporous zeolites exhibited high photocatalytic reactivity for the formation of CH_3OH, its reactivity being much higher than bulk TiO_2.

Studies of the photocatalytic formation of HCOOH and HCHO from CO_2 and H_2O was first reported by Fujishima et al. on a series of semiconductor catalysts such as TiO_2 and $SrTiO_3$.[1] Anpo et al. found that on highly dispersed Ti-oxide/Vycor glass catalysts prepared by an anchoring method, such reactions led to the selective formation of CH_3OH as the main product.[2] The Ti-silicalite zeolite having Ti-O moieties highly dispersed on the framework has been shown to exhibit unique catalytic reactivity distinctively different from bulk titania.[3,4]

Recently, we have found that such Ti-zeolites are able to initiate the decomposition of NO at 295 K under UV irradiation, the selectivity being very different from bulk TiO_2.[3,5] Ti-zeolites can be prepared with uniformly dispersed Ti-O units so that detailed investigations into the relationship between the photocatalytic reactivity and the dispersion state as well as the local structure of metal oxide catalysts can be carried out. In the present study, Ti-MCM-41 and Ti-MCM-48 mesoporous zeolites have been employed as photocatalysts for the reduction of CO_2 with H_2O.

Ti-MCM-41 and Ti-MCM-48 were hydrothermally synthesized according to procedures reported in previous literature.[4] The resulting solid product was recovered by filtration, washed with distilled water several times and dried at 373 K for 12 h. The calcination of the sample was performed under a flow of dry air at 810 K for 6 h in order to remove the remaining template materials. The mole ratio of Si/Ti was found to be 100 for Ti-MCM-48 and 80 for Ti-MCM-41, respectively. TS-1 and bulk TiO_2 (P-25, Degussa Co. with the ratio of anatase/rutile = 7:3) were used as reference materials.

Prior to spectroscopic measurements and photoreactions, the Ti-MCM-41 and Ti-MCM-48 samples were calcined at 723 K for 5 h, degassed at the same temperature for 6 h, then calcined once in O_2 for 8 h and finally degassed at 473 K for 2 h.

The XAFS spectra of Ti-MCM-41 and Ti-MCM-48 catalysts are shown in Figure 1. In contrast to bulk TiO_2, the preedge peaks in XANES spectra of these catalysts are very high. The appearance of these peaks has been shown to correspond to the 4-fold coordinated Ti-O moieties.[5,6] In the FT-EXAFS spectrum, a strong peak due to the neighboring O atoms appeared at about 1.5 Å (without phase correction), however, the peak due to Ti-O-Ti could not be observed for the Ti-MCM-41 and Ti-MCM-48 zeolites. These results indicate that the dispersion level of the Ti-O moieties is high in the present Ti-mesoporous zeolites. Curve fitting analysis of the FT-EXAFS spectra provided coordination numbers about 4 for both Ti-mesoporous zeolites samples and slightly longer Ti-O distances (1.83 Å for Ti-MCM-41 and 1.84 Å for Ti-MCM-48) than for TS-1 (1.81 Å), the results being in good agreement with the literature.[4]

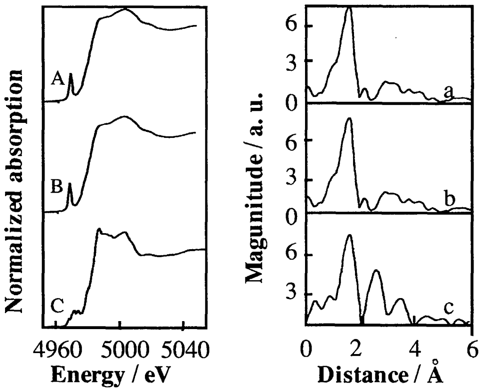

Figure 1. The XANES (left) and FT-EXAFS (right) spectra of Ti-MCM-41 (A, a), Ti-MCM-48 (B, b), and bulk powdered TiO_2 (C, c).

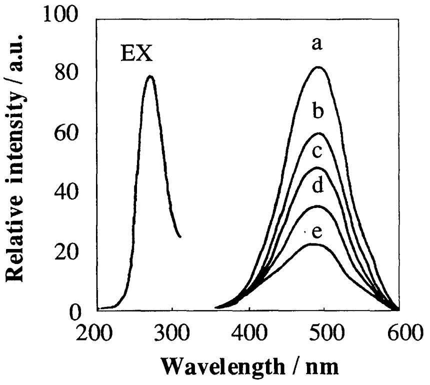

Figure 2. The effect of the addition of CO_2 and H_2O on the photoluminescence of the Ti-MCM-48. (a) 0, (b) H_2O; 0.5 , (c) H_2O; 5.0, (d) CO_2; 0.5, and (e) CO_2; 10.0 Torr added on the catalysts. Spectra were recorded at 77 K. (a-e) exicited at 280 nm, (EX) monitored at 480 nm.

