

Synthesis, characterization and photocatalytic reactivity of Ti-containing micro- and mesoporous materials

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Abstract Ti-oxides incorporated within the framework of microporous zeolites and mesoporous molecular sieves were found to exhibit high and unique photocatalytic activity for the decomposition of NO into N₂ and O₂ as well as the reduction of CO₂ with H₂O to produce CH₄ and CH₃OH. Spectroscopic investigations of these catalytic systems using photoluminescence, UV-vis, XAFS (XANES and FT-EXAFS) and IR analyses revealed that the charge transfer excited state of the isolated tetra-coordinated Ti-oxides plays a vital role in these photocatalytic reactions. The reactivity of such Ti-oxides was found to depend strongly on their local structures which were controlled by the unique framework structures of the micro- and mesoporous material supports.

Keywords Photocatalysis · Zeolites · Mesoporous molecular sieves · Ti-oxides · NO decomposition · CO₂ reduction

1. Introduction

The design of highly efficient and selective photocatalytic systems that work under clean and safe solar light without any loss of energy is especially vital for future energy needs. In particular, the development of photocatalytic systems which are able to decompose NO directly into N₂ and O₂ or to reduce CO₂ with H₂O into chemically valuable compounds such as CH₃OH or CH₄ are among the most desirable and

challenging goals in the research of environmentally-friendly catalysts [1, 2]. Much attention has, therefore, been focused on useful applications of Ti-oxide photocatalysts, mainly as TiO₂ semiconductors, thin films as well as isolated tetrahedrally coordinated Ti-oxides [1, 3]. Meanwhile, the unique and fascinating properties of micro-/mesoporous zeolites and silicates involving transition metal ions within their framework structures have opened new possibilities for applications in catalytic [4, 5] and photochemical processes [6, 7]. Recently, we have reported on highly dispersed tetrahedrally coordinated Ti-oxides as compared with bulk TiO₂ powder, and it was found that they exhibit much higher photocatalytic reactivity for NO decomposition as well as the reduction of CO₂ with H₂O [3, 6, 8, 9]. It is especially important to understand the mechanism and relationship between the local structure of the Ti-oxides, their photocatalytic reactivity and selectivity among various types of Ti-oxide catalysts.

The present study aims to elucidate the distinct characteristics of Ti-oxides incorporated within zeolites and mesoporous molecular sieve frameworks and their photocatalytic reactivity including their selectivity for NO decomposition and the reduction of CO₂ with H₂O at the molecular level using various in situ spectroscopic techniques such as photoluminescence, UV-vis, XAFS (XANES and EXAFS) and FT-IR spectroscopy.

2. Experimental

Ex-Ti/Y-zeolite and imp-Ti/Y-zeolite were prepared by ion-exchange and impregnation of the Y-zeolite with an aqueous titanium ammonium oxalate solution. The Ti-containing porous silica thin films were synthesized by a solvent evaporation method [10]. Ti-PS(h) and Ti-PS(c) with a H₂O/Si ratio of 1/3 and 4/3 and pores of hexagonal and cubic structures,

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respectively, were synthesized. Ti-MCM-41 (0.15~2.0 wt%) were prepared by an ambient temperature method [11, 12]. A TiO₂ powdered catalyst, JRC-TIO-4 (anatase 80%, rutile 20%), supplied by the Catalysis Society of Japan was used. Prior to photocatalytic reactions and spectroscopic measurements, the catalysts were heated in O₂ at 723 K and then evacuated at 473 K. The XAFS (XANES and EXAFS) spectra were obtained at the BL-7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba, Japan. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K with a ring energy of 2.5 GeV. Photoluminescence (Spex 1943D3), UV-vis (Shimadzu UV-2200A) and FT-IR (adsorbed NH₃; Jasco FT/IR 660) spectroscopic measurements were carried out at 295 K and 77 K. The photocatalytic decomposition reactions of NO and the reduction of CO₂ with H₂O were carried out under UV and visible light irradiation using a high pressure Hg lamp ($\lambda > 240$ nm and 420 nm) at 295 K or 323 K, respectively, and a water bath was employed to keep the reaction quartz cell at a constant temperature.

