

# Dehydrogenation of propane over a bimetallic carbide catalyst



Thomas Cotter, Annette Trunschke and Robert Schlögl  
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

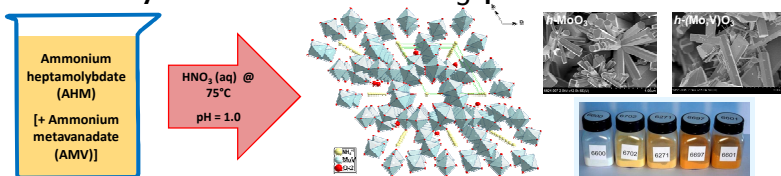
## Introduction

Early transition metal carbides are interesting candidates for use in a number of catalytic reactions. They have been shown to exhibit similar reactivities to those of noble metals under a range of catalytic conditions.<sup>1</sup> Much of the subsequent research has focused on hydrocarbon transformation reactions, but they also demonstrate potential in oxidation chemistry. In such non-oxidic systems there exists the potential to probe the role of surface and subsurface oxygen in catalysis (cf. Mars van Krevelen mechanism). In order to study these materials, molybdenum carbide was chosen as a basis material from which to generate polymetallic doped-carbides. It is anticipated that such doping will confer improved catalytic properties to the final material.

## Objectives

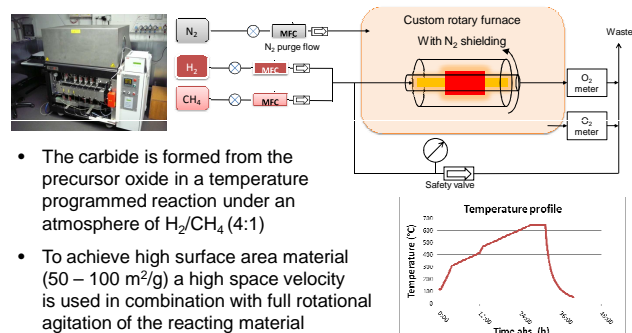
- Develop a flexible synthetic route to molybdenum carbide with high surface area
- Explore synthesis of bimetallic Mo/V carbide in order to tune reactivity
- Test and compare carbide materials for reactivity in the dehydrogenation (DH) and oxydehydrogenation (ODH) of propane
- Study the influence of feed conditions on the carbide activity and stability

## Synthesis of *h*-MoO<sub>3</sub> precursors



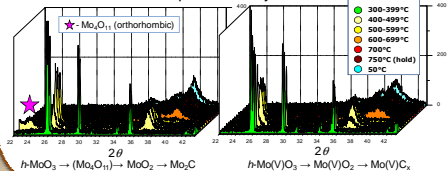
Synthesis of the complex molybdate is carried out by a controlled precipitation in acidic media followed by an aging period (2h)

## Temperature programmed reduction-carburisation



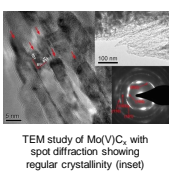
- The carbide is formed from the precursor oxide in a temperature programmed reaction under an atmosphere of H<sub>2</sub>/CH<sub>4</sub> (4:1)
- To achieve high surface area material (50 – 100 m<sup>2</sup>/g) a high space velocity is used in combination with full rotational agitation of the reacting material
- Quantities of material (>10g) may be produced using this method and additionally treated in O<sub>2</sub> - free conditions

## In situ powder X-ray diffraction

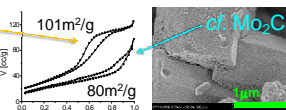
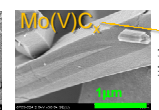
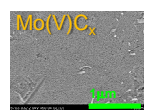


## Characterization of Mo<sub>2</sub>C and Mo(V)C<sub>x</sub>

Influence of precursor on mesostructure and morphology

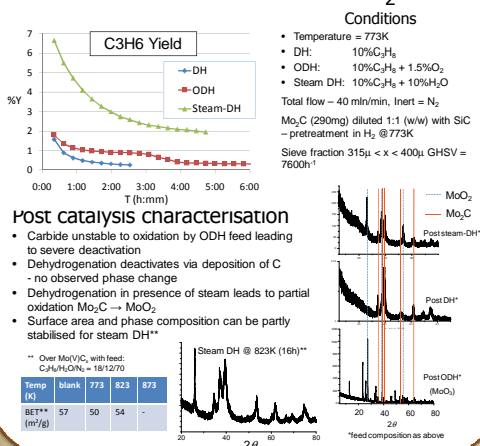


- Electron microscopy indicates the V-containing material has a fibrous, high aspect ratio morphology
- N<sub>2</sub> sorption measurements show exceptional surface area (100 – 110 m<sup>2</sup>/g) of the V-modified carbide
- SEM and porosity calculations indicate a more highly ordered mesostructure for V modification
- X-ray spot diffraction shows ordered crystallinity over a large spot, indicative of a topotactic transformation

