

Photooxidation of Methane to Methanol by Molecular Oxygen On Water-preadsorbed Porous TiO₂-based Catalysts

Xihui Chen and Shuben Li*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

(Received October 15, 1999; CL-990880)

At the temperature below 350 K, methanol was formed from the photooxidation of CH₄ by molecular oxygen on water preadsorbed porous TiO₂-based catalysts, Mo-containing porous TiO₂ catalysts exhibit higher catalytic activity than pure TiO₂.

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 CO₂ over TiO₂ (P25) at room temperature and atmospheric pressure under UV irradiation¹; The selective photooxidation of methane over anatase TiO₂ produced a small amount of HCHO (0.5 μmol h⁻¹) at 493 K under UV irradiation²; the selective photooxidation of methane over MoO₃/SiO₂ and ZnO produced a small amount of CH₃OH at 473-530 K under UV irradiation, the yield of CH₃OH was 0.7 and 0.4 μmol h⁻¹ respectively.^{3,4} In these reports, the yield of CH₃OH is very low. So it is necessary to find out new photocatalysts and reaction routes by which CH₃OH can be directly synthesized from CH₄ and O₂ under mild conditions. It is interesting to study the photooxidation of CH₄ by O₂ using water preadsorbed porous oxide semiconductors catalysts. Now, the study on the photooxidation of CH₄ on water preadsorbed porous oxide semiconductors has not been reported. Here, we report the photooxidation of CH₄ by O₂ on water preadsorbed made home porous TiO₂-based catalysts at the temperature below 350 K and atmospheric pressure.

The porous TiO₂-based catalysts were prepared by simple sol-gel hydrolysis of titanium butyloxide (Ti(OC₄H₉)₄) - 2-propanol solution (alkoxide : alcohol molar ratio 1:32). The determined amount of H₂O and (NH₄)₆Mo₇O₂₄ 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 TiO₂ samples were 0.23 wt%. The crystal form of the porous TiO₂ was determined as anatase by XRD (Figure 1). The textural properties of the porous TiO₂-based samples were listed in Table 1. Commercial TiO₂ (rutile mass component 36%, TiO₂(C)) was used as a reference catalyst.

The photocatalytic reactions were carried out in a quartz glass cell with volume of 50 mL. Prior to the photoreactions,

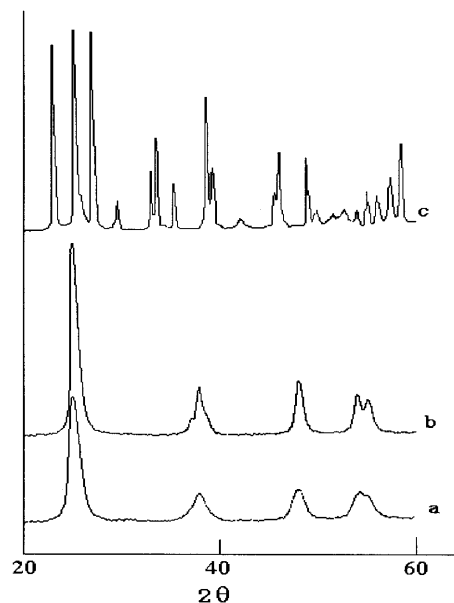


Figure 1. XRD patterns of TiO₂-based catalysts. (a) TiO₂. (b) 0.23 wt% Mo/TiO₂. (c) MoO₃.

Table 1. The textural properties of TiO₂-based catalysts

Catalyst	BET/m ² g ⁻¹	Pore volume /cm ³ g ⁻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		

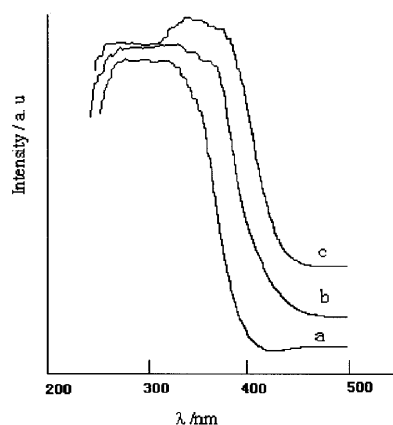
the catalysts were evacuated at 473 K for 2 h. Slurry of catalyst was made by adding a small amount of water to the catalyst in the cell, the slurry was coated on the inter-surface of the cell and dried. After the catalyst in the cell adsorbed water, the cell was cleaned by passing pre-mixed reaction stock (CH₄: O₂: 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 (K₃Fe(C₂O₄)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 CH₃OH 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 CO_x was detected when dehydrated TiO₂ was used as catalyst. It is consistent with the result reported by M. Grätzel et al.¹ Methanol was detected besides CO_x when water-preadsorbed TiO₂ was used as catalyst. According to the reaction results,

Table 2. Photooxidation of CH₄ on water preadsorbed porous TiO₂-based catalysts

Catalyst	T ^d /K	CH ₄ conv./%	Yield/μmol		
			CH ₃ OH	HCHO	CO _x
blank ^a	333	0.1	--	--	--
TiO ₂ ^b	333	0.2	--	--	--
TiO ₂ ^c	333	11.0	--	--	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. ^aUV irradiation without catalyst. ^bWithout UV irradiation. ^cDehydrated sample. ^dReaction 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) TiO₂. (b) 0.23 wt% Mo/TiO₂. (c) MoO₃.

the Mo-containing TiO₂ catalyst exhibits higher photocatalytic activities than pure TiO₂ catalysts. The XRD patterns of the catalysts show in Figure 1. In Figure 1, the XRD pattern of the Mo-containing TiO₂ catalyst is similar with that of TiO₂, but is completely different with that of MoO₃. It shows that MoO₃ crystal is not formed in the Mo-containing catalyst. In Figure 2, the UV-vis diffuse reflection spectra of the Mo-containing TiO₂ sample is different with those of TiO₂ and MoO₃, suggesting the molybdenum oxide species dispersed on the TiO₂. In Figure 2, a significant shift to the longer wavelength in the absorption band is also observed in the Mo-containing TiO₂ sample as compared to that of pure TiO₂, suggesting the molybdenum oxide to sensitize the TiO₂. These may be responsible for the higher catalytic activity of the Mo-containing TiO₂ catalyst. On the other hand, the photooxidation rate of CH₃OH over molybdenum-oxide containing TiO₂ reduces slightly as compared to that over TiO₂.⁵ It might be one of cause that the yield of CH₃OH increased slightly when the Mo-containing TiO₂ was used as catalyst. Table 2 also shows the conversion of CH₄ and the yield of CH₃OH 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).