3. Results and discussion

3.1. Photocatalytic decomposition of NO into N₂ and O₂

3.1.1. Ti-containing zeolite with different Si/Al ratios

Figure 1 shows the diffuse reflectance UV spectra of the Ti/Y-zeolites prepared by an ion-exchange method with various Si/Al ratios. In Fig. 1, the UV absorption of the samples was observed to shift to longer wavelengths with the increase in the ratio of Si/Al. This means that the Ti-oxide species became aggregated with the increase.

Figure 2 shows the XANES spectra of the samples having different Si/Al ratios. Ex-Ti/Y(5.6) exhibits an intense single pre-edge peak, indicating that the Ti-oxides in this

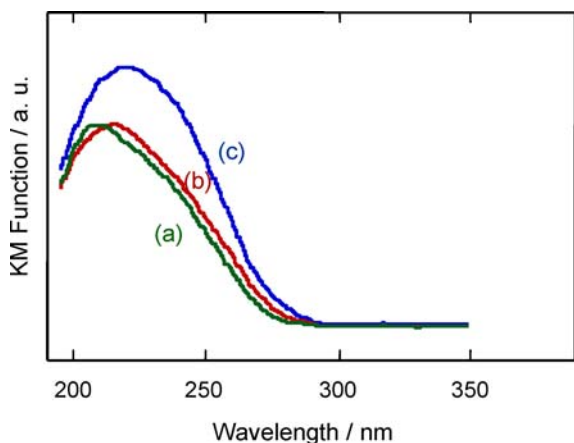


Fig. 1 Diffuse reflectance UV-vis absorption spectra of: (a) ex-Ti/Y (5.6); (b) ex-Ti/Y (13.9); and (c) ex-Ti/Y (390)

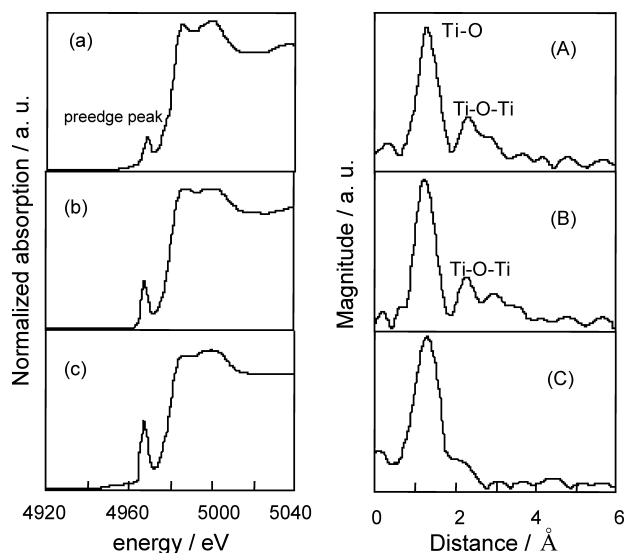


Fig. 2 XANES (left) and FT-EXAFS (right) spectra of: (a, A) ex-Ti/Y (390); (b, B) ex-Ti/Y (13.9); and (c, C) ex-Ti/Y (5.6)

catalyst form a tetrahedral coordination [3, 13]. The intensity of the pre-edge peak decreases with an increase in the Si/Al ratio, suggesting that the average coordination number of Ti atoms increased with an increase in the Si/Al ratio. For the ex-Ti/Y-zeolite (390), the single pre-edge peak is rather weak, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated Ti-oxide species.

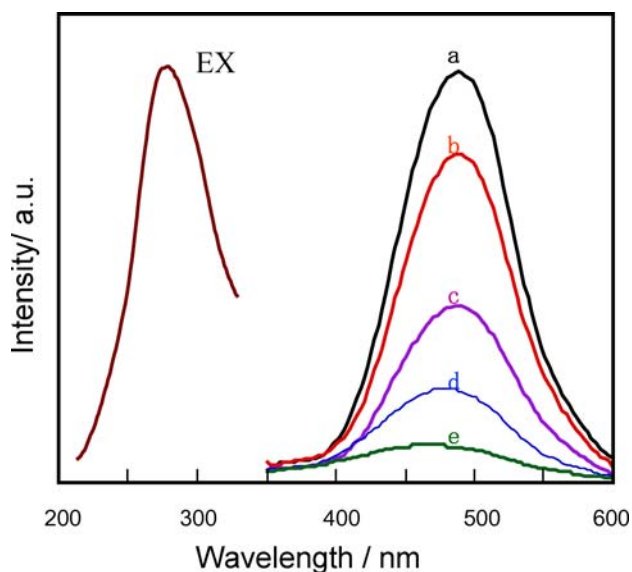
Moreover, in the FT-EXAFS spectra of the catalysts, ex-Ti/Y(5.6) exhibits only a Ti-O peak, while ex-Ti/Y(390) exhibits an intense peak at 2.7 Å assigned to the aggregated Ti-oxide species in the catalyst. From these results, it can be seen that ex-Ti/Y(5.6) contains isolated four-coordinate titanium ions, while in ex-Ti/Y(390), the presence of the aggregated octahedral titanium oxide species was clearly suggested.

