Electronic Supplementary Material (ESI) for Catalysis Science & Technology

An aqueous-phase catalytic process for the selective hydrogenation of acetylene with a catalyst of monodispersed water soluble palladium nanoparticles

Huoli Zhang,[a] Yuanyi Yang,[a,b] Wei Dai,*[b] Dong Yang,[b] Shuliang Lu,*[b] and Yuanyuan Ji[b]

Supporting Information

Beijing University of Chemical Technology, Beijing 100029, China
Sinopec Beijing Research Institute of Chemical Industry, Beijing 100013, China

S1. XPS characterization

X-ray photoelectron spectroscopy (XPS) was used to analyze PdNPs stabilized by CMC in water. And the sample for XPS characterization was prepared by placing a drop of the obtained solution before or after reduction onto a copper sheet, followed by drying in vacuum at room temperature. The XPS of the sample was shown in Figure S1. Before reduction, the binding energy of Pd 3d(5/2) is at 337.1 eV. After reduction, the binding energy of Pd 3d(5/2) is at 335.5 eV, a -1.6 eV shift from the oxidation state palladium (337.1 eV). Therefore, in the case of PdNPs stabilized by CMC, Pd 3d(5/2)-core level has already been strongly modified. The binding energy of PdNPs stabilized by CMC after reduction is also higher (335.5 eV) than that of metallic Pd(0) (335.0 eV). It is close to the binding energy of Pd-C phase (335.6 to 335.7 eV), which is carbon-containing stable phase on the palladium surface of solid catalysts. The Pd-C phase is selective in alkyne hydrogenations. [1-3] XPS characterization was performed by using the Thermo VG Sigma Probe equipped with dual anode (Mg and Al K_{α} source).

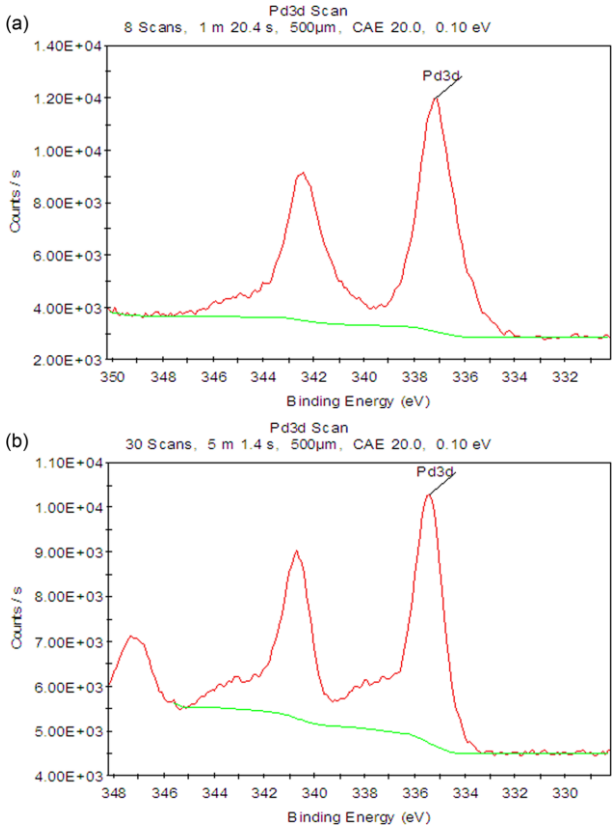

Figure S1. XPS of the obtained PdNPs stabilized by CMC: (a) before reduction; (b) after reduction.

S2. Electrosteric stabilization

The electrostatic and steric stabilization, together formed electrosteric stabilization, can maintain metallic nanoparticles stable in solution.[4] Nanoparticles with a high negative zeta-potential in water can be well dispersed.[5] PdNPs stabilized by CMC in water has a high negative zeta-potential (-31.5 mV), which was shown in Figure S2. The zeta-potential was detected by using the Malvern Zetasizer Nano ZS.

