In situ XPS study on Mo-based oxides under conditions of selective oxidation of C3 hydrocarbons

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Introduction:

Molybdenum oxide is an essential component of multi-metal oxide catalysts applied in selective oxidation of C3 hydrocarbons and oxygenates. Examples are the industrially performed oxidation of propylene to acrolein over promoted bismuth molybdates and the oxidation of acrolein to acrylic acid over promoted MoVW oxide catalysts. MoVTeNb oxides convert propane directly into acrylic acid with high selectivity. Supported molybdenum oxide and various metal molybdates have been studied in oxidative dehydrogenation of propane and direct oxidation of propane to acrolein, respectively.

Experimental:

The experiments were performed at the U49/2-PGM2 beamline (BESSY). The $(Mo_{0.68}V_{0.23} W_{0.09})_5O_{14}$ and $(Mo_{0.91}V_{0.09})_5O_{14}$ catalysts were prepared by spray-drying technique mixed solution of ammonium heptamolybdate, ammonium metatungstate and vanadyl oxalate.[1.] The samples were investigated a variety of reaction mixtures. 0.5 mbar of propylene-oxygen (1:2; 1:1) mixtures, ~0.6 mbar propylene-oxygen-water (1:2:1; 1:1:1), 0.5mbar acrolein-oxygen 1:2 and 0.6mbar acrolein-oxygen-water (1:2:1). Mo 3d, O 1s, V 2p, W 4f, C 1s and valence band spectra were recorded under reaction conditions. In addition in-situ Nexafs spectra were taken at OK-edge and VL-edges. Selected mass numbers were recorded simultaneously with the XPS and absorption spectra, which allowed us to correlate the XPS and absorbtion results with the catalytic activity of the material.
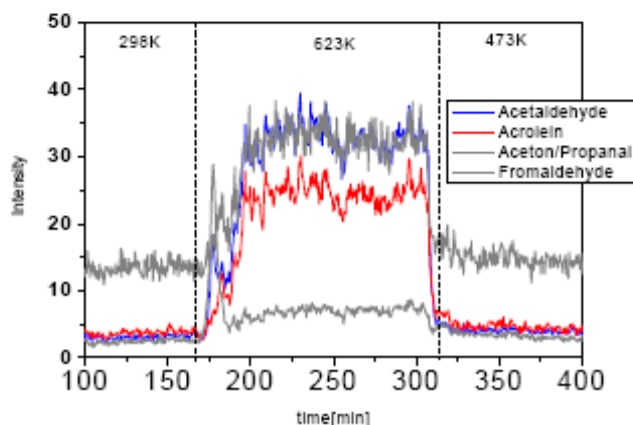

Fig.1. Catalytic MS trace

$(Mo_{0.91}V_{0.09})_5O_{14})$ and $(Mo_{0.68}V_{0.23} W_{0.09})_5O_{14}$ showed lower activity at 1:1 propylene/O_2 ratio in the feed. Under our conditions, both catalysts produced – other than CO_2 – only aldehydes and no acids (Fig1.). The reason might be a pressure barrier existing between atmospheric and mbar conditions.
Further investigations are under progress to examine the effects of pressure dependence on the reaction.

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During acrolein oxidation reaction the tungsten containg sample was produced acrylic acid, meanwhile the other catalyst produced only total oxidation products.
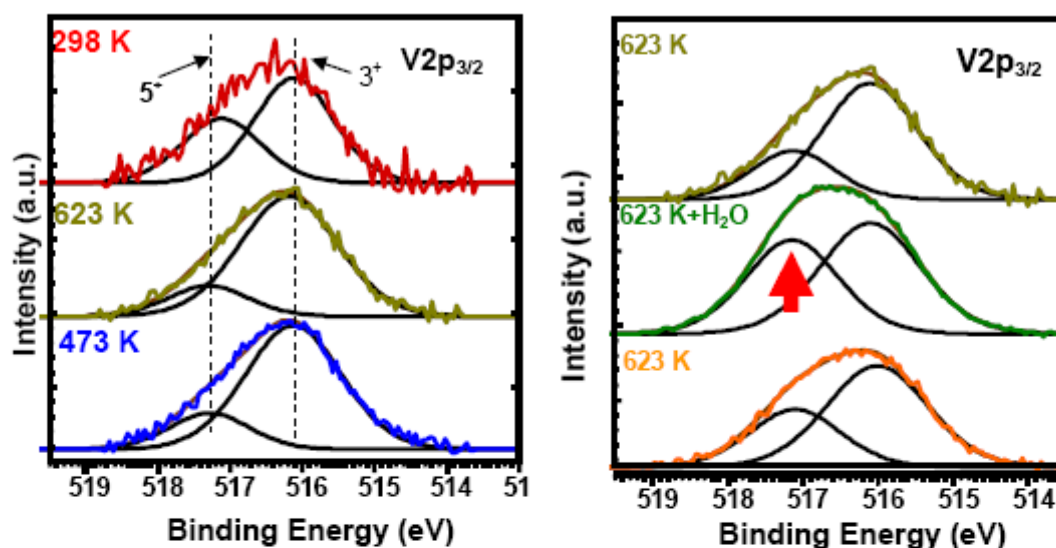Before reaction Mo was in a mixed 5+/6+ state, V was mainly 3+ and W 6+.

Fig2. Vanadium core level spectra with and without adding steam to the feed.

Non-destructive depth-profiling was performed by varying the excitation energy at which the spectra were recorded XPS indicated V enrichment on the catalyst surface as well as significant changes in V oxidation states. Under reaction condition Mo became oxidized and the W oxidation states were not changed. As water was added to the feed vanadium was further enriched at the surface. Moreover V became clearly oxidized to 5+ after switching off H_2O V reduced back to 3+. Showing that the change was reversible. (Fig2.)

Conclusion:

It can be concluded from the result that $(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$ has higher activity and selectivity than the tungsten free sample in both propylene and acrolein selective oxidation reaction. The W containing catalyst shows greater structure stability and is therefore less sensitive to the presence of water.

References:

[1] S. Knobl, G. A. Zenkovets, G. N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl, G. Mestl, Journal of Catalysis **215** (2003) 177