Soft X-ray Spectroscopy Studies of Adsorption and Reaction of CO in the presence of H₂ over 6 nm MnO Nanoparticles Supported on Mesoporous Co₃O₄

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Abstract

MnO nanoparticles (6 nm) were supported on mesoporous spinel Co₃O₄ and studied using ambient pressure X-ray photoelectron spectroscopy (APXPS) and *in situ* X-ray absorption spectroscopy (XAS) during hydrogenation of CO. The nature and evolution of surface adsorbed species as well as the oxidation states of the metal oxide surfaces were evaluated under oxidizing, reducing, and H₂+CO (2:1) reaction atmospheres. From APXPS, MnO nanoparticle surfaces were found to be progressively reduced in H₂ atmospheres with increasing temperature. Surface adsorbed CO was found to be formed at the expense of lattice O under H₂+CO reaction conditions. *In situ* XAS indicated the dominant oxide species were Co(OH)₂, Co (II) oxides, MnO, Mn₃O₄ under reaction conditions. *In situ* XAS also indicated the formation of gas phase CO₂, the disappearance of lattice O, and the further reduction of Mn₃O₄ to MnO upon prolonged reaction in H₂+CO. Mass spectroscopy measurements showed the formation of CO₂ and hydrocarbons. The spent catalyst was investigated using scanning transmission X-ray microscopy and (scanning) transmission electron microscopy; the catalyst grains were found to be homogeneous.

Keywords: ambient pressure X-ray photoelectron spectroscopy, *in situ* x-ray absorption spectroscopy, manganese oxide nanoparticles, mesoporous spinel cobalt oxide, CO hydrogenation

Abbreviations: ambient pressure X-ray photoelectron spectroscopy (APXPS), X-ray absorption spectroscopy (XAS), total electron yield (TEY), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS), electron energy loss spectroscopy (EELS), scanning transmission X-ray microscopy (STXM), nanoparticles (NPs), Fischer-Tropsch (F-T).

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1. Introduction

Understanding and controlling a catalyst's surface has long been the goal of fundamental research in heterogeneous catalysis. However, understanding an industrial catalyst is complex; not only is the surface non-homogeneous, but they often contain multiple components. To overcome this complexity, yet retain the catalytic nature of the surface, model nanoparticle catalysts with controlled size [1–10,3,11], shape [12–20] and composition [12,21–23] are used.

In addition to model surfaces, *in situ* techniques are vital to probing surface properties as catalytic reactions take place. The study of these materials' surfaces was made possible with the proliferation of high intensity X-ray sources (ref) and specialized instrumentation allowing for *in situ* spectroscopic characterization at pressures above high vacuum. Ambient pressure X-ray photoelectron spectroscopy (APXPS) [24,25,10,26,22] is among the surface techniques widely employed to investigate nanoparticle surfaces under relevant conditions. Structure-function correlations can be made using model nanoparticle surfaces and these *in situ* surface techniques.

The dynamic nature of surfaces has been well-documented [25,27], highlighting the importance of studying a model nanoparticle catalyst's surface under reaction conditions. For example, under CO oxidation conditions, spinel Co_3O_4 was found to form an active interface with Pt NPs; *in situ* X-ray spectroscopy uncovered the formation of CoO during the catalytic turnovers [28]. CoO supported on TiO_2 was also found to be active under CO hydrogenation conditions; APXPS measurements showed increased CoO coverage compared to metallic Co on TiO_2 [29].

Recently, 6nm MnO_x nanoparticles supported on mesoporous Co_3O_4 was reported to produce high yields of methanol from a H_2/CO_2 (3:1) feed, where the enhanced catalytic activity towards methanol was attributed to the unique oxide-oxide interface [30]. Bimetallic Co-Mn nanoparticles supported on carbon nanofibers [31], titania [32], and silica [33] have been studied under CO hydrogenation conditions (Fischer-Tropsch synthesis), where the addition of Mn is reported to promote the formation of long chain hydrocarbons over methane. These studies over Co-Mn systems have captured unique catalytic behaviors and trends for well-defined, model hybrid systems; yet the understanding of catalysis at the molecular level remains less understood, as the focus was on metal/oxide surfaces, rather than adsorbed species. Towards this end, adsorption and reaction of CO in the presence of H_2 (Fischer-Tropsch synthesis) were studied to gain molecular insight into the oxide adsorbate interaction.

