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Structural dynamics of an iron molybdate catalyst under redox cycling conditions studied with \textit{in situ} multi edge XAS and XRD$^\dagger$

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The structural dynamics and phase transformations of an iron molybdate catalyst with excess molybdenum trioxide (Mo/Fe = 2.0) were studied during redox cycling of the catalyst using \textit{in situ} multi-edge X-ray absorption spectroscopy (XAS) at the Mo K-edge (transmission mode) and Fe K-edge (fluorescence mode) in combination with X-ray diffraction (XRD). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis showed that heating under reducing conditions with methanol up to 400 °C produced MoO$_2$ and FeMoO$_4$. Linear combination fitting (LCF) analysis showed that iron was reduced completely, while molybdenum remained partly oxidized (60% as Mo(v)). Complementary \textit{in situ} XRD also supported the phase transformation due to reduction of Fe$_2$(MoO$_4$)$_3$ and MoO$_3$ to FeMoO$_4$ and MoO$_2$. Subsequent heating under oxidative conditions from 200 to 500 °C transformed the catalyst into its initial state via Fe$_2$O$_3$ and extra MoO$_3$ as intermediate phases. This underlines the segregation and iron enrichment during redox cycling. MoO$_3$ volatilization, observed under industrial reaction conditions of a methanol and oxygen containing atmosphere, causes this segregation to be permanent. Complete regeneration could only be achieved at 500 °C, which is significantly higher than industrial reaction temperatures. Overall, multi edge \textit{in situ} XAS along with complementary XRD was found to be an ideal tool for tracing the different amorphous and crystalline phases present during redox cycling of the catalyst.

1. Introduction

Iron molybdate with an excess of molybdenum oxide (denoted FeMo throughout the paper) is an industrially important catalyst for the selective oxidation of methanol to formaldehyde, which has led to a number of fundamental studies concerning its structure, activity, mechanism, stability and deactivation.$^{1-6}$ To improve the performance of a catalyst on a knowledge-based approach, it is critical to understand the structure and structural dynamics of the catalyst under reaction conditions. Commercial iron molybdate catalysts are typically formulated with an excess of molybdenum(vi)oxide, since Mo is known to volatilize from the reactor inlet and hot spot$^7$ during the reaction, leaving an unselective Fe rich surface.$^8$ The FeMo system contains multiple distinct phases including bulk $\alpha$-MoO$_3$ and Fe$_2$(MoO$_4$)$_3$, as well as a surface layer of MoO$_x$ on the Fe$_x$(MoO$_4$)$_3$ surface.$^9$ Hence, it is difficult to assess the nature of the active sites and role of Fe$_2$(MoO$_4$)$_3$, specifically whether it merely acts as a support for the active MoO$_x$ or whether it has its own inherent activity. The catalytic behavior of FeMo catalysts was observed to be mainly dependent on their Mo/Fe atomic ratio.$^{2,10}$ The most active phase composition of the bulk iron molybdate catalyst was proposed to have the stoichiometric Mo/Fe ratio of 1.5$^3$ and the function of excess MoO$_3$ is speculated to maintain the active phase of the catalyst
at this ratio. The activity and selectivity of bulk iron molybdate catalysts for methanol oxidation was examined as a function of Mo/Fe ratios from 0.02 to 4,\(^2\) revealing that Mo/Fe ratios greater than 1.5 are required for high catalytic activity and selectivity to formaldehyde. The presence of an octahedral Mo oxide overlayer has been reported,\(^1\) which corresponds to one monolayer. Various groups have proposed that this overlayer structure is the fundamental, active surface for the selective oxidation of methanol to formaldehyde.\(^1,5,11\) The presence of two terminal oxygen atoms double bonded to Mo in such coordination allows the reacting methanol molecules to be bonded simultaneously at two points to the surface. The formation of several molybdenum oxy-methoxy compounds was also reported\(^12\) and it was argued that hydrogen abstraction of the methanol hydroxyl group produces methoxy species that are intermediates in formaldehyde formation. The role of Fe in iron molybdate catalysts would be to favor the transfer of O\(_2\) and H\(_2\)O between in situ multi-edge XAS at the Mo K- and Fe K-edges combined with complementary XRD. Using redox cycling in methanol and under oxidizing conditions insight into the structural dynamics can be received. The combination of multi-edge XAS and XRD allows for investigating the effect of over-reduction followed by re-oxidation of the catalyst, corresponding to one cycle of the selective oxidation of methanol to formaldehyde. For this purpose we exploited the advanced beamline set-ups available at the synchrotron radiation sources which allow obtaining high quality bulk structural data by XAS and XRD from catalysts under dynamic conditions when simultaneously using multiple techniques.

