

Synthesis of nanostructured mixed transition metal carbides



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Aims:

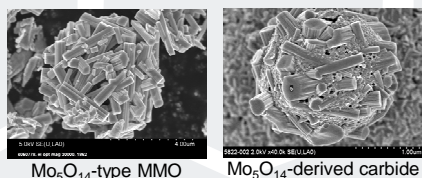
- (1) To investigate the temperature programmed carburisation of mono- and polymetallic molybdenum-oxo species
- (2) Compare and develop an understanding of the structural role of the oxide precursor in determining the reaction pathway
- (3) Concieve and demonstrate a scalable synthesis to generate large quantities of high surface area material for characterisation and testing

Introduction

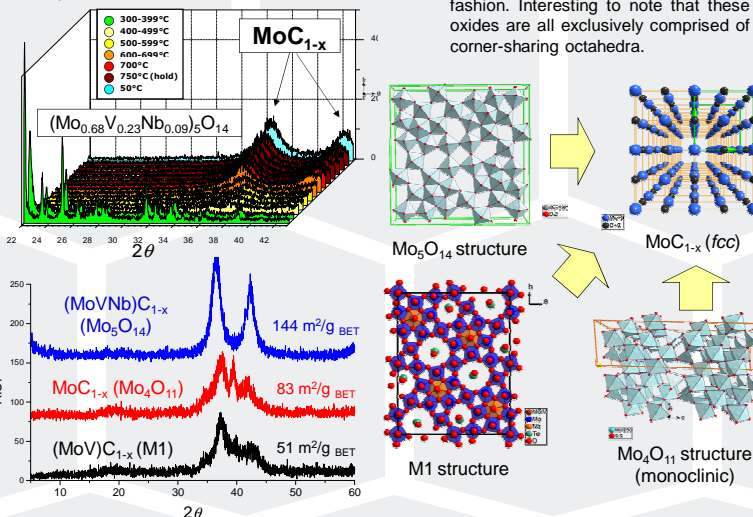
Molybdenum carbides are known to exhibit catalytic activity similar to that of the noble metals. In general it is recognized that Mo carbides and oxycarbides are effective in the activation of C-O, N-N, C-C and H-H bonds making them attractive candidates for a number of hydrocarbon transformation reactions.

Molybdenum participates in an extensive chemistry with oxygen providing numerous potential approaches to mono- and polymetallic carbides via multi-metal oxide (MMO) and complex oxide precursors. Using an appropriate precursor material we are able to tune the chemical compositions and also direct the phase formation of produced carbides.

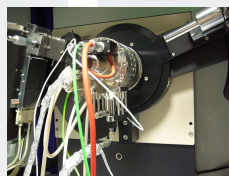
Mo₅O₁₄ structures and related complex oxides



Under carburisation conditions, a pseudomorphic and topotactic transformation to MoC_{1-x} (fcc) is observed with no intermediate phase. This reaction pathway is also observed for Mo₅O₁₁ which can be considered a building block for the structure of Mo₅O₁₄. Likewise, a MoV_x analogue of the M1 phase behaves in a similar fashion. Interesting to note that these oxides are all exclusively comprised of corner-sharing octahedra.

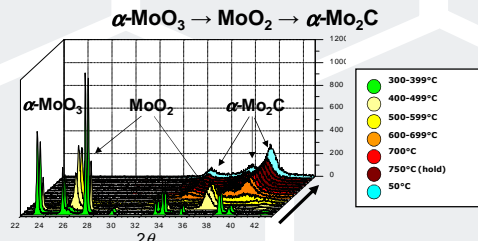


Temperature programmed carburisation



Anton Paar XRK-900 cell

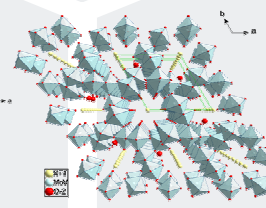
Oxidic precursors are carburised in a temperature programmed reaction (TPR) under a mixture of H₂ and CH₄ (80:20 v/v%). The reaction is characterised *in situ* in a Anton Paar XRK-900 cell seated in a STOE powder X-ray diffractometer.