In this study, we investigated the surface chemical structure of 6nm MnO nanoparticles supported on a mesoporous Co_3O_4 co-catalyst under CO hydrogenation conditions using ambient pressure X-ray photoelectron spectroscopy (APXPS) and *in situ* X-ray absorption spectroscopy (XAS) in the total electron yield (TEY) mode. Measurements were made under

oxidizing (O_2), reducing (H_2) and reactive ($H_2 + CO$; 2:1) conditions. In addition, *ex situ* electron and X-ray spectro-microscopy techniques were employed to determine morphology, chemical compositions and elemental distributions for the pre- and post-reaction catalysts.

2. Experimental

2.1. Synthesis of MnO Nanoparticles / Mesoporous Co_3O_4 Catalyst

The synthesis of 6 nm MnO NPs [34] and mesoporous Co_3O_4 support [35] has been described in detail elsewhere. Briefly, MnO NPs were synthesized by refluxing 1.24 g manganese oleate (~ 2 mmol) dissolved in 10 g of 1-octadecene for 10 min. MnO NPs were stored in 10 ml of hexane until further use.

Mesoporous Co_3O_4 , (m- Co_3O_4) was prepared using a hard template. A mixture of cobalt (II) nitrate hexahydrate (4.7 g) in 8 ml of water and KIT-6 (4.0 g) dissolved in 50 ml of toluene were evaporated at 65 °C and the precipitated solid was subsequently calcined at 300 °C for 6 h in air. The KIT-6 template was dissolved using an aqueous solution of 2 M NaOH at 60 °C.

The MnO NPs/m- Co_3O_4 catalyst was prepared via the capillary inclusion method [36,37]. To produce a catalyst of nominally 10 weight % Mn, 2 mL of the colloidal MnO_x NPs were diluted with 40 mL of *n*-hexane and mixed with 250 mg of m- Co_3O_4 . The mixture was sonicated for 3 h at room temperature. The precipitate was collected by centrifugation and washed with a 50:50 v/v mixture of acetone and ethanol. The precipitated solid was dried at 80 °C overnight.

2.2. Soft X-ray Absorption Spectroscopy

Soft X-ray absorption spectroscopy (XAS) studies were performed in beamline 6.0.2 of the Advanced Light Source (ALS). A purpose-built XAS end-station (detection of Electrons, Photons, and Ions for Chemistry and Catalysis: dEPIC²) was employed for the measurements. The end-station consists of three vacuum chambers: the beam entrance chamber, an ambient pressure (AP) cell, and a mass spectrometry chamber.

The entrance chamber consists of a variable aperture exit slit and an aluminum mesh for I_0 correction. A base pressure of 10^{-8} Torr is maintained in the entrance chamber at any time. A monochromator exit slit of 50 μ m diameter was used for the measurements reported in this paper. The entrance chamber is separated from the AP cell with a 100 nm thick Si_3N_4 window (1 mm by 0.5 mm, Silson Inc.).

Gases were mixed in a pre-mixing line and introduced to the AP cell with measured volumes. Gas pressure in the AP cell and pre-mixing line were monitored via capacitance (Baratron, MKS) and cold cathode (Pfeifer and Granville-Phillips) gauges located on the pre-mixing line and the AP chamber, respectively. To ensure a continuously well-mixed gas environment, a motorized fan is placed in close proximity to the sample holder.

