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Original Research

Observation of Pt-{100}-p(2 × 2)-O reconstruction by an environmental TEM

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ABSTRACT

The surface structure of noble metal nanoparticles usually plays a crucial role during the catalytic process in the fields of energy and environment. It has been studied extensively by surface analytic methods, such as scanning tunneling microscopy. However, it is still challenging to secure a direct observation of the structural evolution of surfaces of nanocatalysts in reaction (gas and heating) conditions at the atomic scale. Here we report an in-situ observation of atomic reconstruction on Pt {100} surfaces exposed to oxygen in an environmental transmission electron microscope (TEM). Our high-resolution TEM images revealed that Pt-{100}-p(2 × 2)-O reconstruction occurs during the reaction between oxygen atoms and {100} facets. A reconstruction model was proposed, and TEM images simulated according to this model with different defocus values match the experimental results well.

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1. Introduction

As a typical catalyst, platinum nanoparticle has been widely studied because of its great performance in heterogeneous catalysis [1–6]. In general, the catalytic performance of catalyst nanocrystals is strongly related to their composition [7,8], shape [9–12], size [9], and, more importantly, their surface structure [12–15], which is in direct contact with environmental reactants. The activity of a catalyst may be very different if the atomic arrangement or coordination of its surface changes [16], such as when reconstruction occurs [17–20]. With respect to Pt nanoparticles, several low-index surfaces (e.g., {100} [18,21], {110} [17,22], and {111} [23–25]) have been observed to reconstruct under different reaction conditions [25–27]. In particular, when these surfaces are exposed to certain gases, surface reconstruction can be induced or reversed [27–30]. Thus, understanding the response of the surface to variable gas environments is important. Although great efforts to study the surface reconstruction on Pt have been exerted, information regarding reconstruction under different reaction conditions at the atomic scale remains limited.

In situ methods, including in situ environmental TEM (ETEM) and in situ scanning tunneling microscopy (STM), are efficient and powerful tools for materials research; thus, they have been extensively employed to investigate the structural evolution of catalyst surfaces under chemical reaction conditions at the atomic scale over the last few decades [31–36]. In this letter, we report the direct observation of a new (2 × 2) reconstruction on the Pt {100} surfaces in an ETEM equipped with a gas-heating holder that allows for introducing pure oxygen (~0.1 Pa) into the TEM column. Our in situ TEM images indicate that the (2 × 2) reconstruction is triggered by the reaction between Pt surfaces and oxygen.

2. Experimental

Using a previously published procedure [37], Pt nanocrystals with an average diameter of 6 nm were synthesized and dispersed in methanol. The solution (1 mg/mL) was then drop-casted onto the edge of a SiN supporting substrate, which is an amorphous holey chip. In-situ observation of the reconstruction on Pt surfaces was carried out in an ETEM (H-9500, Hitachi Company) under an oxygen pressure of 0.1 Pa at 400 °C. Simulation images were obtained using the Multislice program [38] included with the JEMS software [39]. Crucial simulation parameters are all used same as the experiment: accelerating voltage = 300 kV, Cs = 0.7 mm. For HRTEM simulating, we employed a (001) surface slab model, having 37 Pt monoatomic layers with a reconstructed first Pt layer induced by oxygen adsorption (Fig. S1). More details can be found in the Supporting Information.

3. Results and discussion

A series of in situ TEM images shows the structural evolution of Pt surfaces upon oxygen reaction at 400 °C, is depicted in Fig. 1a.

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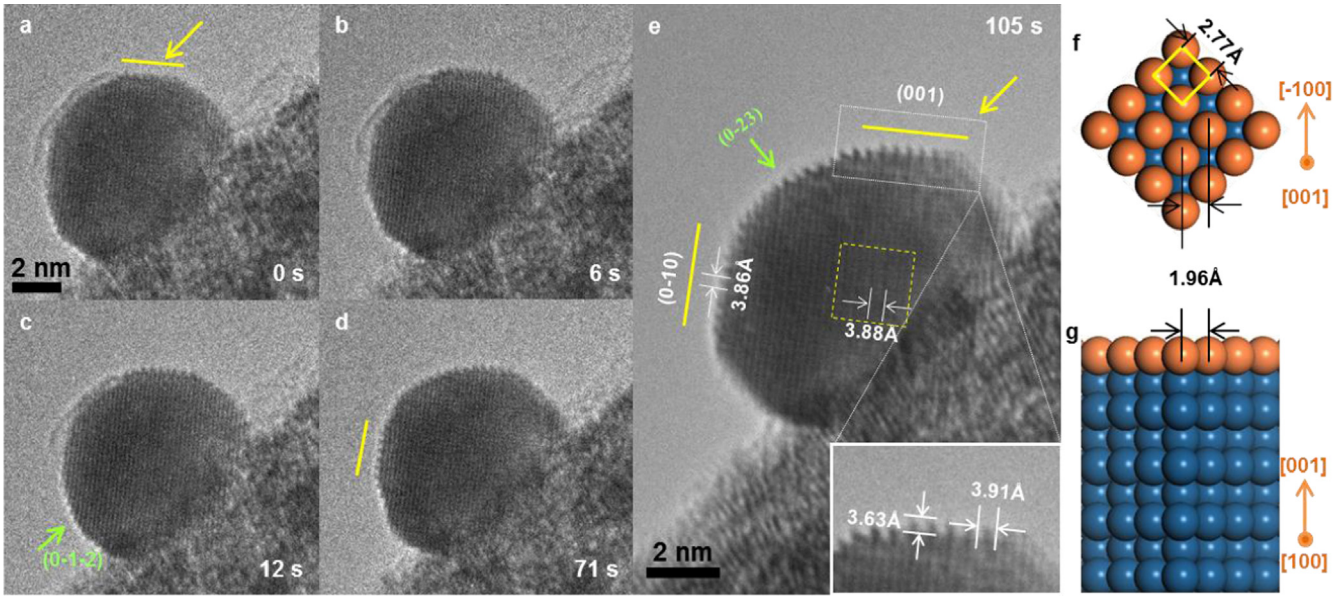

