**Highly Active Subnano Pd Clusters Supported on Ferric Hydroxide for CO-Tolerant Hydrogen Oxidation**

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**Introduction**

The finite resources of fossil liquid fuels and its impact on climate change have long been realized. As a result, fuel cells have emerged as alternatives to combustion engines [1]. Proton-exchange membrane fuel cell (PEMFC) has attracted most attention due to its advantageous features. However, a major issue for PEMFC is that a small amount of residual CO in the H2 stream can severely poison the anode. Therefore, development of CO-tolerant anode catalysts is highly desired and has practical applications.

Due to the fact that Pt is not only expensive but also has limited supply searching for alternative anode catalysts is of importance [2]. Palladium, as a member of the Pt-group metal, can adsorb and dissociate H2, and when modified with oxides or alloyed with other metals possesses a better CO-tolerance property. Furthermore, it has been demonstrated that Pd anodes facilitate the oxidation of alcohols with a remarkable electrochemical stability [3]. Therefore, development of a CO-tolerant Pd anode catalyst is attractive and significant. In this work, we studied a novel FeOx supported subnano Pd cluster catalyst which showed an excellent CO-tolerant H2 oxidation activity at a wide temperature range (20 to 120 °C) and was stable at 80 °C.

**Materials and Methods**

The Pd/FeOx catalyst with a 4.8 wt% Pd loading was prepared with a simple co-precipitation method at room temperature and a 5 wt% Pd/C (Vulvan XC-72) was also prepared with a wet-impregnation method as a reference. The CO-tolerant H2 oxidation reaction was conducted in a fixed-bed reactor with 80 mg of catalyst. The fuel stream gas composition was 40 vol% H2 + 1 vol% CO + 1 vol% O2 balanced with helium. The gas flow rate was 25ml/min. The yield of H2O (YH2O) was used to characterize the activity of CO-tolerant H2 oxidation. The maximum YH2O is 100% if all O2 is converted to H2O.

**Results and Discussion**

Figure 1a shows the CO-tolerant H2 oxidation results on 4.8 wt% Pd/FeOx and 5 wt% Pd/C. Clearly, the Pd/FeOx catalyst was more active than the reference Pd/C catalyst and the yield of H2O can reach about 96% in temperature range of 80 – 120 °C, the typical working temperature for PEMFC. Since both catalysts showed similar activity when pure H2 feed was used, Fig. 1a suggests that the Pd/FeOx catalyst is highly tolerant to CO during the H2 oxidation reaction. The higher CO tolerance of the Pd/FeOx catalyst may originate from a weaker CO adsorption on Pd, confirmed by the microcalorimetric measurement. The initial CO adsorption heat on Pd/FeOx is only about 73 KJ/mol while that on Pd/C is about 110 KJ/mol. The in situ FT-IR spectra of CO adsorption on Pd/FeOx (Fig. 1b) shows that linear adsorption of CO on Pd sites, which is much weaker than the bridged or multi-bonded adsorption [4], dominates, resulting in lower CO adsorption heat on the Pd/FeOx catalyst. The high portion of CO linear adsorption on the Pd/FeOx catalyst may be attributed to the presence of subnano or even atomically dispersed Pd clusters [5], as shown in Fig. 2b,c while the Pd/C catalyst contains primarily nanoparticles with 1– 5 nm in diameter (Fig. 2a).

**Significance**

A subnano Pd/FeOx catalyst was developed with high activity and high CO-tolerance for H2 oxidation. The knowledge obtained from this study can be used to develop better and less expensive PEMFC for portable energy applications.

**References**