A synthesis of high-efficiency Pd-Cu-Cl_x/Al_2O_3 catalyst for low temperture CO oxidation

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Support information

1. Catalyst preparation

$PdCl_2$-$CuCl_2$/Al_2O_3 (1.7wt.%Pd-3.3wt.%Cu-Cl_x/Al_2O_3) was prepared by the NH_3 coordination-impregnation (CI) method. Weighed $PdCl_2$ (AR, Heraeus Materials Technology Shanghai Ltd.) and $CuCl_2$ (AR, Sinopharm Chemical Reagent Co., Ltd.) were dissolved in 2 ml ammonia aqueous solution (25%, Sinopharm Chemical Reagent Co., Ltd.) under ultrasonic at room temperature, and this $PdCl_2$ and $CuCl_2$ mixed solution was diluted to 8 ml with de-ionized water or isopropanol (AR, Sinopharm Chemical Reagent Co., Ltd.). Then 1 g Al_2O_3 (WHA-204, BET surface area of 194 m^2/g, from Wen-Zhou Jingjing aluminum Ltd.) was impregnated in this solution. After being aged for 24 h, the catalyst was dried at room temperature and calcined at 300 °C for 4 h. This process of preparing catalyst can be discribed as Fig.S1. The $PdCl_2$-$CuCl_2$/Al_2O_3 catalyst prepared by the CI method is denoted as PC-CI/H_2O or PC-CI/Isopropanol.

This catalyst was also prepared by the conventional wet impregnation (WI) method, in which de-ionzed water and isopropanol were used as the diluter. The catalyst prepared was denoted as PC-WI/H_2O or PC-WI/Isopropanol.

2. CO oxidation reaction

The activity of catalyst for CO oxidation was measured in a (Ø5 mm) quartz U-tube reactor, and 0.2g catalyst (20-40 mesh) was used and a glass wool was pluged in both sides of catalyst. The feed gas of 1500 ppm CO in air at a flow rate of 50 ml/min was directly through a water vapor saturator immersed in ice-water bath, and then flowed into the reactor. The concentration of moisture in the feed was about 1000 ppm. Changing the temperature of cold trap can adjust the concentration of moisture in the feed. After the steady operation for 10 min, the activity of catalyst was tested. The reaction temperature was controlled as follows: below room temperature was obtained by using ethanol/liquid nitrogen mixture in a vacuum bottle, and above room temperature was achieved by using warm water bath.

3. Catalysis characterization

The powder X-ray diffraction patterns (XRD) of the samples were performed on a Brook D8 focus diffraction spectrometer using CuKα radiation at room temperature. The average crystalline size was determined by the Scherrer formula based on the diffraction peak broadening.

H_2-temperature programmed reduction (H_2-TPR) was performed in a quartz U-tube with 100 mg catalyst. The catalysts prepared by CI were firstly pretreated in N_2 flow at 300 °C for 1 h, and then cooled down to room temperature; the catalysts prepared by WI were pretreated in N_2 flow at room temperature for 1 h. The reduction gas was consisted of 5% H_2/N_2 (45 ml/min). The heating rate was 10 °C/min. The uptake amount of H_2 was measured by a thermal conductivity detector (TCD), which was calibrated by the quantitative reduction of CuO to the metallic copper.

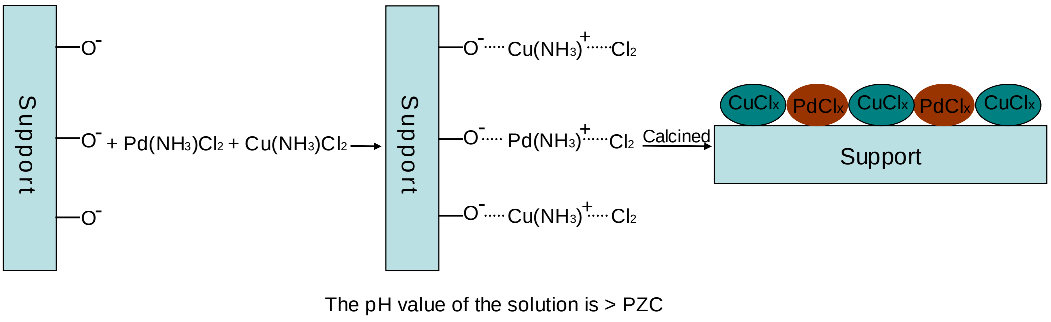

Fig.S1. Schematic representation of preparing catalyst by the NH_3 coordination-impregnation method.