2. Experimental

The catalyst was prepared by hydrothermal synthesis with special interest paid to the precise adjustment of the atomic molybdenum to iron ratio.\(^7\) The Mo/Fe ratio was 2.0, which resulted in an active and selective catalyst in a broad temperature range, typically 250–400 °C, at a feed concentration of 5 vol% CH\(_3\)OH with about 10 vol% O\(_2\).\(^7\) The catalyst was calcined at 535 °C in air, resulting in a BET surface area of 4.7 m\(^2\) g\(^-1\) and Rietveld refined particles size of 133 nm for the MoO\(_3\) phase and 375 nm for the Fe\(_2\)(MoO\(_4\))\(_3\) phase. The catalyst was crushed and ground with silica in a 1/5 catalyst/silica weight ratio. This mixture was pressed as a pellet, crushed and sieved to 100–150 μm. Combined XAS/XRD studies during temperature programmed experiments were conducted at the SNBL beamline BM31 at ESRF, Grenoble, France.\(^21\) Fig. 1 shows the schematics of the advance experimental setup used for the in situ multi-edge XAS/XRD experiments. As optics requirements for high quality XAS and XRD are quite different, the beamline is equipped with a channel-cut monochromator (CCM) for a high-resolution powder diffraction and a second double crystal monochromator (DCM) for XAS (interchanged within 10 s).\(^21\) Measurements were performed by means of a fixed-bed micro-reactor based on quartz glass capillaries\(^22\) for mimicking optimal heat and mass transfer.\(^23,24\) The catalyst in the form of powder was loaded in a glass capillary with inner diameter of 1.5 mm with the total bed length inside the capillary of 1 cm and the catalyst was fixed from both sides by quartz wool. XAS was performed at the Fe K-edge (7.112 keV) in fluorescence mode and at the Mo K-edge (20.000 keV) in transmission mode quasi-simultaneously by using the fast edge changing facility at the beamline. A molybdenum foil was measured simultaneously as a reference compound for energy calibration. The measurements were conducted in a loop that consisted of two Mo K-edge scans (4 min each), three Fe K-edge scans (5 min each) and one XRD pattern (1 min). Switching between Fe K- and Mo K-energies took approximately 30 s and switching from XAS to XRD monochromator and detector took 60 s.
The overview of the experimental procedure followed during in situ experiments is given in the ESI,† Fig. S1. The catalyst was first heated to 100 °C in a flow of 10% O₂/He. Then the flow was changed to 5% MeOH/He and the sample was heated to 400 °C at 1 °C min⁻¹ for temperature programmed reduction (TPR) and was kept at 400 °C for 1 hour. The sample was cooled to 200 °C after which the flow was changed back to 10% O₂/He. In the next step, the sample was heated to 500 °C at 1 °C min⁻¹ for temperature programmed oxidation (TPO) and after a stabilization period of 1 hour finally cooled to 100 °C.

XAS data were treated with the software package IFEFFIT.²⁵ The spectra were energy calibrated, normalized, and background subtracted in Athena. Linear combination fitting (LCF) of XANES spectra was performed in a range of −20 to +50 eV at the Mo K- and Fe K-edges, respectively. EXAFS fitting was performed in Artemis by using model structures obtained from references of Fe₂(MoO₄)₃ and MoO₃, in the case of Mo. At the Fe K-edge, spectra were only measured in the XANES region due to high noise in the EXAFS region. Fittings at the Mo K-edge were performed in R – as well as k-space for determining the structural parameters which included energy shift of the path (ΔE₀), change in the half path length (ΔR), amplitude reduction factor (S₀²), number of identical paths (N) and relative mean-square displacement of the atoms included in the path (Debye–Waller factor, σ²).

