Supporting Information
For

Super-thermostable Platinum Nanoparticles on Fluorinated Clay

Dharmesh Varade, and Kazutoshi Haraguchi*

Material Chemistry Laboratory, Kawamura Institute of Chemical Research, 631 Sakado, Sakura, Chiba 285-0078 (Japan)

* Corresponding Author
E-mail: hara@kicr.or.jp

EXPERIMENTAL SECTION

Materials. Fluorinated inorganic clay used in this study ([Mg_{5.34}Li_{0.66}Si_{8}O_{20}(F)_{4}]Na_{0.66} was purchased from Rockwood, Ltd., UK, and used after being washed and vacuum-dried. Analytical-grade potassium tetrachloroplatinate (II) (K_{2}PtCl_{4}), 4-nitrophenol (C_{6}H_{5}NO_{3}), and NaBH_{4} were purchased from Wako Pure Chemical Industries, Japan. All chemicals were used as supplied. Ultrapure water, supplied by a PURIC-MX system (Organo Co., Japan), was used for all experiments.

Preparation of Pt/f-clay NC. A typical experimental procedure for preparing the nanostructured Pt/f-clay NC is described in Scheme S1. The dispersion was prepared by swelling the fluorinated clay (0.1 g) in deionized water (10 g) at 40 °C for 60 min. In the resulting dispersion (1 wt%), aged K_{2}PtCl_{4} solution (50 µL; 5 wt%) was added with continuous stirring for 2 min. Mixtures containing fluorinated clay and Pt species were stored in the dark under static conditions at room temperature (25 ± 1 °C). The formation of Pt nanoparticles was indicated by a color change in the reaction solution from light brown-yellow to opaque black within 24 h of mixing.

Catalytic Reduction of 4-Nitrophenol: A 0.5 mL sample of aqueous sodium borohydride (60 mmol/L) was added to 2.5 mL sample of aqueous 4-nitrophenol (0.12 mmol/L) in a quartz cuvette. Subsequently, 0.01 g of as-prepared Pt/f-clay material was added. Immediately after adding the composite particles, UV spectra of the sample, from 300–500 nm, were recorded at
1 min intervals at 25 °C. For comparison, analogous measurements were performed with f-clay alone, instead of the Pt/f-clay NC.

**Characterization.** UV-vis absorption spectra of the Pt nanoparticles in the fluorinated clay dispersion were acquired in a 1 mm quartz cuvette at room temperature using a Hitachi U-4100 UV-visible double-beam spectrometer. For the reference blank, a solution with the same composition as the sample but without the added metal precursor was used. The morphology of the nanoparticles was examined using a high-resolution field-emission transmission electron microscope (JEM-2200TFE, JEOL) operating at 200 kV. Samples were prepared by depositing single drops of the dilute sample solutions onto carbon-coated Cu grids and drying them at room temperature. Energy dispersive X-ray spectroscopy (EDS) was performed using a scanning transmission electron microscopy (STEM) detector fitted on a JEOL JEM-2200TFE instrument operating at 200 kV. XRD patterns were obtained using a Rigaku SmartLab X-ray diffractometer with monochromated Cu Kα radiation (40 kV, 100 mA). Nitrogen adsorption–desorption data was obtained using a BELSorp-mini II (BEL JAPAN Inc.) operated at 77 K. Prior to measurement, the sample was added to the measurement cell, which was placed in a drying machine and maintained at 80 °C overnight. After drying, helium gas was added to the cell.
Figure S1: TEM image of the Pt/non-fluorinated clay NC upon calcination for 1 h in air at 500 °C. The non-fluorinated clay used was laponite XLG.
Figure S2: TEM image of the Pt/SiO$_2$ NC upon calcination for 1 h in air at 300 °C.
Figure S3: (a) DTA curves for f-clay and non-fluorinated clay (laponite XLG) and Pt/f-clay NC. (b) Thermogravimetric analysis (TGA) for f-clay and Pt/f-clay NC.
Figure S4: N$_2$ adsorption-desorption isotherm for f-clay and Pt/f-clay NC.