Supporting Information

Synthesis of alumina supported Pd-Cu alloy nanoparticles for CO oxidation via a fast and facile method[†]

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1. Experimental section

1.1 Catalyst preparation

A solution of $Pd(NO_3)_2$ (AR, Tianjin Kemiou Chemical Reagent Co., Ltd.) was prepared by adding a certain amount of $Pd(NO_3)_2$ into HNO_3 aqueous solution under stirring until complete dissolution. Then $Cu(NO_3)_2$ (AR, Tianjin Kemiou Chemical Reagent Co., Ltd.) was dissolved in the $Pd(NO_3)_2$ solution. γ-Al_2O_3 pellets (40-60 mesh, S_{BET}=267.2 $m^2 \cdot g^{-1}$) was pretreated at 600 °C for 5 h to be investigated.

Pd/Al_2O_3-C sample was prepared by simple incipient wetness impregnation followed by thermal reduction at 300 °C in H_2 for 2 h using $Pd(NO_3)_2$ as Pd precursor. Pd-Cu/Al_2O_3-P catalyst was fabricated by simple incipient wetness impregnation followed by the process of 6-min atmospheric-pressure cold plasma reduction using $Pd(NO_3)_2$ and $Cu(NO_3)_2$ as Pd and Cu precursors, respectively. As a comparison, Pd-Cu/Al_2O_3-C sample was also prepared by thermal reduction at 300 °C in H_2 for 2 h rather than plasma reduction. Both of the nominal Pd and Cu loading amounts were 1.3wt% in this study.

The schematic diagram of the atmospheric-pressure DBD cold plasma device for preparing Pd/Al_2O_3 and Pd-Cu/Al_2O_3 catalysts had been described previously.[1] A mixture of Ar (>99.999%) and H_2 (>99.999%) with a total flow rate of 100 ml·min^{-1} was used as the working gas. In the gas mixture, H_2 content was 50%. Before the cold plasma treatment, 0.3 g sample was uniformly put in the reaction tank. The plasma treatment was conducted by applying a 36 kV sine-wave high voltage at a frequency of 14.1 kHz for 6 min.

1.2 Catalyst characterization

The samples were characterized by powder X-ray diffraction (XRD) on a Dandong Haoyuan DX-2700 X-ray diffractometer at 40 kV and 30 mA for graphite-monochromatized Cu $K_{\alpha 1}$ radiation (λ=1.54178 Å). The chemical compositions of the samples were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAN250 Thermo VG) using a monochromatized $Al_{K\alpha}$ (1486.6 eV) X-ray source. All binding energies were referenced to the XPS peak of carbon 1s at 284.6 eV. Temperature programmed reduction (TPR) experiments were carried out with Micromeritics AutoChem II 2920 Automated Catalyst Characterization System using a 30 ml·min^{-1} flow of H_2/Ar mixture (10%H_2). 100 mg catalyst was used. Before each experiment, the catalyst was pretreated at 600 °C in Ar gas flow for 0.5 h, then cooled to 50 °C. Subsequently, the Ar gas flow was switched to the H_2/Ar mixture, and the reduction was performed from 50 to 800 °C at a constant rate of 10 °C·min^{-1}. The rate of H_2 gas consumption was monitored by a thermal conductivity detector (TCD). Pore size distributions, BET surface areas and pore volumes were measured by nitrogen adsorption/desorption using a NOVA 2200e gas sorption analyzer (Quantachrome Corp.). Prior to the adsorption analysis, the samples were outgased at 200 °C for 5 h in the degas port of the adsorption analyzer. The sorption data were analyzed using the Barrett-Joyner-Halenda (BJH) model with Halsey equation. The samples were observed by high resolution transmission electron microscopy (HRTEM, Tecnai G^2 F20, Philips) at 200 kV accelerating voltage.

