

Catalysis Science of Bulk Mixed Metal Oxide Catalysts: An *Operando* IR-TPSR Spectroscopic Study

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Introduction

Even though bulk mixed metal oxides find wide application in catalysis, there has still been a lack of fundamental understanding of how bulk mixed oxide catalysts function in the literature [1]. In order to obtain insights into how bulk mixed metal oxides function, the model bulk FeVO_4 catalyst system was investigated for CH_3OH oxidation to HCHO. Special emphasis was placed on obtaining surface information by employing *operando* IR-temperature programmed surface reaction (TPSR) spectroscopy with the CH_3OH chemical probe molecule.

Materials and Methods

The bulk FeVO_4 and supported 4% $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ were prepared by co-precipitation and incipient impregnation methods respectively [2, 3]. Bulk V_2O_5 was synthesized by thermal decomposition of NH_4VO_3 in flowing air at 300 °C for 4h.

Results and Discussion

The *in situ* IR spectra for CH_3OH chemisorbed on bulk V_2O_5 , Fe_2O_3 , FeVO_4 and supported 4% $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ were collected after adsorbing methanol at 100 °C. Chemisorption of CH_3OH on Fe_2O_3 at 100 °C gives rise to two strong IR peaks at ~ 2924 and 2820 cm^{-1} characteristic of the C-H stretches for surface methoxy (CH_3O^*) species and bands at ~ 2950 and $\sim 2850\text{ cm}^{-1}$ characteristic of the C-H stretches for intact methanol (CH_3OH^*) species on Lewis acid sites. *Operando* IR-TPSR spectroscopy revealed that the intact surface CH_3OH^* species desorbs as CH_3OH (Tp \sim 188 °C) and that the surface CH_3O^* species reacts to desorb as dimethyl ether (Tp \sim 242°C). For bulk V_2O_5 , methanol adsorption also results in both intact CH_3OH^* (2962 and 2854 cm^{-1}) and surface CH_3O^* species (2930 and 2828 cm^{-1}), with the surface methoxy species giving rise to a much a stronger IR signal compared to intact surface CH_3OH^* species. Both surface species, however, give rise to HCHO (Tp \sim 201 °C) from bulk V_2O_5 . Bulk FeVO_4 and supported 4% $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ also form both intact CH_3OH^* (2956 and 2828 cm^{-1}) and surface CH_3O^* (2930 and 2828 cm^{-1}), with the surface methoxy species being more dominant. During *operando* IR-TPSR spectroscopy (shown in Figures 1 and 2), the bulk FeVO_4 and 4% $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ catalysts both exclusively yield formaldehyde with Tp \sim 201 °C and \sim 215 °C, respectively.

The methanol chemical probe molecule reacts with surface redox, acidic and basic sites to produce formaldehyde, dimethyl ether (DME) and carbon dioxide, respectively. The formation of DME and only small amounts of HCHO and CO_2 from Fe_2O_3 during CH_3OH -TPSR reveals that the Fe_2O_3 primarily possesses surface acidic sites. In contrast, the vanadia-containing catalysts almost exclusively yield HCHO as the reaction product indicating that they contain surface redox sites. The very similar Tp values, 201-215 °C, for the V-containing catalysts

suggest that the bulk FeVO_4 catalyst is surface enriched with VO_x . This is also supported by the CH_3OH -IR spectra only showing the presence of surface V-OCH₃ species on bulk FeVO_4 .

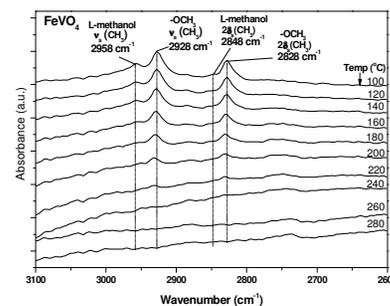


Figure 1. *Operando* IR-TPSR spectra from CH_3OH chemisorbed on bulk FeVO_4 in flowing He.

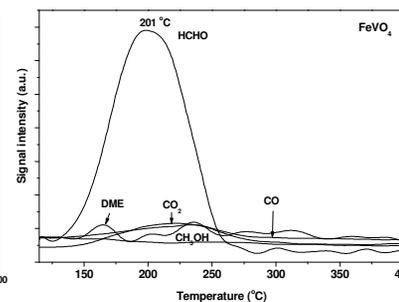


Figure 2. *Operando* MS-TPSR spectra from CH_3OH chemisorbed on bulk FeVO_4 in flowing He.

Significance

New insights about the catalytic contributions of the bulk and surface of bulk mixed metal oxide catalysts were obtained for methanol oxidation by the Fe-V-O system with *operando* IR-TPSR spectroscopy studies. The catalyst *surface* sites are responsible for the nature of the methanol surface species, surface CH_3O^* or intact CH_3OH^* , and their reaction products (HCHO or DME). The presence of surface redox sites for the V-containing catalysts primarily results in the formation of HCHO. Furthermore, since both the monolayer 4% $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ and bulk FeVO_4 catalysts give comparable results this suggests that it is the *surface* characteristics of bulk mixed metal oxide catalysts (surface sites, surface intermediates and their reaction pathways) that dominate the catalytic properties of bulk mixed metal oxide catalysts.

References

1. Wachs, I.E. *Catal. Today*, 100, 79 (2005).
2. Wachs, I.E., Briand, L.E., U.S. Patent 7,193,117.
3. Gao, X., Bare, S.R., Weckhuysen, B.M., Wachs, I.E., *J. Phys. Chem. B* 102, 10842 (1998).