Size Effect of Carbon-Supported Pd Nanoparticles in the Hydrogen Production from Formic Acid

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Abstract: The particle size dependence in the hydrogen production from formic acid was investigated over Pd/C catalysts with nanoparticle sizes ranging from 2.7 to 5.5 nm. A volcano type relationship between catalytic activity and nanoparticle size was obtained and the average size of 3.9 nm exhibited the highest activity under mild reaction conditions. By performing calculations on the Pd crystallites, decomposition of formic acid is considered as a structure-sensitive reaction, and high-coordination sites principally act as catalytically active species in this size range.

Keywords: Hydrogen, Size-effect, Palladium nanoparticles.

1. Introduction

Hydrogen is a worldwide accepted energy vector whose widespread limitation is mainly associated with its storage in a compact, safe, and cost-effective manner. Formic acid (FA) has recently appeared as a stable and readily available liquid-phase chemical hydrogen storage material, whose high gravimetric and volumetric hydrogen capacities (4.4 wt.% and 52 g l^{-1}, respectively), together with its non-toxicity make it a promising candidate to be used to this end[1]. Diverse approaches have been addressed to efficiently boost the FA dehydrogenation, but the use of Pd-based catalysts is considered one of the most favorable alternatives[2]. In this work, we investigate the size sensitivity in the hydrogen production from FA over carbon-supported PVP-capped Pd nanoparticles (NP) by assessing the catalytic behavior of five Pd/C catalysts with sizes ranging from 2.7 to 5.5 nm.

2. Experimental

Pd NPs were initially prepared in colloidal form by means of the polyol method. The control of the NP size was achieved by using different experimental conditions in terms of PVP/Pd molar ratio, reduction temperature and time, as well as metal precursor concentration[3]. Afterwards, five Pd/C catalysts were prepared by conducting the standard impregnation method during 3 days at room temperature, and using the adequate amount of Pd colloids so as to achieve catalysts with 0.5 wt.% of Pd loading. Once the Pd NPs were loaded, the samples were washed with H_2O/EtOH (50/50 vol/vol) and dried overnight at 60 ºC. The as-prepared catalysts, denoted as Pd/C(1)-(5), were characterized and their catalytic performance on the FA dehydrogenation reaction was assessed by monitoring the hydrogen production while the pertinent liquid phase reactions at 30 ºC were conducted.

3. Results and discussion

Results of the Pd/C characterization obtained by TEM revealed that the NPs size ranged from 2.7 nm (in sample Pd/C(1) to 5.5 nm (in samples Pd/C(5)). Then, the relative proportion of low-coordinated defect atoms (LC; edge and corner) and high-coordinated atoms (HC; terrace) with respect to the total number of surface atoms is different for the studied samples (Figure 1).

The hydrogen production achieved after 3 h of reaction together with the NP size for the five Pd/C catalysts is plotted in Figure 2 (a). Sample Pd/C(3) with average particle size of 3.9 nm exhibited the best catalytic performance among investigated, producing 183 µmol of H_2. Samples Pd/C(2), Pd/C(4) and

Pd/C(5), whose average NPs sizes are 3.6, 4.2 and 5.5 nm, respectively, showed similar H_2 evolution profiles, although the generated H_2 in sample Pd/C(4) (158 μmol) was slightly higher than those obtained with Pd/C(5) and Pd/C(2) (142 and 134 μmol, respectively). On its side, sample Pd/C(1) with the smallest NP size, displayed the poorest catalytic performance among studied.

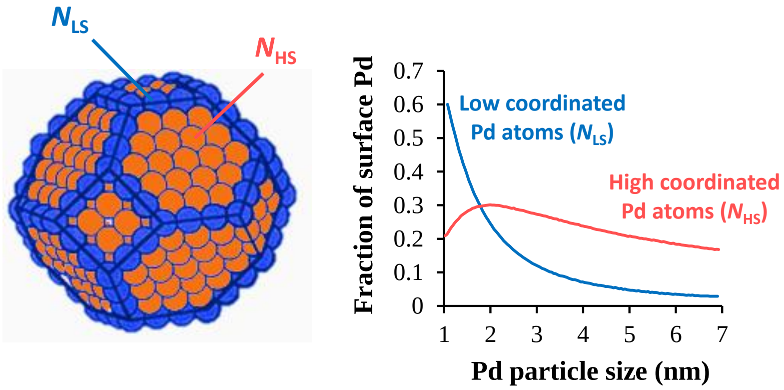

Figure 1. Schematic illustration of N_{HS} and N_{LS} and their fraction of surface area.

TOF values calculated on the basis of low and high-coordination number sites are displayed in Figure 2 (b). According to these results, the dehydrogenation of FA is considered “structure-sensitive” and the high-coordinated Pd atoms at terrace sites act as the key active species within a regular arrangement of the Pd NPs.

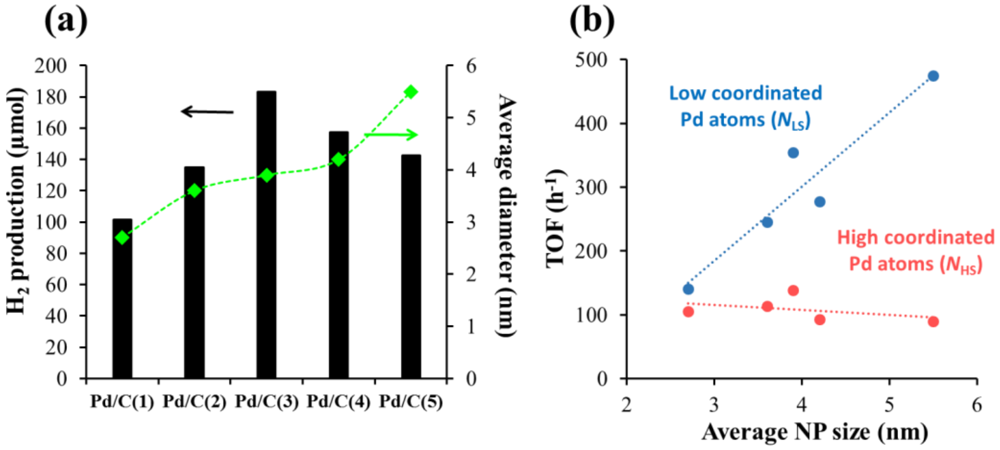

Figure 1. (a) Relationship between H_2 production after 3 h of reaction at 30 ºC and the average NP size; (b) Normalized TOF values calculated on the basis of high-coordinated (terrace) and low-coordinated (edge and corner) as a function of the average Pd NP size.

4. Conclusions

A volcano type relationship between the catalytic activity and the NP size was obtained for the Pd/C catalytic system studied in this work and the average size of 3.9 nm exhibited the highest activity under mild reaction conditions. The results obtained indicated that the decomposition of FA is a structure-sensitive reaction, and high-coordination sites principally act as catalytically active species in the Pd NP size range studied in the present work.

References

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