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ZnO Nanowire Supported Metal Single Atoms for CO oxidation

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Supported noble metal nanoparticles (NPs) are excellent catalysts for a variety of important chemical transformations and are widely used in industrial applications. Noble metals are, however, expensive and thus efficient utilization of noble metals as catalysts is critical to reducing the cost of goods of many products. Downsizing noble metal NPs to small clusters or even single atoms is highly desirable provided that their catalytic performances are not compromised. Recent success in synthesizing single-atom catalysts (SACs) and the subsequent testing of their catalytic properties have unambiguously demonstrated that SACs can be highly active, selective and stable [1-3]. The active centers in SACs consist of isolated individual metal atoms and their immediate neighbor atoms of the support. The strong metal-support interaction results in charge transfer and thus generates new ensembles which may possess unique catalytic properties different from those of the corresponding supported metal NPs. In order to understand how single atoms of different noble metals dispersed on the same support material affect a specific catalytic reaction we dispersed various single noble metal atoms on ZnO nanowires (NWs). CO oxidation was used to evaluate the catalytic properties of the various noble metal SACs.

The SACs were synthesized by a modified adsorption method. Briefly, noble metal precursors were mixed with the pre-formed ZnO NWs. The resultant precipitate was filtered, washed with deionized water and dried in an oven. The nominal loading level of the various noble metals was ~0.05 wt% and the corresponding SAC catalysts were denoted as 0.05Pd/ZnO, 0.05Pt/ZnO, 0.05Rh/ZnO, and 0.05Ir/ZnO, respectively. The CO oxidation reaction was evaluated in a fixed-bed, plug-flow reactor. The feed gas composition was 1vol% CO + 1vol% O_2 and balance He with a flow rate of 33 ml/min. For all the catalytic tests, 50 mg catalyst was directly used without further treatment. The outlet gas composition was on-line analyzed by a gas chromatograph and the CO conversion was calculated based on the inlet and outlet CO concentrations. Aberration-corrected high-angle annular dark-field STEM (HAADF-STEM), indispensable for investigating the atomic level structures of nanostructured catalysts [4], was used to examine the synthesized SACs.

HAADF-STEM images of the synthesized SACs were obtained to provide information on the dispersion and distribution of the noble metal atoms on the ZnO NWs. Two representative images are shown in Figure 1. The isolated and highly dispersed individual Pt (indicated by the yellow arrows in Figure 1a) and Ir (indicated by the yellow arrows in Figure 1b) atoms are clearly revealed. At low levels of noble metal loading the synthesized SACs contained only single noble metal atoms. Figure 2 displays the CO conversion vs. temperature for the as-synthesized SACs. The bare ZnO NWs were also tested as a reference. The ZnO surfaces can be considered inactive for CO oxidation. The catalytic test data clearly show that all the fabricated noble metal SACs are active for CO oxidation. Their activities, however, were very different. Among the four noble metals (Rh, Pd, Ir and Pt) the Pd_1/ZnO SAC is most active while the Ir_1/ZnO shows the lowest activity. The ZnO NW based SACs were also stable during the CO oxidation reaction since the 2nd run overlaps that of the 1st run on both the Pt_1/ZnO and Ir_1/ZnO SACs. These test results clearly demonstrate that different noble metal atoms interact differently with the ZnO {10-10} surfaces and hence generate different types of active centers for CO oxidation [5].

