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HIGH RESOLUTION, IN-SITU CONTROLLED ATMOSPHERE TRANSMISSION ELECTRON MICROSCOPY (CATEM) OF HETEROGENEOUS CATALYSTS

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A catalyst has been imaged with lattice resolution whilst surrounded by flowing gas, using a specially constructed in-situ cell for an electron microscope. This advancement demonstrates the feasibility of directly studying atomic rearrangements in catalysts and catalyst supports under reaction conditions by electron microscopy. Such studies show promise of providing a detailed understanding of the mechanisms involved in certain types of heterogeneous catalyst.

Modern transmission electron microscopes (TEMs) can permit structural characterisation of solids at near-atomic resolution. However, the high vacuum required for their operation makes the dynamic study of heterogeneous chemical reactions difficult, and the performance of the TEM is usually compromised. It is recognised that, if this limitation could be overcome, a major area which would benefit greatly from the application of CATEM is heterogeneous catalysis. To date, with a few notable exceptions, technical constraints and the severity of electron/gas interactions have led to the data obtained being of insufficiently high resolution to help solve problems of fundamental interest. We report here results which demonstrate that poor resolution need not be an inherent property of CATEM studies. Using a narrow-gap, windowed cell in conjunction with a 400kV TEM, images of the crystal lattice of ceria (0.31 nm) were recorded under flowing nitrogen gas at 20 Torr. To our knowledge, this is the first time that such high resolution has been achieved under conditions not far removed from those typical of in situ use. Moreover, a deeper significance lies in the fact that, at around 0.3 nm, structural information of chemical significance becomes discernible, and thus the technique begins to offer real hope of carrying out fundamental dynamic studies of the activation, reaction and passivation of gas/solid systems at close to the atomic level.

CATEM has been pursued as an adjunct to TEM for almost as long as TEM itself [1]. The original impetus for such work was to enable biological samples to be studied in the hydrated state, to avoid the introduction of artefacts by

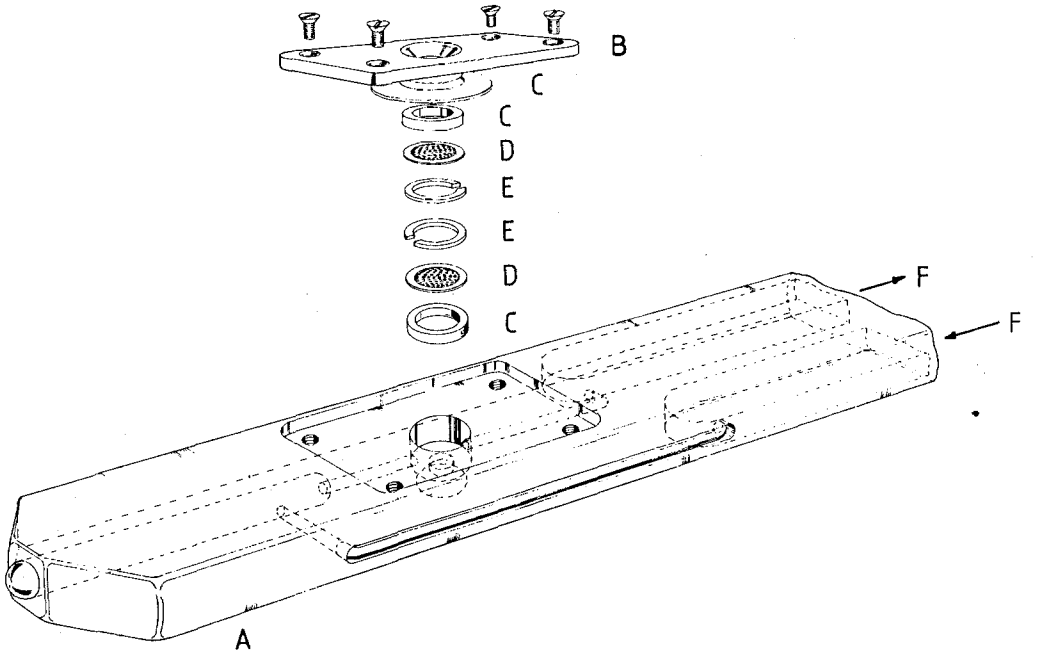

Fig. 1. Schematic, showing A) tip of the environment cell, B) top plate, which is screwed into place, C) silicone rubber gaskets, D) support grids and carbon windows, E) C-spacers, F) gas inlet/outlet pipes.

