Supporting Information

Metallic ruthenium nanoparticles for hydrogenation of supercritical carbon dioxide

T. Umegaki, Y. Enomoto, Y. Kojima

Experimental Procedures

Chemicals

Ruthenium chloride hydrate ($RuCl_3$ ・ nH_2O (n ≈ 1.87)), methyl alcohol (Kanto Chem. Co., > 99.9%), triethylamine (Kanto Chem. Co., > 99.9 %), (Kanto Chem. Co., > 99.5 %)

Characterization

The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded using an FTIR-8400S spectrophotometer (Shimadzu Co. Ltd.) with a resolution of 4 cm^{-1}. The dissolved Ru content into the solution after the catalytic reaction were measured by Inductively coupled plasma (ICP) analyser using an ICPS-8100 (Shimadzu Co. Ltd.). X-ray photoelectron spectra (XPS) were acquired with an ESCA-3400 spectrometer (Shimadzu Co. Ltd.) equipped with a Mg K_α X-ray exciting source (1253.6 eV) operating at 10 kV and 10 mA. The binding energies (BE) referred to the C 1s peak at 285.0 eV.

Activity test with triphenylposphine

Triethylamine (4 mL), distilled water (2 mL), and triphenylphosphine (PPh_3, g) were added to the ruthenium suspension prepared by the method in this paper. The molar ratio of PPh_3 to Ru was 1. The autoclave was heated to 353 K, and the reactor was then pressurized to 5 MPa with H_2. Subsequently, carbon dioxide was introduced from a cooled (268 K) reservoir by a high pressure liquid chromatography pump and the total pressure was increased to 13.0 MPa at which point the reaction was considered to have started. After the reaction (3 h), ethyl acetate (2 mL) was added to the mixture as an internal standard for the quantitative analysis of product, and the liquid mixture from the autoclave was analysed with a Shimadzu GC 8A gas chromatograph equipped with a Flusin T column (Shimadzu, 2m×3mm) and a thermal conductivity detector. The yield is expressed in terms of the turnover number (TON) of formic acid, which is the number of moles of formic acid produced per mole of ruthenium.

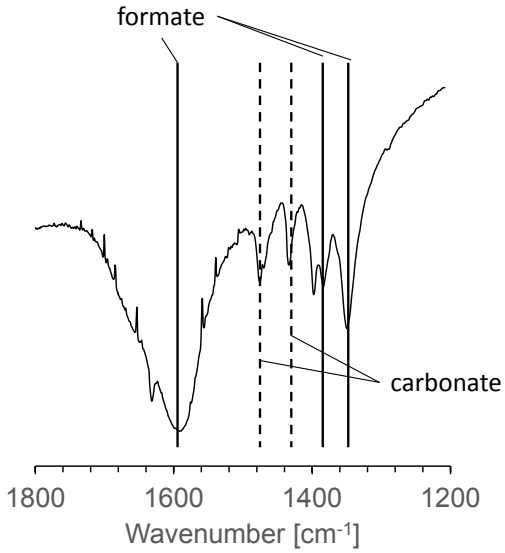

Fig S1 FTIR spectra of Ru nanoparticles prepared with reduction procedure after the reaction with 2 mL of water after hydrogenation of supercritical carbon dioxide.

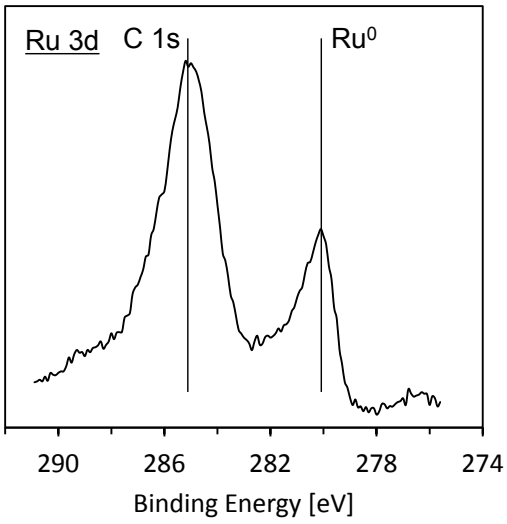

Fig. S2 XPS spectrum of Ru nanoparticles prepared with reduction procedure after the reaction with 2 mL of water after hydrogenation of supercritical carbon dioxide.