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Pt_1/CeO_2-ZnO Nanowire Single-Atom Catalysts for Water-Gas Shift Reaction

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Ceria supported Au and Pt nanocatalysts have demonstrated superior activity, selectivity and stability for water-gas shift (WGS) reaction [1-2]. Downsizing noble metal nanoparticles (NPs) to small clusters or even single atoms is highly desirable for maximizing the effective use of rare and expensive noble metals provided that their catalytic performances are not compromised. It is believed that the active center in a supported metal single atom catalyst (SAC) consists of the isolated individual metal atom plus its immediate neighbor atoms of the support [2-3]. Therefore, it is highly desirable to fabricate SACs that are composed of individual metal atoms supported on small clusters of an appropriate metal oxide which are supported on another relatively inert and inexpensive material. In this work, we demonstrate the feasibility of this new approach by dispersing Pt single atoms onto CeO_2 nanoclusters which are supported on ZnO nanowires (NWs) and test the synthesized Pt_1/CeO_2-ZnO SACs for the WGS reaction.

ZnO NWs were fabricated by a thermal evaporation-condensation method in a high temperature tube furnace [4]. The CeO_2-ZnO NW nanocomposites (5wt% of CeO_2) were prepared by adsorbing Ce salt onto the ZnO NWs via a wet chemistry method. The Ce-containing precipitates were then washed with deionized water, dried at 60°C overnight and calcined at 400°C for 4 h. The as-prepared CeO_2-ZnO NWs were then soaked into deionized water and a specific amount of Pt salt precursor was dropwise added into the solution and the resultant precipitates were filtered, thoroughly washed and dried at 60°C for 5h. The final Pt_1/CeO_2-ZnO SACs contained a nominal amount of 0.5wt% Pt. The activity tests were conducted in a fixed-bed reactor with 50 mg of catalysts and the reaction feed gas composed of 2vol% CO/10vol% H_2O balanced with helium. The gas hourly space velocity (GHSV) was 48,000 ml/g_{cat}/h. The reaction feed gas mixture was preheated to 165°C. The effluent gas compositions were on-line analyzed by a gas chromatograph (HP 7890) equipped with a HayeSep DB column. The CO conversion was calculated based on the difference between inlet and outlet CO concentrations.

Figure 1a displays a HAADF image of a typical CeO_2-ZnO NW, revealing aggregates of small CeO_2 NPs with an average size of ~ 5 nm. Atomic resolution HAADF images, for example, Fig. 1b, of the CeO_2-ZnO nanocomposites reveal that the CeO_2 NPs are well-faceted with primarily exposed {111} surfaces. Because of the 4 h calcination treatment at 400°C there were few Ce single atoms on the ZnO NWs. Single Pt atoms were atomically dispersed onto both the CeO_2 NPs and the ZnO NWs as clearly revealed in Fig. 1c (indicated by the red arrows). We did not observe any Pt clusters or NPs dispersed onto either the CeO_2 nanocrystallites or the ZnO NWs. Therefore, we have successfully synthesized a 0.5 wt% Pt_1/CeO_2-ZnO NWs SAC. Figure 2 shows the CO conversion profile as a function of reaction temperature over the as-synthesized $0.5Pt_1/CeO_2$-ZnO SAC. The CeO_2-ZnO nanocomposites were also tested as a control. The addition of the Pt single atoms clearly significantly enhanced the CO conversion rate in the temperature range of 280°C - 500°C. The strong interaction between the Pt_1 atoms and the CeO_2 surfaces may be responsible for the observed activity enhancement. The activity drop at reaction temperatures > ~ 440°C is related to the activation of the reverse WGS reaction. It is expected that when the sizes of the supported CeO_2 clusters become much smaller (< 1 nm) the catalytic properties of the Pt_1/CeO_2-ZnO SACs will be significantly modified [5].

