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Size-dependent catalytic activity over carbon-supported palladium nanoparticles in dehydrogenation of formic acid

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ABSTRACT

Hydrogen generation from formic acid (FA) under mild conditions has received significant attention, where Pd-based catalysts have been widely employed due to their superior activities. However, the Pd particle size effect has been much less systematically investigated. In this study, carbon-supported Pd nanoparticles (NPs) with five different Pd particle sizes, ranging from 2.1 to 4.5 nm were synthesized using sodium citrate as the stabilizing agent. The Pd particle sizes were determined by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The FA dehydrogenation reaction was conducted in a FA-sodium formate (SF) aqueous solution in a batch reactor at room temperature. We found that decreasing the Pd particle size from 4.5 ± 0.5 to 2.1 ± 0.3 nm remarkably boosted the catalytic activity by about 3.6 times, resulting in a turnover frequency of 835 h^{-1}, which is among the highest values for supported monometallic Pd catalysts in the literature. Our results suggest that both low- and high-coordination Pd surface atoms participated in the reaction. The remarkably higher activity of smaller Pd NPs was attributed to both higher Pd dispersion and the presence of a larger proportion of Pd species with positive charge, through which the Coulomb interaction between the positive Pd species and negative charged formate ions, the key reaction intermediate, is enhanced. Finally, the deactivation and regeneration of Pd/C catalysts were also discussed.

1. Introduction

Hydrogen, an environmentally clean energy carrier, has been regarded as one of the most promising candidates to meet the increasing demands for an efficient and clean energy supply [1]. Developing technologies for controlled storage and release of hydrogen in a safe manner are an urgent need for the utilization of H_2 as transportation fuel, especially in low-temperature fuel cells. Compared with the classic pressurization or cryogenic liquefaction, using a proper chemical as the hydrogen carrier is currently the more desired approach [2,3].

Among the hydrogen storage chemicals investigated recently, formic acid (FA), which contains 4.4 wt% hydrogen, has attracted much attention because FA is a renewable, nontoxic source as a major product of biomass processes, and is stable at room temperature [4–8]. Hydrogen stored in FA can be released using a highly efficient catalyst through the dehydrogenation pathway ($HCOOH \rightarrow CO_2 + H_2$) under a mild reaction condition. A number of experimental and theoretical studies suggested that formate (HCOO) is the key reaction intermediate [9–15]. Thus increasing the concentration of formate ion using sodium formate (SF) as an additive turned out to be an efficient way to accelerate H_2 release [14,16–19]. On the other hand, HCOOH dehydration may also occur and generates low levels of the undesired product, CO ($HCOOH \rightarrow CO + H_2O$) [3,5,20,21]. The worst scenario is that CO can even poison and deactivate the catalysts [22–27]. Hence, development of a catalyst to actively and selectively catalyze FA dehydrogenation to produce CO-free H_2 at near ambient temperature is highly desirable [14,17,28–34].

Among other supported metal catalysts (e.g. Au, Rh, and Pt) [15,34–37], Pd-based heterogeneous catalysts have attracted significant attention due to their superior catalytic activities for FA decomposition [17,29–31,38–42]. Tremendous efforts have been devoted to improving the catalytic activities. One way is to import

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other elements to form alloys or core-shell structures. For instance, Tsang et al. reported that coating a thin layer of Pd atoms onto Ag nanoparticles (NPs) to form an Ag@Pd core-shell structure can enhance the activity by about 5 times at 20 °C compared with pure Pd or PdAg alloy nanoparticles in FA decomposition without any additive. The enhanced activity was attributed to both the presence of terrace sites in the Pd shell and electronic promotion by the Ag core [8]. Cai et al. reported that the boron-doped Pd catalyst (Pd-B/C) was about 4 times more active than pure Pd, showing a turnover frequency (TOF) of 1184 h^{-1} from a FA-SF aqueous solution (FA:SF = 1.1:0.8) at 30 °C [17]. Xu et al. demonstrated that AuPd bimetallic nanoparticles immobilized in metal-organic framework had a much higher catalytic activity and a higher tolerance to CO poisoning than monometallic Au and Pd counterparts [42]. Chen et al. successfully synthesized carbon-supported AuPd alloy NPs with different sizes, and they found that the catalyst with smaller AuPd particle size had much higher catalytic activity than the larger ones in a FA-SF solution (FA:SF = 1:1) at 25 °C [43]. Jiang and coworkers showed that the $Co_{0.3}Au_{0.35}Pd_{0.35}/C$ trimetallic nanoalloy catalyst had significantly higher activity than that of monometallic (Pd/C, Au/C, and Co/C) and bimetallic ($Au_{0.50}Pd_{0.50}/C$, $Co_{0.30}Pd_{0.70}/C$, and $Co_{0.30}Au_{0.70}/C$) counterparts in FA decomposition without any extra additive at room temperature [39].

