

## Supporting Information

# Unexpected Pd-catalyzed Hydrogenation of Phenol into 2-Cyclohexene-1-one: Enhanced Activity and Selectivity Assisted by Molecular Oxygen

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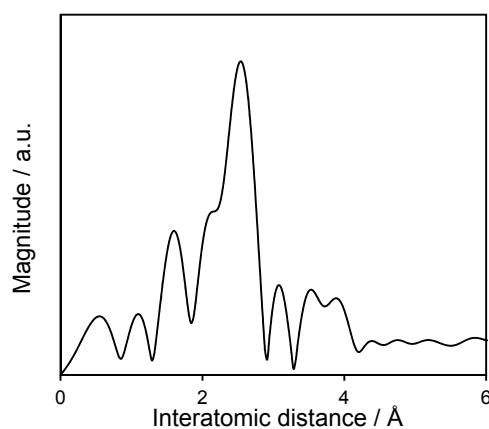
## 1. Experimental

**1.1. Characterization:** Powder X-ray diffraction patterns were recorded using a Rigaku Ultima IV diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Reflectance spectra were collected using a Shimadzu UV-2450 spectrophotometer. The elemental composition was determined by inductively coupled plasma (ICP) analysis using a Nippon Jarrell-Ash ICAP-575 Mark II. BET surface area measurements were performed using a BEL-SORP max (Bel Japan, Inc.) at 77 K. The sample was degassed in vacuum at 343 K for 24 h prior to data collection. TEM micrographs were obtained with a Hitachi Hf-2000 FE-TEM equipped with a Kevex energy-dispersive X-ray detector operated at 200 kV. Pd K-edge XAFS spectra were recorded using a fluorescence-yield collection technique at the beam line 01B1 station with an attached Si (311) monochromator at SPring-8, JASRI, Harima, Japan (prop. No. 2011B1107). The EXAFS data were normalized by fitting the background absorption coefficient, around the energy region higher than the edge of about 35–50 eV, with the smoothed absorption of an isolated atom. The EXAFS data were examined using the Rigaku EXAFS analysis program. Fourier transformation (FT) of  $k^3$ -weighted normalized EXAFS data was performed over the  $3.5 \text{ \AA} < k/\text{\AA}^{-1} < 11 \text{ \AA}$  range to obtain the radial structure function.

**1.2. Synthesis of Pd catalyst:** Mesoporous silica (MCM-41) was prepared by a previously reported method. The MCM-41 obtained was washed with deionized water (2 L) and dried under vacuum before further treatment. The as-synthesized MCM-41 (0.5 g) without calcination underwent template-ion exchange (TIE) treatment with an aqueous  $(\text{NH}_4)_2\text{PdCl}_4$  solution (0.4 mM, 50 mL) for 1 h with stirring and kept at 353 K for *ca.* 20 h. The resultant solid was recovered by filtration, washed with deionized water (1 L), and dried under vacuum. Finally, reduction with an aqueous  $\text{NaBH}_4$  solution (2.8 mM, 25 mL) in an Ar atmosphere followed by filtration, washing with water (1 L), and drying under vacuum, afforded Pd/MCM-41 (Pd 0.5 wt%). In order to reproduce the sample, special attention should be paid in the washing process.

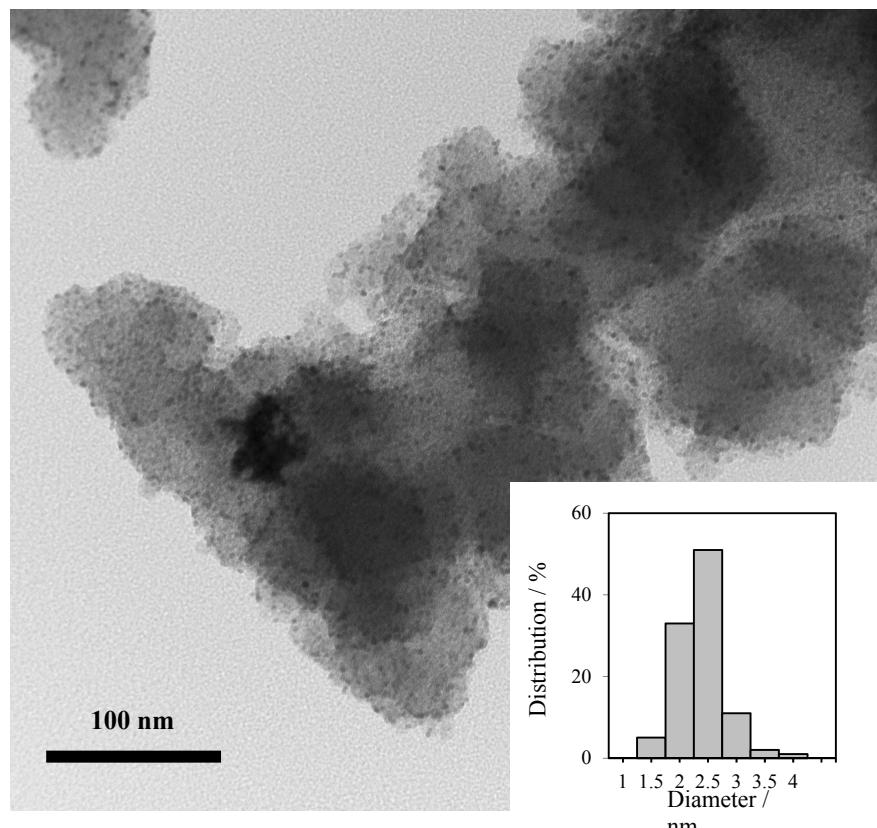
**1.3. Catalytic reaction:** In order to perfume the catalytic reaction using H<sub>2</sub>/O<sub>2</sub> gas mixture with high safety, appropriate precautions should be taken. In particular, the H<sub>2</sub>/O<sub>2</sub> gas mixture should not be added to dry catalyst directly. Hence the catalytic reaction was carried out as follows in a protective draft chamber. The catalyst (0.05 g, Pd:  $2.3 \times 10^{-3}$  mmol), phenol (1.0 mmol), and acetonitrile (20 mL) were placed into a reaction vessel (50 mL) fitted with a reflux condenser. Then, H<sub>2</sub> and O<sub>2</sub> (20 mL/min) gases were bubbled separately into the reaction mixture through Teflon tube and reacted at 333 K for 6 h with magnetic stirring. The reaction progress was monitored using a gas chromatographer (GC; Shimadzu GC-MS-QP 2012 Plus) equipped with TC-5HT columns with an internal standard technique.

## 2. Pd K-edge XAFS



**Figure SI (A)** Pd K-edge FT-EXAFS spectra for as-synthesized Pd/MCM-41.

### 3. TEM



**Figure S2** TEM image and size distribution diagrams of as-synthesized Pd/MCM-41.