

The Stability of High Metal-Loading Pt₁/Fe₂O₃ Single-Atom Catalyst Under Different Gas Environment

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Single-atom catalysts (SACs), which maximize the efficiency of the active metals, are of interest for both fundamental study and industrial applications [1]. Supported single metal atoms are thermodynamically not stable and easy to sinter during catalytic reactions, especially at high reaction temperatures. Investigation of the stability of supported single metal atoms under specific gas environment can help us understand the sintering mechanisms of SACs during catalytic reactions and thus provide insights into developing stable SACs for practical applications [2-3]. We report here the investigation of the mobility of high number-density Pt single atoms in a Pt₁/Fe₂O₃ SAC at a moderate temperature (250°C) under different gas environments that are relevant for CO oxidation, water-gas shift and hydrogenation reactions.

The high loading Pt₁/Fe₂O₃ SAC was synthesized by a modified adsorption method [4]. Briefly, designated amount of H₂PtCl₆ solution was finely mixed with the pre-formed α-Fe₂O₃ nanocrystallites under a specified pH value. The Pt loading was determined by ICP-MS to be ~ 1.66 wt%. The stability of the as-prepared Pt₁/Fe₂O₃ SACs under various gas environments was evaluated in a fixed-bed reactor at 250 °C for 2 hours. The feed gas composition was 1vol% of the target gas and balance He with a flow rate of 33 ml/min. For each test, ~ 20 mg Pt₁/Fe₂O₃ SAC was directly used without any pretreatments. Aberration-corrected high-angle annular dark-field (HAADF) STEM was used to characterize the as-prepared and the gas-treated Pt₁/Fe₂O₃ SACs.

The atomic resolution image of Fig. 1a and the analyses of many similar images reveal that in the as-synthesized Pt₁/Fe₂O₃ SACs only isolated Pt single atoms were found and that the Pt single atoms were uniformly dispersed onto the surfaces of the α-Fe₂O₃ nanocrystallites. After annealing the as-prepared Pt₁/Fe₂O₃ SAC in 1vol% O₂, all the Pt single atoms remained isolated (Fig. 1b). The presence of O₂ molecules did not sinter the Pt single atoms. After annealing the as-prepared Pt₁/Fe₂O₃ SAC in 1vol% H₂, however, the initially isolated Pt single atoms agglomerated to form small clusters (Fig. 2a), clearly suggesting that the reduction treatment facilitated the sintering of the Pt single atoms. Similarly, under the CO gas treatment, the Pt single atoms moved to form subnano Pt clusters (Fig. 2b). Atomic resolution HAADF images showed that the Pt clusters were highly disordered or amorphous-like. When water was added into the feed gas of CO, the Pt sintering process was accelerated and some larger Pt particles appeared (Fig. 2c). The size distributions of the sintered Pt clusters are displayed in Fig. 2d-2f for the various gas treatments. From these size distributions, we concluded that at 250°C 1) O₂ does not sinter the Pt single atoms, 2) both CO and H₂ facilitate the movement of the Pt atoms with a stronger effect by H₂, and 3) the presence of H₂O molecules significantly accelerates the sintering of the Pt single atoms. It is interesting to note that although the Pt single atoms sintered under H₂, CO and CO-H₂O gas treatment, isolated Pt single atoms persisted on the Fe₂O₃ surfaces, presumably due to strong anchoring by surface defect sites such as cation vacancies. These isolated single Pt atoms could also be a consequence of Oswald ripening process. When we extend the CO treatment to 24h, the Pt clusters grew

into well-crystallized Pt nanoparticles with sizes in the range of 5-10 nm. These experimental data suggest that the presence of CO and H₂ molecules in the gas environment weakens the Pt-support interaction and thus facilitates the sintering of Pt atoms. The presence of O₂ molecules, however, does not sinter the Pt atoms. The addition of H₂O molecules significantly modifies the mobility of the Pt single atoms supported on α -Fe₂O₃ nanocrystallites. The effects of long-term gas treatment of supported Pt₁ SACs have been investigated [5].

References:

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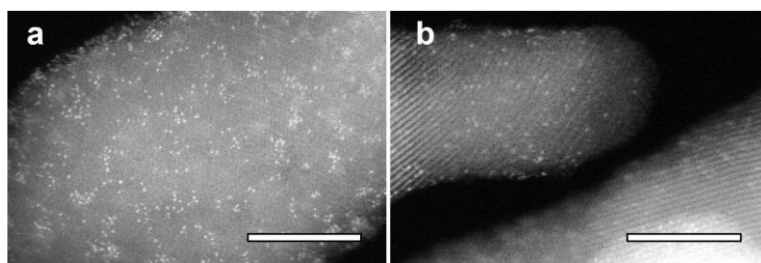


Figure 1. High magnification HAADF images of (a) as-prepared 1.66 wt%Pt₁/Fe₂O₃ SAC and (b) a 1.66 wt%Pt₁/Fe₂O₃ SAC after annealing in 1vol% O₂ (balance He) at 250°C for 2h. Both the as-prepared and the O₂ treated Pt₁/Fe₂O₃ SAC consist of only isolated single Pt atoms. Scale bar: 5 nm.

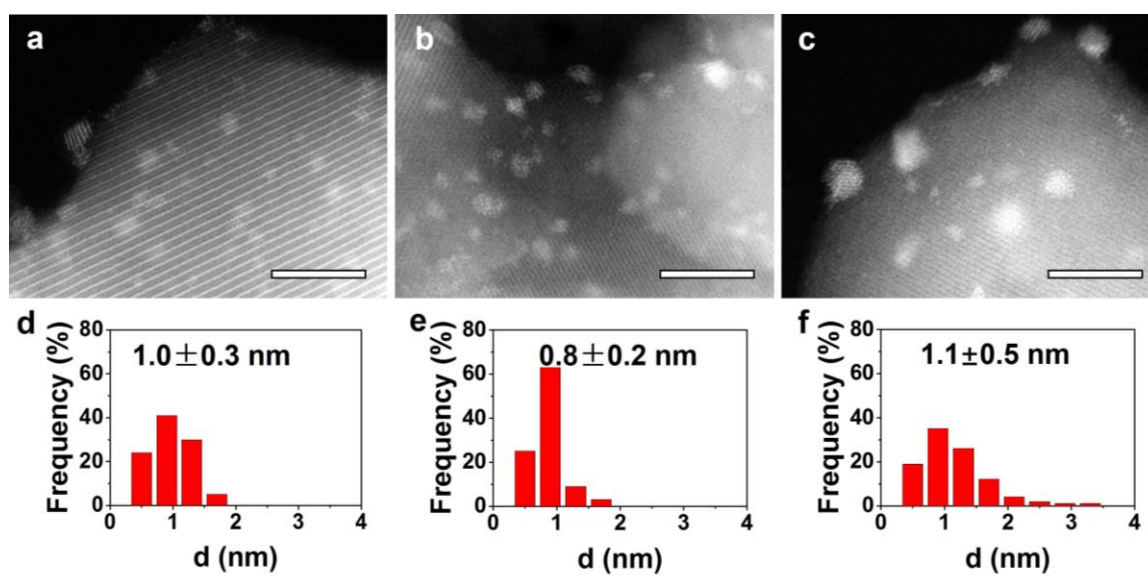


Figure 2. HAADF images (a-c) and the corresponding size distributions (d-f) of a 1.66 wt%Pt₁/Fe₂O₃ SAC after being treated with (a, d) H₂, (b, e) CO and (c, f) CO + H₂O at 250°C for 2h. The addition of H₂O significantly enhances the sintering of the Pt atoms. Scale bar: 5 nm.