Sample holder is installed on a 2.75" CF flange with four mini flange ports and is mobilized on a top-mounted XYZ Ω stage. Samples of nanoparticle films on 200 μm Si wafers or ~ 200 μm pelletized powders are secured between a 1/16" metal plate, which is used for total electron yield current measurements, and a 1/16" cylindrical ceramic spacer (Al_2O_3). A 1/32" metal foil with a central hole ($\varnothing=1/4$ ") is attached to the front end of the ceramic spacer, and used to apply a potential bias to sample. The metal current plate sits on a PID-controlled ceramic heater ($\varnothing=1$ " and 10-16 ohm resistance, Momenive), which allows sample temperatures in the 25-550°C range. A photodiode (SXUV100, Opto Diode Corp.) is placed on a Z-manipulator and adjusted towards or away from sample for fluorescence measurements.

The mass spectrometer chamber is separated from the AP cell with a gate valve. An on-line quadrupole mass spectrometer (RGA, Stanford Research Systems) is used for continuous detection. To achieve this, 1/8" stainless steel capillary tubing, heated to 100°C, is run between the sample front and the mass spectrometer ionizer. The distance between the capillary and the sample is manually adjusted to optimize detection sensitivity.

In a typical XAS experiment, Co L_3 , Mn L_3 , O K, and C K absorption edge spectra were monitored in a total electron yield (TEY) mode in oxidizing, reducing, or reaction conditions. The current to sample was measured using an amplifier with a bias potential of 250 V. Before measurements samples were treated for 0.5 hours in oxidizing or reducing conditions, or for 1 to 12 hours under reaction atmospheres. Acquisition times for TEY spectra were approximately 7 minutes, and spectra showed no significant changes from the beginning to the end of any measurement condition. All spectra were normalized for I_0 .

2.3. Ambient Pressure X-ray Photoelectron Spectroscopy

The APXPS chamber in beamline 9.3.2 at the ALS has been described elsewhere [38]. Various photon energies were used to probe the 2p and 3p levels of Co and Mn, in addition to the 1s levels of C and O. The order of the APXPS experimental conditions was as follows: oxidation in 200 mTorr O_2 at 350°C, reduction in 200 mTorr H_2 at 250°C, reaction conditions of 300 mTorr H_2+CO (2:1) at 225°C, followed by higher reduction temperatures of 350 and 480°C under 200 mTorr H_2 each followed by reaction conditions at 225°C.

After the previous experimental conditions, the reversibility of the surface changes was studied whereby the catalyst was re-oxidized in O_2 at 350°C, reduced in H_2 at 250°C, and run under reaction conditions at 225°C. Energy calibrations were performed using valence level XPS spectra at each photon energy. XPS peaks for gas phase O_2 and CO were also used for energy calibration. XPS data and error analysis was carried out using CasaXPS software. Error analyses for peak fitting parameters and peak ratios were performed using the built-in 'Monte Carlo simulations' function within the CasaXPS software package. Briefly, noise-added synthetic data was iteratively used to find uncertainties in fitted peak model and peak parameters derived from the fits to real data.

Typical exposure times for any condition in the APXPS experiments were on the order of hours, during which multiple measurements at the aforementioned core and valence levels were taken. Each core or valence level was measured until no further changes in the spectral features could be observed. Similarly to XAS TEY measurements, APXPS spectra showed no significant changes from the first to the last measurement at any measurement condition. The steady-state was reached rather quickly in the timescale of both APXPS and XAS techniques.

2.4. Scanning Transmission X-ray Microscopy (STXM)

STXM experiments were performed at the molecular environmental sciences beamline (11.0.2) at the ALS [39]. Samples were dropcasted from suspensions in methanol on to 100 nm thick Si_3N_4 windows, and air-dried before measurements. Multiple catalyst grains, each measuring approximately 500 nm, were measured at both Mn L and Co L absorption edges with spatial resolutions better than 40 nm. Image stacking, alignment, and spectral integrations were carried out using AXIS software.

2.5. Scanning Transmission Electron Microscopy (STEM) with Energy Dispersive Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS)

TEM and STEM measurements were performed at an accelerating voltage of 200 kV using a Jeol2100F transmission electron microscope equipped with an INCA energy dispersive spectrometer and a Gatan Tridiem electron energy loss spectrometer. TEM samples were prepared by dropcasting catalyst suspensions in methanol on to lacey carbon supported on Cu grids and vacuum-dried at 100°C for 2 days before measurements. EDS was carried out by monitoring Co and Mn K lines. EELS was carried out using convergence and collection semi-angles of 12 mrad with ~1 eV energy resolution at a dispersion of 0.2 eV per channel. Standard Gatan software was utilized for the analysis of EELS spectra; the pre-edge background was subtracted using a power-law fit while Hartree-Slater cross-sections were used to subtract step edges before quantification.

