



Experiment title: Operando XAS/XRD/Raman-MS study of iron molybdate catalysts for the selective oxidation of methanol to formaldehyde

Experiment number:
MA-3711

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Report:

Formaldehyde is an important chemical intermediate in the production of a large array of industrial products including thermosetting resins, adhesives, paper, and fertilizers [1]. This underlines the importance of the industrial production of formaldehyde. The most effective industrial process in terms of yield and cost is the Formox process, which uses a bulk iron molybdate catalyst with an excess of molybdenum oxide ($\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3, \text{FeMo}$). It has been proposed that the excess MoO_3 primarily acts to replace molybdenum oxide lost through reaction with methanol, due to formation of volatile species at elevated temperatures, and to improve the selectivity, as iron oxide is known to catalyze the complete oxidation of methanol [2]. Understanding the molybdenum volatilization is important since industrially it leads to shutdown, cleaning and catalyst replacement due to pressure drop increase by molybdenum oxide precipitating from the gas phase downstream in the reactor. Recently, it has been shown that the surface layer of such catalysts are composed of octahedral Mo units, compared to the tetrahedral Mo centers found in $\text{Fe}_2(\text{MoO}_4)_3$ [3]. This over-layer structure has been proposed to be the active surface for the selective oxidation of methanol to formaldehyde [4-5].

This operando XAS/XRD and Raman spectroscopic study investigates the structural changes of the FeMo catalyst at industrially relevant reaction conditions, which is important for rational improvement of the catalysts and reaction conditions. The reaction was operated at high space velocity, in order to achieve uniform changes throughout the catalyst bed and to simulate conditions near the inlet of the industrial reactor where MoO_3 volatilization is most significant. By measuring XAS at the Mo K- and Fe K-edges, we have investigated the atomic environment and oxidation states of all involved phases during the various steps of the catalyst life at industrially relevant conditions. The obtained in-operando information is important because mobile Mo oxide species have been found, which can lead to a deactivation of the catalyst.

For the operando XAS/XRD studies, a FeMo catalyst prepared by a hydrothermal method (with Mo/Fe ratio 2.0) was calcined at 535 °C in air, subsequently crushed and grounded with silica in a 1:5 weight ratio. This mixture was pressed to form a pellet, crushed and sieved to 100-150 µm. Experiments were performed by means of a fixed-bed micro-reactor using 1 mm (0.01 mm wall thickness) quartz capillaries. Operando XAS measurement at Mo K-edge (20.0 keV) and Fe K-edge (7.112 keV) in combination with XRD was carried

out at the Swiss–Norwegian beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France operated at energy of 6 GeV and with a current of 200 mA. Three ionization chambers were used to detect the incident intensity (I_0), transmitted intensity (I_1), and reference Mo foil transmitted intensity (I_2). XRD patterns were recorded with a CMOS-Dexela 2D detector at an X-ray wavelength of 0.04934 nm (25.13 keV). For each diffractogram, five bright and five dark images for background subtraction were recorded in the 2θ range of $2 - 35^\circ$ with a data point spacing of approximately 0.01° and averaged. The sample to detector distance was calibrated with a LaB_6 reference.

Heating of catalyst in the flow of 5 % MeOH/He caused reduction which can be observed from the Mo K-edge XANES features (figure 1 (a)). The edge position shifted to low energies indicating decrease in the oxidation state of Mo. The decrease in intensity of peak A shows rise in octahedral Mo centers, i.e., $\text{Fe}_2(\text{MoO}_4)_3$ was reduced to FeMoO_4 and thereby forming MoO_x species (MoO_2 , MoO_3 and intermediate phases). Linear combination fitting (LCF) analysis during TPR at the Mo K-edge (figure 1 (b)) shows that reduction of Mo starts at $\sim 280^\circ\text{C}$ and with increase in temperature, the contribution from Mo(red) and MoO_2 increases. Under TPR, the Fe K-edge XANES spectra (figure 1(c)) also show shift towards lower energies indicating reduction of $\text{Fe}_2(\text{MoO}_4)_3$ to form FeMoO_4 . From LCF, it has been found that reduction of Fe also starts at $\sim 280^\circ\text{C}$ parallel to Mo and at some temperatures presence of Fe_2O_3 and FeO were also observed as intermediate phases. In-situ XRD (figure 1(d)) also shows that initial phase of catalyst at 100°C show presence of $\text{Fe}_2(\text{MoO}_4)_3$ as well as MoO_3 and FeMoO_4 was formed above 280°C which is in accordance with Mo K- and Fe K- XAFS.

