In-situ environmental (scanning) transmission electron microscopy of catalysts at the atomic level

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Abstract. Observing reacting single atoms on the solid catalyst surfaces under controlled reaction conditions is a key goal in understanding and controlling heterogeneous catalytic reactions. In-situ real time aberration corrected environmental (scanning) transmission electron microscopy (E(S)TEM permit the direct imaging of dynamic surface and sub-surface structures of reacting catalysts. In this paper in-situ AC ETEM and AC ESTEM studies under controlled reaction environments of oxide catalysts and supported metal nanocatalysts important in chemical industry are presented. They provide the direct evidence of dynamic processes at the oxide catalyst surface at the atomic scale and single atom dynamics in catalytic reactions. The ESTEM studies of single atom dynamics in controlled reaction environments show that nanoparticles act as reservoirs of ad-atoms. The results have important implications in catalysis and nanoparticle studies.

1. Introduction

Chemical reactions catalysed by solid surfaces in heterogeneous catalysis take place at the atomic level and play a major role in the development of industrial chemicals, energy sources and environmental emission controls. Dynamic active atomic structures at the surface of the solid catalyst under reaction conditions underpin the performance of the catalysts. Insights into the dynamic evolution of structural changes in heterogeneous catalysts under controlled gas and temperature reaction conditions at the atomic level in real time are therefore crucial in the development of efficient catalysts. The direct observation of the surface structure, chemical evolution and the live reaction mode of operation of catalysts under controlled reaction conditions of gas and temperature at the atomic level is therefore a powerful scientific method but extremely challenging.

Previously Gai and Boyes reported the first development of atomic resolution-Environmental transmission electron microscope (atomic resolution-ETEM) which enabled atomic resolution studies of gas-solid reactions at operating temperatures under controlled conditions and for in-situ nanosynthesis [1,2]. Highlights of this development included their novel and now widely used ETEM design with objective lens polepieces incorporating radial holes for differential pumping with the regular sample chamber as the controlled reaction environmental cell or reactor (Figure 1) [2]. The direct real time imaging of dynamic interactions between hydrocarbons and oxide catalysts and how the gas molecules move and rearrange the catalyst surface in the selective hydrocarbon oxidation has resulted in the discovery of an atomic scale reaction site mechanism resulting from a simple atomic movement, called the “glide shear reaction mechanism” shown in Figure 2 [1]. During the selective oxidation the glide defects are formed to accommodate the shape misfit between the reduced anion-deficient catalyst surface and the subsurface without collapsing the catalyst structure which is critical...
to the sustained operation. The authors’ ETEM development paved the way to atomic resolution studies of gas (or liquid)-solid reactions at operating temperatures worldwide [3].

The subsequent development of double aberration corrected ETEM (AC ETEM) utilising a large gap objective lens polepiece has been reported earlier [4,5,6]. The critical role of atomic level defect structures formed by the glide shear mechanism in biofuel synthesis has been demonstrated recently using double aberration corrected-ETEM ((AC-ETEM) [7]. The evolution of atomic scale glide-shear defects occurs at the nanocatalyst surface during activation, creating active sites. The direct linear correlation between the surface glide defect density and the improved catalytic performance has offered a new route to energy efficient catalysts for biofuel synthesis [7]. Hydrogen reduction of...
cobalt oxide catalysts using AC-ETEM has shown advancing atomic scale interfaces of reduced oxides [8].

Recently Boyes et al have reported the development of the ESTEM method for single atom imaging in catalyst reaction studies [9]. With the new AC-ESTEM capability it is now possible to analyse real space STEM Z-(atomic number), especially single atom contrast high angle annular dark field imaging (HAADF) diffraction and spectroscopy, under transient conditions [9].

In this paper we present our original E(S)TEM research into working oxide catalysts and supported nanocatalysts. Supported cobalt based nanoparticles are of interest in a number of hydrogenation reactions including Fischer-Tropsch (F-T) process for synthetic fuel technologies and in environmental control [10,11]. The F-T process contains a series of chemical reactions involving the hydrogenation of CO over solid catalysts to produce various hydrocarbons. More recently cobalt based oxides have been employed for the reactions. Supported platinum nanocatalysts are important in the chemical industry, including in fuel cells, where reactions with hydrogen and oxygen are important, and as part of vehicle exhaust emission control measures [12,13].

2. Experimental Procedures

Co$_3$O$_4$ powder was obtained from Aldrich. TEM and diffraction analysis of the powder showed primarily Co$_3$O$_4$ [8]. Specimens for conventional EM analysis were made by dispersing Co$_3$O$_4$ powder in ethanol which was then treated in an ultrasonic bath for 2 minutes. The suspension was deposited onto holey-C grids. For in-situ ETEM studies, bare (unfilmed) Cu grids were used because the C films are known to buckle and react with oxide samples under H$_2$. For high resolution imaging, the Cu grids were plasma cleaned at 75% power for 5 minutes using a Diener Femto unit to remove the inevitable contamination. After depositing the Co$_3$O$_4$ powder, the specimens were further plasma cleaned at 10% power for 30 seconds. Crystals protruding over the edge of the grids were employed in the in-situ studies. Model Pt nanocatalysts were prepared by sputtering Pt on carbon supports.