In case of monometallic Pd catalysts, the size of the Pd NPs can play an important role in catalyst activity. Xu et al. showed that highly dispersed Pd NPs (~2.3 ± 0.4 nm) on nanoporous carbon MSC-30 had a much higher activity toward FA decomposition (a TOF of 750 h^{-1} at 25 °C) than a 3.6 ± 0.6 nm Pd catalyst on the same support in a FA-SF aqueous solution (FA:SF = 1:1) [44]. They further demonstrated in a later study that when the Pd particle size was reduced to ~1.5 nm through potent alkalization of reduced graphene oxide with diamine, the TOF was also as high as ~740 h^{-1} at 25 °C [14]. Independently, Jiang et al. also reported that decreasing the Pd size to about 2.8 nm with citric acid as dispersing agent significantly improved catalytic activity [19]. However, to our best knowledge, Yamashita and coworkers are the first ones to systematically investigate the Pd particle size effect by comparing the activities of carbon-supported Pd NPs ranging from 2.7 to 5.5 nm in FA decomposition without any additive. Therein, the Pd/C catalysts were synthesized by the polyol method using polyvinylpyrrolidone (PVP) as the protective agent [45]. They found that the 3.9 nm Pd/C catalyst had the highest activity and suggested that the reaction may primarily occur at the terrace Pd atoms with high coordination numbers based on a model of cuboctahedron-shape Pd NPs with a cubic close-packed structure. However, the use of PVP as a protective surfactant might be an issue, since the PVP capping agent can strongly bind to the surface of Pd NPs to largely reduce their activities. Indeed, such an issue has been reported in other studies [8,19]. For instance, Jiang et al. reported that the Pd/C catalyst with a Pd particle size of 2.3 nm, synthesized with PVP as a stabilizing agent, exhibited the lowest activity for the reaction. A dramatic enhancement in its activity was observed once the PVP was washed off [19].

In our present work, we synthesized Pd/C catalysts with five different Pd particle sizes in a range of 2.1–4.5 nm using a much weaker stabilizing agent of sodium citrate to eliminate the capping agent effect. The Pd particle sizes were determined by HAADF-STEM measurements. Evaluating their activities in FA decomposition from a FA-SF aqueous solution at room temperature, we found that reducing the Pd particle size could remarkably improve both catalytic activity and FA conversion. Herein, a TOF of 835 h^{-1} at 25 °C was observed on the 2.1 nm Pd/C catalyst, which is among the highest values for supported monometallic Pd catalysts reported in the literature.

2. Experimental

2.1. Catalyst preparation

The Pd/C catalysts were prepared using sodium borohydride ($NaBH_4$, 96%, Sinopharm Chemical Reagent Co. Ltd) as a reducing agent, and sodium citrate (Sinopharm Chemical Reagent Co. Ltd) as a stabilizing agent according to a procedure reported previously [40,46]. Carbon black (Vulcan XC72R, Carbot Corp.) was used as the catalyst support as received. The size of Pd nanoparticles was carefully controlled by varying the ratio of sodium citrate to palladium chloride ($PdCl_2$, Aladdin) and by adjusting the reduction temperature by $NaBH_4$. For instance, the procedure for the 2.1 nm Pd/C catalyst synthesis was as follows: 0.1 mmol $PdCl_2$ (dissolved in 0.1 M HCl solution) and 0.8 mmol sodium citrate were dissolved into 150 mL water. 400 mg carbon black was then added. After stirring the mixture for 20 min, followed by 30 min sonication, 15 mL of 0.1 M $NaBH_4$ solution was added into the suspension dropwise under vigorous stirring at 5 °C for 8 h. Next, the precipitate was filtered, and washed with deionized water several times to remove the weakly bonded sodium citrate agent. The obtained materials were then dried overnight in a vacuum oven at 25 °C to obtain the 2.1 nm Pd/C catalyst. For the 2.6 nm and 3.2 nm Pd/C catalysts, the $NaBH_4$ reduction temperatures were 25 °C and 60 °C, respectively. The 3.8 nm Pd/C catalyst was obtained by changing the ratio of sodium citrate to $PdCl_2$ to 2:1 and maintaining the reducing temperature at 25 °C. Finally, the 4.5 nm Pd/C catalyst was obtained by treating the 3.8 nm sample in 10% H_2 in Ar at 300 °C for 60 min.

2.2. Catalyst characterization

The Pd loadings and the possible B impurity were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES). The morphologies of the Pd/C catalysts were characterized on an aberration-corrected HAADF-STEM at 200 kV (JEOL-2010F, University of Science and Technology of China (USTC)). The Pd particle size distribution was obtained by counting more than 200 particles from the HAADF-STEM images at different locations. Powder X-ray diffraction (XRD) measurements were carried out on a Philips X'Pert Pro Super diffractometer at the Structure Research Center at USTC, with a Cu-Kα radiation (λ = 1.5418 Å), operated at 40 kV and 50 mA.

Ex-situ X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo-VG Scientific Escalab 250 spectrometer, equipped with an aluminum anode (Al Kα = 1486.6 eV) (Hefei University of Technology). In order to investigate the impact on the catalyst activity by the changes of oxidation states of Pd NPs through reduction at different temperatures, i*n situ* XPS measurements were further carried out at the photoemission end-station at the beamline BL10B in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. Briefly, the beamline is connected to a bending magnet and covers photon energies from 60 to 1000 eV. The end-station consists of four chambers, i.e., analysis chamber, preparation chamber, quick sample load-lock chamber and a high pressure reactor. The analysis chamber, with a base pressure of $<2 \times 10^{-10}$ torr, is connected to the beamline and equipped with a VG Scienta R3000 electron energy analyzer and a twin anode X-ray source. The samples were treated with different gases in the high pressure reactor. After sample treatment, the reactor can be pumped down to a high vacuum ($<10^{-8}$ torr) for sample transfer. In the current work, each sample was first treated with the 10% H_2 in Ar at 25 °C and 200 °C for 0.5 h in the high pressure reactor. Then the sample was transferred to the analysis chamber for XPS measurements without exposing to air. The binding ener-