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无表面活性剂条件下一锅法制备金属/氧化锌复合材料用于催化二氧化碳加氢制甲醇反应

刘艳芳，胡兵，尹雅芝，刘国亮*，洪昕林*

武汉大学化学与分子科学学院，湖北武汉 430072

One-Pot Surfactant-free Synthesis of Transition Metal/ZnO Nanocomposites for Catalytic Hydrogenation of CO_2 to Methanol

LIU Yanfang, HU Bing, YIN Yazhi, LIU Guoliang *, HONG Xinlin *

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China.

*Corresponding authors. Email: hongxl@whu.edu.cn (H.X.); liugl@whu.edu.cn (L.G.)

1 Experimental

1.1 Materials

All chemicals (Ethylene glycol, sodium chloropalladite, chloroauric acid, silver nitrate, copper acetate, zinc acetate, acetone, ethanol, *N*-hexane, sodium bicarbonate) are AR and purchased from Sinopharm Chemical Reagent Co., Ltd and used as received without further purification.

1.2 Preparation of M/ZnO nanohybrids

Typically, Pd/ZnO samples were synthesized in ethylene glycol under the refluxing condition. A certain amount of sodium chloropalladite (Na_2PdCl_4), 0.1 g of sodium bicarbonate ($NaHCO_3$), 5 mmol of zinc acetate ($Zn(OAc)_2$) and 45 mL of ethylene glycol were added into a 100ml three-neck flask. The mixed solution was heated to boiling point and maintained refluxing for 30 min under magnetic stirring and under the protection of nitrogen gas. The final Pd/ZnO product was separated by centrifugation and then washed with water, acetone, ethanol and *n*-hexane one by one, followed by a vacuum drying procedure for 24 h. A series of Pd loading were achieved by changing the recipe Pd/Zn molar ratio from 1 : 2, 1 : 3, 1 : 4, 1 : 6, 1: 9 , 1 : 12 to 1 : 48. As for the size control of Pd NPs, the amount of $NaHCO_3$ was investigated, varying from 0.1, 0.4, 0.6, 1.0 to 1.5 g. Apart from Pd/ZnO, other metals including Ag, Au and Cu were also hybridized with ZnO by using silver nitrate, chloroauric acid and copper acetate as precursors, respectively. The conditions for catalytic tests, product analyses and characterization can be found in supporting information.

1.3 Catalytic tests

Catalytic tests were carried out in a tubular fixed bed reactor (12.7 mm OD, WFSM-3060, Tianjin Xianquan Industry and Trade Development Co., LTD). Typically, 0.24 g of a catalyst (M/ZnO mixed with Al_2O_3 (33.3% (*w*)) was used to fill in the middle of the reactor. Before each test, the catalyst was pretreated in a flow of pure hydrogen gas at 573K for 2 h. After that, a mixed gas flow (H_2/CO_2 volume ratio = 3) was fed into the reactor at a rate of 15 mL/min. The reaction pressure was initially set at 5 MPa. The product components were analyzed with an on-line gas chromatograph (Donam model DS 6200) equipped with a TCD detector.

2 Characterizations

Transmission electron microscopy (TEM) images were taken with a Philips G2 microscope at an operation voltage of 200 kV. The samples were dispersed into ethanol under ultrasonic and then placed onto a carbon-coated copper grid. XRD analysis was performed on a Shimadzu XRD-6000 diffractometer using Cu Ka radiation (λ = 1.5418 Å) from a generator operating at 40 kV and 30 mA. Elemental analysis was operated with an Agilent Plasma Mass Spectrometer (ICP-MS 7700). Before tests, a certain amount of the samples were dissolved into aqua regia and then diluted to 100 mL with deionized water. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher ESCALAB 250Xi with an achromatic AlKa (1486.6 eV) X-ray source. The samples were analysed with reference to adventitious carbon 1s peak.

3 Supplementary figures

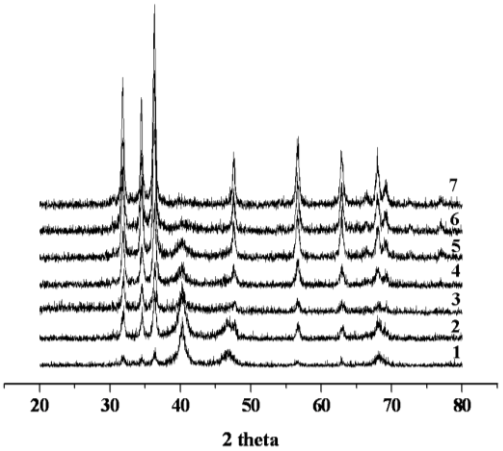

Fig. S1 XRD patterns of Pd/ZnO synthesized at various Pd/Zn molar ratios.