3. Results and Discussion

3.1. Characterization of the As-Prepared Catalyst

The 6 nm MnO NPs/m- Co_3O_4 catalyst was characterized prior to in situ studies using a combination of techniques. TEM and STEM images show ordered mesopores of about 10 nm in size (Figures S1a and S1c). TEM and HRTEM images display nanocrystalline grains with sizes in the 5-10 nm range (Figures S1a and S1b). Individual MnO NPs could not be discerned from these TEM images. TEM image and a particle size histogram for MnO NPs is shown in Figure S2. Mesoporous particles were measured to be in the range of 0.2-2 μm , based on TEM images. STEM/EDS elemental maps indicated random and uniform distributions of Mn over the Co matrix (Figures S1c-S1e). STEM/EDS maps and averages of multiple STEM/EELS point spectra show Mn:Co ratios of 1:10, which is consistent with the nominal mixing of MnO NPs and mesoporous Co_3O_4 .

STXM images taken pre- and post- metal edges (Mn L and Co L) indicated random and uniform distribution of Co and Mn components across single particles, and thus was consistent with STEM/EDS maps. STXM also indicated particle cores and shells were chemically uniform; spinel Co_3O_4 and mixtures of Mn^{2+} and Mn^{3+} species, obtained from a qualitative inspection of STXM spectra (Figure S3).

3.2. Ambient Pressure X-ray Photoelectron Spectroscopy

3.2.1 Co and Mn spectra

Figure 1a shows Mn and Co 3p core levels monitored using 630 eV photons, and demonstrates invariably larger fractions of MnO_x ($1 < x < 2$) on the surface under all conditions studied. The strong peak around 48 eV was assigned to the Mn 3p transition, while the weaker peak around 60 eV was due to the Co 3p transition. The peaks in the 63-65 eV window were attributed to Mn satellites in agreement with Oku and Hirokawa [40].

Surface fractions of Co probed by APXPS progressively decreased with both increasing reduction temperature and $\text{H}_2 + \text{CO}$ reaction conditions. The 2p spectra of Co and Mn (shown in Figures 2b and 2c) were taken at photon energies of 900 and 760 eV, respectively, to give photoelectrons with kinetic energies of 120 eV. Co 2p core level spectra had very low and eventually no signal intensity after reduction in 200 mTorr H_2 at 350°C, as shown in Figure 1b. The absence of Co 2p/3p signal is believed to be the result of a shadowing effect (loss of Co surface area and closer packed MnO_x NPs) or by the formation of a continuous layer of MnO_x NPs (wetting of CoO_x) preventing the Co photoelectrons from reaching the analyzer. This can be argued considering the inelastic mean free paths of the emitted photoelectron from Co through Mn oxides which are found to be 0.6 nm (KE: 120 eV) and ~1.7 nm (KE: ~800 eV) [41].

Fig. 1 Successive APXPS spectra showing (a) 3p core levels of Mn and Co, (b) 2p core levels of Co and (c) 2p core levels of Mn under various conditions. The spectra are stacked from bottom to top in the order of acquisition and color-coded as the key in the middle. Conditions are as described in the experimental section. In (a), Mn 3p and Co 3p levels are marked with dashed lines and Mn satellites with a dashed box. Dashed lines in (c) indicate the approximate peak positions for the respective oxidation states of Mn.

Mn 2p spectra indicated the progressive reduction of $\text{MnO}_{1<x<2}$ ($1<x<2$) NPs. Figure 1c shows shifts to lower binding energies with increasing reduction temperature and subsequent reaction conditions. Figure 1c also includes the Mn $2p_{3/2}$ peak assignments according to Nesbitt *et. al* [42]. The dominant oxidation state on the surface was identified as Mn^{3+} in H_2 atmospheres at 250°C and 350°C, and the following reactions at 225°C. In H_2 atmospheres at 480°C and the reaction conditions run afterward, MnO is the dominant surface species.

