Dynamic atomic structures of solids under reaction conditions are critical to understanding and controlling their properties. We have successfully developed atomic resolution-environmental TEM (ETEM) for direct probing of gas-solid reactions at the atomic level [1,2]. The novel ETEM designed by Gai and Boyes with objective lens pole pieces incorporating radial holes for differential pumping [1,2], has been adopted by TEM manufacturers FEI for commercial production and later versions of the Gai and Boyes’ ETEM include, CM200-300 series, Tecnai and Titan (including with aberration correction), used by researchers world-wide. We describe examples of dynamic ETEM studies under controlled reaction conditions of gas pressure and temperature and describe the recent developments of dynamic real time in-situ studies at the Angstrom (0.1 nm) level in an aberration corrected (AC) environment [4]. For in-situ AC EM studies, we used a modified double aberration corrected JEOL 2200 FS TEM/STEM with a wider gap objective lens pole piece and gas tolerant pumping system [4].

Active ruthenium (Ru) nanocatalysts supported on nano-rutile titania are of interest the hydrogenation of aliphatic dinitriles at ~ 300°C in the production of linear polymers. Atomic resolution-ETEM has been used to probe the effect of hydrogen and the catalyst stability. Dynamic atomic images Ru/titania at room temperature (RT) and at 280°C in hydrogen reacting for 2 hours in 2 mbar of gas pressure are shown in FIG 1(a) and (b), respectively. The dynamic data illustrate that Ru atomic structures remain intact even after the prolonged reaction, indicating a stable nanocatalyst. Aberration correction is particularly beneficial in dynamic in-situ experiments [4]. FIG2 illustrates in-situ AC images of a performance critical gold nanoparticle at room temperature (RT) showing both the internal perfection and (111) surface terraces. FIG2 (b) and (c) illustrate three Au nanoparticles at RT and their sintering into a larger agglomerate at 500°C, respectively, with the parallel alignment of (111) planes in adjacent nanoparticles in FIG2 (c). We believe that the sintering occurs due to the initial reduction of the surface disorder. These atomic scale interactions have implications in CO oxidation catalysis and fuel cells applications.

Many countries have set challenging targets for the partial replacement of conventional fossil fuel sources with renewable biofuels to combat energy shortages. Biodiesel is one such clean biofuel that can be synthesised via transesterification vegetable oils. We have studied magnesium oxide (MgO) nanocatalysts for the transesterification of plant oils to biodiesel. Nano-MgO powder catalysts were prepared from (Mg(OH)(OCH3)). FIG3(a),(b) and (c) show in-situ images at RT, and extended defects at 500 °C and 700 °C, respectively. Detailed Burgers vector analyses revealed that the defects are formed by glide shear in (110) planes along <111> directions and have displacement vector $\mathbf{R}$ of the type, $\pm a/2 <\mathbf{111}>$. Based on the in-situ observations,
we considered the critical role of the defects in the production of biofuels [5].

FIG. 1 Atomic resolution-ETEM in hydrogen atmosphere: (a) Nano Ru over nano-titania catalyst in \( H_2 \) at room temperature (RT) and (b) shows the dynamic reaction at \( \sim 250 \, ^\circ C \) in hydrogen, indicating 0.2 nm lattice of Ru nanoparticles (arrowed) and a relatively stable catalyst.

FIG. 2 Dynamic in-situ studies of gold nanoparticle sintering in aberration corrected EM. (a) Image detail of performance critical gold nanocatalyst showing both internal perfection and (111) surface terracing at RT; (b) gold particles at RT; (c) the same particles at 500 °C, with the alignment of (111) planes (with 0.23nm spacing) near the arrow.

Fig. 1: In-situ, real time dynamic aberration corrected TEM (in-situ AC-TEM) studies of calcination of MgO nanocatalysts showing : (a) nanograins at RT; and defects at (b) 500 °C and (c) 700 °C.

References