Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

1. XPS

The surface of supported noble metal particles in UT- and HT-samples was examined by X-ray photoelectron spectroscopy using a selected couple of UT- and HT-Rh/Al_2O_3 catalysts, which were different in the size of metal particles (Figures 1 & 2). The sample was ground in a mortar, pressed onto a sample holder, and measured by a JEOL model of JPS-9200 without such a pretreatment as argon sputtering. The charge-up shift correction of binding energy for Rh was made by setting the C 1s binding energy at 248.5 eV.

The XPS spectra measured are compared in Figure S1, which indicates no significant difference. The average sizes of the supported Rh particles are different but not so markedly; thus, the XPS spectra are very similar for these UT- and HT-samples.

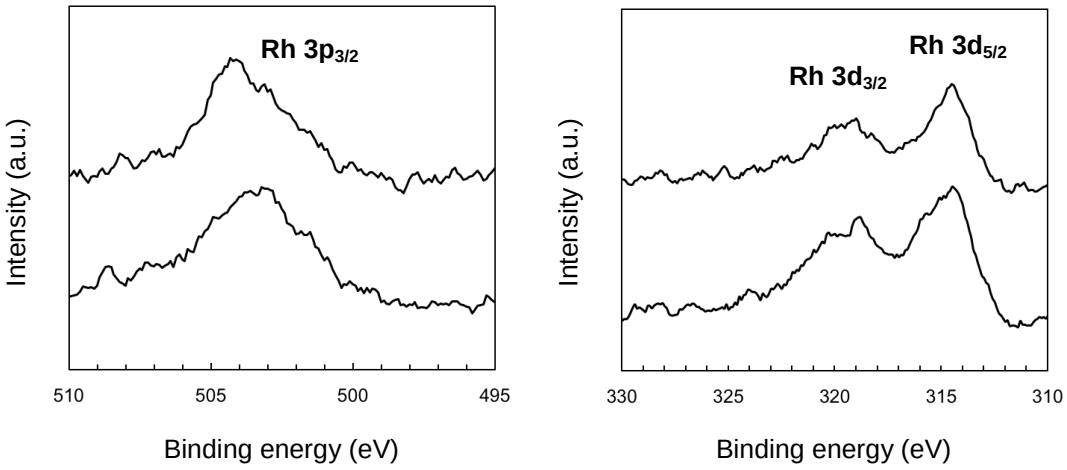

Figure S1 XPS spectra of UT- and HT-Rh/Al_2O_3 catalyst samples

The authors also tried to measure the XPS spectra with UT- and HT-Pt/Al_2O_3 catalyst samples. However, unfortunately, the intensities were weak and so the comparison between these two samples was impossible.

2. FTIR with metal-free Al_2O_3

The surface of metal-free Al_2O_3 was examined by FTIR and the spectra obtained are given in Figure S2. The sample was treated by H_2 in the same way as used for the reduction of noble metal supported Al_2O_3 samples. The spectra were collected before (1) and after (2) this treatment. Then, the spectra were further measured in the presence of either 4 MPa H_2 or 4 MPa H_2 + 4 MPa CO_2. One can see such species as carbonate (1650 cm^{-1}) and carboxylate (1400 cm^{-1}) ones. These species should exist on the surface of Al_2O_3 but not on the metals in the metal supported Al_2O_3 samples as well.

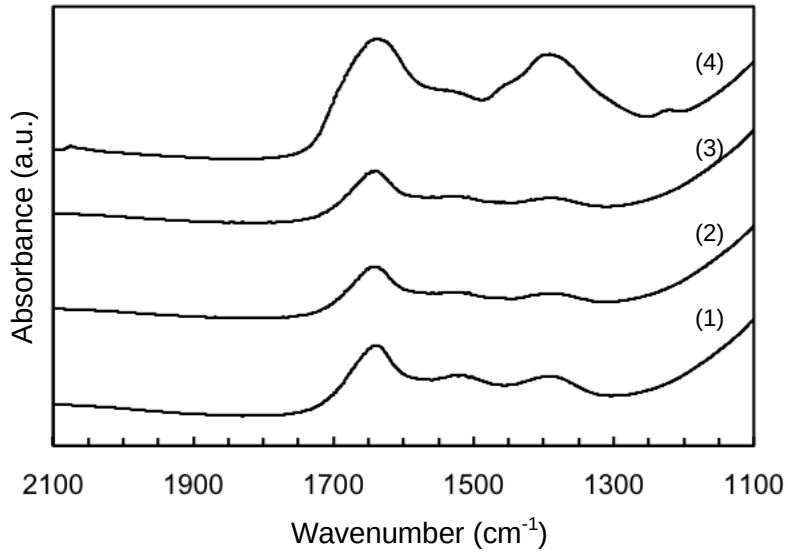

Figure S2 FTIR spectra for metal-free Al_2O_3 sample

3. FTIR in the range of 4000 cm^{-1} – 2500 cm^{-1}

Typical FTIR spectra for meta-free Al_2O_3 and UT-Pt/Al_2O_3 samples are given in Figure S3, which are to examine the possibility of distinguishing between water molecules adsorbed on the support and those on the metal by FTIR measurements. The existence of water species on the catalyst may be indicated by an absorption band at frequency values smaller than 3950 cm^{-1}. Unfortunately, this absorption band is very broad mainly due to hydrogen bonding, which was also the

case for the other noble metal supported Al_2O_3 samples. In this work, however, the influence of water on the adsorption of CO formed from CO_2 and H_2 is discussed by the FTIR spectra of the CO absorption frequency region in the presence of either H_2O or D_2O.

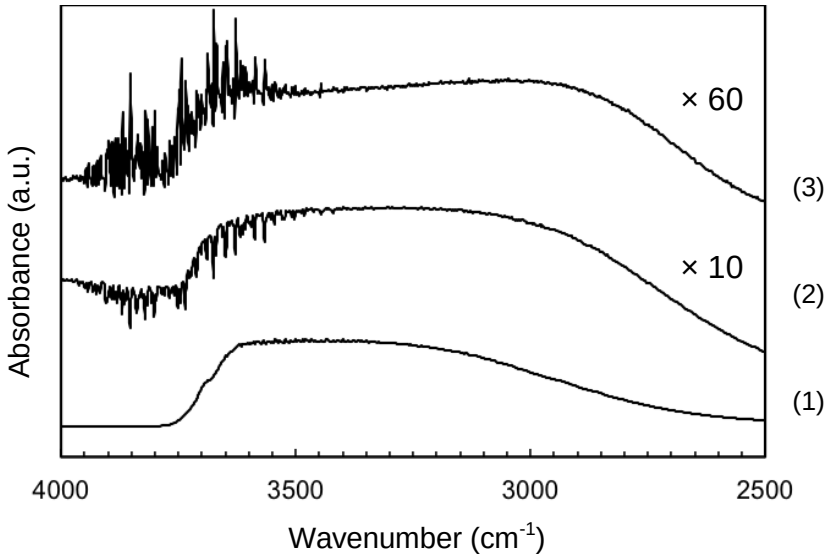

Figure S3 Typical FTIR spectra for (1) metal-free Al_2O_3, (2) UT-Pt/Al_2O_3 in the absence of water and (3) UT-Pt/Al_2O_3 in the presence of water (H_2O) after reduction with H_2 at 323K.