Principal component analysis (PCA) at the Fe K-edge was performed using XANES spectra in the range of −20 to +80 eV using the PCA subroutine of Demeter.²⁵ XRD patterns were recorded with a CMOS-Dexela 2D detector at a short X-ray wavelength of 0.4934 Å (25.13 keV) so that the penetration of X-rays is optimal. For each diffractogram, five bright and additionally five dark images for background subtraction were recorded in the 2θ range of 2–35° with a data point spacing of approximately 0.01° and subsequently averaged. The sample to detector distance was calibrated with a LaB₆ reference. For XRD data treatment, the diffractograms were normalized to the most intense reflection of the SiO₂ dilutant, and a normalized diffractogram of only the dilutant measured at the same temperature was subtracted using an in-house Matlab script.

3. Results and discussion

3.1 Initial state and temperature programmed reduction (TPR)

3.1.1 In situ observations at the Mo K-edge. Fig. 2 shows the in situ Mo K-XANES spectra of the FeMo catalyst during heating under reducing conditions of 5% MeOH/He (TPR).
For comparison, *ex situ* XANES spectra of the FeMo catalyst at 100 °C along with spectra of the reference samples Fe$_2$(MoO$_4$)$_3$ and α-MoO$_3$ are shown in ESI,† Fig. S2. The Mo K-XANES spectra exhibit a pre-edge peak A at ~20.007 eV and another feature B at 20.027 eV. The pre-edge peak A is attributed to the dipole-forbidden/quadrupole-allowed 1s–4d transition, which is associated primarily with tetrahedral geometry. The feature is also present but to weaker extent in distorted octahedral geometry. Feature B at 20.027 eV is assigned to the dipole-allowed 1s–5p transition, a characteristic feature of Mo species with octahedral/distorted octahedral geometry.‡ A comparison of the XANES spectrum of the FeMo catalyst with MoO$_3$ showed that the catalyst had a slightly stronger feature A than for MoO$_3$ and weaker intensity for peak B. Also, the intensity of peak A for the catalyst was considerably lower compared to the reference spectrum of Fe$_2$(MoO$_4$)$_3$.‡ This showed that in the FeMo catalyst, Mo had both tetrahedral (Fe$_2$(MoO$_4$)$_3$ nature) and as well as octahedral geometry (MoO$_3$ nature, i.e., molybdenum oxide with an average oxidation state between Mo(vi) to Mo(v)).

As the initial state of the FeMo catalyst at 100 °C indicated mixed Mo(v) phases, linear combination fitting (LCF) of the XANES spectrum was performed with standards Fe$_2$(MoO$_4$)$_3$ and α-MoO$_3$. This showed 76% contribution from ferric molybdate and 24% contribution from molybdenum trioxide. This is in agreement with the composition of the fresh catalyst as determined by XRD containing 83 wt% Fe$_2$(MoO$_4$)$_3$ and 17 wt% α-MoO$_3$, which corresponds to 22 mol% of the Mo bound as MoO$_3$ and 78 mol% as Fe$_2$(MoO$_4$)$_3$.†

The XANES features of the spectra during TPR (Fig. 2) showed that the edge position shifted to lower energies, from 20012.3 to 20010.2 eV, revealing partial reduction of Mo. The decrease in intensity of peak A and simultaneous increase in the intensity of feature B showed a rise in the octahedral nature of Mo centers, corresponding to Fe$_2$(MoO$_4$)$_3$ being decomposed to FeMoO$_4$ and thereby forming MoO$_3$ species e.g. MoO$_2$ and intermediate MoO$_x$ (x = 2–3) species. However, it can be seen that after TPR, peak A was still present showing that Mo(vi) was not completely reduced to Mo(nv), which does not have this feature. Since MoO$_3$ has a strictly octahedral field, the 1s–4d transition is forbidden and no pre-edge peak would be observed.‡

The corresponding Fourier transformed EXAFS spectra during TPR are shown in the inset of Fig. 2 where in the initial state of the catalyst a high amplitude of the first peak (Mo–O$_1$) indicated strong tetrahedral nature due to a high content of Fe$_2$(MoO$_4$)$_3$. Metal backscattering at ~3 Å (Fe) additionally indicated the presence of Fe$_2$(MoO$_4$)$_3$.§ The fitting results for the initial state of the catalyst at 100 °C in 10% O$_2$/He (see ESI,† Table S1) also supported the presence of multiple Mo phases (see also ESI,† Fig. S3(a)). At about 290 °C, this metal backscattering disappeared due to the reduction of Fe$_2$(MoO$_4$)$_3$, (Fig. S3(b), ESI†). In the final state during TPR at 350 °C, the amplitude of the Mo–O$_1$ contribution was highly reduced showing the presence of disordered Mo oxide phases (Fig. S3(c), ESI†).