It should also be noted that MnO_x ($1<x<2$) NPs were reversibly oxidized in O_2 atmospheres at 350°C. However, Co was not fully recovered from H_2 treatment at 480°C and the following H_2+CO reaction. This could be a result of dramatic morphology changes of the MnO_x NPs from successive lattice expansions and contractions.

3.2.2 C and O 1s spectra

APXPS also indicated adsorption of CO on oxide surfaces. The C 1s and O 1s core levels were monitored using 630 eV photons; clean C 1s XPS spectra were obtained in H₂ atmospheres following the oxidation in O₂ at 350°C. Under reaction conditions, two C 1s peaks were observed (Figure 2a); a peak at 291 eV from gas phase CO and a broader peak at 289 eV, which was attributed to CO adsorbed on MnO_x nanoparticles given their larger surface fractions. Furthermore, O 1s XPS spectra confirmed the above finding of: surface CO (component at 531.5 eV) and a decrease in lattice O (slight decrease of component at 530.5 eV) under reaction conditions (Figure 2b). Combined C and O 1s normalized peak areas, as shown in Figure 2c, are indicative of CO adsorption on MnO_x (1<x<2) NPs, where a strong correlation exists for the increase of surface CO at the expense of lattice O.

Therefore, we believe that more CO is adsorbed for high manganese valences (i.e. after 250 and 350°C reductions), while surface uptake of CO showed a minimum for MnO in Mn²⁺ state (after reduction at 480°C). It should also be noted that CO uptake of the catalyst substantially increased after O₂ recovery. This could be attributed to defect formation and lattice strain due to expansion/contraction of MnO_x NPs, as suggested previously.

Fig 2. Successive APXPS spectra showing (a) C1s and (b) O1s core levels under various conditions. (c) Plots of normalized peak areas for lattice O and surface CO (from O1s [top] and C1s [bottom]). Spectra in (a) and (b) are stacked from bottom to top in the order of acquisition, and color-coded as in the middle key. Surface and gas phase CO are indicated in (a) and lattice O, surface CO, gas phase CO, and O₂ are indicated in (b). Arrows in (c) indicate successive reaction conditions following H₂ atmospheres at 250, 350 and 480°C from left to right.

3.3. In Situ Soft X-ray Absorption Spectroscopy (XAS)

3.3.1 Co and Mn L₃ edges

In situ XAS, probing the near surface regions of the MnO_x/Co₃O₄ catalyst, was used to quantitatively determine the oxidation states present on the surface through a linear combination fitting of reference compounds. Mn L₃ absorption edge spectra and the linear combination fittings are shown in Figure 3. Samples were run at both 7.8 (Figure 3a and b) and 32 (Figure 3c and 3d) Torr total reaction pressure after different reduction pre-treatments. The reduction temperature appears to have no significant effect on the oxidation state of MnO_x NPs during the CO hydrogenation reaction conditions, as shown in Figures 3a-c. The dominant oxidation states present measured after one hour under the reaction conditions are MnO and Mn₃O₄; however, prolonged reaction time in 32 Torr total reaction pressure produces MnO and MnO₂ at the expense of Mn₃O₄.

Fig. 3 (a-d) XAS TEY spectra at the Mn L₃ absorption edge during H₂+CO (2:1) reaction conditions. Black connected diamonds are experimental spectra, red line is the fit, and the colored lines are the reference spectra. (e) Fractions of manganese species determined from the linear combination fittings in (a-d). XAS TEY spectrum in (a) was acquired following H₂ reduction at 250°C. XAS TEY spectra in (b-d) were acquired following H₂ reduction at 350°C. Spectra in (a-c) were acquired after the first hour under reaction conditions; (d) was acquired after 12 hours in the feed. The x-axis in (e) is numbered with the same codes as in the XAS TEY spectra; condition 2 is in H₂ atmosphere (TEY spectrum not shown) and is indicated with an arrow in (e). Arrows in (d) indicate the spectral changes relative to the previous spectrum.

