Role of Excess MoO_3 in Iron-Molybdate Methanol Oxidation Catalysts

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Introduction

It has been recognized for sometime that the presence of excess crystalline MoO_3 in bulk mixed metal oxide catalysts enhances the resulting catalytic performance during selective oxidation reactions [1, 2]. To account for this interesting catalytic phenomenon several different hypotheses have been put forth: contact potential [1], remote control or oxygen spillover [2], etc. In spite of the numerous studies on this interesting and important observation, its origin has not been resolved because none of the studies examined the intrinsic surface characteristics of the catalysts. This catalytic enhancement phenomenon is most widely employed in commercial bulk mixed MoO_3-$Fe_2(MoO_4)_3$ oxide catalyst for CH_3OH oxidation to HCHO [3]. Although the active phase is generally considered to be the crystalline bulk $Fe_2(MoO_4)_3$ phase, the highest catalytic performance is obtained in the presence of excess crystalline MoO_3 (Mo/Fe > 1.5) [4].

In order to investigate this interesting catalytic phenomenon, CH_3OH oxidation to HCHO was undertaken with both CH_3OH-temperature programmed surface reaction (TPSR) spectroscopy and steady-state methanol reactivity studies. The CH_3OH oxidation reaction was selected since metahnol is also a 'smart' chemical probe molecule that can discriminate between different types of surface sites (redox, acid or base) [5], determine the number of exposed sites [6], and the surface reaction mechanism is well understood [7]. This is especially true of the kinetics and mechanism of the bulk $Fe_2(MoO_4)_3$ catalyst that is commercially employed for methanol oxidation to formaldehyde. Consequently, the mixed bulk MoO_3-$Fe_2(MoO_4)_3$ oxide catalyst system was chosen to investigate this interesting catalytic phenomenon for the selective oxidation of CH_3OH to HCHO.

Experimental

The bulk $Fe_2(MoO_4)_3$ catalyst was synthesized by co-precipitation of aqueous $Fe(NO_3)_3.9H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$. The thermal treatment and other details about the synthesis of the bulk $Fe_2(MoO_4)_3$ catalyst have been previously presented [6]. The crystalline MoO_3 phase was prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24}.4H_2O$ at 500 °C. Physical mixtures of MoO_3 and $Fe_2(MoO_4)_3$ were ground to increase the Mo/Fe ratio from 1.5, the stoichiometric ratio for $Fe_2(MoO_4)_3$, to 3.7 and 5.5. It was previously demonstrated that the same catalytic enhancement is obtained independent of the specific preparation method [8]. The experimental procedure followed for the CH_3OH-TPSR as well as the mathematical expression used for kinetic parameter estimation have previously been discussed [9]. The steady-state methanol oxidation reactions were carried out at atmospheric pressure and 300 °C. A reactant stream of $CH_3OH/O_2/He$ of composition (in percentage) 6/13/81 with a total flow rate of 100 mL/min was used for the oxidation reaction studies. Detailed information about the methanol steady-state oxidation system has been described earlier [5].

Results and Discussion

CH_3OH-TPSR The results from CH_3OH-TPSR experiments of $Fe_2(MoO_4)_3$ and the MoO_3 enriched Mo/Fe= 3.7 and 5.5 catalysts are presented in Table 1. During the reaction the exclusive formation of HCHO as the reaction product, no DME or CO/CO_2 formation, reflects the redox nature of the catalytic active sites in this series of iron-molybdate catalysts. The addition of excess MoO_3 shifts the HCHO Tp value from 178 to 189 °C, which corresponds to slightly less active catalytic sites (see Table 1). This temperature shift corresponds to a slight decrease in the specific first-order k_{rds}, by as much as a factor of ~2, and reflects the lower catalytic activity of crystalline MoO_3 (Tp=220 °C) compared to $Fe_2(MoO_4)_3$ for methanol oxidation.

Table 1: Influence of excess MoO_3 on iron-molybdate catalyst parameters

Sample	Tp for HCHO (°C)	k_{rds} (s⁻¹)	Exposed Ns redox sites/gm	Selectivity	
				HCHO	DME
$Fe_2(MoO_4)_3$	178	26	3.9×10^{-7}	74	26
Mo/Fe= 3.7	185	16	4.6×10^{-7}	96	4
Mo/Fe=5.5	189	12	4.7×10^{-7}	95	5

The number of exposed redox catalytic active sites/gm, Ns, is proportional to the area under the CH_3OH-TPSR curve for HCHO formation. The Ns redox sites of the iron-molybdate catalysts normalized per gram of catalyst are presented along with their corresponding k_{rds} values in Table 1. The Ns values reveal that the number of exposed sites in the bulk iron-molybdate catalysts just slightly increases with increasing excess MoO_3 in the catalyst. Table 1 also shows that with addition of MoO_3, the HCHO selectivity increases from 74 to 96% while the DME selectivity decreases from 26 to 5%. This HCHO selectivity enhances is related to covering of the exposed unselective Fe sites in $Fe_2(MoO_4)_3$ by the excess MoO_3.

Significance

The excess MoO_3 in MoO_3-$Fe_2(MoO_4)_3$ catalysts serves to slightly decrease k_{rds}, slightly increases the Ns redox sites, and significantly increases HCHO selectivity by suppressing the DME formation. The enhanced selectivity performance of excess MoO_3 is, thus, primarily related to surface MoOx species covering exposed unselective Fe sites from $Fe_2(MoO_4)_3$.

References
1. Haber, J., and Lalik, E. *Catal. Today* 33, 119 (1997).
2. Delmon, B., and Froment, G. F. *Catal. Rev.-Sci. Eng*. 38, 69 (1996).
3. Adkins, H., and Peterson, W.R. *J. Am. Chem. Soc*.53, 1512 (1931).
4. Okamoto, Y., Morikawa, F., Oh-Hiraki, K., Imanaka, T., and Teranishi, S. *J.C.S. Chem. Comm*. 19, 1018 (1981).
5. Badlani, M.; Wachs, I.E. *Catal. Lett*. **2001**, 75, 137-149.
6. Briand, L. E.; Hirt, A. M.; Wachs, I. E. *J. Catal*. **2001**, 202 268-278.
7. Holstein, W. L.; Machiels, C.J. *J. Catal*. **1996**, 162, 118-124.
8. Wachs, I.E.; Briand, L.E. U.S. Patent 6,037,290, 1999.
9. Wachs, I.E.; Jehng, J.-M.; Ueda, W. *J. Phys. Chem.B*. **2005**, 109, 2275-2284