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Surface modified phase pure M1 $MoVTeNbO_x$ catalysts

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The rather complex mixed oxide $MoVNbTeO_x$ was found to be very potent in the partial oxidation of propane to acrylic acid [1]. The excellent catalytic properties have been attributed to a crystalline phase called M1. M1 can be prepared by hydrothermal synthesis as phase-pure polycrystalline material [2]. This crystal structure has been argued to provide the active centers for propane activation. However, the surface of the solid might differ in both structure and composition from the XRD probed bulk [3, 4]. As the processes involved in the heterogeneous catalysis are certainly occurring on the exposed surface of the solid, elucidation of the surface termination of the catalyst is essential for any mechanistic understanding.

By chemical treatment of phase pure M1 we attended to modify the surface keeping the bulk structure unaffected. One batch of phase-pure M1 has been divided into five portions, which have been dispersed in different aqueous solutions and shaken for 2 h under ambient conditions. The solutions were:

- distilled water
- 0,1 M H_3PO_4 (acidic, complexing)
- 0,1M Tetramethylethylenediamine (complexing and basic)
- 0,1M $NaBrO_3$ (oxidizing)
- 0,1M $N_2H_4 \cdot H_2O$ (reducing, basic)

The catalysts were recovered by filtration and drying. By means of XRD, no change of the crystal structure has been observed. On the other hand, the analysis of the filtrate solutions (pH, UV-VIS, XRF) revealed leaching of different elements depending on the solution applied. Characterization by SEM and EDX revealed neither significant difference in morphology, nor in the elemental composition of the bulk.

The catalysts were tested in a tubular quartz reactor operated under plug-flow conditions with a feed gas composition $C_3H_8/O_2/H_2O/N_2$=3/6/40/51 vol%. The reaction was carried out at 400°C and different space velocities in order to achieve different conversions. We observed that all the modified samples show very similar catalytic performances in terms of propane conversion and acrylic acid selectivity, except for the bromate-treated (oxidized) sample (Figure 1). The XAS experiment showed that the V^{4+} in the bromate-treated sample is partially oxidized to V^{5+}, while the oxidation state of the other metal ions seem to be the same, irrespective of the treatment method. The catalytic performance will be discussed further with respect to XPS and micro-calorimetric investigations of propane adsorption.

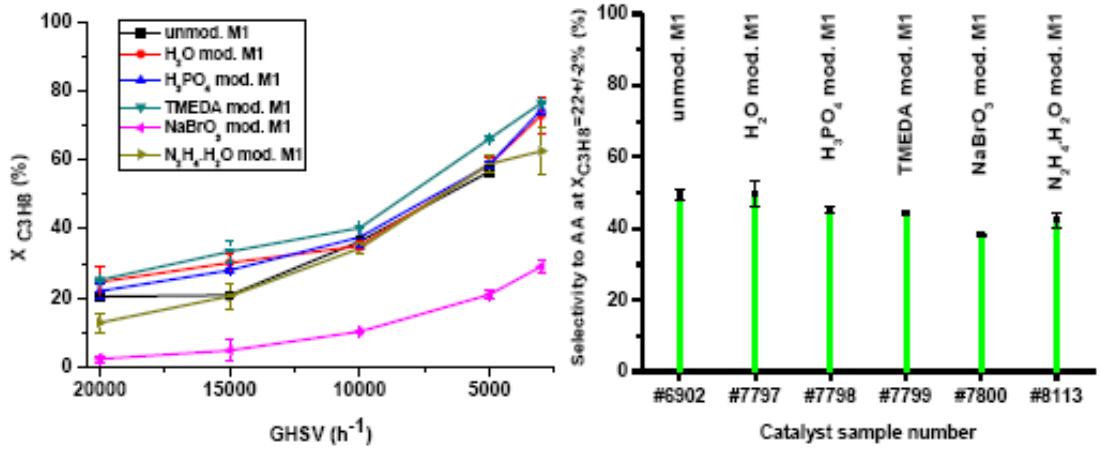

Figure 1. The catalytic performance of the differently treated $MoVNbTeO_x$ catalysts. Left: the conversion of propane as a function of GHSV. Right: the selectivity to acrylic acid at similar (22 ± 2%) propane conversion.

References:

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