In order to determine the contribution of different phases during the TPR, LCF was performed using standard spectra of Fe$_2$(MoO$_4$)$_3$, MoO$_3$ and MoO$_2$. FeMoO$_4$ was not available as reference due to unavailability of this compound commercially and its instability during synthesis. Also, at the Mo K-edge weak XANES features present in the FeMoO$_4$ phase were found to be overlapping with strong features of the Mo(vi) phases Fe$_2$(MoO$_4$)$_3$ and MoO$_3$ (for details see ESI,† Fig. S4). Thus, the formation of FeMoO$_4$ and associated reduction of iron, is measured and discussed more clearly using Fe K-edge XANES in Section 3.1.2. It is worth mentioning here that PCA cannot be applied at Mo K-edge due to the unavailability of set of proper standard spectra. The contributions of the different phases obtained from LCF analysis of the XANES spectra at the Mo K-edge during TPR are shown in Fig. 3(a). Reduction of Mo started at approximately 270 °C and the contribution from MoO$_2$ was observed at the expense of an initial decrease in MoO$_3$ content. In the final state at 400 °C, contributions from Fe$_2$(MoO$_4$)$_3$, MoO$_3$ and MoO$_2$ were observed to be 43%, 20% and 37%, respectively. Note that MoO$_3$ and Fe$_2$(MoO$_4$)$_3$ together represent the Mo(vi) present as FeMoO$_4$ after reduction, see also Fe K-edge XANES and XRD results in Section 3.1.2. Thus, at 400 °C, about 40% of the Mo(vi) species were reduced to Mo(nv) species, represented by MoO$_2$. Some MoO$_x$ (x = 2–3) may also be presented by a combined contribution from MoO$_2$ and MoO$_3$ as it is hard to detect these species by their XANES fingerprint. More than 50% of the Mo was still present in oxidation state VI, which is in agreement with a previous *in situ* catalytic study at 250 °C, which showed that during formaldehyde production only Mo(v) was present throughout the experiment, indicating that gas phase oxygen transfer to molybdenum is rapid under reaction conditions at temperatures near the lower range of industrial conditions (typically 220 to 350 °C).

Corresponding EXAFS spectra were analyzed by performing fitting in R-space and variation of selected obtained parameters are given in Fig. 3(b). Initially at 100 °C, the CN of Mo–O$_1$ was found to be 5.0 (±0.4) at 1.76 Å, which indicates strong contribution from the tetrahedral Mo centers present in Fe$_2$(MoO$_4$)$_3$. A considerable decrease in the CN of Mo–O$_1$ was observed at approximately 290 °C (see also Fig. S3(b, c) and Table S2, ESI†).
Also, the DW factor for Mo–O1 started increasing in parallel with the reduction process and was almost doubled at the end of TPR, showing higher disorder in these bonds. Conversely, the DW factor for the longer Mo–O2 bonds (axial position), which corresponds to octahedral Mo centers, decreased at higher temperature showing stronger axial bonds due to an increase in octahedral nature of Mo centers present in MoO$_x$ species (the CN of each of Mo–O2 bond were fixed to 1). Hence, with increasing temperature, a decrease in Mo oxidation state and an increase in octahedral nature of Mo centers were observed. These structural changes point towards formation of MoO$_2$ and as well as MoO$_x$ species during TPR (see also Fe K-edge XANES and XRD results in Section 3.1.2).

