Synthesis and reactivity of molybdenum-based transition metal carbides in the dehydrogenation of propane

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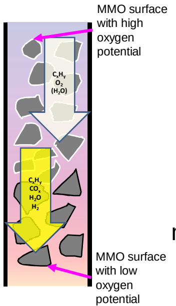
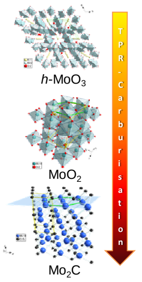
Introduction and Motivation

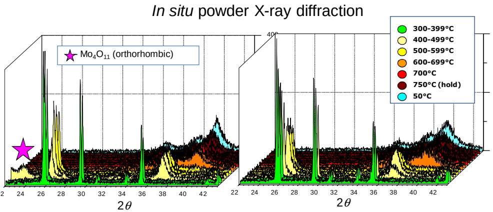


Selective or partial oxidation reactions of light alkanes and oxygenates are regularly carried out over transition metal oxide surfaces. Such reactions in which total oxidation of the substrate molecule is undesired are uniquely problematic and the rigorous conditions under which the catalyst operates often confound comprehensive understanding. Molybdenum-based mixed metal oxides (MMOs) constitute an important class of such catalysts and in particular the oxyfunctionalisation of propane to acrylic acid relies upon the action of a novel class of MoVTe catalysts. Here we present molybdenum carbide (Mo_2C) as a model for a highly reduced oxide surface under conditions of total oxygen conversion in a carbon-enriched atmosphere. The activation of propane under the influence of various feed conditions is studied in conjunction with the observed surface properties of the catalyst.



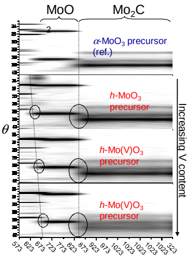
Objective 1: Develop and characterise a MMO system to compare the kinetics of reduction-carburisation

In situ powder X-ray diffraction



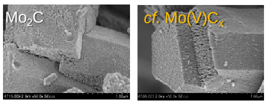
h-MoO_3 → (Mo_4O_{11})→ MoO_2 → Mo_2C h-Mo(V)O_3 → Mo(V)O_2 → Mo(V)C_x

In situ TPR-Carburisation of 100-200mg h-Mo(V)O_3 under 100 sccm He/H_2/CH_4 (50:40:10)



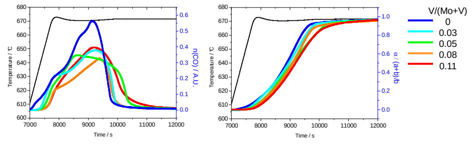
In situ synthesis of Mo(V)C_x materials was carried out in a STOE XRD equipped with a Parr XRK900 cell to determine the influence of vanadium on the reaction kinetics.

Increasing vanadium was found to stabilise the initial reduction
MoO_3 -> MoO_2 and additionally it was observed that the vanadium influenced the nanostructure of the as produced carbides (see below and inset).



Influence of vanadium on MoO_2 -> Mo_2C

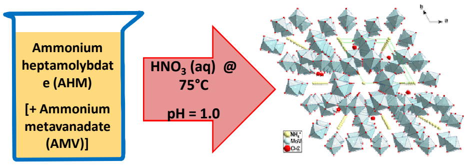
TPR-Carburisation of 500mg h-Mo(V)O_3 under 200 sccm H_2/CH_4 (80:20)



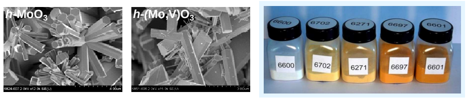
To observe differences in the kinetics of carburisation, the evolution of CO during the carburisation step was observed to give the reaction coordinate α vs. time.

- Vanadium substitution is observed to stabilise the reduction-carburisation of the precursor oxides
- The influence of vanadium substitution also served to modify the nanostructure and resulting mesoporosity of the product carbides

Note 1: Synthesis and characterisation of a mixed Mo-V oxide series

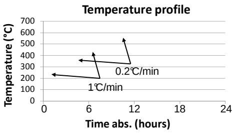


Synthesis of the complex hexagonal molybdate ($Mo_{(1-x)}V_xO_y.xNH_4$) is carried out by controlled precipitation in acidic media followed by aging (2h)

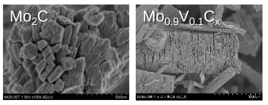


A series of Mo/V oxide precursors were synthesised with a common crystalline phase and progressively substituted V content (0-11%)

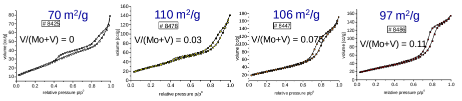
Note 2: Synthesis and characterisation of mixed Mo-V carbides



Scale up reaction to multi-gram quantities in rotating furnace – transfer to glovebox optimise temperature ramp, gas flow and concentration: 360sccm H_2, 90sccm CH_4

