Photooxidation of Methane to Methanol by Molecular Oxygen On Water-preadsorbed Porous TiO_2-based Catalysts

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At the temperature below 350 K, methanol was formed from the photooxidation of CH_4 by molecular oxygen on water preadsorbed porous TiO_2-based catalysts, Mo-containing porous TiO_2 catalysts exhibit higher catalytic activity than pure TiO_2.

Although the photocatalytic directly conversion of methane into oxygen-containing organics over solid oxide semiconductors has been studied for many years, few attempts to convert directly methane with high conversion and high selectivity have been successful.[1,2] On selective photooxidation of methane using semiconductor oxides as catalysts, the photooxidation of methane only produced CO_2 over TiO_2 (P25) at room temperature and atmospheric pressure under UV irradiation[1]; The selective photooxidation of methane over anatase TiO_2 produced a small amount of HCHO(0.5 μmol h^{-1}) at 493 K under UV irradiation[2]; the selective photooxidation of methane over MoO_3/SiO_2 and ZnO produced a small amount of CH_3OH at 473-530 K under UV irradiation, the yield of CH_3OH was 0.7 and 0.4 μmol h^{-1} respectively.[3,4] In these reports, the yield of CH_3OH is very low. So it is necessary to find out new photocatalysts and reaction routs by which CH_3OH can be directly synthesized from CH_4 and O_2 under mild conditions. It is interesting to study the photooxidation of CH_4 by O_2 using water preadsorbed porous oxide semiconductors catalysts. Now, the study on the photooxidation of CH_4 on water preadsorbed porous oxide semiconductors has not been reported. Here, we report the photooxidation of CH_4 by O_2 on water preadsorbed made home porous TiO_2-based catalysts at the temperature below 350 K and atmospheric pressure.

The porous TiO_2-based catalysts were prepared by simple sol-gel hydrolysis of titanium butyloxide ($Ti(OC_4H_9)_4$) - 2-propanol solution (alkoxide : alcohol molar ratio 1:32). The determined amount of H_2O and $(NH_4)_6Mo_7O_{24}$ aqueous solution were added to alkoxide alcohol solution respectively to form sol under vigorous stirring at room temperature, then 100 mL of acetic acid aqueous solution(1 mol/L) was added into the sol under stirring to produce white precipitate. After having been aged for 3 days at room temperature, the gel was washed with a large amount of distilled water to remove the alcohol and dried at room temperature, then calcined at 723 K for 8 h. Chemical analysis using ICP atomic emission spectroscopy the Mo content in the porous TiO_2 samples were 0.23 wt%. The crystal form of the porous TiO_2 was determined as anatase by XRD (Figure 1). The textural properties of the porous TiO_2-based samples were listed in Table 1. Commercial TiO_2 (rutile mass component 36%, TiO_2(C)) was used as a reference catalyst.

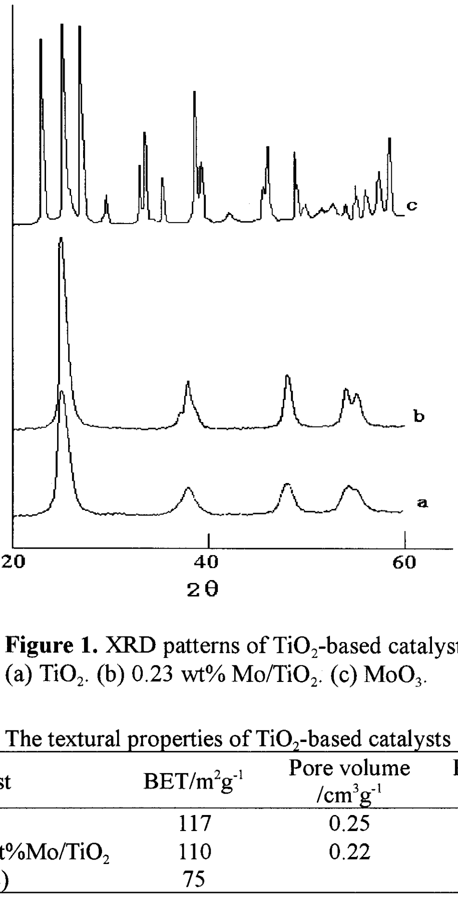

Figure 1. XRD patterns of TiO_2-based catalysts. (a) TiO_2. (b) 0.23 wt% Mo/TiO_2. (c) MoO_3.

