Photocatalytic decomposition of NO on Ti-HMS mesoporous zeolite catalysts

Jinlong Zhang [*], Madoka Minagawa, Masaya Matsuoka, Hiromi Yamashita and Masakazu Anpo [**]

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan
E-mail: anpo@ok.chem.osakafu-u.ac.jp

Received 18 January 2000; accepted 19 April 2000

Titanium oxide species were loaded within the framework of mesoporous materials (Ti-HMS) by hydrothermal synthesis. These Ti-HMS exhibited high and unique photocatalytic reactivity for the decomposition of NO into N_2 and O_2 at 275 K. *In situ* diffuse reflectance absorption and XRD investigations indicated that the titanium oxide species were dispersed well within the zeolite framework and isolated in tetrahedral coordination with low Ti content.

Keywords: titanium oxide, Ti-HMS, photocatalyst, decomposition of NO

1. Introduction

A variety of Ti-containing materials having high surface areas and high pore volumes such as Ti-MCM-41 and Ti-MCM-48 have been developed as unique catalysts in recent years [1]. However, there are only few reports [2,3] on the photocatalytic activity of these materials, though anatase TiO_2 as well as highly dispersed titanium oxides are known as effective photocatalysts [4,5]. These Ti-HMS catalysts exhibit high reactivity and selectivity due to their unique structural characteristics. Extensive investigations on the relationship between the local structure and photocatalytic reactivity have been conducted on Ti silicalites [6] and Y-zeolites involving Ti oxides in their cavities [7,8]. In such materials, Ti oxides have tetrahedrally coordinated TiO_4 units, and their charge transfer excited complexes exhibit high photocatalytic activity and selectivity for the decomposition of NO into N_2 and O_2 [7], as well as the reduction of CO_2 with H_2O to form CH_4 and CH_3OH [9]. The structural characterizations of the Ti-HMS had been already studied by Pinnavaia et al. [10] and Kresge et al. [11]. However, the structural characteristics of the Ti oxide species loaded within the framework of mesoporous material (Ti-HMS) and their photocatalytic reactivity and selectivity have yet to be investigated. The present investigation focuses on the relationship between the structures of mesoporous Ti-HMS and their photocatalytic reactivities.

2. Experimental

In this study, the synthesis of Ti-HMS was carried out successfully by the method reported by the Pinnavaia research group [10]. Tetraethyl orthosilicate (TEOS), tetraisopropyl orthotitanate (TIPOT), and a long-chain alkylamine surfactant (DDA) were used as the source of silica, titanium, and template, respectively. The TEOS/TIPOT solution was added to the DDA solution in water and ethanol under vigorous stirring. The molar compositions of the reaction mixture were 0.01–0.10Ti : 1.0Si : 0.20DDA : 9.0EtOH : $160H_2O$. The final catalysts were denoted as Ti-HMS(x), where x is the Ti content, wt% in gel. The actual composition of Ti was determined by atomic absorption spectroscopy. TiO_2 powdered catalyst (JRC-TIO-4: anatase 92%, rutile 8%) was supplied as a standard reference catalyst by the Catalysis Society of Japan. Prior to photoreactions and spectroscopic measurements, the catalysts were degassed at 725 K for 2 h, heated in O_2 at the same temperature for 2 h, and finally evacuated at 475 K to 10^{-6} Torr. UV irradiation of the catalysts in the presence of NO (7.8 mmol) was carried out by using a 75 W high-pressure Hg lamp ($\lambda > 280$ nm) at 275 K. The reaction products were analyzed by gas chromatography. The UV absorption spectra were recorded with a Shimadzu UV-2200A spectrometer at 295 K. XRD patterns were observed with a Shimadzu XD-D1 using Cu Kα radiation.

3. Results and discussion

Figure 1 illustrates the XRD pattern of the calcined Ti-HMS materials. All materials exhibit well-defined (100) reflections in their XRD patterns. The relatively well-defined pattern in figure 1 is typical, though also described by Pinnavaia et al. [10] and the XRD reflections can be indexed on a hexagonal lattice. From figure 1, it can also be seen that the intensity of the XRD peaks decreases with an increase in the Ti concentration. This suggests the hexagonal lattice may be destroyed by the incorporation of Ti into the

---

[*] Permanent address: Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China.

[**] To whom correspondence should be addressed.

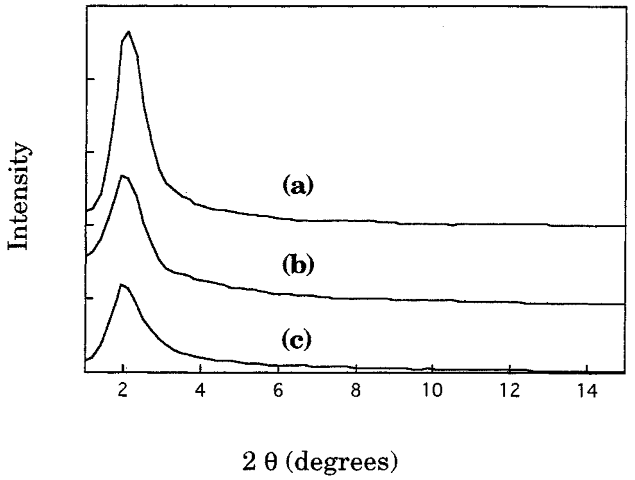

Figure 1. Powder XRD patterns for different Ti-HMS samples prepared at ambient temperature: (a) Ti-HMS(1), (b) Ti-HMS(2), and (c) Ti-HMS(10).