Upon excitation with UV light at around 260-290 nm, both Ti-MCM-41 and Ti-MCM-48 exhibit photoluminescence spectra at around 450-650 nm, as shown in Figure 2. The Stokes shifts of these photoluminescence are in good agreement with the 4-fold coordinated titanium oxide species and these absorption and photoluminescence correspond to the following scheme:[3,5,7]

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

The addition of CO_2 or H_2O onto these Ti-mesoporous zeolites results in a significant quenching of these photoluminescence spectra, suggesting the excellent accessibility of the Ti-O sites 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-O moieties.

UV irradiation of the Ti-mesoporous zeolites and TS-1 zeolite in the presence of CO_2 and H_2O led to the immediate formation of CH_3OH and CH_4 and other products were formed only in trace amounts. The yields of the photoformed products increased at an almost constant rate, parallel to the irradiation time. Without any catalyst or under dark conditions, no product could be detected. After prolonged UV irradiation, the amount of CH_3OH and CH_4 evolved may exceed the amount of Ti ions incorporated in these zeolites. These results clearly show that the reaction proceeded photocatalytically. The yield of CH_4 and CH_3OH per unit weight of the various Ti-based catalysts are shown in Figure 3. It can be seen that under the same conditions, Ti-MCM-41 exhibits a total reactivity of about 20 times higher, Ti-MCM-48 about 30 times higher and TS-1 about 18 times higher than bulk TiO_2. These findings indicate that by the dispersion of Ti species on the wall of zeolite materials, the reactivity of the titanium oxide unit is greatly enhanced compared with bulk TiO_2. Only Ti-MCM-48, Ti-MCM-41 and TS-1 which involve the 4-fold coordinated titanium oxide species exhibit the photocatalytic reactivity for the formation of CH_3OH.

It was found that Ti-MCM-41 exhibits similar reactivity to the TS-1 catalyst while the Ti-MCM-48 catalyst is much higher than either TS-1 or Ti-MCM-41. Furthermore, on bulk TiO_2, CH_4 was the main product and only trace amounts of CH_3OH was formed while on Ti-mesoporous zeolites, the selectivity for methanol was enhanced to 30%, which was higher than for TS-1 (21%) and significantly higher than for bulk TiO_2 (1.4%).

Besides having the titanium oxide species in a higher dispersion state, 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; and Ti-MCM-48 has both a large pore size (>20 Å) and three-dimensional channels. Thus, the high reactivity and high selectivity for the formation of CH_3OH observed with the Ti-MCM-48 zeolite than with any other catalyst used here may be a combined contribution of the high dispersion state of Ti-O moieties and the large pore size having the three-dimensional channel structure.

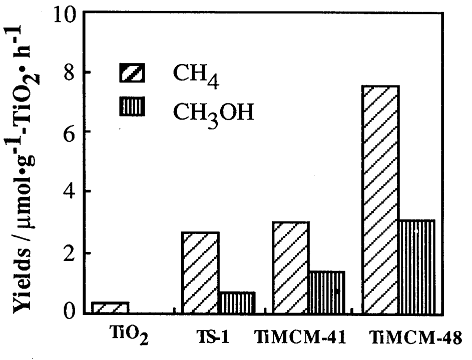

Figure 3. The yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O at 328 K on various Ti-based catalysts.

These distinctive properties are associated with the remarkable results obtained and it can be concluded that changes in the local structure of the titanium oxide species as well as the charge transfer nature of their excited states may greatly modify both the reactivity and/or the selectivity of the catalyst towards the formation of CH_3OH. The dispersion state may also affect the excited state of the Ti-zeolite as compared with bulk TiO_2. We have measured the lifetime of the photoluminescence of the titanium oxide species in the TS-2 catalyst and found it to be about 0.2 ms, a relatively long lifetime corresponding to the recombination time of the photoformed electrons and holes, while for bulk TiO_2 the combination of the photoformed electrons and holes occurred within a time scale of ns. A long lifetime can undoubtedly be considered to favor the interaction between the catalyst and the reactants, further providing pathways to form the reaction products.

It can thus be seen that the dispersion state as well as the local structure of the titanium oxide species on the zeolite framework can significantly modify the separation of the photoformed electrons and holes which results in an enhancement of the photocatalytic reactivity.

In summary, we have demonstrated that titanium oxide species highly dispersed on the zeolite framework can greatly modify not only the catalytic properties but also the photocatalytic properties of the titanium oxide catalyst. Ti-MCM-41 and Ti-MCM-48 mesoporous zeolites exhibited a higher reactivity and selectivity towards CH_3OH production in the photocatalytic reduction of CO_2 with H_2O at 328 K. Although the detailed reaction mechanisms behind the present reaction deserves further scrutiny, the present results strongly indicate that mesoporous zeolites with Ti-O moieties highly dispersed on their framework are promising candidates to serve as effective photocatalysts for the photoreduction of CO_2 with H_2O.

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