3.1.2 In situ observations by Fe K-edge XAS and XRD. Fig. 4(a) shows the in situ Fe K-XANES spectra during TPR, measured in the loop with Mo K-edge spectra to simultaneously probe the oxidation state and phase transitions of Fe. The features observed for the initial state of Fe at 100 °C show similarity with the Fe$_2$(MoO$_4$)$_3$ spectral features reported earlier.$^{29}$ Initially, the Fe K-edge absorption peak maxima was observed at 7131.8 eV, which is similar to the value reported in literature.$^{29}$ At higher temperature, the spectra exhibited a gradual shift towards lower energy indicating a change in the average oxidation state of Fe from III to II, mainly corresponding to formation of FeMoO$_4$, however the presence of other Fe(II) species cannot be ruled out. In the temperature range 200–300 °C, the presence of iron oxides such as Fe$_2$O$_3$ and FeO were also expected as intermediate phases. Hence, PCA was performed over Fe K-edge XANES spectra measured in this temperature range to confirm the number components required to fit the spectra by LCF analysis.

PCA uses matrix operations on an experimental spectra data matrix, to give two main outputs in the form of eigenvectors and eigenvalues, thereby providing the minimum number of significant components required to satisfactorily regenerate the data matrix.$^{30}$ Thus, absorbance in a set of spectra can be mathematically modelled as a linear sum of individual components, called factors, which correspond to each one of the species present in the sample, plus noise. The PCA result at 275 °C is given as an example in the ESI,$^\dagger$ Fig. S5 and Table S3. The figure shows the different components weighted by their eigenvalues where the first two components clearly dominate the spectra and the contribution from the third component is
also significant. The fourth component appears to be noise, indicating that 3 components were required to fit the data. Thus, both FeO and FeO2 were evaluated as standards during LCF, but FeO was shown to give better fit results, confirming its presence as an intermediate phase during TPR (200–300 °C).

Results obtained from LCF analysis performed using these XANES spectra are given in the ESI† Fig. S6. It was observed that the reduction of Fe starts at approximately 270 °C, parallel to reduction of Mo. FeO (FeO) is the initial state which mainly corresponds to Fe23[MoO4]3 and FeO(red) is the final state after TPR, which have been taken as the standards for LCF analysis. The final reduced state of Fe, having features similar to FeMoO4, was observed at 330 °C, showing faster reduction of Fe compared to Mo. These results, combined with the Mo K-edge results, indicate that at the end of TPR at 400 °C, the phases present were Fe23[MoO4]3, FeMoO4, and MoO2 (possibly including intermediate phases MoO3), which confirm the presence of both Mo(IV) and Mo(VI) species.

Due to the fast interchange between the monochromators, DCM for XAS and CCM for XRD, the XAS measurements at the Mo K- and Fe K-edges were further supported by quasi-simultaneously recorded XRD patterns of the FeMo catalyst during TPR under 5% MeOH/He, as shown in Fig. 4(b). An XRD pattern characteristic for Fe23[MoO4]3 (most intense reflection at 2θ = 7.32° and other significant reflections at 6.93, 7.55–7.63, 7.92, 8.16, 8.73–8.82°) at the beginning of the TPR was observed, which disappeared almost completely at 310 °C and reflections corresponding to FeMoO4 appeared (reflections at 8.32 and 8.50°). Furthermore, at the end of TPR a weak reflection from MoO2 was also observed at 11.6°. In the initial state, reflections from FeMoO4 were observed as well (reflections at 7.43 and 8.16–8.23°), partly overlapping with the reflections of Fe23[MoO4]3, which disappeared as well. Thus, in situ XRD confirms that the phase transformation of Fe23[MoO4]3 to FeMoO4 started at around 280 °C, in agreement with XAS results at the Mo K- and Fe K-edges.

3.1.3 Gas phase composition during TPR. The corresponding evolution of the gas phase composition during TPR, overlaid with the fraction of Mo (v) (from Mo K-edge LCF), Fe(ii) and Fe(iii) (from Fe K-edge LCF) is shown in Fig. 5 (feed gas composition of 5% MeOH/He). It can be observed from the figure that at ~270 °C reduction of Fe started almost simultaneously with Mo. Here, the Fe(ii) fraction obtained from Fe K-edge LCF represent FeMoO4 as no other Fe(ii) species were confirmed by LCF, which indicate formation of FeMoO4 from Fe23[MoO4]3. Looking at the MS trace, the concentration of MeOH was observed to decrease in this temperature range, confirming the reaction of methanol with the catalyst in the temperature range from 260 to 400 °C. When staying at this temperature for 1 h, the methanol concentration increased to almost its initial value as shown in the extended X-axis of Fig. 5 for the isothermal period (red line) starting at 400 °C.

