Chapter 29
Environmental Transmission Electron Microscopy

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Keywords In situ observation · Differential pumping · Sealing membrane
Gas · Liquid

29.1 Principle

ETEM is a dynamic observation technique based on transmission electron microscopy (TEM). In normal TEMs, specimens are placed under a vacuum condition because electron scattering by residual gas molecules must be minimized. In contrast, ETEM enables to observe specimens exposed to gas or liquid environments. Therefore, ETEM can reveal nature of materials under the conditions in which they are formed or utilized, for example, catalysts in gas, battery electrodes in liquid electrolyte, and so on. ETEM has two types of system to keep specimens in gasses or liquids. One is an open-type with differential pumping system for gas experiments [1–3], and the other is a close-type for both gas and liquid flow [4–6]. The former is incorporated in TEM vacuum column where electron beam goes down (Fig. 29.1a). By adding orifices and pumping lines, gas molecules spreading from the specimen chamber can be mostly evacuated. In the latter type (Fig. 29.1b), a small space inside a specimen holder, called an environmental cell (E-cell), is separated from a vacuum with two thin membranes that permit electrons to pass through but forbidden gas/liquid molecules to leak out. These systems provide the

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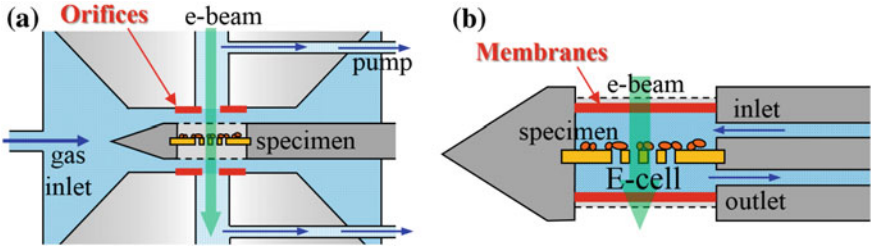

Fig. 29.1 Schematic illustrations of two types of ETEM; **a** open-type and **b** close-type

special conditions only around the specimens but keep the other parts of the TEM vacuum.

29.2 Features

- Materials in gas or liquid environments can be dynamically observed.
- Observations in gas/liquid can be realized with the other actions on specimens such as heating, applying voltage, and so on.
- This technique can be applied not only to TEM but also to the other electron microscopies, e.g., scanning electron microscopy (SEM), etc.
- Atomic resolution is achievable by reducing thickness of gas/liquid layer and pressure of gasses.
- Analysis techniques such as EELS (electron energy loss spectroscopy) and EDX (energy dispersive X-ray spectroscopy) can be combined.

29.3 Instrumentation

In the open-type ETEM, the differential pumping system is assembled in a TEM vacuum system (Fig. 29.2a). A gas control system is connected to the specimen chamber to introduce gas inside the TEM, which consists of variable leak valves, mass flow meters, pressure gauges, etc. Achievable gas pressure around the specimen depends on performance of the differential pumping. Multistage differential pumping is needed for higher pressure, e.g., a several kPa. This ETEM system suits for various specimen holders such as double-tilting, heating, biasing, and so on. In the close-type (Fig. 29.2b), the high vacuum of TEM is maintained. Instead, the specimen holder must be dedicated; containing the E-cell space for specimens in which two membranes can be attached to pack gas/liquid, and pipes for inlet/outlet. A gas (or liquid) control system is connected to the specimen holder. The pressure inside the E-cell can be increased to that higher than ambient by using highly

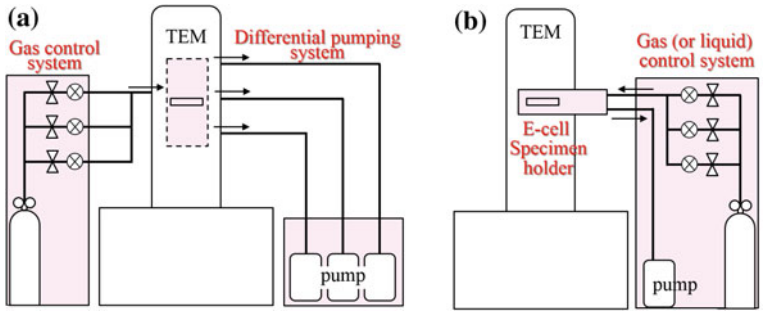

Fig. 29.2 Schematic illustrations of configurations of the **a** open- and **b** close-type ETEMs. Parts modified from the original TEMs are shown in *red*

durable membranes even when the thickness is less than a few tens nanometers. Amorphous silicon nitride membranes fabricated with the microelectromechanical system (MEMS) technique are recently utilized, on which electrodes can be patterned for heating and biasing specimens.

