Supplementary Material (ESI) for Chemical Communications

Highly selective alcohol oxidation over ordered mesoporous carbon containing molecular level dispersed Pd clusters in the carbon walls

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Experimental

Synthesis procedure

The synthesis of SBA-15 template is described elsewhere.[1] The SBA-15 was evacuated at 150°C for 6h and then infiltrated with acrylonitrile solution in the presence of an AIBN initiator by the incipient wetness technique. The mixture was maintained at 40 °C and then at 60 °C each for one day under static conditions in argon atmosphere. After polymerization, the white powder was subjected to air oxidation at 230 °C for 10 h. The obtained dark brownish powder (1.5 g) was impregnated with $Pd(NO_3)_2$ acid solution (10 wt% HNO_3 solution), using 0.5 ml for high Pd loading and 0.2 ml for low Pd loading, mixed with 50 ml of distilled water, stirred for 24h. The powder was collected after filtration and extensive washing with distilled water, and dried overnight at 80 °C. Subsequently, for the production of nanosized Pd clusters embedded in OMC, the as-prepared composites were thermally treated at the desired temperature (650 or 750 °C) for 3 h under argon. The black powder was recovered after leaching with NaOH or HF aqueous solution, filtration, washing and drying. Samples were labeled Pd-OMC (high Pd loading) and Pd-OMC* (low Pd loading.)

Characterization

TEM images of the samples were obtained with a HF2000 microscope (Hitachi) equipped with a cold field emission gun. The acceleration voltage was 200 kV.

Samples were prepared dry on a lacey carbon grid. X-ray diffraction patterns of samples were recorded with a STADI P diffractometer (Stoe) in the Bragg-Brentano (reflection) geometry. Nitrogen adsorption isotherms were measured with an ASAP2010 adsorption analyzer (Micromeritics) at liquid nitrogen temperature. Prior to the measurements, all the samples were degassed at a temperature of 250 °C for 6 h. The IR spectra of Pd-OMC were collected on a Magna-IR 750 Nicolet FTIR spectrometer. The samples were prepared as KBr-wafers, measured from 4000 – 400 cm^{-1}.

Alcohol oxidation on Pd-OMC

Catalytic tests were carried out in 36 ml volume stainless-steel high pressure reactors. After adding the desired alcohol (0.25-0.3 g) substrate and catalyst (65mg) into the autoclave, the reactor was pressurized with a defined amount of the CO_2/O_2 (8.5% O_2 in CO_2) mixture and heated under vigorous stirring to the desired temperature for 13 h. The molar ratio of substrate to palladium is about 320 for all reactions.

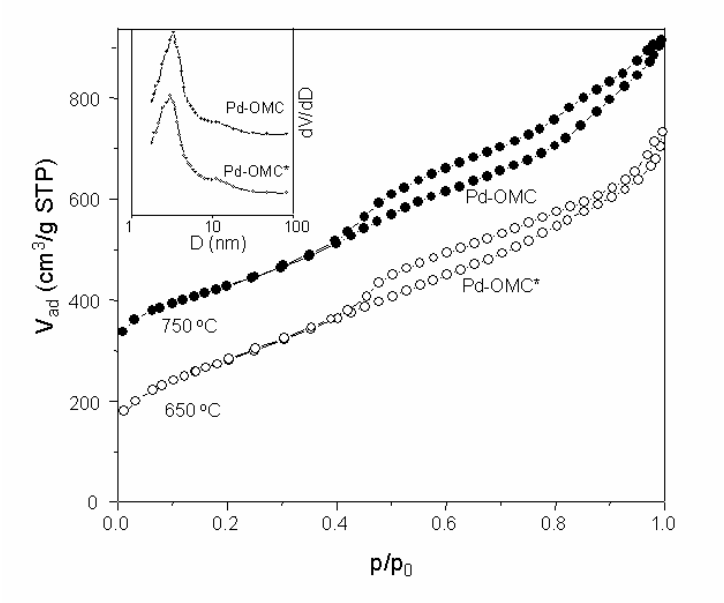

Fig. S1. Nitrogen sorption isotherms (insert are the pore size distributions) of Pd-OMC (high loading of Pd) and Pd-OMC* (low loading of Pd). The isotherms of Pd-OMC is offset vertically by 200 cm^3 g^{-1} STP.

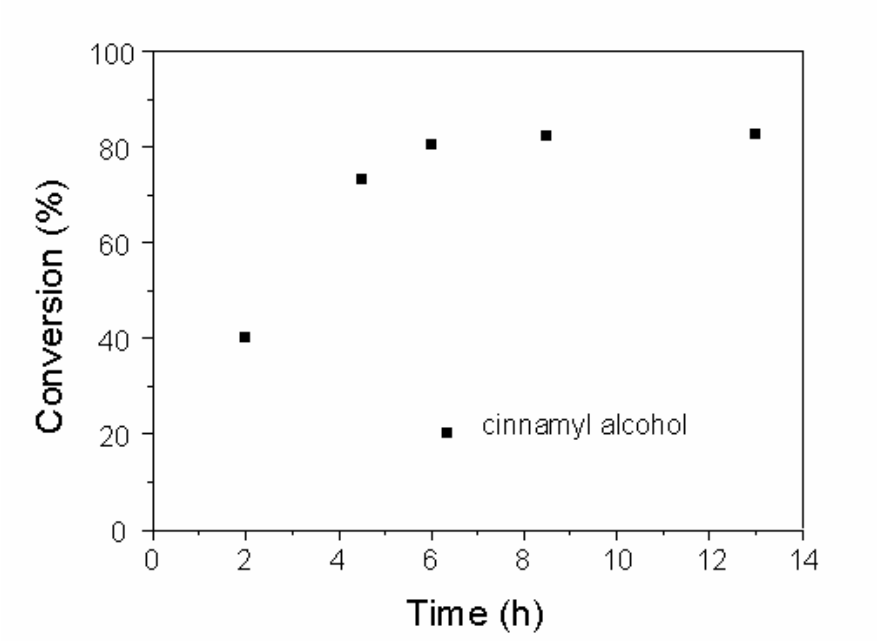

Fig. S2. The conversion of cinnamyl alcohol with time on the Pd-OMC catalyst at 80^{o}C

[1] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548.