ODH of Ethane to Ethylene on a MoO_x Sphere Bed Investigated by Spatial Reactor Profiles and Raman Spectroscopy

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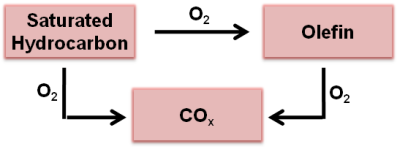
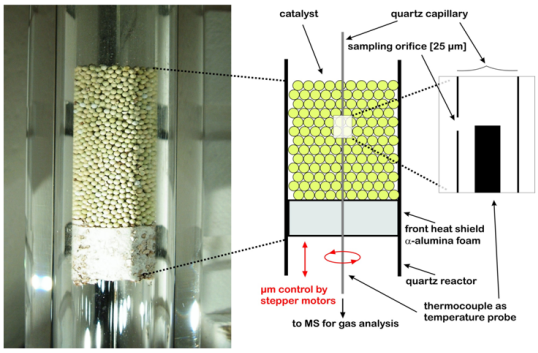
Motivation

Oxidative dehydrogenations (ODH) of saturated hydrocarbons to olefins are characterized by a network of consecutive and parallel reactions.



To study the interrelation between catalytic performance and catalyst structure we present spatial reactor profiles for ethane ODH on γ-alumina supported MoOx as model catalyst and correlate them to the catalyst structure studied by Raman spectroscopy of the quenched catalyst bed.

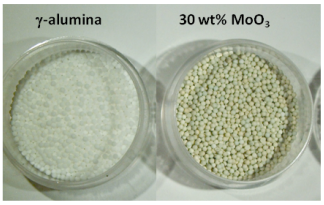
Setup[2] and reaction conditions



- 66 ml/min : 4 ml/min C_2H_6, 4 ml/min O_2, 58 ml/min Ar → GHSV: 520 h^{-1}
- 132 ml/min : 8 ml/min C_2H_6, 8 ml/min O_2, 116 ml/min Ar → GHSV: 1040 h^{-1}
- oven temperature set to 485 °C to keep the maximum reaction temperature around 500 °C to minimize MoO_3 sublimation
- 30 mm bed length with spheres of about 1 mm diameter
- 300 µm spatial resolution per mass spectrum
- 1 h activation in pure oxygen at 500 °C before each experiment

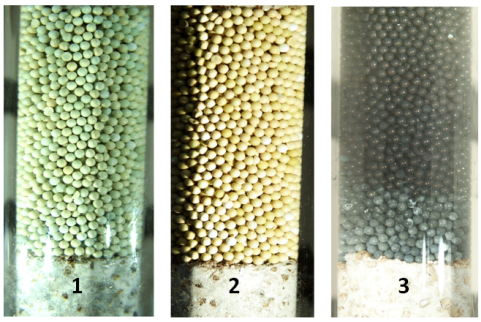
Catalyst preparation

Catalysts are prepared by incipient wetness from an aqueous solution of Ammonium heptamolybdate tetrahydrate. For the 30 wt% catalyst nine impregnation steps were necessary with 2 h drying at 120 °C between each step followed by calcination at 540 °C in air for 12 h.



BET surface area decreased from 157 m^2/g for the pure support to 107 m^2/g after calcination but remains stable under reaction.

Catalyst reaction stages and characterization by XRD

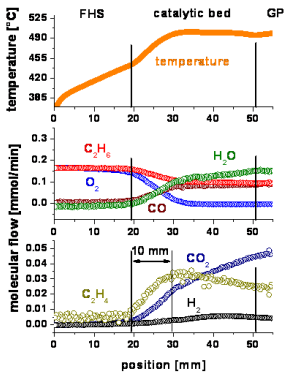


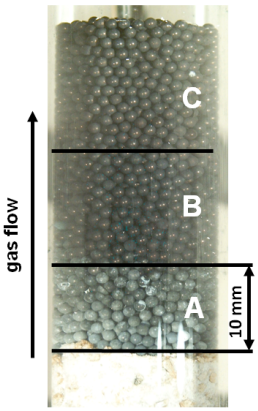
- after preparation (1) the spheres were activated for 1h in pure O_2 at 500 °C prior reaction resulting in the dehydrated state (2)
- depending on flow conditions during the reaction color and oxidation state of the MoO_x species changed (3) as function of position inside the catalyst bed
- XRD diffractograms of the "as prepared" 30 wt% MoO_3 catalyst (1) shows the presence of only γ-alumina and $Al_2(MoO_4)_3$ but no crystalline MoO_3 phase
- XRD analysis of the used catalyst (3) shows $Al_2(MoO_4)_3$ species only in the reaction zone containing gas phase oxygen (3 – grey spheres), the dark spheres in (3) show MoO_2 as major species