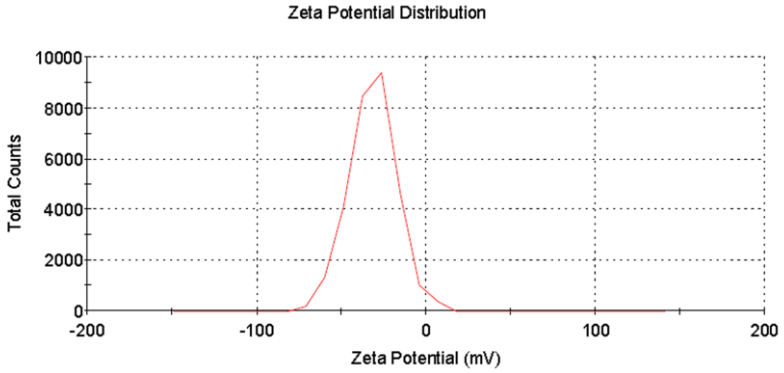

Figure S2. Zeta-potential of PdNPs stabilized by CMC in water.

S3. Evaluation method of catalysts

PdNPs stabilized by CMC in water was a very efficient and stable catalyst in the aqueous-phase catalytic process for the selective hydrogenation of acetylene. The catalytic performance was also evaluated at a total gas flow rate of 160 mL/min when the temperature increased from 40 to 70℃. The solution of PdNPs stabilized by CMC (200mL) was placed in a 500-mL stainless steel autoclave for use. Feed gas was introduced at the bottom of the autoclave and flowed out from the top (1 atm). Sampling is online. When the reaction temperature was kept at a certain centigrade temperature, the reactor outlet products were analyzed by gas chromatography (Agilent 6890) with a FID and a HP-PLOT/Q column (30 m × 0.535 mm × 40.00 μm). Meanwhile, the side reaction was found due to the detected small amounts of C_4 hydrocarbons by gas chromatography (GC). No deactivation or green oil was observed for 24 hours. The typical GC spectra were shown in Figure S3.

The acetylene conversion[6] was calculated by:

$$X_{C_2H_2} = \left[1 - \frac{x_{C_2H_2}}{x^0_{C_2H_2}}\right] \times 100\%$$

The ethylene selectivity[7] was calculated by:

$$S_{C_2H_4} = -\frac{\Delta C_2H_4}{\Delta C_2H_2} \times 100\%$$

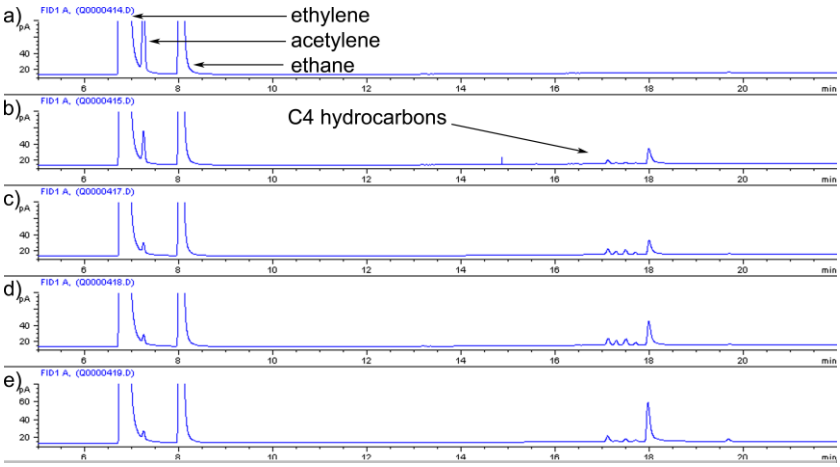

Figure S3. GC spectra: (a) the feed gas; (b) the reaction products at 40℃; (c) the reaction products at 50℃;(d) the reaction products at 60℃;(e) the reaction products at 70℃.

S4. Picture

PdNPs stabilized by CMC was stable in water. No precipitation was found for 10 months. However, the Pd particles immediately precipitated in water without adding CMC. The picture was shown in Figure S4.