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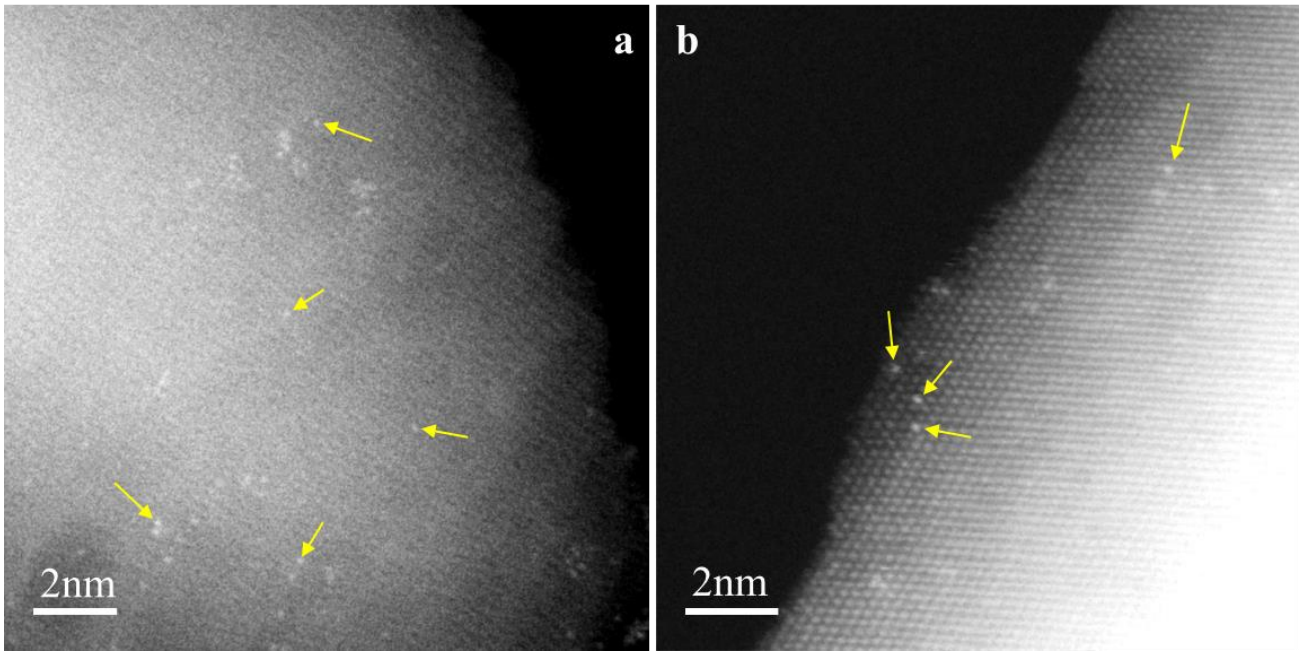

Figure 1. STEM-HAADF images of (a) Pt_1/ZnO and (b) Ir_1/ZnO nanowires clearly show that the isolated Pt and Ir single atoms (indicated by the yellow arrows) occupy Zn positions of the ZnO support.

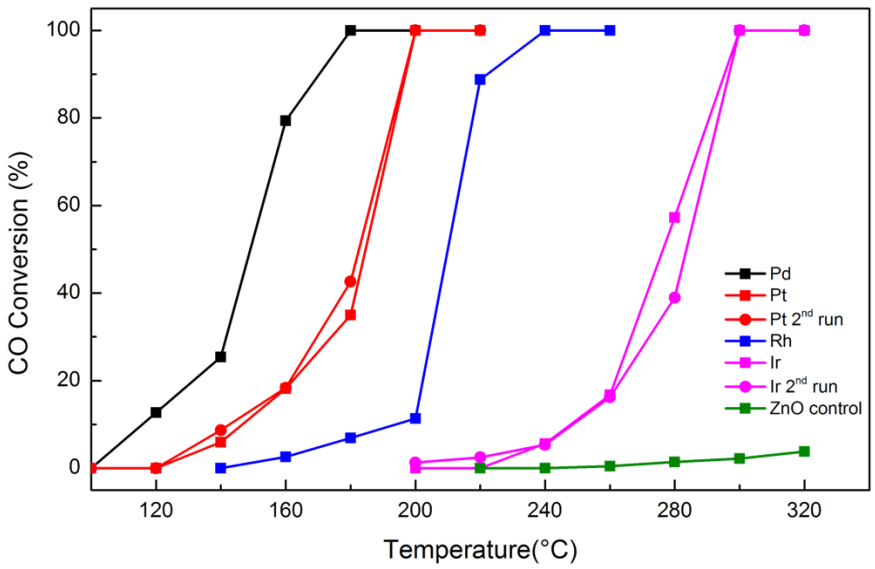

Figure 2. CO conversion vs. reaction temperature for various noble metal M_1/ZnO SACs, clearly demonstrating the differences in activity of ZnO NW supported noble metal SACs. The nominal metal loading for all the SACs was 0.05wt%. The condition for the CO oxidation was the same for all the tested noble metal SACs. Among the four SACs tested, the Pd_1/ZnO NW is most active. The noble metal SACs were stable as well.

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