In situ investigations of the formation of a (MoVW)$_5$O$_{14}$ type mixed molybdenum oxide catalyst

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Goals:
• Development & characterization of model systems for catalysts industrially applied in the selective oxidation of propene
• Elucidation of the function of different metal centers for phase formation and stabilization

Approach:
• Mo$_{14}$ type structure as model system for more complex mixed oxide catalysts
• Studies on the local structures of the metal centers during phase evolution of the Mo$_{14}$O$_{14}$ structure
• Investigations on the stability of the Mo$_{14}$O$_{14}$ phase

Methods:
• In situ XRD (CuK$_\alpha$) in Bragg-Brentano geometry, Bühler HDK combined with MS
• In situ XAS at HASYLAB, Hamburg. In situ XAS cell combined with online monitoring of gas phase composition by MS

Normalization of absorption

Intensity

Normalized absorption

0.0 0.5 1.0

Photon energy [keV]

5.46 5.48 5.50 5.52

10% propene

20% propene

Reduced from (MoVW)

Re-oxidation of tungsten containing metal oxide to (MoVW)$_5$O$_{14}$ corroborates the redox-stabilizing effect of tungsten in molybdenum based catalysts under selective oxidation reaction conditions.

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The precursor to the (Mo$_{14}$V$_2$)$_5$W$_{5}$O$_{20}$ was prepared by spray-drying of aqueous solutions of ammonium heptamolybdate, ammonium metavandate and vanadyl oxalate.

Heating in 0% synthetic air to 623 K followed by heating in helium to 733 K.

Increasing crystallinity of the (MoVW) oxide material at 773 K in helium.

Isotermal redox experiment at 773 K

Heating of sample to 773 K in inert, at 773 K reduction in 10% propene followed by re-oxidation in 20% oxygen.

In situ XAS

In situ XRD

Redox properties of two Mo$_{14}$O$_{14}$ structured samples with different cation composition at 773 K. Only the (MoVW) oxide containing tungsten is re-oxidized to the (MoVW)$_5$O$_{14}$ type material obtained from the re-oxidation of tungsten containing metal oxide to (MoVW)$_5$O$_{14}$ corroborates the redox-stabilizing effect of tungsten in molybdenum based catalysts under selective oxidation reaction conditions.

Conclusions

HASYLAB is acknowledged for providing beamtime for this work

The long range ordered structure of the bulk is completely described with the Mo$_{14}$O$_{14}$ structure using refined lattice constants and site occupancy factors.

The metals contained in the catalyst under investigation have different characteristic coordination geometry and atomic radii. They may prefer one or the other coordination geometry of oxygen ligands and (de-)stabilize the short metal-metal distances at the pentagonal bipyramidal block units.

Formation of (MoVW) mixed oxide

The XANES at the V K edge. The pre-edge peak height goes through a minimum at 500 K. This is attributed to a minimum of the average valence of V in the precursor.

Experimental data

Difference

Calculated data

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