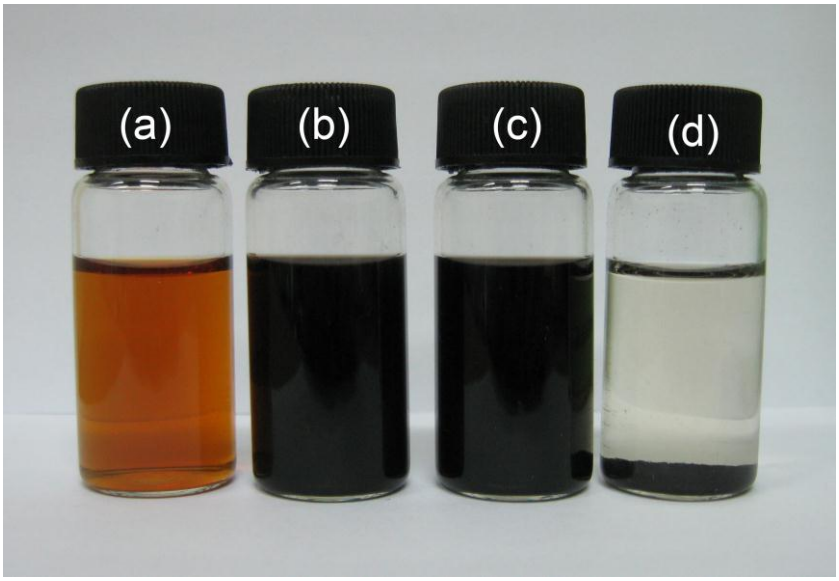

Figure S4. (a) an aqueous solution of Pd(Ⅱ) ions; (b) PdNPs stabilized by CMC in water; (c) PdNPs stabilized by CMC in water; (d) the Pd(0) particles in water without adding CMC.

S5. Catalytic test (time on stream and recycling results)

The catalyst of PdNPs stabilized by CMC was used on stream for 12 hours each time. The catalyst was recycled one time. The results were shown in Figure S1, which proved that the catalyst of PdNPs stabilized by CMC in water had a high activity. And acetylene conversion was always kept at 100%, which means that acetylene content in the reactor outlet products is lower than 1 ppm. However, the initial selectivities of the catalyst are different from the selectivities under steady-state conditions. When reaction time was at 2 hours on stream, ethylene selectivity was the best. After 8 hours on stream, the catalyst was under steady-state conditions.

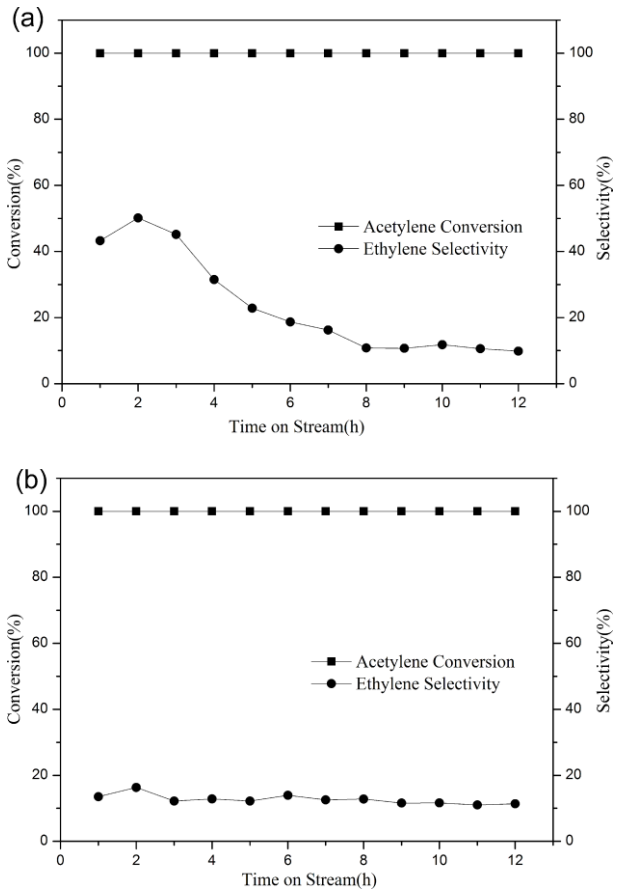

Figure S5. The stability and recycling of the catalyst of PdNPs stabilized by CMC: (a) the initial use of the catalyst; (b) the catalyst recycling. Reaction condition: the total gas flow rate was 12 mL/min and the stirring speed was 600 rpm.The gas ethylene-rich stream containing 0.45 % C_2H_2, H_2/C_2H_2 = 2.0.