In Fig. 3, the ex-Ti/Y-zeolite exhibits a photoluminescence spectrum at around 490 nm by excitation at around 280 nm at 77 K. The observed photoluminescence spectrum is attributed to the radiative decay process from the charge transfer excited state (Ti³⁺—O⁻)^{*} to the ground state (Ti⁴⁺—O²⁻) of the highly dispersed Ti-oxides in tetrahedral coordination [3]. The addition of NO, CO₂, or H₂O onto the ex-Ti/Y-zeolite catalyst led to an efficient quenching of the photoluminescence as well as a shortening of the lifetime of the charge transfer excited state, its extent depending on the amount of added gasses. These results indicate not only that tetrahedrally coordinated Ti-oxides locate at positions accessible to these added molecules but also that the added molecules easily interact with the Ti-oxides in their excited states.

UV irradiation of the ex-Ti/Y-zeolite with various Si/Al ratios, ex-Ti/ZSM-5, and imp-Ti/ZSM-5 in the presence of NO was found to lead to the formation of N₂, O₂, and N₂O in the gas phase with different yields and product selectivities.

Table 1 The yields of N₂ and N₂O and their selectivities in the photocatalytic decomposition of NO on the various types of the Ti/zeolite catalysts

Catalysts	Ti content (TiO ₂ wt%)	Yield ($\mu\text{mol/g-TiO}_2 \text{ h}$)			Selectivity (%)	
		N ₂	N ₂ O	Total	N ₂	N ₂ O
Ex-Ti/Y (5.6)	1.0	23	6	29	79	21
Ex-Ti/Y (13.9)	1.0	19	7	26	73	27
Ex-Ti/Y (390)	1.0	17	8	25	68	32
Ex-Ti/ZSM-5	1.1	14	2	16	88	12
Imp-Ti/ZSM-5	1.0	8	11	19	42	58
P-25		3	8	11	27	73

**Fig. 3** Effect of the addition of NO on the photoluminescence spectrum of ex-Ti/Y (5.6). (a) 0; (b) 0.1; (c) 3.2; (d) 6; and (e) 8 Torr

The yields of the products increased in proportion to the irradiation time and the reaction immediately stopped when irradiation ceased. Table 1 shows the yields and selectivities of the photoformed N₂ (O₂) and N₂O in the decomposition of NO on these catalysts. From Table 1, it is clear that the efficiency and selectivity for the formation of N₂ strongly depend on the type of catalyst used. The photocatalytic reactivity and selectivity for the formation of N₂ was found to be much higher in low ratios than for high ratios of Si/Al. Table 1 also shows that the selectivity of N₂ is much higher on ex-Ti/ZSM-5 than on imp-Ti/ZSM-5. From these results, the photocatalytic reactivity and selectivity for the formation of N₂ were found to decrease with an increase in the aggregated titanium oxides in the photocatalysts. Polymerization of the titanium oxide species to form aggregated titanium oxides when they are loaded by an impregnation method led to a decrease in the concentration of the Ti-oxide species having Ti-O-Si bonds, resulting in a significant decrease in the photocatalytic reactivity for the catalyst. Thus, under UV irradiation of the isolated tetra-coordinated TiO₄ species, two NO

molecules can be activated on a photoexcited TiO₄ species, resulting in the formation of N₂ and O₂. However, in the case of the aggregated hexa-coordinated Ti oxide particles, the photoformed electrons and holes react with NO molecules at different sites, respectively, resulting in the formation of N₂O and/or NO₂ but not N₂ and O₂, since N and O formed in the primary processes of the decomposition of NO immediately react with other NO molecules to form N₂O and NO₂ [3].

