

## Synthesis of stable V-doped Mo<sub>2</sub>C with high surface area

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### Introduction

Since Levy and Boudart first demonstrated the Pt-like catalytic properties of tungsten carbide [1], there has been increasing interest in early transition metal carbide and nitride catalysts as substitutes for expensive noble metals in industrial catalytic processes. In particular, molybdenum carbide has long been shown to have promising catalytic properties in a number of hydrocarbon transformation reactions [2]. There are a number of routes to molybdenum carbide reported in the literature, however, the preparation of powders with high surface area devoid of surface impurities remains challenging [3]. Another important challenge from a synthetic point of view is to overcome the intrinsic instability of the aforementioned compounds with respect to oxidative sintering. This is reflected in catalytic studies where stability of the catalytic material is paramount.

In this study a series of single-phase bimetallic carbides have been synthesised by carbothermal reduction, and their phase development monitored *in situ*. By changing the dopant concentration in the precursor oxide, it is possible to tailor the morphological and textural properties of the resultant carbide.

### Materials and Methods

The hexagonal modification of molybdenum trioxide (*h*-MoO<sub>3</sub>) was used as a precursor material for the carbothermal reduction process. Doped and undoped *h*-MoO<sub>3</sub> was synthesised using reported methods [4] with varying concentrations of V as a dopant metal. These oxides were subsequently carburized *via* temperature-programmed-reaction [5] using an Anton Paar XRK-900 *in situ* cell equipped with a STOE diffractometer under a flowing atmosphere of He/H<sub>2</sub>/CH<sub>4</sub> (5:4:1). The carbide materials were characterized using BET measurements, SEM-EDX, TEM and elemental analysis. The catalytic activity of the products was tested in the dehydrogenation reaction of propane to propene.

### Results and Discussion

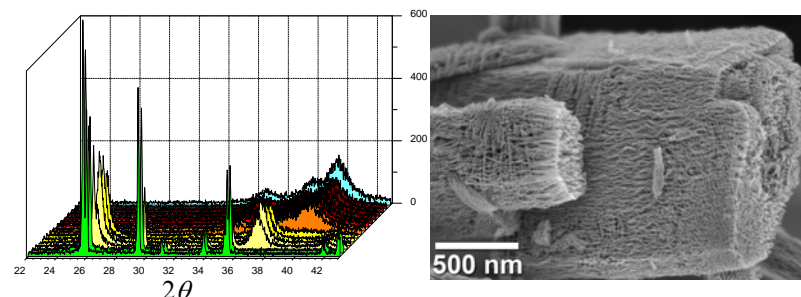
Figure 1 shows the *in situ* powder X-ray diffraction results of the carbothermal reduction of V-containing molybdenum carbide with a dopant concentration of ca. 7% (metals basis). The doped oxide smoothly undergoes carbothermal reduction according to: *h*-MoO<sub>3</sub> → MoO<sub>2</sub> → β-Mo<sub>2</sub>C. In contrast, the reaction of the V-free reference material is characterized by an additional monoclinic MoO<sub>x</sub> phase appearance prior to MoO<sub>2</sub> formation. This difference in the reaction pathways is likely attributed to the increased content of ammonium ions, present in the channels of the V-doped *h*-MoO<sub>3</sub> to balance the charge. The doped carbide is formed as porous, fibrous structures consisting of highly associated crystallites with average size of 3.5 nm, also retaining the overall hexagonal-prismatic morphology of the parent oxide (Fig. 2). It exhibits a high specific surface area of 95 m<sup>2</sup>/g. Whereas undoped Mo<sub>2</sub>C tends to decrease

markedly in surface area over a period of weeks in atmospheric conditions, no reduction in surface area is detected for the doped carbide even after 4 months. This observation indicates an exceptional stability of the title compound towards oxidative sintering. The catalytic performance of derived materials is investigated in the dehydrogenation of propane to propene and the respective results are discussed.

### Significance

The use of multi-metal oxides (MMOs) as precursors for carbides is a largely unexplored area of transition metal carbide chemistry. In particular it offers interesting possibilities to produce stable polymetallic carbides with high specific surface areas – promising substitute materials for noble metals [1].

To the best of our knowledge this is the first report of *in situ* monitoring of the carbothermal reduction of a molybdenum oxide to molybdenum carbide. A strategy for the synthesis of polymetallic carbides was successfully explored *via* a synergetic effect between the doping and structural properties of a MMO precursor. The synthesized carbide is indeed a stable, nanocrystalline material which exhibits high surface area – an important step to enhanced catalytic performance.



**Figure 1. (left)** *In situ* XRD plot showing the phase development in 50K increments from 573K to 1023K with final scan at 323K; **Figure 2. (right)** SEM image showing fibrous β-(Mo<sub>0.93</sub>V<sub>0.07</sub>)<sub>2</sub>C

### References

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