The Co mesoporous oxide support was also found to actively change during reduction and reaction. Figure 4 displays the Co L₃ absorption edge and the resulting linear combination fits under various conditions. The dominant phase after reduction at 250°C and during reaction conditions of 7.8 Torr total pressure was spinel Co₃O₄ (Figure 4a). Following reduction at 350°C (Figure 4e, condition 2) Co₃O₄ was completely reduced to Co²⁺ species, namely CoO and Co(OH)₂, as shown in Figure 4 b-d. Upon increasing the total reaction pressure from 7.8 to 32 Torr, the relative amounts of Co(OH)₂ and CoO change by approximately 10%. However, unlike

the MnO_x NPs, the Co does not undergo any further changes during prolonged reaction time (Figure 4d).

The XAS signal for Co was strong compared to the APXPS measurements mainly because of the deeper probing depth of the XAS TEY technique. However, it should be noted that Mn L edge TEY signal (10 nA) was about two orders of magnitude higher in intensity than Co L edge TEY signal (0.1 nA).

Fig. 4 (a-d) XAS TEY spectra at the Co L_3 absorption edge during $\text{H}_2+\text{CO}(2:1)$ reaction conditions. Black connected diamonds are experimental spectra, red line is the fit, and the colored lines are the reference spectra. (e) Fractions of cobalt species determined from the linear combination fittings in (a-d). XAS TEY spectrum in (a) was acquired following H_2 reduction at 250°C . XAS TEY spectra in (b-d) were acquired following H_2 reduction at 350°C . Spectra in (a-c) were acquired after the first hour under reaction conditions; (d) was acquired after 12 hours in the feed. The x-axis in (e) is numbered with the same codes as in the XAS TEY spectra; condition 2 is in H_2 atmosphere (TEY spectrum not shown) and is indicated with an arrow in (e). XAS contributions for Co^{2+} in (e) was decomposed into two components in (a-d): Co^{2+} in octahedral sites, indicated with dark green; and Co^{2+} in tetrahedral sites, indicated with light green. Arrows in (b) and (c) indicate the spectral changes relative to the previous spectrum.

3.3.2 C and O K edges

C and O K absorption edge spectra are shown for various conditions in Figure 5. Pure O_2 spectra were taken while cooling from the oxidation treatment at 350°C , while pure CO and CO_2 spectra were taken at catalyst temperatures of 200°C for reference. The C K edge spectrum under H_2 shows the surface is free of residual carbon. Under 7.8 Torr reaction conditions, no apparent peak due to CO adsorption was observed; however, splitting and chemical shift of the gas phase CO peak (287.0 eV) were observed under 32 Torr reaction conditions, as shown in Figure 5a. In light of the APXPS findings, the splitting and shift of the gas phase CO peak could be due to adsorption of CO. Furthermore, gas phase CO_2 (290.4 eV) appears during reaction

conditions. The gas phase CO₂ peak becomes more pronounced upon prolonged reaction periods (batch reactor mode), suggesting adsorption and reaction of CO on the catalyst surface. The O K edge spectra support this view, with gas phase CO₂ (534.2 eV) appearing at long reaction times. In addition, lattice O shows a substantial decrease at long reaction times, indicative of a qualitative agreement with the APXPS findings of a correlation between lattice O and surface CO.

Fig. 5 XAS TEY spectra at the (a) C K and (b) O K absorption edges under various conditions. CO (gas phase and surface adsorbed) and gas phase CO₂ are indicated in (a) and (b). Lattice O is also indicated in (b). The O₂ spectrum was taken in vacuum after pumping out O₂ while cooling from 350°C. The H₂ spectra were taken in 2.7 Torr H₂ while cooling from 350°C. CO and CO₂ spectra were acquired in 2.7 Torr of the pure gases at 200°C. All H₂+CO(2:1) spectra were collected at 225°C. The spectra are shown in the order of acquisition from bottom to top.