specimen preparation techniques. Subsequently, the technique was applied to materials science for the study of gas/solid reactions [2,3]. More recent work, using 1 MeV TEMs, has demonstrated the potential of CATEM for studying heterogeneous catalysis dynamically at a resolution approaching 2 nm [4,5]. However, the limited availability of 1 MeV TEMs and the fact that their inherent resolution is inadequate for many CATEM studies, have reduced the impact of the technique on heterogeneous catalysis to date. The purpose of the present work is to assess the potential of CATEM when carried out using a high resolution, medium voltage TEM (JEM 4000EX).

Environmental cells were constructed for two TEMs: a JEM 2000FX (200 kV) and a JEM 4000FX (400 kV), both fitted with side-energy goniometers. The designs were based on that published by Fukami et al. [6]. The key features are that the gas is contained between very thin (ca 5–10 nm), evaporated carbon windows, and the path length of the beam is kept small (10–50 μm) by using thin, C-shaped, spacers (fig. 1). The cell is able to support a pressure differential of ca 1 atmosphere because the window film is left unsupported over only small areas of the electroformed copper grid. Alignment of holes in the top and bottom windows is achieved by tilting the cell. The lower window is used as a support for the sample; at high magnification ($> 50\,000$) the holes do not limit the field of view and location of sample particles is straightforward. A gas handling system

was constructed to allow control of pressure of gas within the cell (up to one atmosphere) and flow rate (up to 50 ml/min) and for the cell to be evacuated (to ca 10^{-2} Torr by rotary pump).

A sample of cerium oxide (CeO_2), a typical catalyst support and sacrificial catalyst which operates by release of structural oxygen [7], was chosen as a test specimen to measure the resolution attainable by the cells at 200 and 400 kV. The average crystallite size was 5 nm and, when oriented with the ⟨110⟩ zone parallel to the electron beam, lattice fringes from the {111} planes (separation = 0.312 nm) are clearly resolvable at 200 and 400 kV in the absence of gas.

High vacuum is achieved in the specimen area of both TEMs by sputter ion pumping. Because of the nature of this type of system, only very small leak rates from the environmental cells could be tolerated; this limited operation of the cells to pressures lower than they could intrinsically sustain. The micrograph in fig. 2 was obtained under conditions of flowing (ca 10 ml/min) nitrogen gas at 20 Torr. This does not necessarily represent the maximum gas pressure at which the obtained lattice resolution of 0.31 nm may be realised: that is determined by a combination of accelerating voltage, the nature of the gas, and its pressure, beam path length, window thickness and type of specimen. Indeed, with a diffusion pumped system (which can cope with a higher leak rate of gas from the cell), it is anticipated that 0.3 nm could be resolved under a significantly higher pressure of gas, particularly for low molecular weight gases such as hydrogen, where electron scattering is less pronounced.

Repeated attempts were made to resolve the ceria lattice in the presence of gas at 200 kV. This was done on both the JEM 4000EX with the accelerating voltage reduced to 200 kV, and also on the JEM 2000 FX. Under identical conditions, the ceria planes that were resolvable at 400 kV could not be resolved at 200 kV. This result emphasises the importance of the combination of high accelerating voltage and high resolution for achieving near-atomic resolution CATEM.

Preliminary estimates of the relative increase in resolution between 200 and 400 kV for a given set of cell conditions will be reported in full, elsewhere [8]. Briefly, the effect on resolution caused by the inelastic scattering of electrons by the windows and gas was treated simplistically as an increase in energy spread of the primary electron beam. Hence, the effect of increasing energy spread is to act as progressively severe damping function on the oscillating contrast transfer function of the microscope (this function represents the ability of a TEM to resolve faithfully specimen features for a particular set of microscope operating conditions). On the basis of an estimated energy spread of 10 eV, the resolutions at 200 and 400 kV are calculated to be ca 0.5 and 0.25 nm, respectively. Further experiments are planned to measure the energy spread directly by energy loss spectroscopy; similar experiments offer the promise of being able to measure the window thickness and pressure directly, during CATEM studies [9].