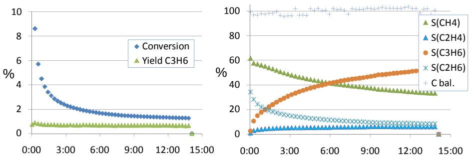


Sample	8425	8478	8447	8486
V/(Mo+V)	0.0	0.03 ± 0.01	0.08 ± 0.01	0.11 ± 0.01
Carbon (%w/w)	5.16	5.21	5.05	5.34
BET (m^2/g)	70	110	106	97



A series of bimetallic carbides (Mo/V) were synthesised on a large scale (~10g) with high surface area and transferred under inert conditions for catalytic testing and characterisation

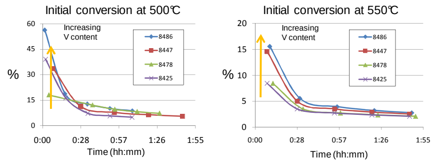
Objective 2: Understand and compare the reactivity of molybdenum-based carbide materials in the activation of propane



Mo_2C pretreated @950K
1 hour; 80:20 H_2/CH_4
10 mL/min C_3H_8
20 mL/min H_2
8 mL/min N_2
450 mg cat. (#9450)
$5000 h^{-1}$ @773K

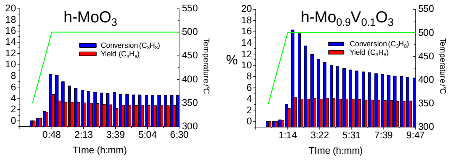
- Initially high activity towards hydrogenolysis
  - ➢Greater than 2:1 ratio of CH_4:C_2H_6
  - ➢Fast deactivation by C deposition
- Steady, but low dehydrogenation observed

Comparison of propane activation on freshly prepared carbide surfaces



- Increasing vanadium content → higher initial activity
- Higher temperature → lower activity (v. fast deactivation?)

Activation of precursor oxide materials in C_3H_8/H_2/N_2 - Temperature programmed reduction-carburisation under reaction conditions



450 mg h-Mo(V)O_x loaded into reactor, ramp 50°C steps under H_2/C_3H_8/N_2 (20/10/8 sccm) to 500°C

- Increasing vanadium content → higher overall activity – mostly hydrogenolysis
- Increasing vanadium content → higher stability to reduction/activation

- Vanadium substitution results in a higher conversion due to increased hydrogenolysis activity
- The oxycarbide appears to be more active precursor for dehydrogenation site

Objective 3: Compare and correlate catalytic activity with observable surface chemistry

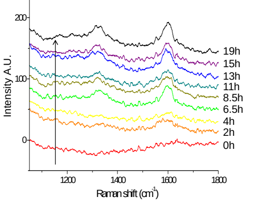
In situ Raman study of surface carbon species

Raman spectra recorded *in situ* SiO_2 cell through 2mm window

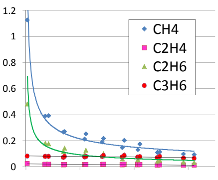
50X ULWD objective
λ=633 nm
Scans: 6
Scan time: 300s

Pressed wafer, 200 mg (#10000)
Re-carburised @950K for1 hour; 80:20 H_2/CH_4

5 mL/min C_3H_8 4 mL/min CO_2
10 mL/min H_2 1 mL/min N_2



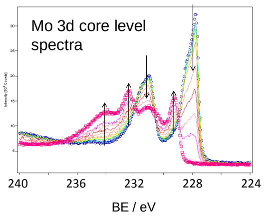
Relative reaction products over time

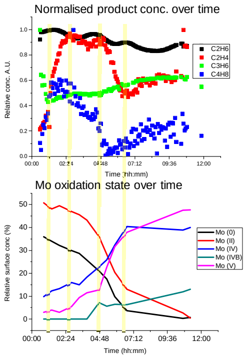


- Oxygen is observed to migrate to the catalyst surface from traces in the bulk
- Adventitious carbon may be removed but at expense of over reduction
- Mo(IV) – Mo (V) species show dehydrogenation
- Indication that the Mo(0) and Mo(IV) phases are correlated
- Hydrogenolysis appears to be on highly active sites and is deactivated via C deposition
- Dehydrogenation is not acutely deactivated by adventitious carbon

In situ XPS at BESSY beamline Mo_2C under C_3H_8/H_2/He

Conditions:
50mg wafer (Mo_2C) at 500°C, 0.3 mbar;
gas flow: C_3H_8 – 2.5 sccm
H_2 – 1.25 sccm
He – 1.25 sccm





ACKNOWLEDGEMENTS

International Max Planck Research School for Complex Surfaces in Material Science
M. Hävecker, D. Teschner, R. Naumann, W. Zhang
A. Trunschke, R. Schlögl

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