For dynamic real-time in-situ studies at the atomic level under controlled gas and temperature conditions, we used a double spherical aberration corrected Environmental (Scanning) TEM (AC-E(S) TEM) developed in-house by Boyes and Gai [4,5,9] in the Nanocentre at the University of York. The AC-E(S) TEM with sub-Angstrom (<100 pm) resolution was developed by modifying a double aberration corrected JEOL 2200FS(S)TEM operating at 200 kV and fitted with a larger gap (HRP) objective lens polepiece and gas tolerant pumping system [4,5,9]. The E(S)TEM development is uniquely equipped to carry out in-situ studies of the structure and stability of single atom catalysts and small nanoparticles [9]. The dynamic nature of in-situ reactions means that it is rarely possible to obtain a complete through focal series of images. By including in the CTF of each image frame a complete range of spatial frequencies, and by minimising delocalisation effects by operating at close to zero defocus, AC-E(S)TEM allows us to clearly observe single atoms, measure more accurately inter-atomic spacings, analyse crystal structures, and especially external surfaces, from a single image. The wider gap pole piece enables hot stage capabilities and an increased sample tilt range [4,5,9]. Further, AC-E(S)TEM under low electron dose imaging and ‘blank’ calibration experiments (without the beam and the beam switched on only to record the final reaction end point and compared to in-situ data) are used to minimise effects of the electron beam on the sample [1-6, 14,15].

3. Results and Discussion

3.1 Atomic level Reduction of cobalt oxides

The reduction of model Co$_3$O$_4$ catalysts has been carried out in H$_2$ from room temperature (RT) to ~ 450°C from the same area of the sample to directly observe the dynamic phase evolution in the reduction process. Figure 3 shows dynamic AC-ETEM images of the reaction sequence of a Co$_3$O$_4$ catalyst crystal at rising temperatures during exposure to H$_2$ in-situ. Figure 3(a) shows Co$_3$O$_4$ at RT which is readily identified from other phases because of the presence of a large 0.47 nm {111} atomic plane spacing. The evolution of CoO was observed at the surface of the catalyst from ~200°C and persisted up to higher temperatures of ~ 400 °C. Figure 3(b) shows the presence of CoO at 400 °C in hydrogen with (002) spacings of 0.21 nm. These direct in-situ observations have provided new insights into the reduction mechanism from Co$_3$O$_4$ to the intermediate CoO. These include the formation of an advancing atomic scale interface between the Co$_3$O$_4$ and CoO regions. There are
Figure 3. Dynamic AC-ETEM image sequence of the same area (near X) of a Co$_3$O$_4$ catalyst in hydrogen gas: (a) Co$_3$O$_4$ at room temperature (RT). 0.47{111} lattice spacings are shown. (b) The formation of CoO recorded at ~400°C in hydrogen gas. CoO {002} spacings of 0.21nm are shown.

reports in the literature that active sites in the F-T process at low temperatures of 225-250 °C are Co metal. Our in-situ observation of CoO at operating temperatures of 250-350 °C has important implications in understanding the catalytic activity of Co-based oxide catalysts in hydrogenation reactions. In our in-situ studies Co is observed only at higher temperatures and higher gas pressures.

3.2 Single atom dynamics

In-situ ESTEM studies were carried out on platinum catalysts supported on carbon in reducing and oxidising atmospheres. Figure 4 (a) displays single atoms and clusters of a Pt catalyst clearly using ESTEM, with the intensity profile of a single atom in (b). The FWHM for the single atom is ~0.11 nm.

A sequence of a small particle (P) undergoing structural rearrangement is shown in Figure 5.

Figure 4. (a) single atoms of a Pt/C catalyst in ESTEM HAADF. (b) Intensity profile of a single atom indicated in (a).
Figure 5. Single atom dynamics: migration of single atoms arrowed in (a) and (b) (e.g. from a cluster/particle P) leading to increased faceting of the particle and the formation of clusters (c).

Figure 5 (b) forms the intermediate stage, indicating the migration of single atoms from the particles (appearing as white dots (arrowed) on the thin amorphous carbon support film. The driving force for the removal of atoms away from the particle is proposed to be minimisation of the particle surface energy, where surface ad-atoms and steps are removed in order to create lower energy facets. The onset of faceting can be seen in (c) and the formation of small clusters.

The reduction-oxidation reactions were carried out at the single atom level and the observations are illustrated in Figure 6. Figure 6 (a) shows single atoms and particles; Figure 6 (b) shows the sample in hydrogen gas at 500 °C. The gas inlet pressure was ~ 200 Pa. Fewer single atoms and some faceting of clusters are observed. The hydrogen was then outgassed and oxygen was inserted at ~200°C with the inlet gas pressure of ~ 190 Pa.

Figure 6. Dynamic ESTEM showing single atom dynamics in Pt/C nanocatalyst in controlled reduction-oxidation reaction environments: (a) RT; (b) Hydrogen gas at ~500 °C showing faceting and fewer single atoms; (c) Oxygen gas at 200°C showing relatively more single atoms indicating that interaction with oxygen inhibits their mobility.

In-situ hydrogen reduction in Figure 6(b) shows the presence of fewer single atoms on the support than in (a), clusters and increased faceting of the nanoparticles. This indicates that the nanoparticles act as a source of potential ad-atoms and clusters. This has important implications in catalysis and understanding the role nanoparticles generally. Recent literature reports based on ex-situ studies indicate excellent catalytic performance in the presence of low coordinated atoms and clusters [16]. Minimisation of surface energy leads to the removal of low coordinated atoms and stable surface facets. This decrease in the low coordinated sites may explain the often observed initial drop in the activity of nanocatalysts [17,18]. In oxygen relatively more single atoms are observed in Figure 6(c)
indicating that the single atom reaction with oxygen prevents their migration.

Conclusions
Using our novel ESTEM development we have demonstrated single atom dynamics in industrially important supported platinum nanocatalysts in reduction and oxidation environments at operating temperatures and atomic level transformations in cobalt oxide catalysts in hydrogen reduction. The results have important implications in catalysis and studies of nanoparticles.

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