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In-situ XPS study on $(MoV)_5O_{14}$ selective oxidation catalysts

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Introduction

Catalytic reactions involving partial oxidation of simple hydrocarbons belong to the most important processes in the chemical industry [1]. Different molybdenum and vanadium oxides as mixed oxides are successfully applied in those reactions. Therefore, Mo based selective oxidation catalysis (propane and propylene to acrylic acid) is one of the main research area in our department. The surfaces of catalytic materials strongly depend on the gaseous environment and temperature. Therefore in-situ experiments under working conditions are necessary to identify the active phase of catalysts. In-situ spectroscopy techniques in the soft X-ray range like XAS and XPS were applied to learn about the electronic structure of the working catalyst surface. In this study we investigated two different catalytic formulations, Mo-V mixed oxides with and without W in the crystal lattice. These are good candidates for these reactions.

Experimental

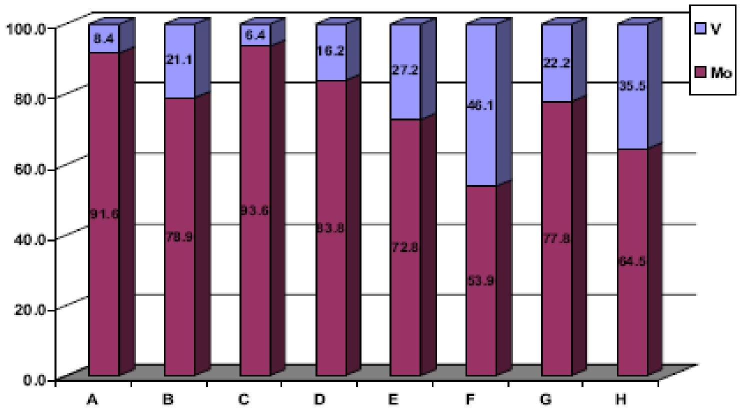
The experiments were performed at beamline U49/2-PGM2. The $(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$ [(MoVW)Ox] and $(Mo_{0.91}V_{0.09})_5O_{14}$ [(MoV)Ox] catalysts were prepared by spray-drying technique from the mixed solution of ammonium heptamolybdate, ammonium metatungstate and vanadyl oxalate. The samples were investigated in a variety of reaction mixtures. At 0.5 mbar, propylene-oxygen ratio (1:2; 1:1) was varied; and water (0.1 mbar) was added to the mixtures. The catalytic reactions were measured at 350°C. Mo 3d, O 1s, V 2p, W 4f, C 1s and valence band spectra were recorded under reaction conditions at different excitation corresponding to different information depth. In addition in-situ XAS spectra were taken at OK-edge and VL-edges. Selected mass numbers were recorded by Proton transfer reaction mass spectrometer, simultaneously to the XPS and absorption spectra, which allowed us to measure the catalytic activity and correlate it to the spectroscopic information.

Results

Other than the total oxidation products CO_2 and water, both catalysts produced aldehydes such as acrolein, acetaldehyde, propanal, formaldehyde however no acids under these low-pressure conditions. On the other hand at higher pressure (1 bar) both catalysts are able to produce acrylic acid as well. The reason to this discrepancy might be a pressure barrier existing between atmosphere and mbar conditions. Further investigations are under progress to examine the reason of this pressure dependence on the reaction.

The catalytic activity was depending on the reaction conditions. In 2:1 oxygen propylen ratio both catalysts showed higher activity. (MoVW)Ox was more active and selective compare to the W-free sample independently from the O_2/propylene ratio.

The elemental composition of the samples measured with bulk sensitive excitation indicated good agreement with the theoretical composition and with the ICP experimental data. XP spectra recorded in surface sensitive mode however revealed vanadium enrichment in the surface near region of both samples (Fig1, Fig2).