3.1.2. Ti incorporated mesoporous materials with different Ti contents

XAFS experiments indicated that for the Ti-MCM-4 catalysts, the Ti(IV) centers are tetrahedrally coordinated to the oxygen anions even for a Ti content as high as 2.0 wt%. The IR spectra of ammonia irreversibly adsorbed on these catalysts at 295 K exhibited a characteristic band at 1608 cm⁻¹ ($\delta_{\text{asym}} \text{NH}_{3\text{ads}}$) due to the NH₃ molecules irreversibly adsorbed on the Ti(IV) centers of the tetra-coordinated Ti-oxide species [14]. The intensity of this band increased with an increase in the Ti content, indicating that the amount of tetra-coordinated Ti(IV) sites exposed at the surface walls of the Ti-MCM-41 materials increased with the Ti loading (Fig. 4(a)). Nevertheless, the photoluminescence spectra exhibited different degrees of dependence on the Ti content. Ti-MCM-41 exhibits a typical photoluminescence spectrum at around 450–550 nm upon excitation at around 220–260 nm at 295 K, which is attributed to the existence of isolated tetra-coordinated Ti-oxide species in the catalyst. As shown in Fig. 4b, the intensity of this photoluminescence increases with an increase in the Ti content up to 0.58 wt%, and then sharply decreases with a higher Ti content while the phosphorescence lifetime decreases from 0.1 ms to 0.025 ms. It can, thus, be seen that only the isolated tetrahedrally coordinated Ti-oxide species exist at low Ti content up to 0.58 wt%, while the dimeric and/or oligomeric tetrahedrally coordinated Ti-oxide species are present at higher Ti content.

Figure 4 shows the effect of the Ti content on the reactivity of the photocatalytic decomposition of NO. The yield and selectivity of N₂ in this reaction is the highest for Ti-MCM-41

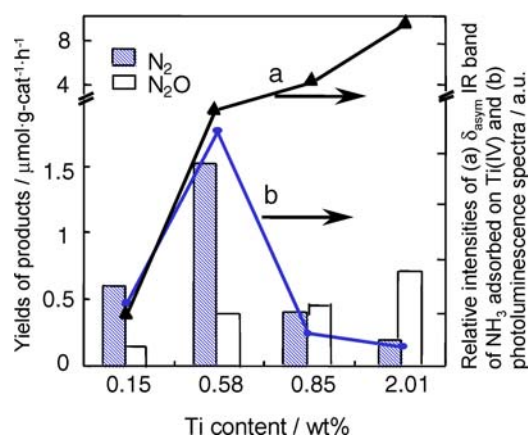


Fig. 4 Relationship among the yields of N₂, N₂O, the intensities of the (a) IR band of $\delta_{\text{asym}}\text{NH}_3$ adsorbed on Ti(IV) and (b) photoluminescence spectra of Ti-MCM-41 with various Ti contents

(0.58 wt%), showing a good correspondence with the photoluminescence yield due to the isolated tetrahedrally coordinated Ti-oxide species. The amount of isolated tetrahedrally coordinated Ti-oxide species, and not the total amount of the tetra-coordinated Ti-oxide exposed at the surface walls of the Ti-MCM-41 channels, appeared to play an important role in this reaction. These results also indicate that only the highly dispersed isolated tetrahedrally coordinated Ti-oxide species act as active sites in the photocatalytic decomposition of NO into N₂ and O₂.

Moreover, the photocatalytic reactivity for the decomposition of NO was found to strongly depend on the types of porous materials. Ti-MCM-41 exhibited much higher activity and selectivity for the formation N₂ in the decomposition of NO than Ti-HMS and TS-1. Considering the higher surface area of Ti-MCM-41, this higher performance for Ti-MCM-41 than other catalysts may be attributed to the higher dispersion state of the Ti-oxide species.

3.2. Photocatalytic reduction of CO₂ with H₂O

3.2.1. Ion-exchanged Ti-zeolite

The XANES spectra of the ex-Ti/Y(1.1 TiO₂ wt%) and imp-Ti/Y(1.0 TiO₂ wt%) showed that the ex-Ti/Y-zeolite exhibits an intense pre-edge peak while the imp-Ti/Y-zeolite exhibits three weak peaks attributed to bulk TiO₂. In the FT-EXAFS spectra of these catalysts, the ex-Ti/Y-zeolite showed only a peak at ~ 1.6 Å due to the neighboring oxygen atoms, and curve-fitting analysis of the EXAFS spectra showed the tetra-coordinated Ti-oxides to have a Ti-O distance of 1.78 Å. Meanwhile, the imp-Ti/Y-zeolite exhibited an intense peak at 2.7 Å assigned to the neighboring Ti atoms, indicating the aggregation of the Ti-oxides in the catalyst.