29.4 Applications

29.4.1 In Situ Observation of Au/CeO_2 Catalyst with Open-type ETEM

Figure 29.3 shows an example of the open-type ETEM observations for a gold nanoparticulate catalyst supported on CeO_2 [7]. These images were taken under three different environmental conditions; vacuum, 100 Pa of 1 vol.% CO/air, and 100 Pa of O_2, by using Cs-corrected ETEM with an acceleration voltage of 300 kV. This result clearly shows with the atomic resolution that the morphology and surface structure of the gold particle are reversibly changed by the surrounding environments. The gold particle appeared to be well facetted in the reaction condition of CO/air, while in pure oxygen gas the particle changed to round shape. During CO oxidation, CO molecules absorbed on the gold surface stabilize the particle with polyhedral shape enclosed by the major facets of {111} and {100}. On the other hand, oxygen molecules dissociated into O atoms or active O-related species induce the formation of rounded surfaces of the gold. This result proves that structural analysis of catalysts should be done in situ during the catalytic reactions.

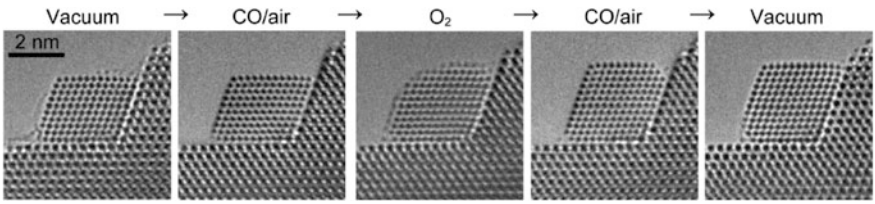

Fig. 29.3 Reversible change in the morphology and surface structure of a gold nanoparticle supported on CeO_2 under different environments. Reprinted from ref. [7], copyright 2014, with permission from Elsevier

29.4.2 Visualization of Reaction Sites of Au/TiO_2 Catalysts with Close-type ETEM

Figure 29.4 shows in situ TEM images of a gold nanoparticulate catalyst supported on anatase TiO_2 [8] as an example of the close-type ETEM observations. In order to reveal reaction sites of this gold catalyst, in situ analyses of catalytic reaction of propene epoxidation (selective oxidation of propene (C_3H_6) to propene oxide (PO; C_3H_6O)) are appropriate. Since the PO has a low vapor pressure of $\sim 5 \times 10^4$ Pa at room temperature, the PO remains in liquid form if the surrounding pressure is controlled to be more than this value. Here, the PO catalytic product might be observed in liquid form, but it is almost impossible to visualize gaseous products. By observing the PO formation, reaction sites on the catalyst surface can be determined directly. The close-type ETEM should be adopted for such relatively high-pressure condition close to 1 atm. The TEM images were taken under a reactant gas environment consisted of C_3H_6 (13%), O_2 (18%), tiny amount of moisture (<0.1%), and N_2 (69%; just for increasing pressure) with a conventional 200 kV-TEM. Before starting the reaction (Fig. 29.4a), surfaces of Au and TiO_2 kept to be clean in a gas environment of O_2, H_2O, and N_2 because of no propene. In contrast, by adding propene to a total pressure of 5×10^4 Pa, the PO product molecules started to be accumulated at the perimeter of interface between Au and TiO_2 substrate, as indicated by arrowheads in Fig. 29.4b. The PO catalytic product disappeared in vacuum because the surrounding pressure became lower than its

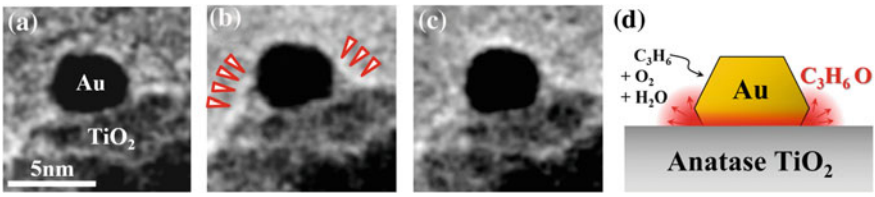

Fig. 29.4 In situ TEM images of Au/TiO_2 observed during propene epoxidation reaction, **a** surrounding gas was O_2, H_2O, and N_2 (not reacted), **b** propene gas was added at a total pressure of $\sim 5 \times 10^4$ Pa and the catalytic reaction started, **c** in vacuum after gas evacuation [8]

vapor pressure (Fig. 29.4c). These results directly proved that the active site where the catalytic reaction occurs is the perimeter of Au/TiO_2 interface, as schematically shown in Fig. 29.4d.

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