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Singly Anchored Pt and Pd atoms on Co_3O_4 and Their Catalytic Performance

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Efficient use of precious metal atoms is ideal for cost-effective catalytic processes. High dispersion of precious metal atoms on a support is one approach to a full use. Catalyst of Co_3O_4 nanorods anchoring singly dispersed Pt or Pd atoms is highly active for reduction of nitric oxide with H_2 at a relatively low temperature. Co_3O_4 with highly dispersed 0.1% Pt exhibits 100% selectivity in reducing nitric oxide to N_2 in the temperature regime of 150^{o}C-300^{o}C. Catalytic in-situ studies using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) showed the active phase is surface doped Co_3O_4 in which a Pt atom bonds with both Co atoms and oxygen atoms. During catalysis in 150^{o}C-300^{o}C Co_3O_4 surface remains its original chemical state. Pd atoms anchored on Co_3O_4 of 0.5% Pd/ Co_3O_4 during catalysis are singly anchored on Co_3O_4 surface, evidenced by the lack of Pd-Pd bonds in in-situ EXFAS studies. During catalysis it forms singly dispersed bimetallic nanoclusters $PdCo_n$. In contrast to pure Co_3O_4 and 0.5% Pd/SiO_2, 0.5% Pd/Co_3O_4 exhibits much higher selectivity to production of N_2 and high activity in reduction of nitric oxide.

The catalysts were prepared by impregnation of Co_3O_4 nanorod with certain amount of H_2PtCl_6 and $Pd(NO_3)_2$ as precursors, respectively, followed by calcination to anchor metal ions to surface of Co_3O_4. Size, shape, and lattice fringe of the as-synthesized 0.1% Pt/Co_3O_4 were characterized with Titan TEM (FEI Titan 80-300, 300 kV FEG TEM with point resolution of 0.2 Å) shown in Figure 1. The measured inter-planar distance of (220), 2.82 Å is the same as pure Co_3O_4 crystal parameter [1], which suggests the impregnation of Pt atoms on Co_3O_4 does not change the lattice of Co_3O_4 since immobilization of notal metal atoms is done upon a well crystallization of Co_3O_4 nanorods through calcination at 450^{o}C. The singly atomic dispersion features were showed in Figure 2 collected in high-angle annular dark-field (HAADF)-STEM mode on JEOL JEM-ARM 200F with a CEOS probe corrector. Bright spots are Pt atoms dispersed on Co_3O_4. The representative images suggested that most of the Pt atoms on Co_3O_4 surface are separately anchored and thus singly dispersed on Co_3O_4 nanorods. We expect that the dispersion of Pt atoms on the surface of Co_3O_4 benefits from the low concentration of the noble metal ions and the generation of oxygen valvancies during calcination even at low temperature and a subsequent filling or/and a restructuring on well crystallized Co_3O_4 nanorods.

0.5% Pd/Co_3O_4 presents morphology similar to 0.1% Pt/Co_3O_4 (Figure. 1). HAADF-STEM does not distinguish Pd from Co atoms due to insufficient Z-contrast resulting from their close atomic numbers. EXAFS and AP-XPS were used to identify the binding environment and oxidation state of Pd in-situ, which showed the lack of coordination of Pd to Pd atoms and Pd to Co atoms, suggesting that Pd atoms are anchored on oxygen atoms of Co_3O_4 and they are singly dispersed under reaction conditions.

References

[1] Xie, X. W. *et al.* *J Phys Chem C* **2010**, *114*, 2116.
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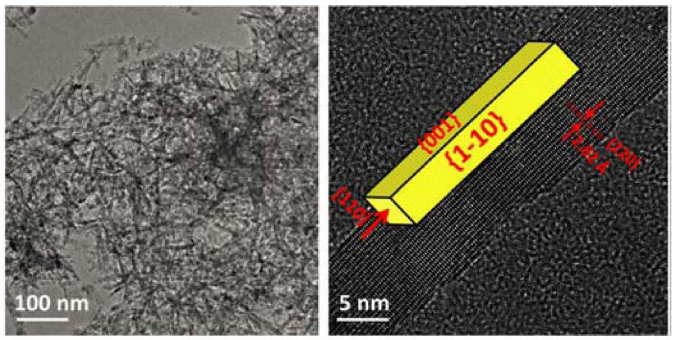

Figure 1. TEM images of Co_3O_4 nanorods anchoring noble metal atoms. (a) Large scale image. (b) High resolution image.

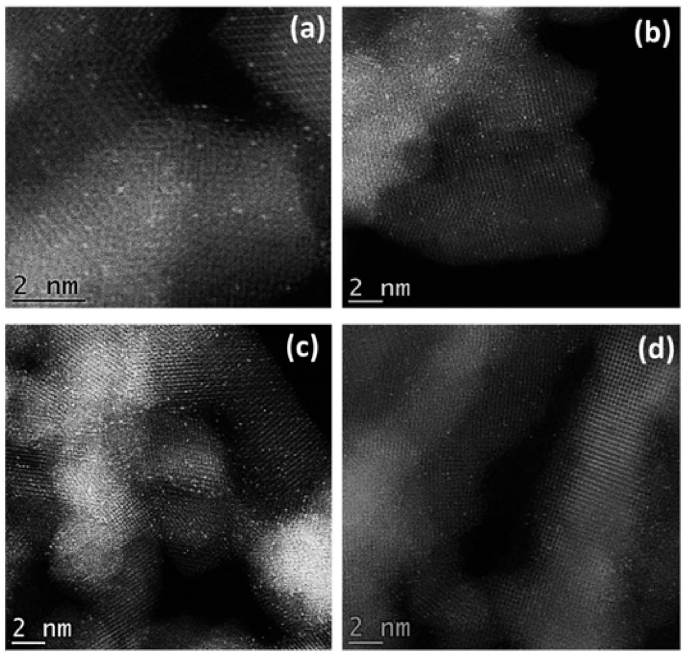

Figure 2. Image of aberration-corrected annular dark-field scanning transmission electron microscopy studies of 0.1% Pt/Co_3O_4 with singly dispersed Pt atoms. Each bright spots with high contrast are Pt atom singly dispersed on Co_3O_4 nanorods.

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