Structure evolution of Mo₂C catalysts upon exposure to oxygen

Jacob Held[1], Mark Sullivan[1], Aditya Bhan[1], K. Andre Mkhoyan[1]

[1.] Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455.

Molybdenum carbide (Mo₂C) formulations have recently received renewed interest as catalysts that can be functionally tuned via surface termination alteration (e.g. Mo, C, or O) [1-4]. In this work, we demonstrate oxygen co-processing as a means of reversibly tuning catalyst acid site density *in situ*. Oxygen co-feed was observed to reversibly alter the dehydration rate of isopropyl alcohol by a factor of about 30 as shown in Figure 1a. Oxygen adatoms both suppressed metallic functionality and generated Brønsted acidity. Nitrogen physisorption measurements in conjunction with XRD peak broadening showed that catalyst particles were composed of 2-5 nm crystallites with BET surface areas of 60 - 100 m^2 g_{cat}^{-1}. However, catalyst X-ray diffractograms (Figure 1b) were inadequate for accurate catalyst phase determination due to the indistinguishability of the proposed hexagonal close-packed and orthorhombic Mo₂C phases.

Here we report on the evolution of the crystal structure of Mo₂C catalysts using analytical scanning transmission electron microscopy (STEM). Crystal structures of the catalyst particles were analyzed by high-angle annular dark-field (HAADF) imaging using an aberration-corrected monochromatic FEI-Titan G2 60-300 equipped with a Gatan Enfinium EEL spectrometer and a Super-X EDX system.

A representative sample of post-reaction Mo₂C catalyst particles was mechanically crushed in an agate mortar and suspended in dimethylformamide. The resulting suspension was then sonicated to break up agglomerates, and was drop cast onto a holey/thin carbon film on a copper grid. HAADF-STEM imaging, shown in Figure 2, revealed that the catalyst particles consist of 1-3 nm crystallites with 1-2 nm pores visible throughout, which corroborates the XRD analyses. Analysis of high-resolution HAADF-STEM images of particles tilted to low-order zone axes were used to evaluate the structure and symmetry of individual crystallites, confirming the presence of orthorhombic Mo₂C in post-reaction samples with lattice parameters that agreed well with neutron scattering analyses by reported by Parthé *et al* [5].

References:

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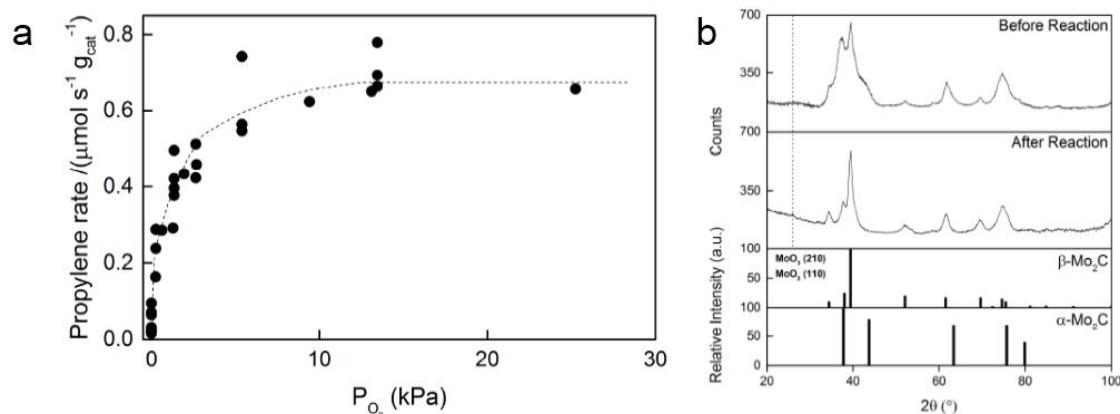
Figure 1. a) Propylene synthesis rate from IPA as a function of co-fed O_2 partial pressure, showing a reversible 30 fold control of Brønsted acid site density. **b)** X-ray diffractograms of Mo_2C catalysts before and after reaction including reference diffractograms for orthorhombic β-Mo_2C [5] and FCC α-Mo_2C phases [6]. The positions of the highest intensity MoO_2 and MoO_3 peaks are also included.
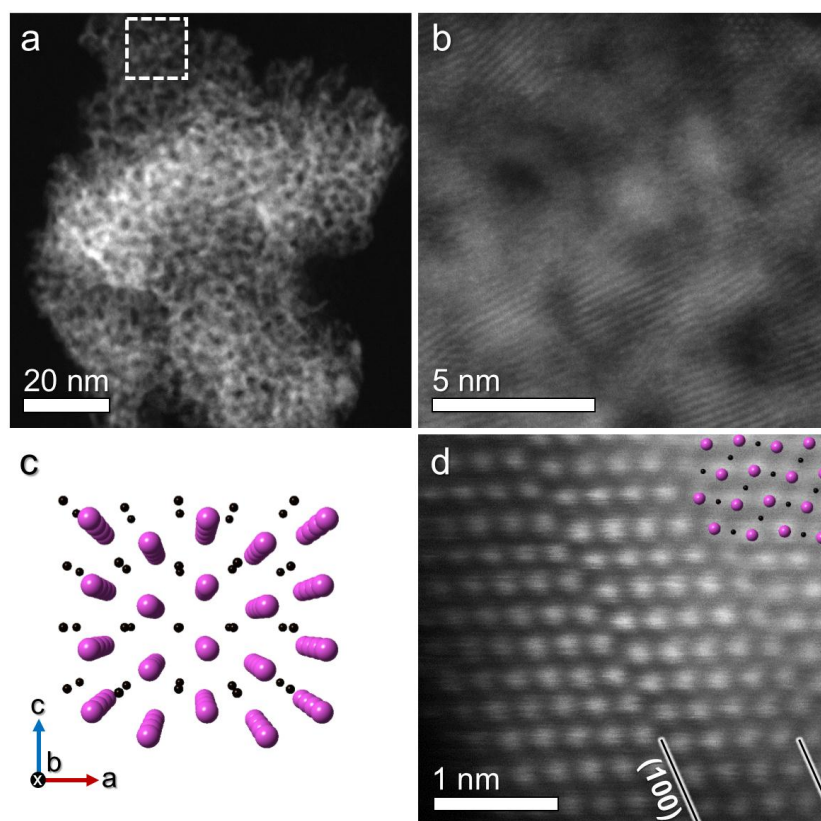

Figure 2. a) HAADF-STEM image of a post-reaction catalyst particle exhibiting visible porosity in the range of 1-2 nm. **b)** High magnification of boxed region of image in a) showing crystallinity, size of grains, and porous features. **c)** Schematic view down the [010] zone axis of orthorhombic Mo_2C [5]. Mo atoms are in pink, while C atoms are in black. **d)** Representative high resolution HAADF-STEM image of [010] zone axis of the same sample. Two stacking faults on the (100) planes are marked with lines.