UV irradiation of the Ti/Y-zeolite catalysts prepared by an ion-exchange or impregnation method in the co-existence

of CO₂ and H₂O led to the evolution of CH₄ and CH₃OH in the gas phase at 328 K, as well as trace amounts of CO, C₂H₄ and C₂H₆, while the yields of these products increased in proportion to the irradiation time. It was found that the reaction rate and selectivity of the products depend strongly on the type of catalyst. The photocatalytic reactivity of the Ti/Y-zeolite catalysts, which were normalized by unit gram of the Ti in the catalysts, were observed to be much higher than bulk TiO₂. The ex-Ti/Y-zeolite exhibited a high reactivity and selectivity for the formation of CH₃OH, while CH₄ was found to be the major product on bulk TiO₂ and imp-Ti/Y-zeolite.

3.2.2. Ti-containing mesoporous materials

We have found that the highly dispersed tetrahedrally coordinated Ti-oxides incorporated in the silica matrix of zeolite and mesoporous silica shows higher reactivity and selectivity for the formation of CH₃OH compared to bulk TiO₂. As shown in Fig. 5, Ti-MCM-48 exhibits much higher reactivity than TS-1 and Ti-MCM-41. Besides the higher dispersion state of the Ti-oxides, the distinguishing properties of these samples are: TS-1 has a micro-pore size of ~ 5.7 Å and three-dimensional channels; Ti-MCM-41 has a mesopore size of >20 Å and one-dimensional channel structure. Thus, the higher activity and selectivity for the formation of CH₃OH observed with Ti-MCM-48 may be attributed to the synergetic effect of a combination of the high dispersion of the Ti-oxide species and the large pore size (>20 Å) with a three-dimensional channel structure.

However, such powdered material systems are difficult to handle for practical use. A morphology that would be more ideal would be photocatalytic thin films of high transparency. We have, thus, synthesized Ti-containing mesoporous silica (Ti-PS) thin films and investigated its reactivity for the photocatalytic reduction of CO₂ with H₂O.

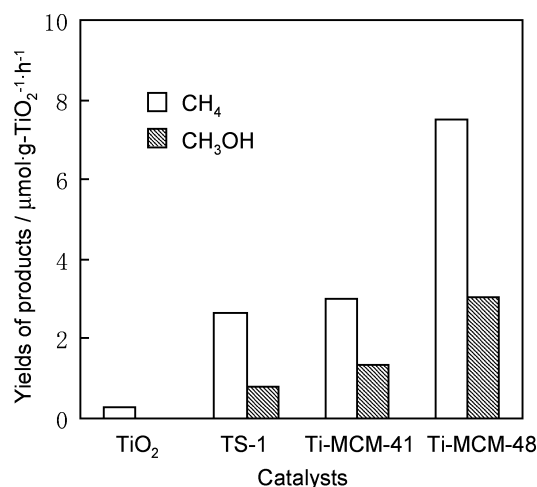


Fig. 5 Product distribution of the photocatalytic reduction of CO₂ with H₂O on various catalysts

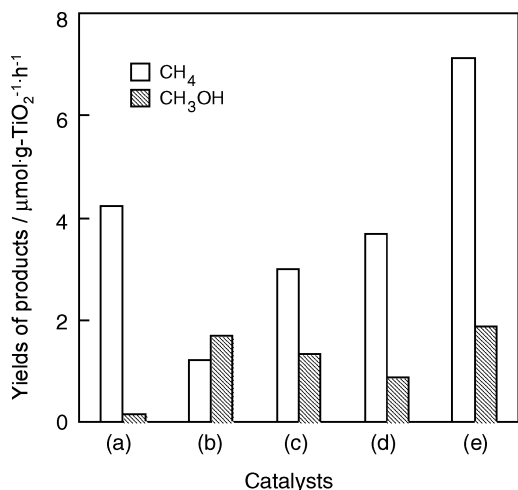


Fig. 6 Product distribution of the photocatalytic reduction of CO₂ with H₂O on: (a) Ti-PS (h, 25); (b) Ti-PS (c, 50); (c) Ti-MCM-41; (d) powdered Ti-PS (h, 50); and (e) Ti-PS (h, 50). Reaction time: 6 h; Intensity of light: 265 μWcm⁻²