Whilst higher accelerating voltages than 400 kV have advantages for CATEM (an atomic resolution 1 MeV TEM is in operation [10]), the high cost and siting

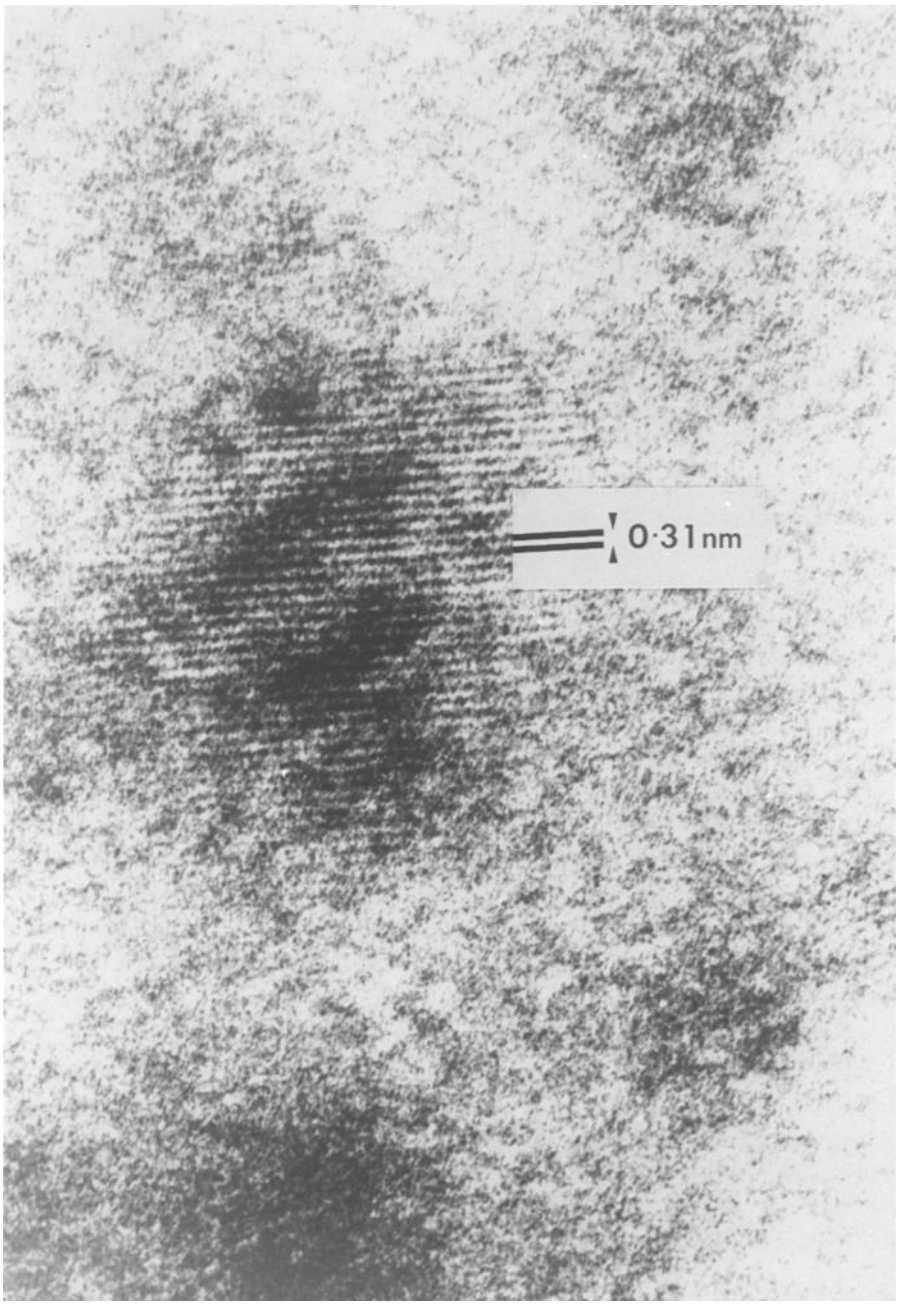

Fig. 2. HRTEM image of ceria lattice, taken under flowing nitrogen at 20 Torr.

constraints make access to such instruments limited. With their relatively lower cost and ease of siting, the new generation of medium voltage TEMs [11] offers the prospect that high resolution CATEM may become a more readily available

technique in the near future. It is hoped that this initial demonstration of the feasibility of near-atomic resolution CATEM will lead to further development of the technique and consequently to a greater understanding of gas/solid interactions at the atomic level.

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