In situ detection of product gas molecules associated with catalytic reactions of fine matallic particles by environmental high-voltage TEM eauipped with quadrupole mass spectrometer

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A 1-MV TEM, called the Reaction Science High-Voltage Scanning Transmission Electron Microscope, JEM 1000K RS was installed in 2010 in the high-voltage electron microscopy (HVEM) laboratory of Nagoya University. This machine is capable of not only conventional high-resolution TEM observation but also bright/dark-field scanning imaging of thick samples, chemical analyses using a Gatan Energy Filter (or electron energy-loss spectrometer), 3D computer tomography, and other *in situ* observations/measurements under a reactive gas atmosphere [1]. The high penetration power of 1-MeV electrons allows clear lattice fringe observation even at a gas (e.g., N_2) pressure of 10,000 Pa.
The new HVEM system has delivered a number of novel and outstanding achievements particularly in studies of industrial materials. One of the most remarkable results is atomic-resolution observations of catalytic reactions [2], where the surface structures of metal catalysts dynamically change under a reaction gas atmosphere at usually elevated temperatures. Although such observations should be informative for the design of catalysts with better performance, there was no direct evidence that the chemical reaction of interest really took place at the observation conditions. To overcome this difficulty we developed a new system that combines the HVEM and a quadrupole mass spectrometer (QMS), JMS-Q1000 to identify the reaction gases *in situ* in the specimen chamber.

In this paper, we introduce the new HVEM-QMS system and show preliminary results of redox reactions where the product gas species are unambiguously detected, associated with the expected structural changes, as follows. The block diagram of the present system is schematically shown in Figure 1. (i) CO_2 as a result of carbon nanotube (CNT) combustion by a Pd nano-particle catalyst in O_2 atmosphere was detected when a mixture of a CNT bundle and Pd fine particles (Fig. 2(a)) was heated in ~10 Pa of O_2 gas. The Pd particles started to move around in CNTs > ~200°C, and it appeared that the Pd particles decomposed the CNTs, because carbon atoms contacting Pd particles surface were burned to CO_2, when QMS of m/Z 44 was detected; a good correlation was obtained between the TEM image and Q-Mass spectra, without a significant delay of the CO_2 detection onset with respect to the start of the Pd particles motion, as shown in Fig. 2(b). (ii) Reduction of Rd_2O_3 nano-particles in vacuum: Rd_2O_3 nano-particles supported on ZrO_2 substrate were heated in vacuum, which was reduced to metal at temperatures > ~200°C, as shown in Figs. 3(a) and (b). Interestingly QMS detected no oxygen even during the transformation of Rd_2O_3 to metallic Rh. Instead species of m/Z 44 (in the form of CO_2) were unambiguously detected, as in Fig. 3(c). This suggests that the emitted oxygen atoms were so chemically active in the atomic form as to instantly react with the surrounding carbon-origin contaminations, forming CO_2. Further demonstrations will be presented.

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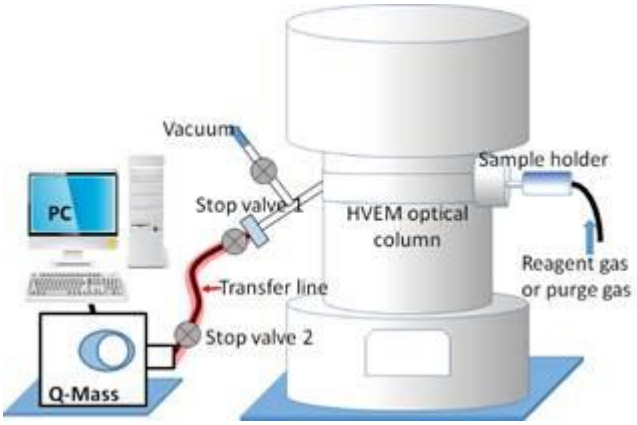

Figure 1 Schematic diagram of the present HVEM-Q-Mass system.

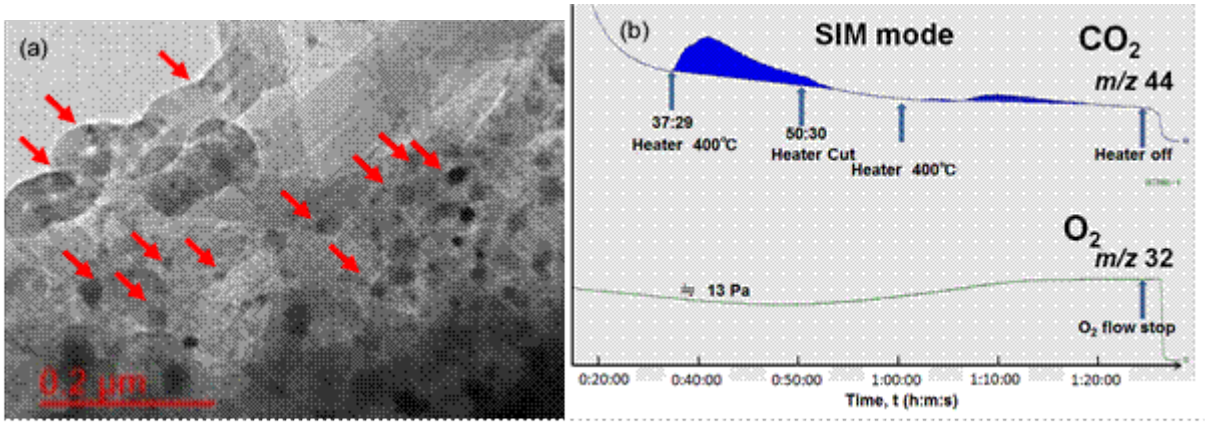

Figure 2(a) TEM image of moving Pd nanoparticles (shown by red arrows) dispersed on CNTs and heated in O_2 atmosphere. (b) Q-Mass spectra at SIM mode, monitoring emission of CO_2 and stable O_2 pressure during Pd/CNT heating.

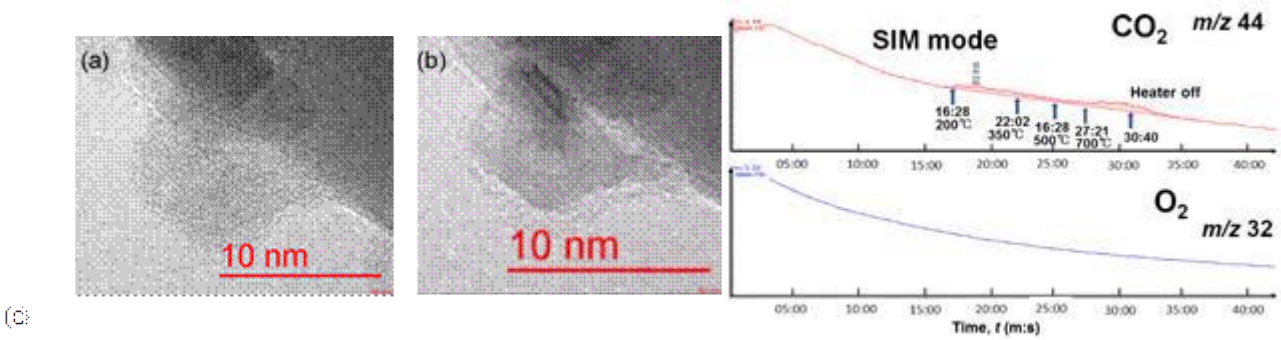

Figure 3 Rh_2O_3 nanoparticle supported on ZrO_2 (a) is reduced to metallic Rh (b) by heating in vacuum.
(c) Corresponding Q-Mass spectra at SIM mode, monitoring CO_2 and O_2.