Figure 6 shows the product distribution in the photocatalytic reduction of CO₂ with H₂O on these Ti-PS thin film catalysts. Among them, Ti-PS(h,50), with a hexagonal mesopore structure, shows the highest apparent photocatalytic reactivity per gram of Ti. Moreover, Ti-PS(h,50) exhibits higher reactivity as compared with powdered Ti-MCM-41 with a hexagonal pore structure. In powdered form, the effect of the scattering of light on the particle surface would be too large and effective light absorption and measurement may not be realized. Therefore, there is a great advantage in using transparent Ti-PS thin film photocatalysts to measure the exact quantum yield of the photocatalytic reaction using chemical actinometers. In contrast to the quantum yield obtained with the Ti-oxides anchored on transparent porous silica glass, Ti/PVG (0.02% at 250 nm), the values obtained with transparent Ti-PS thin films were remarkably improved and Ti-PS(h,50) showed the highest value of 0.28%. Such improvement in the reactivity is attributed to the larger surface area and higher transparency of the Ti-PS thin films compared to Ti/PVG. These results clearly suggest that the photocatalytic reactivity of transparent Ti-PS thin films is quite high and sufficiently effective for utilization in actual photocatalytic systems. It was, thus, clearly seen that the transparency is associated with the extent of the photocatalytic reactivity while the local structure of the Ti-oxide is directly associated with whether the reaction proceeds or not.

3.3. Design of visible light-responsive Ti-oxide/porous materials

Highly dispersed Ti-oxide containing micro- and mesoporous silica showed a high photocatalytic reactivity for the decomposition of NO into N₂ and O₂ as well as the

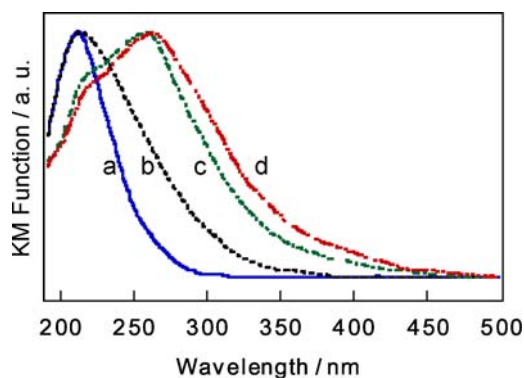


Fig. 7 Diffuse reflectance UV-vis absorption spectra of V ion-implanted Ti-MCM-41. The amount of implanted V ions (μmol/g-cat): (a) 0; (b) 0.66; (c) 1.3; (d) 2.0

reduction of CO₂ with H₂O into CH₃OH. However, a UV light source shorter than 280 nm was necessary. For practical and widespread use, catalyst that can operate efficiently under both UV and visible light irradiation is the most desired. A metal-ion-implantation method was applied to modify the electronic properties of the Ti-oxide species by bombarding them with high-energy metal ions, and it was discovered that implantation with various transition metal ions such as V, Cr, Mn, Fe and Ni by accelerated high voltage makes possible a shift in the absorption band of the Ti-oxides toward the visible light region. The order of the magnitude of the red shift was V > Cr > Mn > Fe > Ni. Figure 7 shows the UV-vis absorption spectra of the V ion-implanted Ti-MCM-41 catalyst. The extent of the shift strongly depended on the amount of V ions implanted. It was found that visible light irradiation (λ > 420 nm) of this electronically modified catalyst led to the decomposition of NO into N₂ and O₂, while NO decomposition did not proceed under UV or visible light irradiation on the V ion-implanted MCM-41 catalyst. These results suggest that the implanted V ions and highly dispersed Ti-oxide species form a Ti-O-V linkage which leads to the modification of the electronic properties of the tetrahedral Ti-oxides,

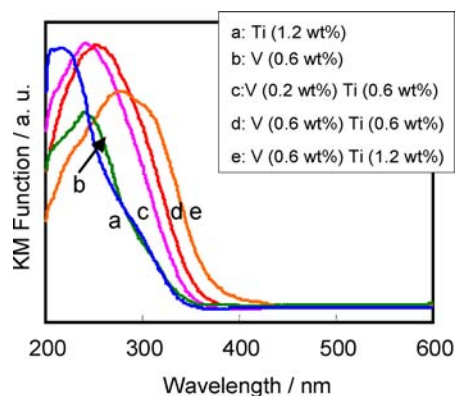


Fig. 8 Diffuse reflectance UV-vis spectra of Ti-MCM-41, V-MCM-41, and V-Ti-MCM-41 prepared under UV light irradiation for 24 h

thus, making it possible to operate as photocatalysts even under visible light irradiation.