S6. **TEM images of the catalyst of PdNPs stabilized by CMC**

The catalyst was recycled on stream for 12 hours, which indicated that the catalyst had a good stability. TEM images of the catalyst of PdNPs stabilized by CMC were provided in Figure S6, which showed that there were no agglomerations after the catalyst was reused.

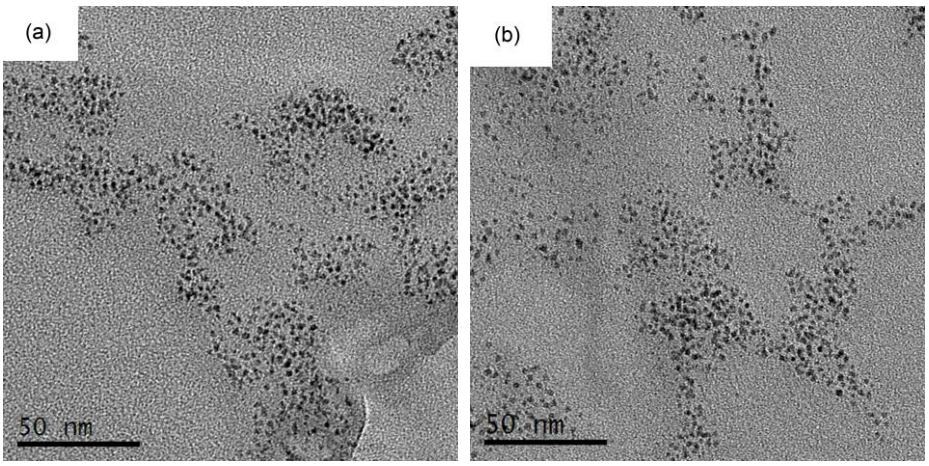

Figure S6. TEM images of the catalyst of PdNPs stabilized by CMC: (a) fresh catalyst; (b) reused catalyst.

S7. **The effects of the CMC concentration on the stability of PdNPs**

TEM images of PdNPs stabilized using 0.03 wt.% CMC and 0.12 wt.% CMC in aqueous solution have been presented in Figure S7. These TEM images indicate that the CMC concentration has no major effect on the Pd particle size within the range (from 0.03 wt.% to 0.12 wt.%).

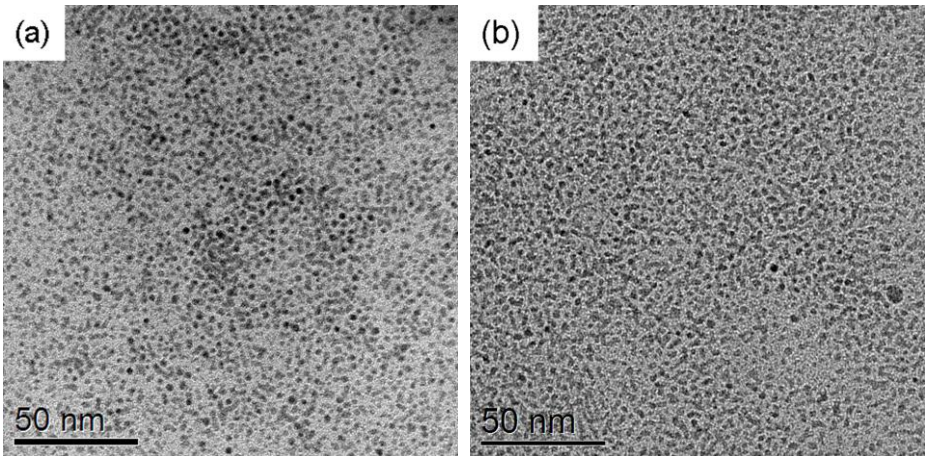

Figure S7. TEM images of PdNPs stabilized by CMC: (a) 0.03 wt.% CMC; (b) 0.12 wt.% CMC.

References

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