

The size-effect of Pd nanocrystals on the EAQ hydrogenation activity

According to the reported literatures, the size-effect of the nanocrystals was not obvious for CO oxidative coupling to dimethyl oxalate (ACS Catalysis, 2013, 3, 118-122). Whereas in some other reactions, such as CO oxidation (Nano Research, 2011, 4, 83-91) and direct hydrogen peroxide synthesis from hydrogenation and oxygen (Journal of Molecular Catalysis A: Chemical, 2014, 383-384, 64-69), the catalytic performance showed a strong dependence on the nanocrystal size. In order to investigate the size-effect of Pd nanocrystals on the EAQ hydrogenation activity, we synthesized Pd cubes with bigger size by increasing the KBr concentration (using 20 mmol KBr as capping agent). As shown in Fig. S1, the average edge length was 13.4 nm ($\delta=1.1$ nm).

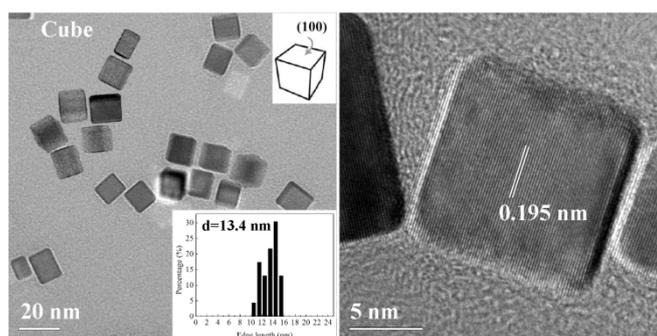


Fig. S1 TEM and the corresponding HRTEM images of Pd cubes with average edge length of 13.4 nm. The insets show the edge length distribution and structural diagram, respectively.

These Pd cubes with average edge length of 13.4 nm were immobilized on Al_2O_3 and evaluated as catalysts for EAQ hydrogenation using the same procedure described in the original manuscript. Their conversions were listed in Fig. S2. The activity of Pd-Cube-13.4 nm/ Al_2O_3 was obviously higher than Pd-Octa-14.1 nm/ Al_2O_3 . To further analysis the original activity of these cubes, the turnover frequency (TOF) of main hydrogenation reaction was also calculated based on the conversion of 5 min. The TOF of Pd-Cube-13.4 nm/ Al_2O_3 (10.2 s^{-1}) was higher than that of Pd-Octa-14.1 nm/ Al_2O_3 (5.3 s^{-1}). Thus we can exclude the size matter in the comparison of catalytic activities between the cubes, cubotahedrons and octahedrons, it is the Pd exposed facets which play a vital role in the EAQ hydrogenation reaction.

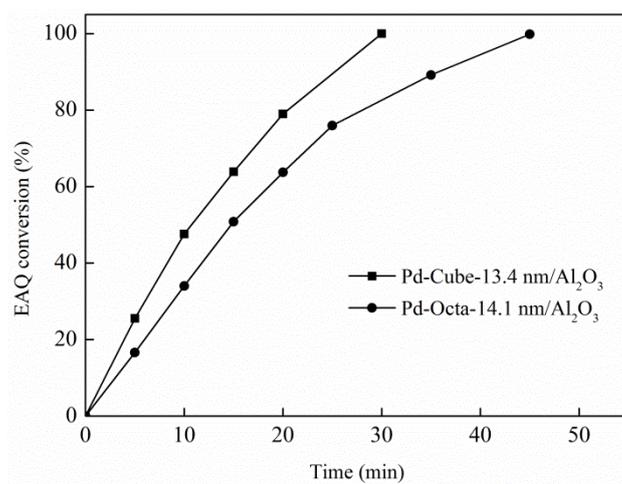


Fig. S2 EAQ hydrogenation as a function of time for Pd cubes with average edge length of 13.4 nm and Pd octahedrons with average edge length of 14.1 nm.

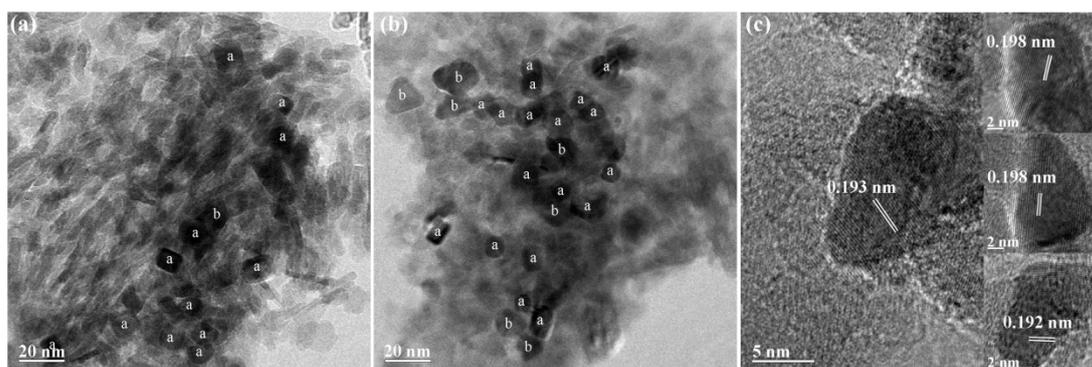


Fig. S3 TEM images of the Pd-Situ/Al₂O₃ (a) (b) and HRTEM images of the irregularly shaped particles, letter **a** for cubic shape and **b** for irregular shape.