Very recently, we have synthesized a V-Ti-MCM-41 catalyst using a simple photo-assisted synthesis method [15] and found a remarkable red shift of the absorption spectrum compared to that of Ti-MCM-41, as shown in Fig. 8. The absorption of visible light on V-Ti-MCM-41 can be seen, and these results clearly indicate that the modification of these Ti-containing materials enabled them to absorb light of longer wavelengths in the near-visible light region. A study of these materials and reactions are now underway.

4. Conclusions

An efficient and selective photocatalytic decomposition reaction of NO into N₂ and O₂ as well as the photocatalytic reduction of CO₂ with H₂O into CH₃OH could be achieved using Ti-containing microporous zeolites and mesoporous silica including a highly dispersed tetrahedrally coordinated Ti-oxide species. For the former reaction, N₂O was the major product while, for the latter reaction, CH₄ was the major product on bulk TiO₂ and the catalysts involving the aggregated octahedral coordinated Ti-oxide species. The reactivity of such Ti-oxides was found to depend strongly on their local structures, which were controlled by the unique structures of the micro- and mesoporous material supports, the preparation method and titanium content. Furthermore, a metal-ion-implantation and photo-assisted synthesis method allowed us to design micro- and mesoporous materials that respond to visible light by incorporating two different transition metal

ions in the framework structures of these porous materials, enabling the utilization of the most efficient energy source, solar light.

References

1. M. Anpo, in *Stud. Surf. Sci. Catal.*, edited by A. Corma, F.V. Melo, S. Mendioroz and J.L.G. Fierro (Proceedings of the 12th International Congress on Catalysts, Granada, 2000) vol. **130**, p. 157.
2. M. Anpo and H. Yamashita, in *Heterogeneous Photocatalysis*, edited by M. Schiavello (Wiley, Chichester, 1997), p. 133.
3. M. Anpo and M. Che, *Adv. Catal.* **44**, 119 (1999).
4. A. Corma, *Chem. Rev.* **97**, 2373 (1997).
5. B. Notari, *Adv. Catal.* **41**, 253 (1996).
6. M. Anpo (Ed.), *Photofunctional Zeolites* (NOVA Science Publishers Inc. 2000).
7. N.J. Turro, X.G. Lei, S. Jockusch, W. Li, Z.Q. Liu, L. Abrams, and M.F. Ottaviani, *J. Org. Chem.* **67**, 2606 (2002).
8. J. Zhang, M. Minagawa, T. Ayusawa, S. Natarajan, H. Yamashita, M. Matsuoka, and M. Anpo, *J. Phys. Chem. B* **104**, 11501 (2000).
9. K. Ikeue, H. Yamashita, T. Takewaki, and M. Anpo, *J. Phys. Chem. B* **105**, 8350 (2001).
10. M. Ogawa, K. Ikeue, and M. Anpo, *Mater. Chem.* **13**, 2900 (2001).
11. W. Zhang, M. Froba, J. Wang, P. T. Tanev, J. Wong, and T. J. Pinnavaia, *J. Am. Chem. Soc.* **118**, 9164 (1996).
12. Y. Hu, S. Higashimoto, G. Martra, J.L. Zhang, M. Matsuoka, S. Coluccia, and M. Anpo, *Catal. Lett.* **90**, 161 (2003).
13. T. Blasco, M.A. Cambor, A. Corma, and J. Perez-Pariente, *J. Am. Chem. Soc.* **115**, 11806 (1993).
14. M.E. Raimondi, E. Gianotti, L. Marchese, G. Martra, T. Maschmeyer, J.M. Seddon, and S. Coluccia, *J. Phys. Chem. B* **104**, 7102 (2000).
15. Y. Hu, N. Wada, M. Matsuoka, and M. Anpo, *Catal. Lett.* **97**, 49 (2004).