A Structure and Catalytic Behavior Study of Boron Doped Palladium Nanoparticles

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Abstract: Palladium **(**Pd) nanoparticles (NPs) with boron (B) interstitial modifications were synthesized. Based on theoretical analysis and experimental characterizations, a series of characterizations including the Solid NMR, X-ray diffraction and Electron Microscopy based techniques demonstrated that the insertion of B elongates the lattice parameter and modifies the surface of Pd NPs. It is evident that B can reside in the interstitial site of the Pd unit cell, rendering the change of electronic distribution of Pd. Consequently, different catalytic behaviour was performed.

Keywords: X-ray diffraction technique, Electron Microscopy, Catalysis

1. Introduction

The catalytic performance of transition metal NPs is usually boosted after addition of a promoter and doping with other elements.[1] Alloying light metalloid elements to metal lattice of the NPs, forming interstitial alloy,[2] such as carbrides,[3] nitride,[4] borides,[5] has been heavily researched. Incorporating a light metalloid element to the metal lattice can downshift the d-band centre of this metal, resulted from the movement of electrons from p orbital to d orbital.[6] For example, Pd-^{int}B/C NPs, have exhibited increased reactivity and selectivity in formic acid decomposition,[7] selective hydrogenation of alkyne to alkene,[8] oxygen reduction reaction.[9] Notwithstanding the intense research activity on the synthesis and catalytic testing of light element doped materials, no many information is available about their physical property and structure. These include the location of the doping sources and variation in lattice parameter of Pd. Herein, we describe this nanomaterial by employing Solid NMR, X-ray scattering techniques, ptychography and electron energy loss spectroscopy (EELS).

2. Experimental procedures

Synthesis of 5%Pd/C**:** $Pd(OAc)_2$ (21.28 mg) and Vulcan ® XC72R (190 mg) were ground until forming a homogeneous solid. The resultant powder was transferred into round bottom flask, followed by degassing over 15 minutes. Then, the powder was heated at 250 ^oC for 1 hour and cooled to room temperature. Subsequently, Pd/C was reduced by 5%H_2 in N_2 for 2 hours at 250 ^oC. The ramping rate was 2 ^oC per minute. Before removing the catalyst from the furnace, it was left under only nitrogen flow for 15 minutes.

Synthesis of Pd-^{int}B/C**:** 5%Pd/C (150 mg) was heated at 40 ^oC to evaporate residual water under N_2 atmosphere, followed by heating at 100 ^oC for 15 minutes under H_2 atmosphere. The resultant powder was wetted with 2 mL of Tetrahydrofuran (THF) before 3 mL of 1M $BH_3{\cdot}THF$ was added via dropwise. The mixture was stirring for 15 minutes and then heated at 40 ^oC under N_2 atmosphere to evaporate all THF. Eventually, the powder was heated at 200 ^oC and cooled to room temperature. After cooling to room temperature, the sample was washed with water (200 mL) and ethanol (200 mL) before leaving to dry overnight.

3. Results and discussion

Experimental Characterization**:** Solid NMR and XRD can confirm the formation of the Pd-^{int}B/C. Low-Mag TEM images illustrated that light element doped Pd NPs with a narrow range of sizes were highly dispersed on the active carbon support. High resolution TEM images of this NPs were obtained and indicated the expansion of d-spacing. The ptychography and EELS were employed simultaneously to ensure the appearance of B in phase image.[10]

4. Conclusions

The structure properties of Pd-^{int}B has been studied by a combined solid NMR, X-ray diffraction and Electron Microscopy techniques. All of techniques illustrate that B atom locates in the interstitial sites. Further catalytic results are processing.

5. References

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