In-situ visualisation and analysis of single atom dynamics in chemical reactions by novel E(S)TEM

GAI, P.[1], Martin, T.[1], Mitchell, R.[1], Lloyd, D.[1] and Boyes, E.[1]

[1] University of York, United Kingdom

Many chemical processes using heterogeneous catalysts take place in gas (or liquid) environments at elevated temperatures at the atomic level. There are postulations that single atoms and very small clusters can act as primary active sites in these chemical reactions. Understanding and control of complex chemical reactions on the atomic level are therefore crucial for the development of improved processes and materials (1). To visualise and analyse gas-catalyst reactions at the atomic level in real time, we designed and constructed the first atomic resolution environmental transmission electron microscope (ETEM) (1), which has been exploited for commercial production and used globally (2,3). We have now developed it further (4,5), to support full ES(scanning)TEM and the other analytical functionalities with aberration correction (AC), (AC ESTEM; Boyes et al, 5, 6). In the ESTEM single atom resolved high angle annular dark field (HAADF) imaging (Fig. 1) and full analytical functionalities including electron diffraction and EDX, are enabled for the first time under controlled chemical reaction conditions of high temperatures in a continuously flowing gas atmosphere around catalysts while retaining single atom sensitivity for critical catalytic processes (4-10).

The novel AC E(S)TEM instrument in our laboratory has been used to obtain new insights into catalytic processes for chemical transformations. These include processes of metal nanoparticle catalyst deactivation which has both economic and other societal importance, including for scientifically informed environmental management; water gas shift (WGS) reaction in CO and water environments for the generation of clean hydrogen energy for fuel cells; transportation fuels and in ammonia manufacture.

In supported nanoparticle catalysts quantitative single atom dynamics in catalyst sintering and deactivation are revealed by the E(S)TEM through single atom detachment, migration and reattachment. In ceria supported noble metal nanocatalysts, the in situ observations in WGS have revealed the formation of clusters of only a few metal atoms resulting from single atom dynamics and the catalytic effect of low coordination surface sites. The new insights have important implications for applications of nanoparticles in chemical process technologies including for transportation fuels and emission control. Reaction dynamics at the atomic scale are basic to ammonia synthesis using supported nanoparticles. Effects of the dynamics on the sintering and size of Ru nanoparticles on different carbon supports of interest in ammonia synthesis are visualised and monitored *in-situ* at the atomic level in real time under controlled reaction conditions using the (E(S)TEM). The findings provide a better understanding of the nanoparticle behaviour on the different supports under ammonia synthesis conditions. Benefits of the E(S)TEM studies include new knowledge and environmentally beneficial technological processes for healthcare, renewable energy and pollution control, as well as improved or replacement mainstream technologies in the chemical and energy industries.

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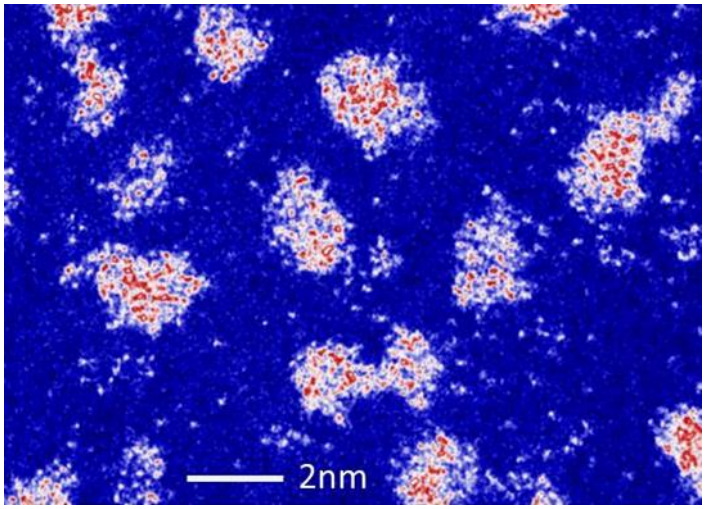

Fig.1 ESTEM-HAADF of single atoms and clusters of Pt on carbon support