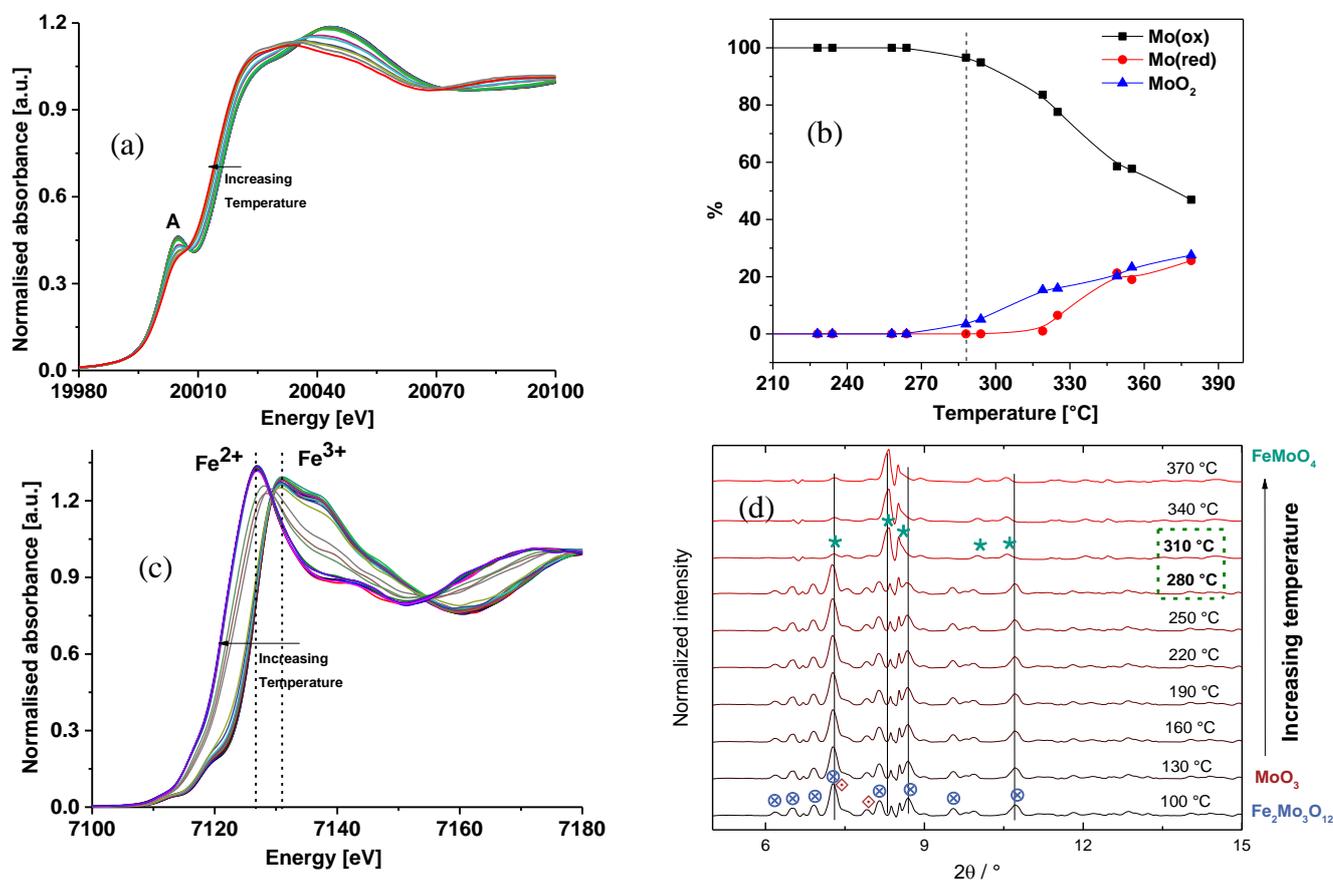


Figure 1. For the catalyst during TPR under 5 % MeOH/He (a) Mo K-edge XANES, (b) corresponding LCF results, (c) Fe K-edge XANES and (d) In-situ XRD.

These primary results shows that $\text{Fe}_2(\text{MoO}_4)_3$ was decomposed into FeMoO_4 and MoO_3 around 280°C . Further, analysis of the data has been done and two manuscripts based on these results is under preparation.

- [1] G. Reuss, W. Disteldorf, A. O. Gamer, and A. Hilt, "Formaldehyde," in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [2] M. Carbuticchio and F. Trifirò, *J. Catal.*, vol. 45, no. 1, pp. 77–85, 1976.
- [3] A. M. Beale *et al.*, *Appl. Catal. A Gen.*, vol. 363, no. 1–2, pp. 143–152, 2009.
- [4] C. Brookes *et al.*, *J. Phys. Chem. C*, vol. 118, no. 45, pp. 26155–26161, 2014.
- [5] C. Brookes, *et al.*, *Catal. Sci. Technol.*, vol. 6, no. 3, pp. 722–730, 2016.