3.3.3 Residual Gas Analysis

Using a multiple ion detection mode on the dEPIC² mass spectrometer, several m/z species were monitored during the reaction of 32 Torr H₂+CO(2:1), after reduction at 350°C. Figure 6 shows the changes in the partial pressures of m/z 16 (CH₄), 18 (H₂O), 27 (hydrocarbon fragments), 28 (CO and hydrocarbon fragments) and 44 (CO₂) from 5 min to 11 hours into the reaction. A decrease in the m/z 28 signal was indicative of consumption of CO, as a corresponding increase in the partial pressure of CO₂ was observed. The observation of CO₂ is consistent with detection of gas phase CO₂ in the XAS TEY spectrum after 12 hours under reaction conditions. Interestingly, the formation of m/z 27 fragments and H₂O could be the result of the catalytic hydrogenation of CO, as water and CO₂ is a typical byproduct of the

Fischer-Tropsch synthesis (C-C bond formation). However, the formation of H_2O from a chemical reaction on the MnO_x surface cannot be ruled out. Also of note is the lack of CH_4 at the mass spectrometer; under low pressure CO hydrogenation conditions, CH_4 is often the most abundant product [31,33]. In agreement with the mass spectroscopy data, no CH_4 is detected in the XAS TEY spectra.

Fig 6. Partial pressures of various species before, during, and after the reaction of 32 Torr H_2 +CO (2:1) at 225°C.

3.4. *Ex Situ* Spectro-microscopy

The catalyst was studied pre- and post-reaction using TEM, STEM/EDS and STXM. No changes to morphology in the post-reaction catalyst were detected by TEM or STEM. Elemental composition, measured by STEM/EDS remained uniform (Figure 7c-e). STEM/EELS spectra, acquired from single grains and multiple particles, indicated that the $\text{O}/(\text{Mn}+\text{Co})$ ratio dropped from 1.3 ± 0.1 for the fresh catalyst to 1.1 ± 0.2 for the spent catalyst, consistent with the reduction of catalyst. Representative energy loss spectra shown in Figure 8 clearly illustrate the loss of O content from the spent catalyst.

Fig 7. (a) TEM, (b) HRTEM and (c) STEM images of the post-reaction MnO_x NPs/m- Co_3O_4 catalyst. EDS elemental maps of the STEM image in (c) showing (d) Co K and (e) Mn K lines. Scale bars are given for each image.

Fig 8. Representative STEM/EELS spectra, pre-O edge background removed, of the pre- and post-reaction (i.e. fresh vs. spent) catalysts. Difference spectrum is also given.

STXM was performed on the pre- and post-reaction catalyst. Figure 9 shows the XAS spectra obtained by integrating over different sections of the STXM image, namely the core of the particle and the outer shell. The corresponding STXM maps are superimposed over the STXM image at the given photon energies. Changes from the pre-reaction to post-reaction catalyst are consistent with the XAS TEY spectra and the STEM/EELS O loss spectra discussed above; namely the Co L absorption edge shows a qualitative reduction from spinel Co_3O_4 in the pre-reaction catalyst (S2) to Co^{2+} species in the post-reaction catalyst (Figure 9b).

A visual inspection of the Mn L absorption edge XAS spectra revealed a weaker peak at 639 eV (i.e. Mn^{2+}) for the spent catalyst, which indicated a post-reaction oxidation of the MnO NPs (see Figure 9a and Figure S2a). This could be a result of exposure to air, as *in situ* XAS found Mn^{2+} (major) and Mn^{4+} (minor) species during reaction. This could also be a difference between the surface and bulk of the catalyst particles, because *in situ* XAS TEY measured the near surface regions as opposed to STXM monitoring the bulk using transmitted X-rays. STXM also indicated that chemical compositions were uniform across single particles and over the entire catalyst, as shown by identical XAS spectra integrated over the core and shell of individual particles. Multiple particles were imaged and show consistent results.