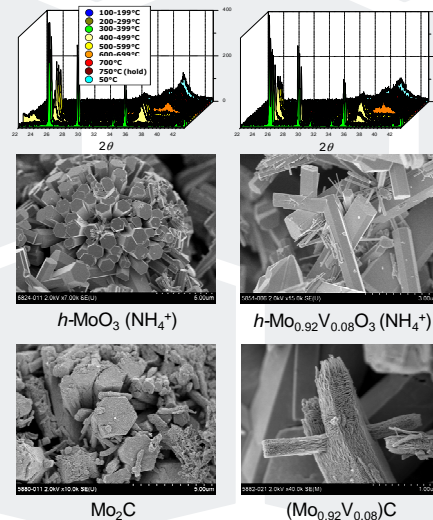
Mo₂C from $\alpha\text{-MoO}_3$

h-Mo(V)O₃ → $\alpha\text{-Mo(V)C}_x$

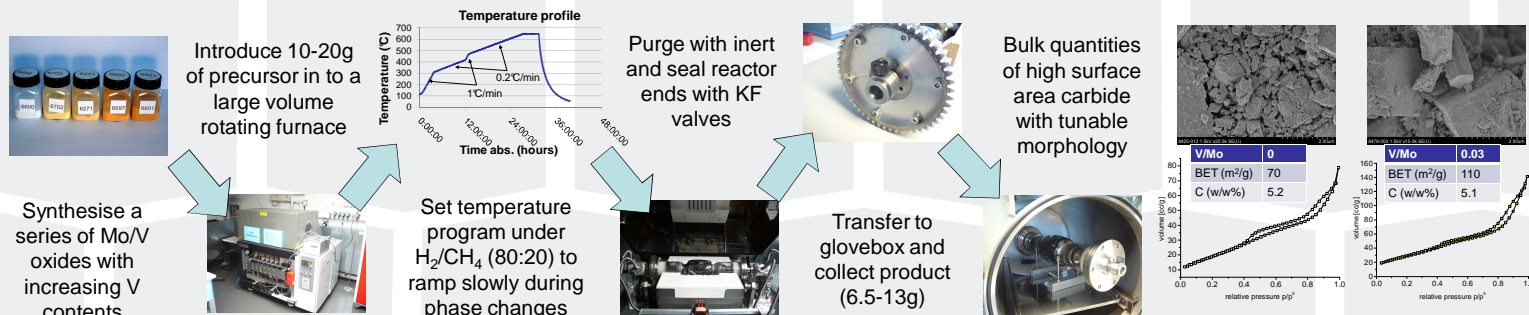
Pseudomorphism and Topotacticity in Mo₂C



Hexagonal MoO₃ is a bronze-like molybdate structure with hexagonal channels. The channels are occupied by cations which stabilise the structure. The structure on the left is undoped h-MoO₃ and on the right is a V-doped h-MoO₃ both with ammonium ions as stabilising cation. Like the orthorhombic $\alpha\text{-MoO}_3$, it is seen that the structure is comprised of ribbons of edge-sharing MoO₆ octahedra which is reduced to MoO₂ during carburisation



Upscaled synthesis of MoVC_x from a mixed-metal oxide precursor h-Mo(V)O₃



Conclusions

- In the temperature programmed carburisation of MoO_x → MoC_x, the choice of precursor oxide can be used to tune the morphological, chemical, and phase properties of the resultant carbide.
- It is seen that in many cases the use of polymetallic molybdenum-based oxides can result in a single phase carbide
- It was observed that the phase (Mo₂C or MoC_{1-x}) is determined by structural motifs in the precursor oxide material relating to the oxygen sharing of the Mo octahedra (edge sharing octahedra exhibit the reducibility; MoO₂ → Mo₂C)
- It is demonstrated that the process can be scaled to multi-gram quantities (>10g) and that the resultant material can be handled and characterised in a pristine state.

References

1. Oyama, S. T., The Chemistry of Transition Metal Carbides and Nitrides. Blackie 1995
2. Oyama, S. T.; Yu, C. C.; Ramanathan, S., Journal of Catalysis 1999, 184, (2), 535-549.
3. Cotter, T., Girgsdies, F., Zhang, W., Timpe, O., Trunschke, A., Schlögl, R., 2010 (In preparation)

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