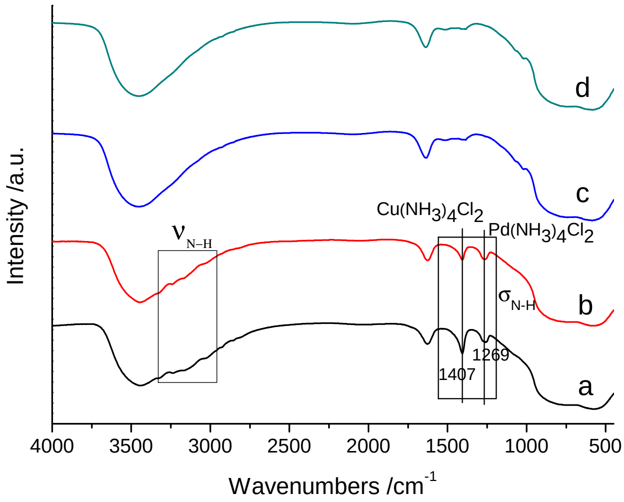

Fig.S2. FT-IR spectra of PC-CI/H_2O (a), PC-CI/Isopropanol (b) before calcination, and PC-CI/H_2O (c) and PC-CI/ Isopropanol (d) after calcination.

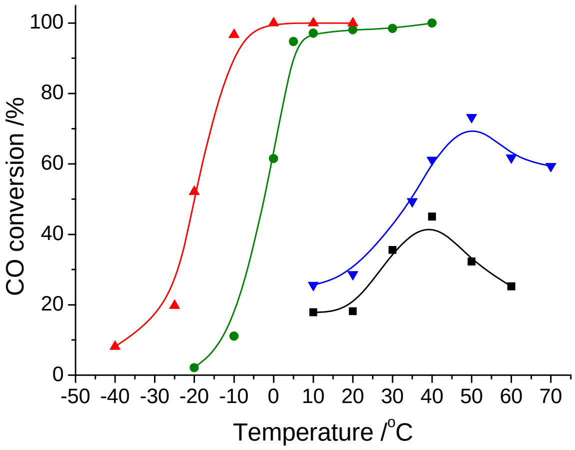

Fig. S3. Influence of preparation method on the activity of Pd-Cu-Cl_x/Al_2O_3 prepared by (●) CI/H_2O, (▲) CI/Isopropanol, (■) WI/H_2O, and (▼) WI/Isopropanol. (1500 ppm CO and ~ 6000 ppm H_2O in air).

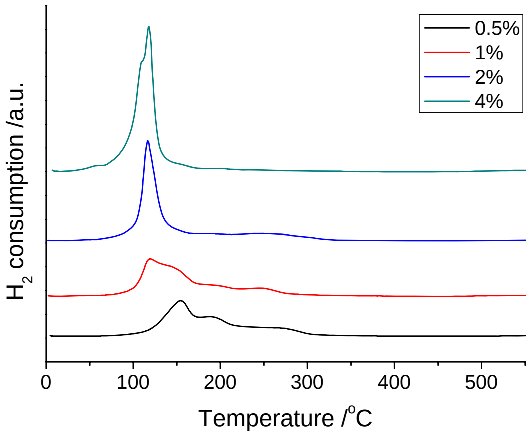

Fig. S4. TPR profiles of PC-CI/Isopropanol with different Pd loadings and 3.3wt.%Cu in the synthesis solution.

Table S1. Pd and Cu loadings, the crystalline size of copper phase, and H_2 consumption in TPR for Pd-Cu-Cl_x/Al_2O_3 catalysts

Catalyst	Pd /wt.% [a]	Cu /wt.% [a]	Crystalline size /nm [b]	H_2 consumption /μmol/g [c]					
				α_1	α_2	β_1	β_2	Total	Theoretical[c]
PC-WI/H_2O	1.4	3.1	34	334	281	–	–	615	620
PC-WI/Isopropanol	1.4	3.2	31	346	279	–	–	625	635
PC-CI/H_2O	1.3	3.2	21	–	99	254	279	632	625
PC-CI/Isopropanol	1.2	3.2	–	–	–	454	167	621	616

[a] Pd and Cu loadings were measured by an ICP-AES instrument (Varian 710);

[b] It is the crystalline sizes of $Cu_2Cl(OH)_3$ in the catalysts, which were calculated from the (101) peak broadening of $Cu_2Cl(OH)_3$ by Scherrer equation.

[c] Theoretical H_2 consumption was calculated according to the Pd and Cu loadings in the catalyst.

Table S2. Apparent activation energy (Ea) and specific reaction rate for CO oxidation over Pd-Cu-Cl_x/Al_2O_3 catalysts

Temperature /°C	Specific reaction rate* /mol g^{-1} h^{-1} × 10^3			
	PC-WI/H_2O	PC-WI/Isopropanol	PC-CI/H_2O	PC-CI/Isopropanol
60	2.4	2.3	-	-
50	1.7	2.1	-	-
40	0.97	1.2	-	-
30	0.81	0.83	-	-
0	-	-	120	180
-25	-	-	50	51
-40	-	-	23	29
Ea /kJ mol^{-1}	32	30	23	23

* The specific reaction rates were obtained after the reaction was run for 30 min. The feed gas consisted of 400 ppm CO, 1000 ppm H_2O and air, and the hourly gas space velocity was in the range of $1.5\times 10^4 - 9\times 10^5$ ml g^{-1} h^{-1}. The conversion of CO was adjusted to below 15% in order to calculate the reaction rates under different reaction conditions.