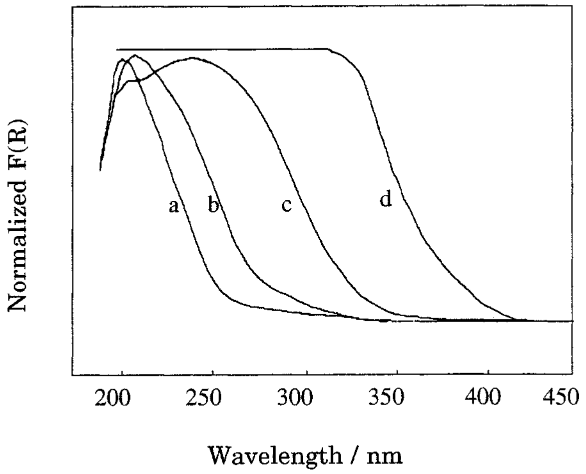

Figure 2. Diffuse reflectance UV-VIS spectra of (a) Ti-HMS(1), (b) Ti-HMS(2), (c) Ti-HMS(10), and (d) JRC-TIO-4.

HMS framework. However, as the Ti/Si ratio approaches 0.1 (Ti-HMS(10)), the (100) peak still appears clearly in the XRD patterns. The XRD patterns of the HMS samples are indexed on a hexagonal lattice, as assigned previously [11].

The diffuse reflectance UV-visible spectra of Ti-HMS are shown in figure 2. Compared to bulk anatase (standard reference catalyst JR-TIO-4), the absorption edges of the Ti-HMS samples exhibit a blue shift of more than 50 nm. For Ti-HMS(1) and Ti-HMS(2), the absorption band centering near 210 nm can be assigned to the ligand-to-metal charge-transfer transition (LMCT) between the oxygen ligands to the tetracoordinated Ti(IV) ions of the Ti oxide species [12–14]. This indicates that the Ti ions are coordinated in the framework of HMS. Only a slight red shift ($\sim$20 nm) of the LMCT transition can be seen from Ti-HMS(1) to Ti-HMS(2), indicating that the coordination geometry rearranges along with changes in the ligand due to Ti in the framework. The spectrum for Ti-HMS(10), on the other hand, shows a red-shifted absorption band between the wavelength of 250 and 300 nm. This indicates that at least a fraction of the Ti oxide in Ti-HMS(10) is in octahedral coordination. However, no significant absorption at around 300–350 nm can be seen, suggesting that a segregated crystalline TiO_2 anatase phase is not present. These results indicate that most of the Ti atoms in the Ti-HMS samples occupy site-isolated positions in the silica framework, except for the high Ti content sample Ti-HMS(10), where some of the Ti species are present in an octahedrally coordinated species. According to previous literature [15,16], the absorption at around 260–270 nm can be attributed to the presence of isolated Ti oxides having a penta- or octahedral coordination.

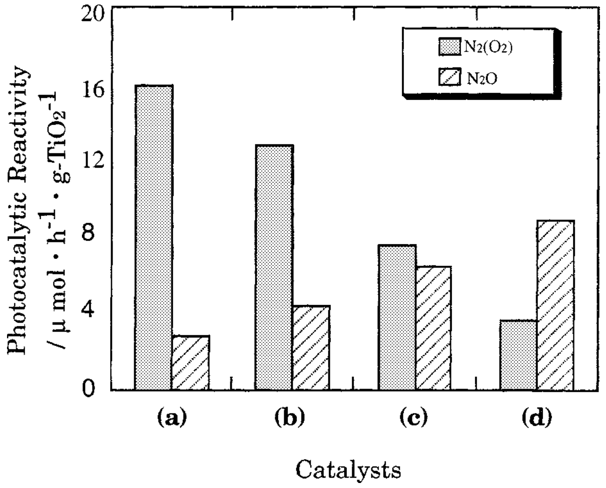

Figure 3. Products distribution of the photocatalytic decomposition of NO on the different photocatalysts: (a) Ti-HMS(1), (b) Ti-HMS(2), (c) Ti-HMS(10), and (d) JRC-TIO-4.

UV irradiation of the powdered TiO_2 and Ti-HMS in the presence of NO was found to lead to the decomposition of NO to form N_2, O_2, and N_2O in the gas phase at 275 K with different yields and product selectivities, showing a good linearity against the UV irradiation time. These results suggest that a photocatalytic decomposition reaction proceeds on these Ti oxide catalysts. Figure 3 shows a comparison of the photocatalytic reactivity and selectivity of the four different types of Ti oxide catalysts. It can be seen that the specific photocatalytic reactivities of the Ti-HMS catalysts, which have been normalized for the unit amount of TiO_2 in the catalysts, are much higher than that of the bulk TiO_2 catalyst.