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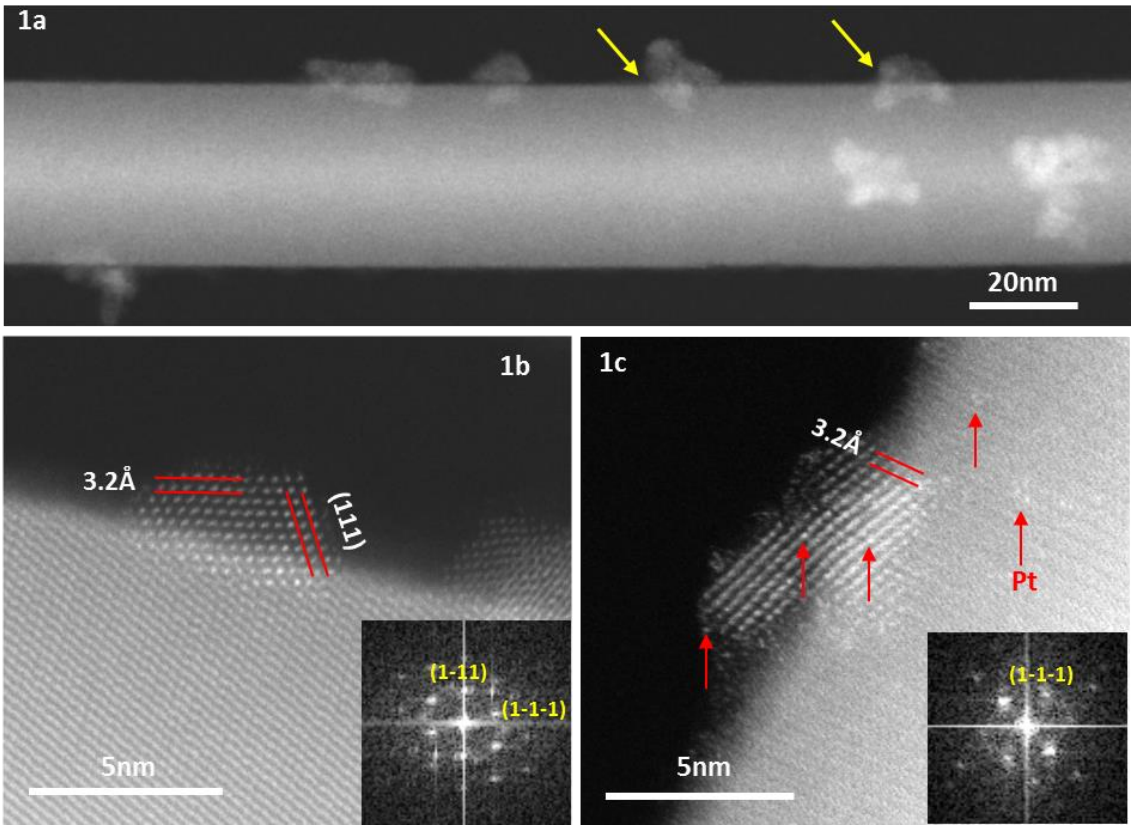

Figure 1. (a) Low magnification HAADF image of a typical CeO_2-ZnO NW. The aggregated CeO_2 NPs are indicated by the yellow arrows; (b) and (c) are atomic resolution HAADF images of a CeO_2-ZnO nanocomposite and a Pt_1/CeO_2-ZnO SAC. The exposed CeO_2 facets were identified as {111}. Atomically dispersed Pt atoms are indicated by the red arrows.

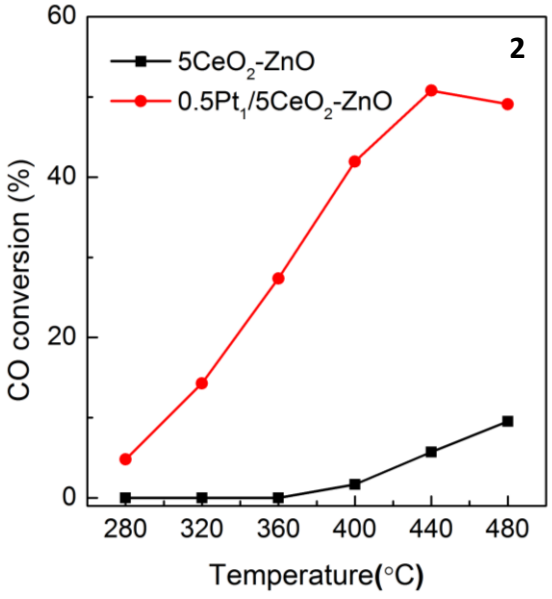

Figure 2. CO conversion vs temperature for WGS reaction on bare CeO_2-ZnO and 0.5wt% Pt_1/CeO_2-ZnO SAC. The SAC exhibited much higher activity.

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