Fig. 1. TEM snapshot images of the P-{100}-(2 × 2) reconstruction (oxygen pressure 0.1 Pa, 400 °C) obtained from a video. The zone axis of (a)–(e) is [100]. (f, g) Top- and side-views of the ideal unreconstructed Pt models, respectively. Orange and blue balls denote the top layer and substrate Pt, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

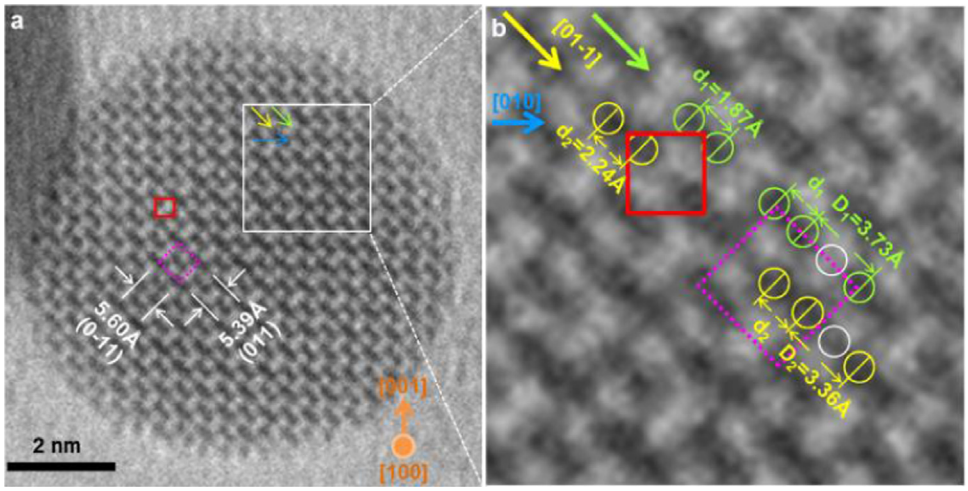

Fig. 2. (a) the reconstruction of Pt (100) surface (at an oxygen pressure of 0.1 Pa, 400 °C). (b) an amplified area of the white square in (a). The distance between the circles are indicated as D1 = 3.73 Å, d1 = 1.87 Å, D2 = 3.36 Å, d2 = 2.24 Å. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

The Pt nanoparticle is located at the edge of the SiN supporting substrate. Graphene layers, which are formed firstly on the surfaces of the Pt nanoparticle (Fig. 1a) due to consecutive electron beam irradiation [40,41], impede direct impingement of oxygen on the Pt surfaces. The graphene layers are gradually removed after reaction with oxygen at elevated temperatures [42], leaving clean Pt surfaces. The structure of the exposed part of the Pt surfaces begins to change after the graphene layers are removed. As shown in Fig. 1a, the (001) facet (indicated by the yellow line) is flat without any obvious reconstruction. As the reaction proceeds, small atomic promontories appear on the (001) surface and arrange regularly. This type of atomic rearrangement can be clearly observed on either (100) or (010) facets and even on some high-index facets, such as (0–1–2) and (0–23) (green arrows in Fig. 1c and e). For simplicity, we only focus on atomic reconstructions on the {100} facets, which consist of three identical surfaces: (001), (010), and (100). A high resolution TEM image of the Pt nanoparticle is presented in Fig. 1e. The inset in this figure shows promontories on the (001) facet with a spacing of 3.91 Å and a height of 3.63 Å. Similar promontories with a spacing of 3.86 Å can be seen on the (0–10) facet. Ideal models of the unreconstructed Pt (001) surface from the top- and side-views are respectively depicted in Fig. 1f and g. The orange (blue) balls are top (substrate) atoms.

According to a previous report [43], the spacing of the (200) facets in this model is 1.96 Å, which is approximately half that of the promontories in Fig. 1e. These results indicate that a 2 × superstructure is formed on the (001) along [010] direction, but it is still not clear about the vertical [100] direction. So a top-view is urgent needed. In fact, similar reconstructions can be observed on the (100) facet, as marked by the yellow dotted square in Fig. 1e, although the image is not very clear due to the non-flat surface.

In Fig. 2a, the (100) surface of the Pt nanoparticle after reconstruction is displayed; here, the reconstruction directly shows the top-view. The lowest period of the surface lattice is marked by a purple dotted square. The spacing of the (011) and (0 − 11) facets

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