1.3 Activity test

The temperature-dependent CO oxidation was performed in a quartz tube (4 mm i.d., 6.0 mm o.d.) at atmospheric pressure with 10 mg catalyst. The reaction was started in flowing CO/O_2 mixture (1.0 vol.% CO, 20.0 vol.%O_2, balance N_2) with a 20 ml·min^{-1} flow rate over the temperature range of 20-200 °C. All data were acquired after 30 min reaction time to allow the attainment of steady state. The effluent was then analyzed online by a gas chromatograph (Tianmei 7890) equipped with a TDX-01 column and a thermal conductivity detector (TCD).

The turnover frequency (TOF) was defined as the number of CO converted over one surface-active Pd atom per second:[2]

$$TOF(s^{-1}) = \frac{M_{CO} \cdot X}{M_{Pd} \cdot D \cdot t}$$

where M_{CO} and M_{Pd} were the amount of CO and Pd in the feed (mol), respectively, X was the conversion of CO, D was the Pd dispersion estimated from the TEM mean particle diameters, assuming spherical particles,[3] t was the reaction time (s).

2. Characterization and activity test of the samples

2.1 XRD

The crystallite sizes of Pd and Pd-Cu nanoparticles were also calculated by Scherrer's formula from the half-maximum peak-width values of the (111) reflections of XRD patterns. They are ca. 9.3 nm, 6.5 nm and 5.9 nm for Pd/Al$_2$O$_3$-C, Pd-Cu/Al$_2$O$_3$-C, and Pd-Cu/Al$_2$O$_3$-P, respectively, which are consistent with the results of TEM.

2.2 BET

Fig. S1 shows the N$_2$ adsorption-desorption isotherms and pore size distributions of the samples, and the specific surface area (S_{BET}), pore volume and pore diameter of the samples are summarized in Table S1. As shown in Fig. S1a, all of the samples showed an adsorption isotherm of type IV according to the IUPAC classification and had a H3 hysteresis loop that was representative capillary condensation of nitrogen within the non-uniform mesoporous structure, which was consistent with the pore size distribution of the samples (Fig. S1b). Compared with the bare Al$_2$O$_3$ support, the BET surface areas of the Pd/Al$_2$O$_3$ and Pd-Cu/Al$_2$O$_3$ samples were decreased after supporting Pd nanoparticles. Furthermore, the BET surface areas of Pd-Cu/Al$_2$O$_3$ samples are higher than that of Pd/Al$_2$O$_3$-C, which indicates that Pd-Cu nanoparticles were well dispersed. However, there is not much difference for the BET surface areas and the pore size distribution of the Pd-Cu/Al$_2$O$_3$ samples due to the low loading amount of Pd (1.3wt%). This also indicated that the pores in the Al$_2$O$_3$ support were not destroyed by cold plasma or thermal reduction, which is in line with previous results.[4]
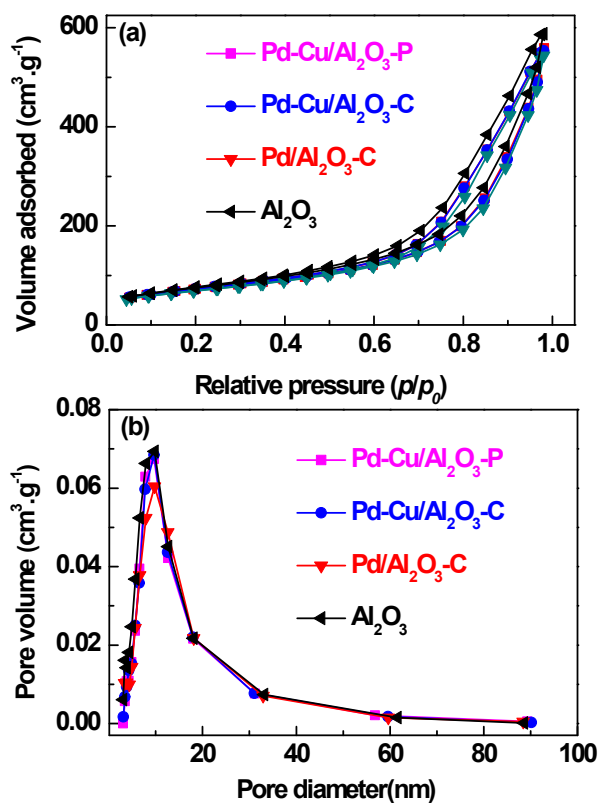
Fig. S1 (a) N_2 sorption isotherms and (b) pore size distributions of the samples.