Results

Catalytic results

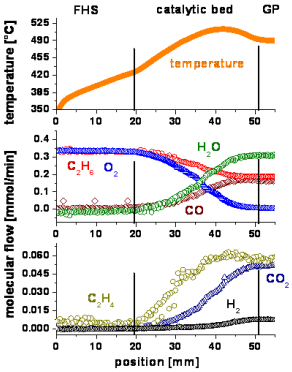
Total flow - 66 ml/min

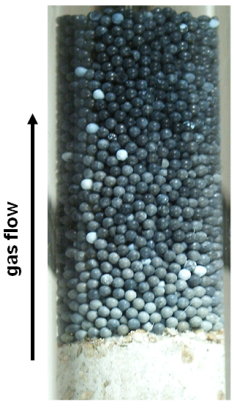




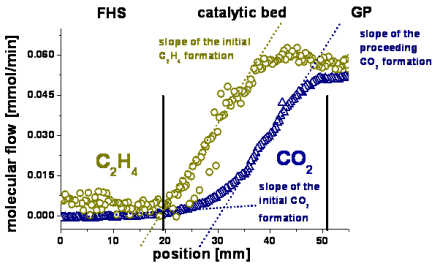
- the high loading of 30 wt% ensures a nearly complete coverage of the acidic centers of the γ-alumina support
- oxygen is fully converted in both experiments
- the main oxidation products are CO and H_2O
- C_2H_4 is formed only in presence of gas phase oxygen and levels off at about 90 to 95 % oxygen conversion
- CO_2 is identified a secondary product by its initial zero slope
- after total conversion of gas phase oxygen ethylene is totally oxidized by lattice oxygen from the molybdate species reducing the catalyst to MoO_2 (violet spheres in area B of the catalyst) as evidenced by Raman and XRD
- the MoO_2 containing spheres show a high electrical conductivity typical for MoO_2

Total flow - 132 ml/min



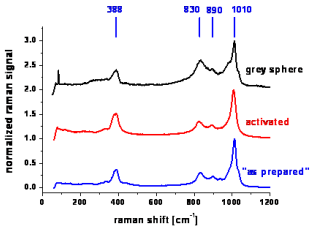


C_2H_4 and CO_2 profiles in the 132 ml/min experiment



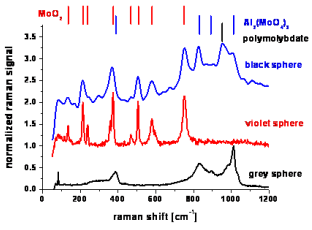
Raman analysis

Oxygen containing atmosphere



Raman spectra of the "as prepared" catalyst (1), under O_2 atmosphere (dehydrated sample, 2) and the grey spheres from the oxidation zone (A). Only Raman bands of $Al_2(MoO_4)_3$ and poly-molybdate species are observed.

Area A, B and C of the 66 ml/min experiment



Violet spheres from area B consist purely of MoO_2. Spheres from area C are a mixture of molybdenum in the +IV and +VI state. With further time on stream also zone C will transform into MoO_2.

Reference wavenumbers taken from: [3]

Conclusion

- in the oxidation zone where C_2H_4 is formed Mo is present as polymolybdate species
- after total oxygen consumption lattice oxygen becomes co-reactant, totally oxidizing C_2H_4 to CO_2 reducing the catalyst to MoO_2, as shown by Raman analysis
- C_2H_6 oxidation by lattice oxygen is less pronounced

Measurement of spatially resolved kinetic and spectroscopic data allows insight into the mechanism of ODH reactions.

References

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[3] J. R. Bartlett and R. P. Cooney, Raman spectroscopic studies in chemisorption and catalysis. In: R. J. H. Clark and R . E. Hester, Editors, *Spectroscopy of Inorganic-based Material*, John Wiley, New York (1987).

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