Fig 9. STXM spectra at (a) Mn L and (b) Co L absorption edges for the post-reaction catalyst. STXM spectra are color-coded as in the STXM images, and show integrated % absorption for the marked areas: particle cores (red) and particle shells (blue). STXM elemental maps are shown at given photon energies: 630 and 770 eV pre-edge; 640 and 780 eV, L_3 edge maxima; and 665 and 805 eV, post edge for Mn and Co, respectively.

3.5 Discussion

From APXPS measurements, the MnO_x NPs show higher degrees of reduction with increased reduction temperature. This decrease in Mn oxidation state is reversible, as shown by the O_2 treatment at 350°C (Figure 1c). Interestingly, the MnO_x NPs irreversibly cover the CoO_x surface after reduction at 480°C , and the Co signal is not regained after re-oxidation at 350°C . The loss of Co signal is attributed to the high loading of Mn (10 weight %) and permanent morphology changes in the MnO_x NPs. The XAS TEY measurements show a much smaller effect of reduction temperature on the catalyst's oxidation state during reaction conditions, indicating the change is localized to the outermost surface layers.

The adsorbates interaction with the surface was followed by monitoring C and O signals in APXPS and XAS TEY measurements. APXPS indicates CO adsorption with corresponding peaks in both the C 1s and O 1s regions (Figure 2a and 2b). CO adsorption is found to correlate with the loss of lattice oxygen and high Mn valences - CO adsorption is highest for the lowest reduction temperature. XAS TEY measurements qualitatively agree, showing gas phase CO_2 and loss of lattice O over long reaction times (12h) in Figure 5. Mass spectroscopy confirms the presence of gas phase CO_2 , H_2O , and indicates possible C-C bond formation. Although C-C bond formation is indicative of the Fischer-Tropsch process, the additional possibilities that CO itself

is reducing the surface forming CO₂ or that MnO_x is participating in the water-gas shift reaction cannot be ruled out.

Previous CO hydrogenation studies on cobalt-manganese systems have focused on the promotional effect of small amounts of MnO, showing increased selectivity to long chain hydrocarbons, lower selectivity to methane, and a decrease in the reducibility of Co [32]. However, these systems are mostly comprised of metal active sites (Co⁰), of which the MnO_x/m-Co₃O₄ catalyst has none. In accordance with previous work, the mass spectrometer results show evidence of C-C bond formation but no methane, indicating a poor hydrogenation activity (lack of metal sites) of the catalyst under low pressure conditions.

Future work will focus on lower Mn loadings such that the nature of the interface and the effect of MnO_x on the Co₃O₄ co-catalyst can be studied. The bonding configuration and site in the oxide-oxide catalyst is not clear in this study; vibrational spectroscopy can shed light on the roles of oxide sites over Fischer-Tropsch synthesis.

4. Conclusion

In this paper, we studied the evolution of oxidation states and chemical compositions of a hybrid oxide catalyst comprised of MnO NPs supported on mesoporous spinel Co₃O₄ under H₂+CO atmospheres. Using tunable X-ray energies and reactive atmospheres in APXPS, we showed that MnO NPs covered cobalt oxide support. Surface adsorption of CO was correlated with high Mn valences and a decrease in lattice O. *In situ* XAS TEY measurements revealed chemical compositions of MnO NPs and the oxide support in the near surface regions and under H₂+CO reaction conditions: MnO and Mn₃O₄ were found dominant species for the nanoparticles, while Co(OH)₂ and Co oxides bearing +2 charge were obtained for the cobalt oxide support. *In situ* XAS TEY measurements also revealed CO₂ formation under 32 Torr H₂+CO (2:1) and at 225°C after 12 hours of reaction. Interestingly, the CO₂ formed at long reaction times coincided with the disappearance of lattice O, as Mn₃O₄ mainly reduced to MnO. Combined APXPS, *in situ* XAS TEY and mass spectroscopy measurements indicated the adsorption and reaction of CO over oxides of manganese and cobalt in the presence of H₂. Morphology and chemical composition of the catalyst were investigated using spectro-microscopy techniques, and found to be uniform across single particles and over particle ensembles.

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