Table S1 The specific surface area (S_{BET}), pore volume and pore diameter of the samples

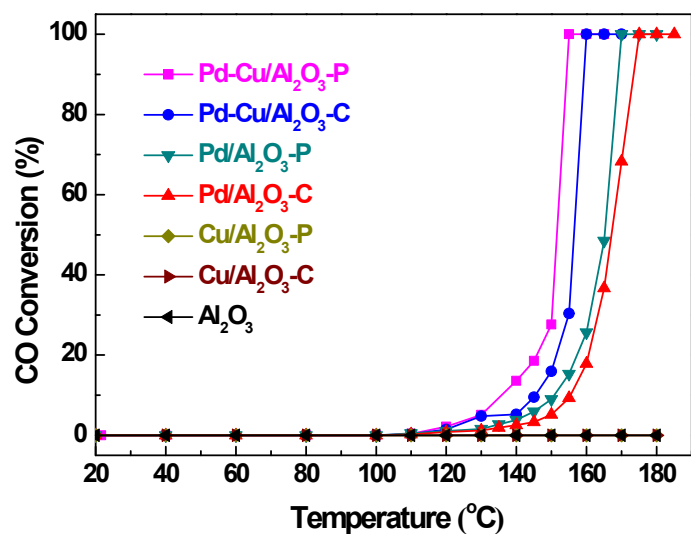| Sample	S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^{-3} \cdot g^{-1}$)	Pore diameter (nm)
Al_2O_3	267.2	0.922	9.76
Pd/Al_2O_3-C	242.2	0.847	9.75
Pd-Cu/Al_2O_3-P	252.7	0.868	9.68
Pd-Cu/Al_2O_3-C	252.8	0.859	9.63

2.3 Activity

Fig. S2 CO oxidation activity over alumina supported Pd, Cu and bimetallic Pd-Cu catalysts prepared by different methods

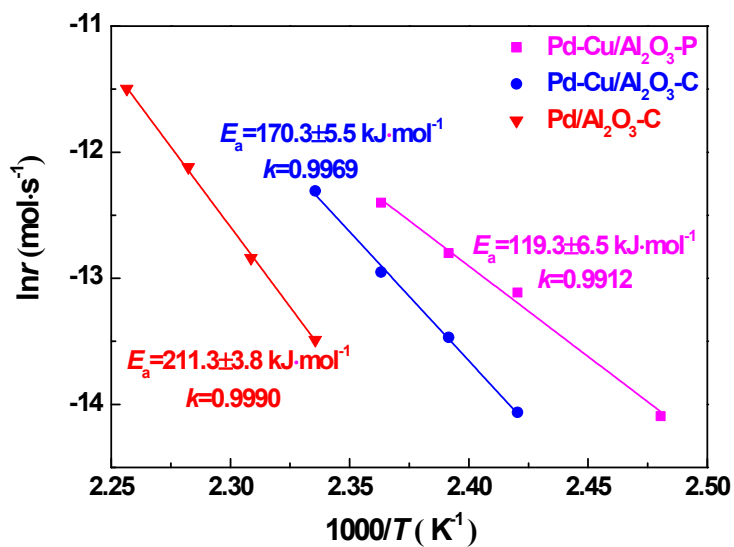As shown in Fig. S2, bare alumina and Cu/Al_2O_3 exhibited no CO oxidation activity below 180 ^{o}C.

Fig. S3 The corresponding Arrhenius plots of the samples.

Reference

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4 W. J. Xu, Z. B. Zhan, L. B. Di, X. L. Zhang, *Catal. Today*, 2015, DOI: 10.1016/j.cattod.2015.01.017