Table 1. The textural properties of TiO_2-based catalysts

Catalyst	BET/m^2g^{-1}	Pore volume /cm^3g^{-1}	Pore size /nm
TiO_2	117	0.25	6.4
0.23 wt%Mo/TiO_2	110	0.22	6.5
TiO_2(C)	75		

The photocatalytic reactions were carried out in a quartz glass cell with volume of 50 mL. Prior to the photoreactions, the catalysts were evacuated at 473 K for 2 h. Slurry of catalyst was made by adding a small amount of water to the catalyst in the cell, the slurry was coated on the inter-surface of the cell and dried. After the catalyst in the cell adsorbed water, the cell was cleaned by passing pre-mixed reaction stock (CH_4: O_2: He molar ratio 9:1:10) and stock gas was introduced into the cell at room temperature and atmospheric pressure. UV irradiation was carried out with a high-pressure mercury lamp (250 W) with a cooling water jacket. Chemical actinometry using potassium ferrioxalate ($K_3Fe(C_2O_4)_3$) revealed that the number of photons irradiated into the cell was 7.2×10^{-9} einstein s^{-1} for 250-500 nm. After photoreaction, the CH_3OH and HCHO were collected by ice-trap (273 K). The products were determined and analyzed by ion trap detector and gas chromatography.

The reaction results were summarized in Table 2. Only COx was detected when dehydrated TiO_2 was used as catalyst. It is consistent with the result reported by M. Grätzel et al.[1] Methanol was detected besides COx when water-preadsorbed TiO_2 was used as catalyst. According to the reaction results,

Table2. Photooxidation of CH_4 on water preadsorbed porous TiO_2-based catalysts

Catalyst	T^d/K	CH_4 conv./%	Yield/μmol		
			CH_3OH	HCHO	COx
blank[a]	333	0.1	--	--	--
TiO_2[b]	333	0.2	--	--	--
TiO_2[c]	333	10.0	--	--	78
TiO_2	299	11.4	0.9	--	88
	333	11.5	1.4	--	88
0.23wt%	293	16.4	1.4	--	127
Mo/TiO_2	333	23.0	2.5	--	175
TiO_2(C)	333	8.6	0.9	--	66

Conditions: catalyst mass 0.40g. [a]UV irradiation without catalyst. [b]Without UV irradiation. [c]Dehydrated sample. [d]Reaction temperature. Irradiation time; 30 min. Amount of water adsorbed in catalyst 0.1-1.0 g.

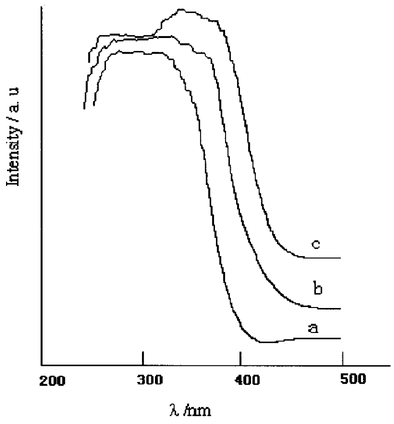

Figure 2. UV-vis diffuse reflection spectra of the catalysts. (a) TiO_2. (b) 0.23 wt% Mo/TiO_2. (c) MoO_3.

the Mo-containing TiO_2 catalyst exhibits higher photocatalytic activities than pure TiO_2 catalysts. The XRD patterns of the catalysts show in Figure 1. In Figure 1, the XRD pattern of the Mo-containing TiO_2 catalyst is similar with that of TiO_2, but is completely different with that of MoO_3. It shows that MoO_3 crystal is not formed in the Mo-containing catalyst. In Figure 2, the UV-vis diffuse reflection spectra of the Mo-containing TiO_2 sample is different with those of TiO_2 and MoO_3, suggesting the molybdenum oxide species dispersed on the TiO_2. In Figure 2, a significant shift to the longer wavelength in the absorption band is also observed in the Mo-containing TiO_2 sample as compared to that of pure TiO_2, suggesting the molybdenum oxide to sensitize the TiO_2. These may be responsible for the higher catalytic activity of the Mo-containing TiO_2 catalyst. On the other hand, the photooxidation rate of CH_3OH over molybdemun-oxide containing TiO_2 reduces slightly as compared to that over TiO_2.[5] It might be one of cause that the yield of CH_3OH increased slightly when the Mo-containing TiO_2 was used as catalyst. Table 2 also shows the conversion of CH_4 and the yield of CH_3OH increase with temperature. It may be one of cause that desorption of products from catalyst surface can be promoted at higher temperature. The systematic investigation on the reaction is underway and will be reported later.

References and Notes

1 K. R. Thampi, J. Kiwi, and M. Grätzel, *Catal. Lett.*, **1**, 109 (1988).
2 K. Wada, K. Yoshida, T. Takatani, and Y. Watanabe, *Appl. Catal. A: General*, **99**, 21 (1993).
3 K. Wada, K. Yoshida, Y. Watanabe, and T. Suzuki, *J. Chem. Soc., Chem. Commun.*, **1991**, 726.
4 K. Wada, K. Yoshida, and Y. Watanabe, *J. Chem. Soc., Faraday Trans.*, **91**, 1647 (1995).
5 Y. C. Liu, G. L. Griffin, S. S. Chan, and I. E. Wachs, *J. Catal.*, **94**, 108 (1985).