Catalysis for Chemicals and Specialty Products (Synergistic Interactions in Alumina-Supported Binary Oxide Catalysts of Mo and W for Alcohol Oxidation Reactions)

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Introduction

Supported mixed transition metal oxide catalysts have been shown to be extremely promising as tunable catalysts for selective hydrocarbon oxidation reactions. The activity of these catalysts is strongly dependent on the surface structures present on the catalyst, which in turn depends on the surface densities of the individual oxides. While methods to elucidate structure-reactivity relationships in supported single metal oxide catalysts have been developed [1,2], limited progress has been made in the study of supported binary oxide catalysts. This work focuses on the use of two techniques – Ultraviolet-visible Diffuse Reflectance Spectroscopy (UV-vis DRS) [1] and ethanol partial oxidation [2] as a probe reaction - to better understand the evolution and reactivity of surface structures in alumina supported binary oxide catalysts of molybdenum and tungsten (MoO_x/WO_x-Al_2O_3) in comparison to alumina-supported single metal oxide catalysts of molybdenum (MoO_x-Al_2O_3) and tungsten (WO_x-Al_2O_3).

Materials and Methods

Ultraviolet-visible (UV-vis) diffuse reflectance spectra of prepared catalysts were obtained under ambient conditions using a Varian (Cary 5000) spectrophotometer with a Harrick-Scientific Praying-Mantis diffuse reflectance accessory (DRP-xxx) and in-situ cell (HVC-DRP). Reflectance measurements were converted into pseudo-absorbance units using the Kubelka-Munk transform using magnesium oxide as a reference.

Reactions were conducted at 180˚C by passing a continuous stream of 0.5% ethanol, 1.5% oxygen (if used), and balance He through a fixed bed, vertical U-tube quartz reactor containing 0.022-0.044 g of 125-250 µm particle catalyst dispersed on a quartz frit. Product analysis was performed using an Agilent 6890GC with FID and TCD detection (HP-PLOT Q column). Redox sites are known to form acetaldehyde (AC) while acidic sites form diethyl ether (DE) [2].

Results and Discussion

Physical mixtures of supported single oxide catalysts or bulk metal oxides result in multiple absorption edges (with edge energies identical to those of the component oxides) (Figure 1) in the UV-vis absorption spectra, indicating that *non-interacting, spatially and compositionally segregated* domains of WO_x and MoO_x can be detected using UV-vis DRS. For coimpregnated binary MoO_x/WO_x-Al_2O_3 catalysts, two edges are obtained for total surface densities below 1 (Mo + W)/nm^2 – one of which is identical to the MoO_x-Al_2O_3 catalyst with the same Mo atom surface density and the other is identical to the WO_x-Al_2O_3 catalyst with the same W atom surface density. This suggests that the two oxides form segregated and compositionally pure domains at these surface densities. For surface densities higher than 4 (Mo+W)-atoms/nm^2, only one edge is obtained in the UV-vis absorption spectra, indicating the presence of a single mixed composition domain at these surface densities (in which the two oxides interact)(Figure 1).

Probing of prepared catalysts using ethanol partial oxidation reaction shows that single MoO_x-Al_2O_3 catalysts have primarily redox character while WO_x-Al_2O_3 catalysts show primarily acidic behavior, as previously reported [2]. AC Selectivities on the MoO_x/WO_x-Al_2O_3 catalysts are found to be greater than those on MoO_x-Al_2O_3 catalysts at submonolayer Mo atom surface densities (Table 1), despite the lack of redox character of the WO_x. This selectivity is greater than that obtained through a linear combination of the AC formation rates over MoO_x and WO_x, suggesting that the redox ability of the WO_x is enhanced in the binary oxide catalyst. The cause of this enhancement was investigated using a variation of the probe reaction in which no oxygen was used in the reactant stream. This allows the examination and if desired, the quantification, of oxygen availability in each catalyst for the formation of AC through a redox mechanism. The AC selectivity under normal operating conditions is found to be dependent on the oxygen availability (Table 2). It is believed that the MoO_x plays a role in increasing oxygen availability for the WO_x in the binary oxide catalysts, which causes an enhancement in the AC production over the WO_x.

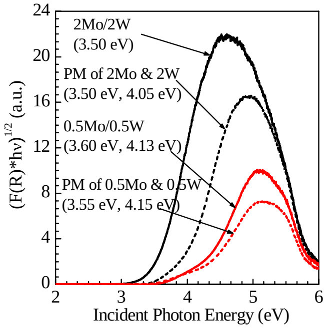

Figure 1. Absorption spectra for physical mixtures (PM) and binary oxide catalysts

Table 1. Acetaldehyde selectivities for MoO_x-Al_2O_3 and MoO_x/WO_x-Al_2O_3 catalysts

Catalyst	Acetaldehyde Selectivity(%)
0.5Mo	18.7
0.5Mo/0.5W	16.9
2Mo	57.1
2Mo/2W	64.5
2Mo/6W	70.0
4Mo	77.3
4Mo/4W	83.3

Table 2. Acetaldehyde selectivities for catalysts in the presence and absence of O_2 (after 8 hrs)

Catalyst and Conditions		Acetaldehyde Selectivity (%)
2Mo	In O_2	57.1
	No O_2	1.3
2W	In O_2	3.0
	No O_2	0.0
2Mo/2W	In O_2	64.5
	No O_2	1.5
6Mo	In O_2	83.1
	No O_2	4.2
Bulk WO_3	In O_2	27.6
	No O_2	4.5

Significance

This work is one of the first systematic investigations into the interaction between the component metal oxides of a binary oxide catalyst. Through a combination of UV-vis DRS and probe reactions, we have been able to gain insight into the catalytically active surface structures in binary MoO_x/WO_x-Al_2O_3 catalysts and the interaction and promotional synergy between WO_x and MoO_x in these catalysts. Such insight is useful for the design of highly selective muti-component oxide catalysts for hydrocarbon oxidation reactions.

References

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2. Briand, L. E.; Farneth, W. E.; Wachs, I. E. *Catalysis Today* 2000, 62, 219.