XAFS Study on Mo/SiO₂ and Mo/Al₂O₃ Photocatalysts for the Selective Oxidation of CO with O₂ in the Presence of H₂ at 293 K

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Introduction
The preferential oxidation (PROX) of CO is one of the most straightforward methods to reduce the CO contamination in H₂-rich gas. For now, noble metals supported catalysts generally have been tested and proposed for thermal PROX reaction. To the best of our knowledge, no attempt has been made to apply photocatalysis for the PROX reaction. Therefore, we have applied the Mo/SiO₂ and Mo/Al₂O₃ photocatalysts for PROX reaction at 293 K.

Experimental
Mo/SiO₂ and Mo/Al₂O₃ (0.60 wt% molybdenum as metal) were prepared by an impregnation method of SiO₂ (aerosil 300; Degussa) or Al₂O₃ (Aluminium Oxide C; Degussa), respectively, using an aqueous solution of (NH₄)₆Mo₇O₂₄•4H₂O. Photocatalytic reactions were carried out in a closed system using quartz reactor under UV irradiation at 293 K using a 100 W high-pressure mercury lamp.

XAFS spectra at Mo K-edge were measured in a transmission mode at room temperature at the BL-10B station. Curve fitting analysis of the EXAFS spectra was conducted on k²g(k) in k-space (k range = 3-12 Å⁻¹) with a REX2000J program (Rigaku).

Results and Discussion
The photocatalytic selective oxidation of CO into CO₂ with O₂ in the presence of H₂ was investigated on Mo/SiO₂ and Mo/Al₂O₃ under UV light irradiation at 293 K. After UV irradiation for 180 min, concentration of CO reached below the detection limit of GC analysis (less than 8 ppm), while the amount of H₂ remained constant.

Mo/SiO₂ and Mo/Al₂O₃ (0.60 wt% molybdenum as metal) were prepared by an impregnation method of SiO₂ (aerosil 300; Degussa) or Al₂O₃ (Aluminium Oxide C; Degussa), respectively, using an aqueous solution of (NH₄)₆Mo₇O₂₄•4H₂O. Photocatalytic reactions were carried out in a closed system using quartz reactor under UV irradiation at 293 K using a 100 W high-pressure mercury lamp.

Moreover, the results of curve fitting analysis of Mo-O bonds suggest that Mo⁶⁺-oxide species on SiO₂ and Al₂O₃ have two short Mo=O double bonds and two long Mo-O single bonds, while Mo⁶⁺-oxide species on Al₂O₃ has longer M=O double bonds and shorter Mo-O single bond than that on SiO₂. The short Mo-O single bond of Mo⁶⁺-oxide species on Al₂O₃ can be ascribed to the large ionic character of framework metal-oxygen bond (Al-O) of Al₂O₃ as compared to that (Si-O) of SiO₂ [2]. The shorter Mo-O single bond also indicates the strong interaction between Mo⁶⁺-oxide species and Al₂O₃.

From the results of XAFS measurements, the weak photoluminescence intensity of Mo/Al₂O₃ can be explained by the efficient thermal deactivation from photoexcited Mo⁶⁺-oxide species to support, which is enhanced by the strong interaction between Mo⁶⁺-oxide species and Al₂O₃, as suggested by XAFS results. The efficient thermal deactivation process of photoexcited state of Mo⁶⁺-oxide species on Al₂O₃ dramatically decreases catalytic reaction rate on Mo/Al₂O₃.

References

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