Figure 3 shows the yields of the photoformed N_2 and N_2O (efficiency) and their selectivity in the photocatalytic decomposition of NO. From figure 3, it is clear that the efficiency and selectivity for the formation of N_2 and O_2 strongly depend on the type of Ti oxide catalysts. Ti-HMS(1) and Ti-HMS(2) exhibit a high reactivity and selectivity for the formation of N_2 and O_2, while the formation of N_2O is found to be the major reaction on the bulk TiO_2 catalyst. The results obtained with the Ti-HMS catalysts thus show a large difference in the selectivity as well as efficiency as compared with the bulk TiO_2 catalyst.

The photocatalytic performance of Ti oxides appears to be completely modified by their incorporation into the framework of HMS, which leads to change in the coordination structure and reaction environment. The unique catalytic performance of highly dispersed Ti oxides in Ti-HMS(1) in comparsion with higher loading Ti-HMS(10) shows a higher photocatalytic reactivity and selectivity for the formation of N_2 and O_2. Pure bulk TiO_2 is not an reactive photocatalyst for the direct decomposition of NO into N_2 and O_2. In the present study, the catalytic activity and selectivity for the formation of N_2 and O_2 in the decomposition of NO on the Ti-HMS photocatalysts are also found to be affected by Ti content, which is associated with the change in the coordination geometry and the aggregation of the Ti oxide species.

From these results, it was found that the photocatalytic activity and selectivity for the formation of N_2 and O_2 decrease with an increase in the Ti content. The highest photocatalytic reactivity and selectivity for the formation of N_2 and O_2 in the decomposition of NO were achieved on the Ti-HMS(1). This indicates that the highly dispersed tetrahedrally coordinated Ti oxide species are the active species for the formation of N_2 and O_2.

4. Conclusions

These results show that a high efficiency and selectivity for the formation of N_2 and O_2 in the photocatalytic decomposition of NO was achieved with the Ti-HMS(1) catalyst having highly dispersed isolated tetrahedral titanium oxide species and this reactivity decreased with an increase in the Ti content. The formation of N_2O in the photocatalytic decomposition of NO was found to proceed on bulk TiO_2 and Ti-HMS(10) catalysts which involve an aggregated octahedrally coordinated titanium oxide species, suggesting that this reaction is characteristic to octahedrally coordinated Ti oxide species.

Acknowledgement

The present work has been supported in part by the Ministry of Education of Japan, Grant-in-Aid for JSPS Fellows (P98096).

References

[1] A. Corma, Chem. Rev. 97 (1997) 2373.
[2] S.G. Zhang, Y. Fujii, H. Yamashita, K. Koyano, T. Tastumi and M. Anpo, Chem. Lett. (1997) 659.
[3] K. Kosuge and P.S. Singh, Chem. Lett. (1999) 9.
[4] M. Anpo, Catal. Surveys Jpn. 1 (1997) 169.
[5] D.-R. Park, J. Zhang, K. Ikeue, H. Yamashita and M. Anpo, J. Catal. 185 (1999) 114.
[6] M. Anpo, Sol. Energy Mater. Sol. Cells 38 (1995) 221.
[7] H. Yamashita, Y. Ichihashi, M. Anpo, M. Hashimoto, C. Louis and M. Che, J. Phys. Chem. 100 (1996) 16041.
[8] H. Yamashita, S. Kawasaki, Y. Ichihashi, M. Harada, M. Takeuchi, M. Anpo, G. Stewart, M.A. Fox, C. Louis and M. Che, J. Phys. Chem. B 102 (1998) 5870.
[9] M. Anpo, H. Yamashita, Y. Fuji, Y. Ichihashi, S.G. Zhang, D.R. Park, S. Ehara, S.E. Park, J.S. Chang and J.W. Yoo, Stud. Surf. Sci. Catal. 114 (1998) 177.
[10] W. Zhang, M. Froba, J. Wang, P.T. Tanev, J. Wong and T.J. Pinnavaia, J. Am. Chem. Soc. 118 (1996) 9164.
[11] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.
[12] A.M. Prakash, H.M. Sung-Suh and L. Kevan, J. Phys. Chem. B 102 (1998) 85.
[13] B. Notari, Adv. Catal. 41 (1996) 253.
[14] M. Anpo and M. Che, Adv. Catal. 44 (2000) 119.
[15] X. Gao, S.R. Bare, J.L.G. Fierro, M.A. Banares and I.E. Wachs, J. Phys. Chem. B 102 (1998) 5653.
[16] D. Trong On, I. Denis, C. Lortie, C. Cartier and L. Bonneviot, Stud. Surf. Sci. Catal. 83 (1994) 101.