Though the MS-traces m/z = 29 and 18 corresponding to the formation of HCHO and H2O, respectively, have also been observed as shown in the ESI† Fig. S7, the MS was slow at pumping down from the previous experiment performed.

Hence there was remarkably high background signal of HCHO and H2O during the TPR up to about 300 °C. Nevertheless, it can be observed from Fig. S7 (ESI†) that during heating up the concentration of MeOH decreased and those of HCHO and H2O increased, as expected, and during the isothermal period, when the reduction was complete, the concentration of MeOH increased and those of HCHO and H2O decreased, both with some delay due to the MS pumping down.

Hence, using in situ XAS/XRD with MS measurements of the gas phase, it can be concluded that during heating under reducing conditions, Fe23[MoO4]3 and MoO2 were observed to reduce thereby forming FeMoO4 and MoO2 which is in agreement with the proposed reactions (1) and (2).

\[
\text{Fe}_2\text{MoO}_4 + \text{CH}_3\text{OH} \rightarrow 2\text{FeMoO}_4 + \text{MoO}_3 + \text{HCHO} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{MoO}_3 + \text{CH}_3\text{OH} \rightarrow \text{Mo}_2\text{O}_7 + \text{HCHO} + \text{H}_2\text{O} \quad (2)
\]

As described earlier, after TPR the catalyst was kept isothermal at 400 °C in 5% MeOH/He for 1 hour. Then the temperature was lowered to 200 °C and after stabilization at 200 °C the gas conditions were changed to 10% O2/He (ESI† Fig. S1). The phases of the catalyst remained mainly intact during the cool down, as well as during switching to oxidizing conditions as indicated by the XAS/XRD results given in the ESI† Fig. S8. At the Mo K-edge a slight shift of the edge was observed towards lower energies owing to a small increase in reduced phases of Mo. At the Fe K-edge in the post edge region some features were enhanced, indicating less distortion in the structure of Fe species after cooling down.
3.2 Heating under oxidizing conditions (TPO)

3.2.1 In situ XAS at Mo and Fe K-edges and XRD. Fig. 6(a) shows the in situ Mo K-edge XANES spectra of the catalyst during heating under oxidizing conditions (TPO) after the TPR and cool down to 200 °C in 5% MeOH/He. The edge position shifted towards higher energies showing an increase in the oxidation state of Mo, as expected. The pre-edge peak A regained intensity lost during TPR, corresponding to an increase in tetrahedral nature of the Mo centers, and the simultaneous weakening of feature B indicated lowering of octahedral nature.

LCF analysis of the XANES spectra using the same standards as during TPR and variations of the parameters obtained from EXAFS analysis are shown in Fig. 6(b) in the temperature range 320–500 °C (for the complete LCF results from 200–500 °C please see ESI,† Fig. S9). The initial composition before TPO at 200 °C was 39% Fe₂(MoO₄)₃, 20% MoO₃ and 41% MoO₂ which is similar to the composition of the final state after TPR (43% Fe₂(MoO₄)₃, 20% MoO₂ and 37% MoO₃) within the margin of error of LCF and considering the temperature difference.

Oxidation of Mo began as soon as the temperature started to rise which is evident from the decreasing MoO₂ and increasing Fe₂(MoO₄)₃ contributions, showing that overall MoO₂ combined with FeMoO₄ to give Fe₂(MoO₄)₃. The content of MoO₃ was quite stable until 380 °C, but in the range of 380–400 °C a sharp increase was observed (Fig. 6(b)), indicating formation of MoO₃ as well.

