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Article

A vicinal effect for promoting catalysis of Pd₁/TiO₂: Supports of atomically dispersed catalysts play more roles than simply serving as ligands

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ABSTRACT

Atomically dispersing metal atoms on supports has been emerging as an effective strategy to maximize the atom utilization of metals for catalysis. However, due to the lack of effective tools to characterize the detailed structure of metal-support interface, the chemical functions of supports in atomically dispersed metal catalysts are hardly elucidated at the molecular level. In this work, an atomically dispersed Pd₁/TiO₂ catalyst with Ti(III) vicinal to Pd is prepared and used to demonstrate the direct involvement of metal atoms on support in the catalysis of dispersed metal atoms. Systematic studies reveal that the Ti(III)-O-Pd interface facilitates the activation of O₂ into superoxide (O₂⁻), thus promoting the catalytic oxidation. The catalyst exhibits the highest CO turn-over frequency among ever-reported Pd-based catalysts, and enhanced catalysis in the combustion of harmful volatile organic compound (i.e., toluene) and greenhouse gas (i.e., methane). The demonstrated direct involvement of metal atoms on oxide support suggests that the real active sites of atomically dispersed metal catalysts can be far beyond isolated metal atoms themselves. Metal atoms on oxide supports in the vicinity serve as another vector to promote the catalysis of atomically dispersed metal catalysts.

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1. Introduction

Minimizing catalytic metals into isolated metal atoms (ions) provides an ideal strategy to maximize the utilization of earth-scarce metals for catalysis [1–4]. Towards this goal, two main practical approaches have been developed. One is to isolate and stabilize by organic ligands, forming homogeneous catalysts. The other is to atomically disperse metals on various supports, yielding heterogeneous catalysts that are easily recyclable [3–10]. The catalytic properties of isolated metal atoms (ions) are heavily determined by their coordination environments [11]. Ligands of mononuclear homogeneous catalysts not only tune the electronic structures of metal centers, but also form geometric barriers to tailor the adsorption behaviors of substances [12–15]. Similar electronic and geometric roles can be identified for the supports of atomically dispersed metals [3,4], in which the supports, to some extent, serve as ligands to stabilize metal centers [5,16–19].

Based on the above argument, it is not surprising that atomically dispersed catalysts based on the same metal showed different

performance in reactions. It is even under debate whether the isolated metal atoms themselves are catalytically active [20]. For instance, while Pd₁/TiO₂ and Pt₁/SiO₂ showed no activity in catalytic CO oxidation even at elevated temperature [21,22], Pd₁/La-Al₂O₃ and Pt₁/FeO_x exhibited high activities [6,23]. It is vital to understand at the molecular level how supports are involved in catalysis [22,24–28]. However, the atomic-resolution characterization of interfacial species surrounding isolated metal atoms remains a grand challenge [29–33], preventing us from addressing the key question of how supports are involved in the catalysis of atomically dispersed metal catalysts.

We demonstrate herein that the metal oxide support of atomically dispersed metal catalysts is readily involved in the catalysis of dispersed metal centers to significantly promote the overall catalysis. An atomically dispersed Pd₁/TiO₂ catalyst with the presence of Ti(III) vicinal to Pd is prepared and used for the demonstration. Both experiments and DFT calculations reveal that the Ti(III)-O-Pd interface facilitates the activation of O₂ into superoxide (O₂⁻), thus promoting the catalytic oxidation. The Pd₁/TiO₂ catalyst exhibits an enhanced activity for CO oxidation and the catalytic combustion of harmful volatile organic compound (i.e., toluene) and greenhouse gas (i.e., methane). Metal atoms on oxide supports

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in the vicinity direct involve in catalytic reactions, which is distinguished from the ligands of homogeneous catalysts.

2. Experimental

2.1. Synthesis of Pd₁/TiO₂-cal

Pd₁/TiO₂-EG (ethylene glycolate) was first prepared by our reported photochemical method [34,35]. The dried Pd₁/TiO₂-EG powder was transferred into an alumina crucible and placed into a muffle furnace with a controlled temperature program. The temperature was heated by 1 K/min from room temperature to 623 K and kept for 4 h. The calcination process was carried out in air. After the temperature was cooled to room temperature, the obtained sample was denoted as Pd₁/TiO₂-cal.

2.2. Characterization of Pd₁/TiO₂-cal

Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 (FEI, Netherlands) operating at 300 kV. High-resolution aberration-corrected scanning transmission electron micrographs (AC-STEM) were acquired using a JEOL ARM-200CF (JEOL, Japan) in high-angle annular dark-field (HAADF) mode. Electron Energy-loss spectroscopy (EELS) experiments were carried out using a Gatan Quantum 965 (Gatan, USA) spectrometer attached to the ARM microscope. The X-ray absorption spectra (XAS), including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) at the Pd K-edge were recorded at the XAS station (BL14W1) of the Shanghai Synchrotron Radiation Facility (SSRF, China). X-band electron spin resonance (ESR) spectra were recorded by an EMX-10/12 microspectrometer (Bruker, Germany) at 90 K. Thermogravimetric analysis (TGA) was operated on Q600 SDT (TA instrument, USA). Fourier-transform infrared spectroscopy (FTIR) was operated on Nicolet IR380 (Thermo Electron, USA). X-ray diffraction (XRD) were recorded by a Rigaku Ultima IV (Rigaku, Japan). Details of characterizations can be found in the supplementary material.