(1) 1 : 2; (2) 1 : 3; (3) 1 : 6; (4) 1 : 9; (5) 1 : 12; (6) 1 : 24; (7) 1 : 48.

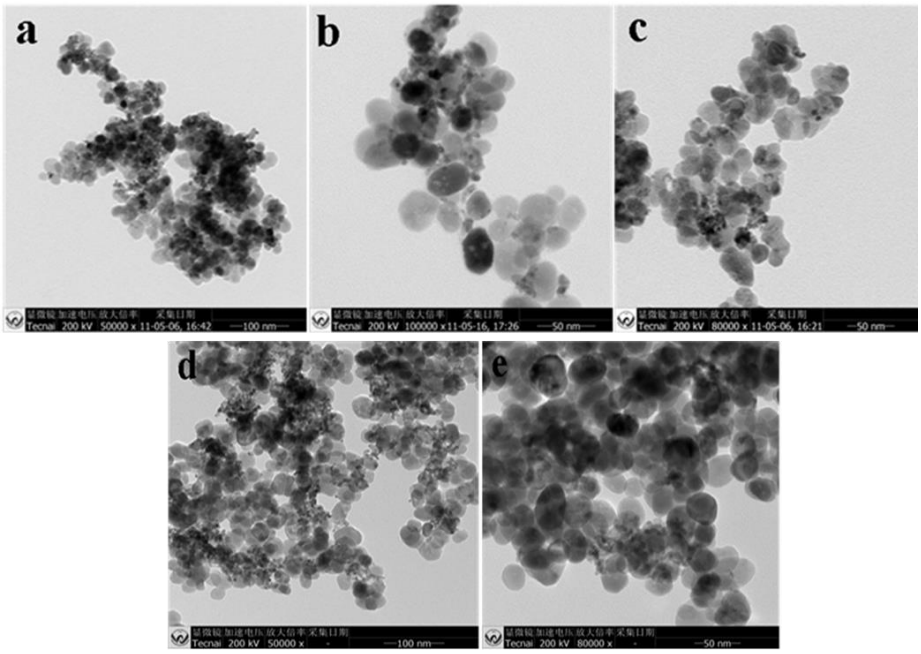

Fig. S2 TEM images of Pd/ZnO synthesized at various Pd/Zn molar ratios.

(a) 1 : 2; (b) 1 : 6; (c) 1 : 9; (d) 1 : 12; (e) 1 : 24.

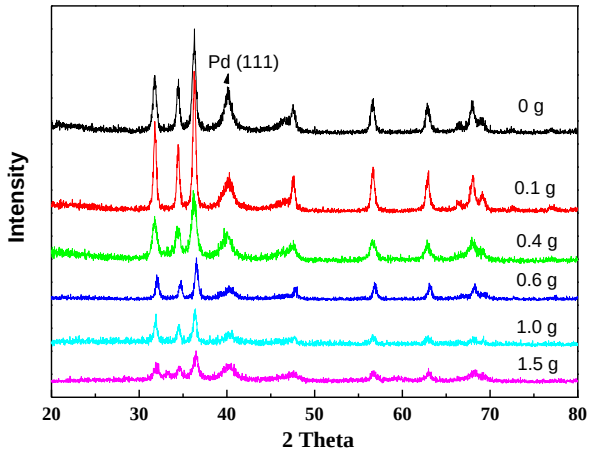

Fig. S3 XRD patterns of the Pd/ZnO sample synthesized at Pd/Zn molar ratio as 1:6 with different amount of $NaHCO_3$.

From up to down, the weight of $NaHCO_3$ is 0, 0.1, 0.4, 0.6, 1.0, and 1.5 g, respectively.