At the same temperature, the EXAFS parameters (Fig. 6(b)) showed a decrease in the DW factor of Mo–O1 and an increase in that of Mo–O2 supporting formation of octahedral Mo centers present in MoO₃. Both FeMoO₄ and MoO₂ continuously decreased and became negligible at around 500 °C, showing that almost all of Mo was in the Mo(VI) state. After the sudden increase at approximately 390 °C, the contribution from MoO₃ fell back to 21%, slightly lower than what was present initially before TPO (24%). The remaining 80% of Mo(VI) was found to be

Fig. 6 For the FeMo catalyst during heating under oxidizing conditions 10% O₂/He (TPO): (a) Mo K-edge XANES spectra, (b) corresponding XANES LCF results and variation in the selected parameters as determined from EXAFS analysis. At the X-axis, the red line after 500 °C represents the isothermal period, (c) Fe K-edge XANES spectra and (d) corresponding XANES LCF results. In (a) and (c) arrows point towards increasing temperature. The vertical dashed lines in (b) and (d) indicate the temperature ~390 °C at which a sudden increase in MoO₃ and Fe₂O₃ content was observed, respectively.
Fe₂(MoO₄)₃, which is slightly higher compared to the initial composition of the catalyst at 100 °C before TPR (76%). It is possible that some MoO₃ formed volatile species and evaporated during the TPR, similar to the evaporation clearly observed under reaction conditions for methanol oxidation.²⁰ EXAFS analysis also confirmed this conclusion since the CN of Mo–O1 at 1.77 Å increased and the corresponding DW factor decreased, showing a rise in tetrahedral nature of Mo. Similarly, the DW factor of the Mo–O2 (axial) concurrently increased, showing a decrease in octahedral nature of Mo centers (the CN of both Mo–O2 bonds were kept fixed to 1).

Fig. 6(c) shows the Fe K-edge XANES spectra during heating under oxidizing conditions. PCA was performed to confirm the number components required to fit the spectra and the results obtained from PCA analysis for Fe K-edge XANES spectrum at 380 °C is given as an example in ESI,† Fig. S10 and Table S4. In this case also, the first two components clearly dominate the spectra, with a significant contribution from the third component and the fourth component appears to be noise, indicating that 3 components were required to fit the data. Thus, Fe₂O₃ was also employed as standard during LCF, which gives better fit results than FeO, confirming its presence as intermediate phase during TPO (300–450 °C). LCF analysis shown in Fig. 6(d) showed that oxidation of Fe effectively started at 280 °C. The contribution from Fe₂O₃ was found to be high (around 30%) between 380–410 °C. In this temperature range LCF at the Mo K-edge also showed a high presence of MoO₃ pointing towards FeMoO₄ reacting with O₂ to give Fe₂O₃ and MoO₂ (eqn (3)) in competition with the reactions regenerating the catalyst (eqn (4) and (5)).³¹ However, like the excess MoO₃, the Fe₂O₃ phase was an intermediate and the contribution was found to decrease at higher temperature. At 500 °C Fe was found mostly as Fe₂(MoO₄)₃, due to recombination of Fe₂O₃ and MoO₂ by solid state reaction (eqn (6)). These redox dynamics explain the formation of Fe₂O₃ observed under reaction conditions for selective oxidation of methanol at 380 to 400 °C, where MoO₃ evaporation competes with the recombination and with extended time on stream MoO₃ eventually evaporates completely.⁷

Corresponding in situ XRD results are given in Fig. 7. They also show the presence of FeMoO₄ and MoO₂ initially, as observed at the end of TPR. During TPO, a phase transition was observed between 380–410 °C where higher presence of MoO₃ (by LCF at Mo K-edge data) and Fe₂O₃ (by LCF at Fe K-edge data) were observed by XANES. Only Fe₂(MoO₄)₃ and MoO₂ were observed as oxidation products by XRD, which agrees with the overall re-oxidation and recombination reactions given in eqn (3), (4) and (6). The Fe₂O₃ detected by LCF of the XANES data was an intermediate, possibly an amorphous, phase and thus was not detected by XRD.

Overall, the results obtained from XRD correspond to those obtained from LCF of XANES showing that FeMoO₄ and MoO₂ were oxidized and recombined to form Fe₂(MoO₄)₃.

3.2.2 Reversibility of the reduction and re-oxidation. To check whether the changes that occurred during the complete cycle of TPR and TPO were reversible, the initial state of the catalyst at 100 °C before reduction, the state of the catalyst at 500 °C after reoxidation and the final state of the catalyst after cooling down to 100 °C were compared. Fig. 8(a–d) show the Mo K-edge XANES spectra, corresponding FT spectra, Fe K-edge XANES spectra and XRD reflections of the catalyst at these different stages of the redox cycle. The identical features observed in the Mo and Fe XANES showed that Mo and Fe have attained their initial state with respect to oxidation state and coordination geometry. Similar conclusions can be drawn from the corresponding XRD patterns showing the presence of identical phases at these stages, though at 500 °C there is a temperature shift.