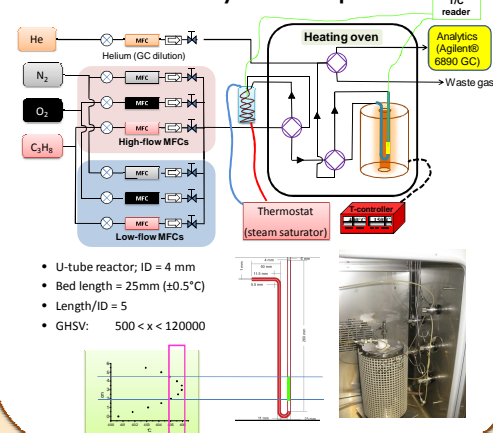


Contrasting SEM micrograph (right) of Mo<sub>2</sub>C shown alongside an N<sub>2</sub> BET isotherm (left) illustrating the carbide porosity and surface area

## DH versus ODH over Mo<sub>2</sub>C



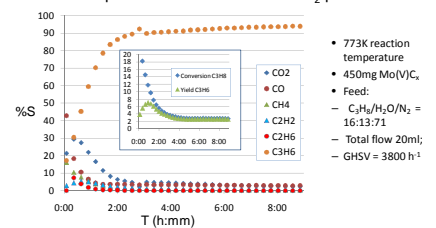
## Catalytic setup



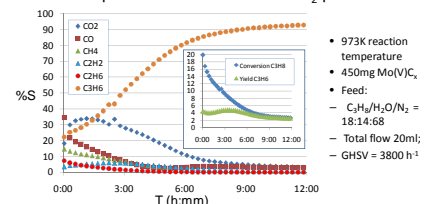
## Reductive pretreatment and surface properties of Mo(V)C<sub>x</sub>

- Mo/V catalysis are pre-reduced in H<sub>2</sub> at different temperatures to explore the influence of surface composition on product distribution

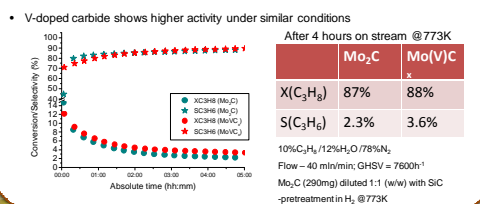
### TOS product selectivities - 773K H<sub>2</sub> pretreatment



### TOS product selectivities - 973K H<sub>2</sub> pretreatment



## Comparison of Mo<sub>2</sub>C and Mo(V)C<sub>x</sub>



## Conclusions

- High surface area Mo<sub>2</sub>C was produced from vanadium-doped *h*-MoO<sub>3</sub> with varying V content
- A novel mesostructured bimetallic carbide was prepared with exceptional morphology
- Reactivity explored for the activation of propane:
- Oxycarbide more active phase for dehydrogenation
- Metallic carbide surface exhibits increased stability to oxidation
- Mo<sub>2</sub>C bulk phase can be preserved in a balance of steam oxidation and carburisation-reduction

- Freshly reduced carbides show similar initial reactivity to hydrogenolysis/dehydrogenation
- Oxycarbide species is more highly selective to dehydrogenation
- More highly reduced material exhibits greater stability to oxidation
- Most active species lies between molybdenum carbide and molybdenum dioxide oxidation state

## ACKNOWLEDGEMENTS

International Max Planck Research School for Complex Surfaces in Material Science  
AC Reactivity Group, Dr. Raoul Naumann, Dr. Olaf Timpe, Edith Kitzelmann, Gisela Lorenz, Daniel Brennecke

## REFERENCES

R.B. Levy, and M. Boudart, Science 181 (1973) 547-549.  
O. Mounj, J.-L. Dubois, F. Mathieu, and A. Roussel, Journal of Solid State Chemistry 152 (2000) 353-360.  
T. Cotter, F. Girgsdes, W. Zhang, A. Trunschke, R. Schlögl, in preparation