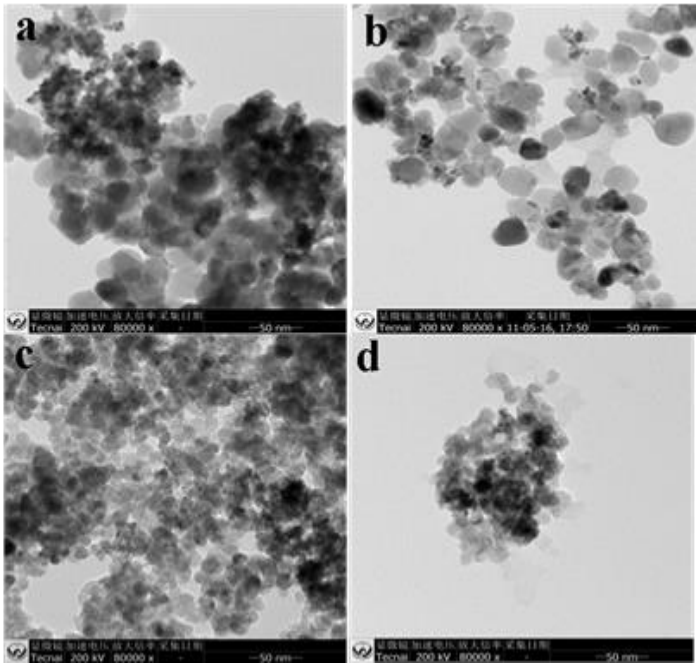

Fig. S4 TEM images of Pd/ZnO synthesized at Pd/Zn molar ratio of 1:6 with different amount of $NaHCO_3$.

(a) 0.4 g; (b) 0.6 g; (c) 1.0 g; (d) 1.5 g.

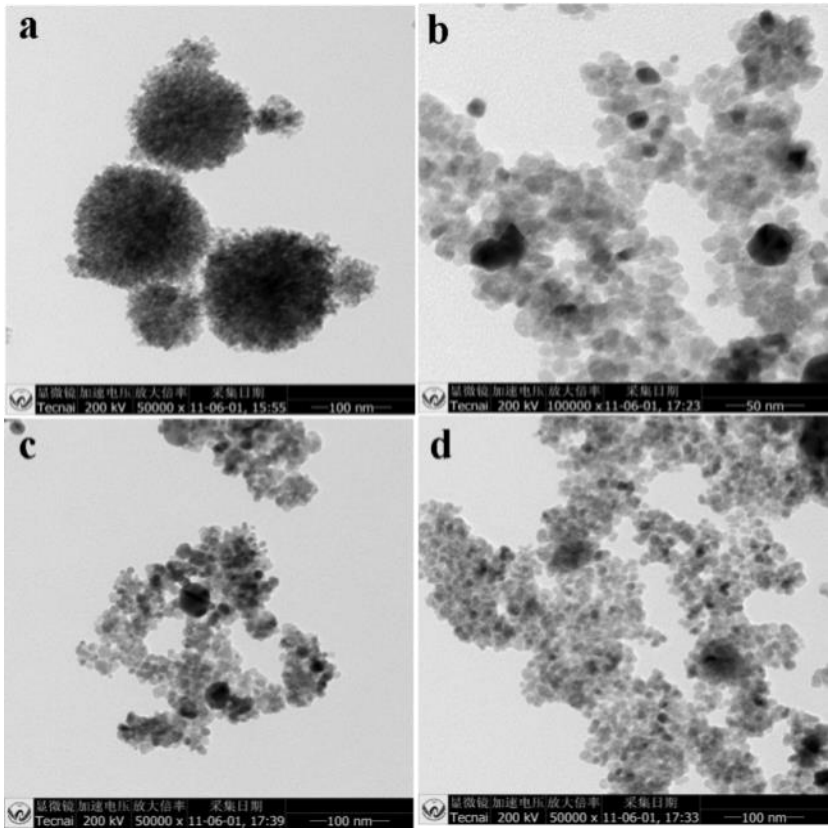

Fig. S5 TEM images of (a) pure ZnO and (b–d) M/ZnO (M = Au, Ag, and Cu) synthesized at the M/Zn molar ratio of 1 : 6.

4 Supplementary tables

Table S1 Comparison of theoretical Pd/Zn ratios with ICP-MS results for Pd/ZnO nanocomposites.

Pd/ZnO samples (recipe Pd/Zn ratio)	Pd/Zn molar ratio from ICP-MS
1 : 3	1 : 2.81
1 : 6	1 : 5.83
1 : 9	1 : 8.82
1 : 12	1 : 11.78
1 : 24	1 : 24.31
1 : 48	1 : 49.05