In Fig. 8(b), the FT EXAFS spectra are given and Table 1 shows the fitting parameters (see also ESI,† Fig. S3(a, e and f)). The major difference was observed in the FT spectra in the region of 2.5–4.0 Å where there are backscattering peaks due to Mo–Fe and Mo–Mo contributions. The Mo–Mo peak at 3.7 Å completely disappeared at 500 °C after the redox cycling, which indicates high distortions in the Mo–Mo metal shells related to the MoO₃ phase. By cooling down to 100 °C, this backscattering peak was observed to be regenerated indicating that the catalyst returns to its crystalline phase. At 500 °C, the CN of the first peak (Mo–O1) was comparatively higher than its value at 100 °C in the initial as well as the final state, which indicate stronger tetrahedral nature of Mo coordination at higher temperature. In case of the longer axial Mo–O2 bonds, a considerable increase in the DW factor was observed between the initial and final states at 100 °C. This indicates loss of octahedral character of the Mo centers during the redox cycle, corresponding to evaporation of some of the excess MoO₃. However, changes in the MoO₃ crystallite particle size or shape during the redox cycling may also occur. As the CN of Mo–O2
bonds were kept fixed to the value of 1, the DW factor obtained from the fitting corresponds to the strength of these bonds.

4. Conclusions

We have shown that the advanced setup at the synchrotron facilities makes it possible to obtain bulk structural as well as chemical information on the catalyst system under investigation. The combination of transmission XAS at the Mo K-edge, fluorescence XAS at the Fe K-edge and XRD at high energy proved to be a successful tool for detection of individual crystalline and amorphous phases in situ during the different stages of redox cycling of an iron molybdate catalyst with excess molybdenum trioxide, thereby providing important information about the phase transformations. The simplified...
Reducing/oxidizing conditions employed in this study are needed to gain deeper insight into the catalytic system and catalytic cycle. Subsequent XAS measurements at the Mo K- and Fe K-edges showed that reduction of Mo as well as Fe started at ~270 °C and at 400 °C MoO₃ and FeMoO₄ were observed as reduced phases. Complete reduction of Fe(III) to Fe(II), forming FeMoO₄, was observed at 330 °C whereas 60% Mo was still present as Mo(VI) after reduction at 400 °C. Quasi-simultaneously recorded in situ XRD at high energy confirmed that the phase transition from Fe₂[MoO₄]₃ and MoO₃ to FeMoO₄ and MoO₂ occurred at about 280–300 °C. Online gas phase analysis recorded simultaneously showed that the concentration of methanol decreased parallel to reduction of Fe and Mo observed by XAS and XRD, confirming the reaction between gas and solid.

Subsequent heating in an oxidative atmosphere from 200 to 500 °C caused Mo and Fe to reoxidize thereby forming Fe₂[MoO₄]₃. Intermediates phases Fe₂O₃ and excess MoO₂ were also formed in parallel reactions, but they recombined above 400 °C to give Fe₂[MoO₄]₃, which was observed to be the most dominant phase at 500 °C. XRD confirmed that the main transition occurred at about 380–400 °C, at which rise in the MoO₂ and Fe₂O₃ contributions were observed by XANES LCF.

The reduction/re-oxidation dynamics observed in this study, particularly the formation of FeMoO₄ and MoO₂ during reduction and Fe₂O₃ during re-oxidation, shows the segregation of iron and molybdenum (forming FeMoO₄ and Fe₂O₃) observed under industrial reaction conditions, where the concurrent MoO₃ evaporation hinders recombination to form Fe₂[MoO₄]₃, which results in catalyst deactivation and selectivity loss by iron enrichment. In the future, it would be helpful to receive complementary insight by more surface sensitive methods, typically only possible under quasi in situ conditions, or using samples with higher surface area that would enhance the sensitivity of XAS for the surface.

Conflicts of interest

The authors declare no competing financial interest.

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