2.3. Catalysis tests

The catalytic reactions of CO oxidation were carried out in a continuous flow fixed-bed glass reactor with an inner diameter of 5 mm. CO conversion was detected by an on-line gas chromatograph (GC9790, Fuli, China). The gas mixture of air (40 mL min⁻¹) and CO (10 mL min⁻¹, 5 vol% in N₂) was governed by mass flow controllers at atmospheric pressure and passed through the catalysts with a space velocity (SV) of 6,000 L g_{pd}⁻¹ h⁻¹. The reactor was heated and the temperature of the catalyst was measured with a K-type thermocouple. The temperature of the reactor was incrementally ramped from room temperature to 453 K. The overall compositions of the TiO₂-supported catalysts used for catalysis comparison studies were as follows: Pd₁/TiO₂ (1.0 wt% Pd), and Pd₁/TiO₂-cal (1.2 wt% Pd, the removal of EG decreased the total weight and the loading content of Pd appears larger).

CO conversion (X_{CO}) is calculated as Eq. (1):

$$X_{CO} \text{ conversion (\%)} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{out}} \times 100, \quad (1)$$

where, [CO]_{in} represents the concentration of CO in the reactant gas flow; [CO]_{out} represents the concentration of CO in the gas after reacting with the catalysts in the fixed-bed reactor.

3. Results and discussion

3.1. Preparation and characterizations of Ti(III)-O-Pd interfaces

To create a catalyst with all Pd atoms situated at the metal/metal oxide interface, an atomically dispersed Pd₁/TiO₂-EG catalyst was first prepared by a photochemical method previously reported [34,35]. The Pd₁/TiO₂-EG catalyst was then subjected to a thermal treatment at 623 K in air for 2 h to remove surface EG on the catalyst (Figs. S1 and S2 online). After calcination, all the EG ligands were removed, as proved by the TGA and FTIR results. The Pd loading in the catalyst was kept at 1.0 wt% to ensure no aggregation of Pd atoms into clusters or nanoparticles, which was confirmed by TEM and XRD (Figs. S3–S5 online). As illustrated by AC-STEM (Figs. 1a and S6 (online)), Pd atoms in Pd₁/TiO₂-cal were still atomically dispersed on TiO₂. The atomic dispersion of Pd was further confirmed by FTIR results of Pd₁/TiO₂-cal after CO pre-adsorption (Fig. S7 online). Only one peak at around 2,100 cm⁻¹ attributed to the linear configuration of CO was observed. The peak at 2,354 cm⁻¹ was attributed to adsorbed CO₂ [36,37], which will be discussed later. The EXAFS analysis also confirmed the atomically dispersing structure of Pd (Fig. 1b–d, Fig. S8 (online), and Table 1). Only one notable peak was observed at 8 Å⁻¹ from the wavelet transform (WT) contour plots of the Pd K-edge, ascribed to the Pd-O path. No peak from the Pd-Pd contribution was observed both in the WT and Fourier-transformed (FT) results. Fitting results of FT R-space further demonstrated the atomically dispersion of Pd, similar to the sample before calcination (Table 1).

In order to probe the vicinal environment surrounding the Pd atoms, high-resolution EELS in AC-STEM was conducted to investigate the electronic structures of neighbor Ti atoms. As shown in Fig. 1e, the L_{2,3} edge of Ti atoms away from Pd (site 1, 3 and 4) showed typical Ti⁴⁺ features with a crystal-field splitting of the three-fold t_{2g} (d_{xy}, d_{yz} and d_{xz} orbitals) and two-fold e_g (3d_{z²-r²} and 3d_{x²-y²} orbitals) states. In contrast, the L_{2,3} edge of the Ti atom adjacent to Pd (site 2) was broadened and moved to lower energies, indicating a decrease in the oxidation state [38,39]. These results suggest the successful construction of atomically well-defined Ti(III)-O-Pd interface, as illustrated in the structural model in Fig. 1e, proving that the surface dispersion of Pd atoms changed the surface state of TiO₂ supports.

3.2. Different reaction kinetics for two Pd₁ catalysts

CO oxidation was first chosen to probe the possible role of adjacent Ti³⁺ sites in catalytic reactions. It is interesting that Pd₁ catalysts with and without pre-reaction calcination exhibited completely different activities. Pd₁/TiO₂-cal showed a high activity and stability at a SV as high as ~6,000 L g_{pd}⁻¹ h⁻¹ (Fig. 2a and S9 (online)). The turnover frequencies of Pd₁/TiO₂-cal were 36 and 60 h⁻¹ at 343 and 353 K (Fig. 2b), respectively. The activity and stability of Pd₁/TiO₂-cal exceeded that of the state-of-the-art Pd₁/La-Al₂O₃ catalyst [6]. In comparison, the Pd₁/TiO₂-EG catalyst displayed negligible activity below 373 K (Fig. 2a). 100% CO conversion was achieved only at temperatures above 433 K. The fitting results of EXAFS data for both catalysts before and after reaction showed that no aggregation was observed (Table S1 online). Since Pd species of both catalysts were atomically dispersed showing similar valences (Fig. S10 online), the difference in activities has to be on account of their local structures: Pd-EG and Ti(III)-O-Pd.

To prove the assumption, Pd₁/TiO₂-EG was calcined for different durations to expose different amounts of Ti(III)-O-Pd sites at 623 K in air (Fig. S11 online). The catalyst obtained after 1 h-calcination showed a similar activity with that of 4 h-calcination; whereas the sample calcined for 10 min displayed a poorer activity than

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