In-situ Reduction of Co$_3$O$_4$ in H$_2$ using Environmental HRTEM

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Abstract. We present an in-situ study of the reduction of Co$_3$O$_4$ to CoO. Co based catalysts are promising for Fischer Tropsch process reactions in which heavy fuels such as diesel are synthesised from CO$_2$ and H$_2$. Co$_3$O$_4$ is the precursor and must be reduced by H$_2$ to Co. Although there have been many studied of this process, both ex-situ and in-situ, there is no consensus on how Co$_3$O$_4$ transforms to CoO including how defects influence the transformation mechanism. Our results show that dislocations are formed between Co$_3$O$_4$ and CoO regions and a fuse-wire like transformation is observed in crystals above 15 nm diameter.

1. Introduction

The commercialisation of synthetic diesel has received much attention since the 1980s [1, 2]. One source of synthetic diesel is from the Fischer-Tropsch process. The Fischer-Tropsch process involves many reactions including hydrogenation and gasification but it allows non-oil resources such as gas, biomass and coal to be converted into liquid diesel fuel. The reaction responsible for the conversion is the Fischer-Tropsch reaction: $(2n+1)$H$_2$ + nCO $\rightarrow$ CH$_{2n+2}$ + nH$_2$O

The Fischer-Tropsch reaction requires a catalyst otherwise the yield of desired product would be low [3]. Ni, Fe and Cu based catalysts were found to be catalytically active in this reaction but they generally had poor yields of heavier hydrocarbons such as diesel at low temperatures [3].

Co based catalysts are now the preferred choice for the production of diesel using the Fischer-Tropsch process [4, 5]. The Co takes the form of nanoparticles which may be loaded onto a support such as Al$_2$O$_3$. The catalysts are usually prepared using a catalyst precursor in the form of Co$_3$O$_4$ [2, 6]. Ultimately, the reduction of Co$_3$O$_4$ determines the activity of the Co catalyst.

It is well known that fcc Co$_3$O$_4$ can transform to an intermediate fcc CoO phase before reducing to either fcc or hcp Co [7, 8, 9]. The fcc phase of Co is believed to dominate at temperatures above 350 °C [10]. The role of defects in the reduction process to CoO is not clear and how it effects the reduction to Co. Here we present aberration corrected environmental TEM (AC-ETEM) study of the in-situ reduction of Co$_3$O$_4$ in H$_2$.
Figure 1. HRTEM reduction sequence of the reduction of Co₃O₄ to rocksalt CoO with (a) showing the Co₃O₄ crystal at room temperature (b) 350 °C and (c) 450 °C. The wavy lines in (a) indicate the presence of stepped Co₃O₄ surfaces which is where the CoO formation is initiated as shown in (b) at 350 °C. At 450 °C the entire parent crystal has transformed.

2. Method
The Co₃O₄ powder used for the in-situ studies originates from Aldrich. For in-situ work (S)TEM specimens were prepared by suspending approximately 20 mg of the powder in ethanol and depositing 5 µl onto an empty Cu TEM grid. C films were not used because they become unstable at high temperatures and can react with H₂.

The microscope used for these studies was a double aberration corrected JEOL 2200FS with extra large pole-piece gap that allows the use of the Gatan 628 heating holder. Extensive modifications were made to the microscope to allow gas to be injected into the specimen chamber which are described elsewhere [11,12]. Aberrations were corrected using a reference sample (Au nanoparticles on 2.5 nm amorphous C).

Regions of the Co₃O₄ were imaged before the gas was added for reference. The temperature was increased in 50 °C increments up to 550 °C. The regions of interest were not exposed to the electron beam during the heating steps. A landmark on the Cu grid far away from the regions of interest was used as a locator when the sample drifted during heating. At each temperature, images were recorded.

The images featured in this paper were all taken in-situ in H₂ at the temperatures indicated.

3. Results
Figure 1 shows a HRTEM reduction sequence of an area of Co₃O₄ at room temperature, 350 °C and 450 °C. The majority of the Co₃O₄ crystals contained a mixture of stepped surfaces and flat surfaces such as those shown in frame (a). The contrast of the similarly aligned grains in the figure is caused by the slight difference in orientation (a few °) resulting in different phase contrast in the HRTEM image.

We observed that CoO formation began at temperatures as low as 200 °C [13] but in general we found that the majority of crystals did not form CoO regions until 350 °C as is the case here. We observed that the CoO formation generally begins at stepped surfaces or at corners as shown in Figure 1(b). The CoO region cuts further into the Co₃O₄ crystal like a fuse-wire as the heating continues and by 450 °C the entire crystal had transformed to CoO. Despite heating to 550 °C we did not observe Co in this experiment. We believe this is because of the low pressure used in this experiment [13].

In the widest part of the crystal, which was about 50 nm wide, dramatic contrast variations...
Figure 2. HRTEM images of a Co$_3$O$_4$ crystal approximately 50 nm wide showing dramatic contrast variations in the centre of the crystal at (a) 350 °C and (b) 400 °C in H$_2$. (c) is the FFT of (a) and (d) shows an example of a defect shown in the filtered image of (a). Defects are highlighted in the images with circles and the defect in (d) is highlighted with an arrow in (a).

were observed. Examples of this contrast is shown in Figure 2. Such oscillations in intensity have been attributed to the presence of defects and the strain associated with them. The HRTEM images in Figure 2 show that the contrast changes between 350 °C and 400 °C. The FFT indicates the simultaneous presence of CoO and Co$_3$O$_4$ as shown in Figure 2(c). There is an additional reflection on the opposite side of the Co$_3$O$_4$ {004} reflection which is caused by the double diffraction of Co$_3$O$_4$ and CoO. This suggests that in the case observed in Figure 2, the Co$_3$O$_4$ to CoO interface is observed parallel to the electron beam unlike in Figure 1 where it is perpendicular.

By Bragg filtering the FFT (selecting one or more set of reflections) it was deduced that the contrast changes observed in the centre of the crystal at the two different temperatures is related to the presence of dislocations. In the filtered image (an example is shown in Figure 2(d)), the dislocations appear as forks. By including more reflections in the filtered image, most of the dislocations were deduced as having Burgers vectors of type $\vec{b} = \frac{1}{2}\{1 1 0\}$ [13]. Dislocations were also found close to Co$_3$O$_4$ to CoO interfaces [13]. We currently do not know the nature of the defects (e.g. edge or screw) but our preliminary data indicate that they play a role in the reduction.
4. Conclusions
We have demonstrated that defects form in the reduction of Co$_3$O$_4$ to CoO and mobile interfacial boundary forms between Co$_3$O$_4$ and CoO in large crystals. We believe the defects originate from the difference in lattice constants of Co$_3$O$_4$ and CoO [13].

Further work is required to deduce the nature of the defects and how they influence the formation of Co. Higher pressure runs are required and ideally a double tilt heating holder is required for deducing the Burgers vector of defects in more zone axes. Environmental HAADF-STEM [12] could also be useful since the contrast originating from the specimen is not dependant on phase contrast unlike HRTEM images which are often non-intuitive.

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