A	2 O_2 : 1 C_3H_6 at RT in **bulk** sensitive mode
B	2 O_2 : 1 C_3H_6 at RT in **surface** sensitive mode
C	2 O_2 : 1 C_3H_6 at 350 C° in **bulk** sensitive mode
D	2 O_2 : 1 C_3H_6 at 350 C° in **surface** sensitive mode
E	2 O_2 : 1 C_3H_6 at 350 C° + H2O in **bulk** sensitive mode
F	2 O_2 : 1 C_3H_6 at 350 C°+ H2Oin **surface** sensitive mode
G	2 O_2 : 1 C_3H_6 at 350 C° off H2O in **bulk** sensitive mode
H	2 O_2 : 1 C_3H_6 at350 C° off H2O in **surface** sensitive mode

Fig1. Molybdenum and Vanadium ratio in "bulk" (~18Å) and "surface" (~8 Å) sensitive mode

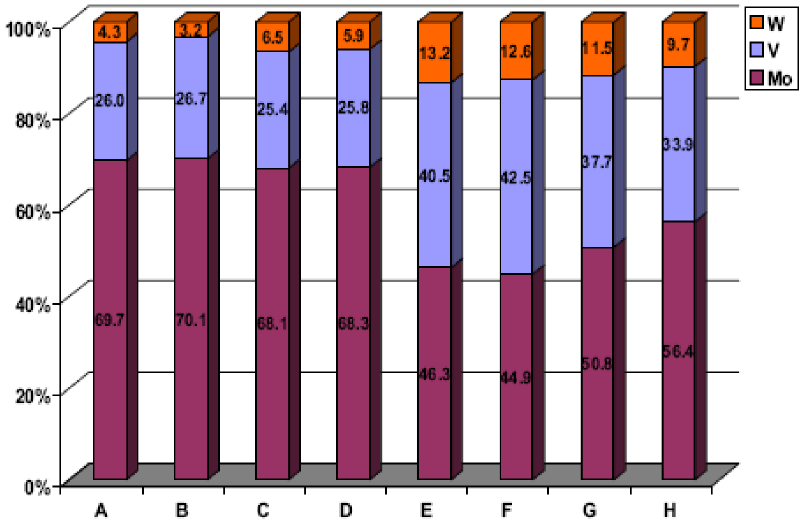


Fig2. Molybdenum, Vanadium and Tungsten ratio in "bulk" (~18Å) and "surface" (~8 Å) sensitive mode

For (MoVW)Ox the Mo3d state was not significantly altered in the different conditions; it was mainly Mo^{6+}.

(MoV)Ox contained different Mo oxidation states at room temperature (Mo^{6+}, Mo^{5+}). During reaction the Mo^{5+} state disappeared. The loss of Mo^{5+} correlates with the removal of surface carbon.

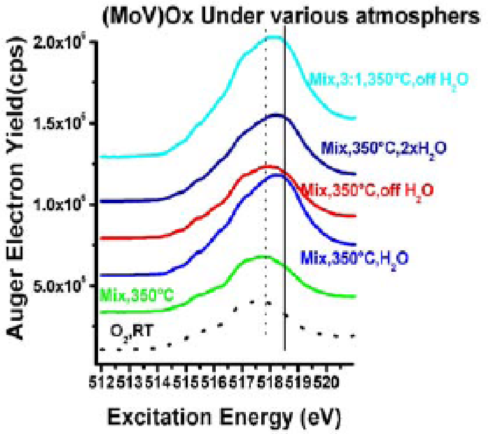


Fig3. (MoV)Ox Auger Electron Yield VL3 spectra

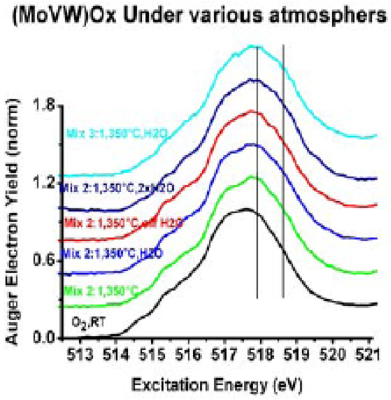


Fig4. (MoVW)Ox Auger Electron Yield VL3 spectra

Vanadium was in a mixed oxide state of V^{5+} and V^{4+} in both samples. The V2p core level indicated more oxidized vanadium under the reaction condition. The ratio of V^{5+}/V^{4+} was higher with W in the oxide lattice. The initial tungsten oxidation state was 6+ and it was not modified under the reaction. From Auger Electron Yield spectra vanadium was clearly more oxidized in the presence of water in the case of (MoV)Ox .

Conclusion

It can be concluded from the result that (MoVW)Ox has higher activity and selectivity than the tungsten free sample in propylene selective oxidation reaction. The W containing catalyst possesses greater structure stability and is therefore less sensitive to the presence of water to strongly modify the surface structure and composition.

Acknowledgement

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