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Spillover enhanced hydrogen uptake of Pt/Pd doped corncob-derived activated carbon with ultra-high surface area at high pressure

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ABSTRACT

Corncob-derived activated carbon (CAC) was prepared by potassium hydroxide activation. The Pt/Pd-doped CAC samples were prepared by two-step reduction method (ethylene glycol reduction plus hydrogen reduction). The as-obtained samples were characterized by N_2-sorption, TEM and XRD. The results show the texture of CAC is varied after doping Pt/Pd. The Pd particles are easier to grow up than Pt particles on the surface of activated carbon. For containing Pt samples, the pore size distributions are different from original sample and Pd loaded sample. The hydrogen uptake results show excess hydrogen uptake capacity on the Pt/Pd-doped CAC samples are higher than pure CAC at 298 K, which should be attributed to hydrogen spillover effects. The 2.5%Pt and 2.5%Pd hybrid doped CAC sample shows the highest hydrogen uptake capacity (1.65 wt%) at 298 K and 180 bar, The particle size and distribution of Pt/Pd catalysts could play a crucial role on hydrogen uptake by spillover. The total hydrogen storage capacity analysis show that total H_2 storage capacities for all samples are similar, and spillover enhanced H_2 uptakes of metal-doped samples could not well support total H_2 storage capacity. The total pore volume of porous materials also is a key factor to affect total hydrogen storage capacity.

Introduction

Hydrogen is a convenient, safe and versatile second energy that can be easily converted to a desired form of energy without releasing harmful emissions. It will be an energy carrier holding tremendous promise as a new renewable and clean energy option and play an important role in future transportation energy sector as the ideal fuel [1,2]. However, several technical hurdles need to be overcome before the economical application of hydrogen. Hydrogen storage is one of the main difficult technical hurdles, which cuts across both

hydrogen production and hydrogen applications and thus assumes a critical role in realization of hydrogen economy. There are several hydrogen storage ways which are being extensively studied, such as cryogenic storage, compression storage at high pressure and different ways of solid storage: physisorption, chemisorption or chemical compound formation [3].

Compared with other storage ways, physisorption offers the advantages of lightweight, low cost material, rapid sorption kinetics and on-board reversibility. In contrast to chemisorption in metal hydrides, physisorption is essentially accumulation of the hydrogen molecules on the surface of sorption materials, and it employs high surface area sorption materials that can effectively adsorb hydrogen, such as activated carbon. Activated carbon is a good candidate for hydrogen storage because of its low cost, high packing density, ready availability and good chemical stability [4—6]. However, common carbon adsorbents with specific surface area less than approximately 2000 m^2/g still can't achieve the gravimetric and volumetric hydrogen storage requirements. Chemical activation offers one effective approach to obtain activated carbon with ultra-high surface area, which is generally made by mixing carbonaceous materials with chemical activating agents (KOH, H$_3$PO$_4$, ZnCl$_2$, etc.), followed by the carbonization at 873—1173 K. Among various chemical reagents, KOH is widely used since it can result in activated carbons (ACs) with defined micropore size distribution, and a very high special surface area (SSA) up to 3000 m^2/g. Thus, KOH activation is considered as one of the effective ways to prepare activated carbons with high SSA [7]. Since the first claim of hydrogen storage properties in carbon nanotubes by Dillon et al. [8], there have been great progresses in preparation of porous carbon materials with high surface areas. However, it has been recognized that the hydrogen storage capacity of carbon-based adsorbents is less than 1 wt% under ambient temperature and even10 MPa for physisorption, which does not meeting the goals of the U.S. Department of Energy (i.e. 5.5%) [9].

Some investigations indicate that the hydrogen uptake property of carbon-based porous materials can be enhanced at ambient temperature via enhancing specific surface area, optimizing pore size [10], and transition metal doping (e.g. Pt, Pd, Ni etc) by spillover effect. The hydrogen spillover phenomenon has been well known in heterogeneous catalysis [11—13], but it has only recently been investigated as hydrogen storage mechanism [14]. Briefly, for hydrogen storage by spillover at ambient temperature, molecular hydrogen is dissociated into atomic hydrogen on the surface of metal particles, and subsequently migrates to the carbon surface, then surface diffuse and adsorbed in pores of carbon. In the previous studies, Carbon nanotubes, carbon fibers and activated carbons were used as carbon supports [15—17], and platinum, palladium, nickel or ruthenium were studied as doping metal catalysts for hydrogen spillover application [18—21]. According to previous results, the hydrogen uptake capacity of metal doped porous materials is not only relative with the texture of porous materials at ambient temperature, but also depends on doped metal type. Both platinum and palladium were considered as the most effective catalysts for hydrogen spillover. In addition, in the most reports, the

hydrogen uptake tests based on hydrogen spillover enhanced effect were performed below 5 MPa. For low-temperature hydrogen uptake, the testing pressure of 5 MPa could be enough. As we know, however, the hydrogen uptake capacity of porous materials was closely relative with testing pressure at ambient temperature. To improve the testing pressure is useful for investigation on hydrogen spillover enhanced hydrogen uptake.

In this work, the Pt/Pd catalysts were deposited on the corncob-derived activated carbon (CAC) with ultrahigh surface area by two-step reduction method. The detailed microstructure of Pt/Pd-loaded CAC samples was not only carefully characterized, but also whose hydrogen uptake performance was investigated at higher testing pressure and ambient temperature.

Experimental

Material synthesis

Activated carbon samples were prepared by the chemical activation of corncob derived char with KOH. Detailed procedures are described in the previous report [22]. After carbonization of corncob powders with typical size of less than 830 μm, the carbonized powders were further ground into small particles with size of less than 25 μm through ball milling, and suspended in KOH saturated solution and magnetically stirred for 2 h at room temperature followed by drying under vacuum at 393 K overnight to evaporate most of the water adsorbed on the sample. Finally, the impregnated mixture was transferred to a furnace and activated for 3 h at the heating rate 5 K/min and 1123 K under flowing nitrogen. The final products were washed with deionized water until the pH value reached about 7.0 and then dried at 383 K under vacuum. The as-prepared product was hereafter designated as CAC.

The Pt/Pd-doped CAC samples were prepared by two-step reduction method. As an example of Pt/Pd-doped CAC, firstly, CAC and H$_2$PtCl$_6$ or PdCl$_2$ were individually dispersed in ethylene glycol (EG). After the H$_2$PtCl$_6$ or PdCl$_2$ and EG mixture were dried at 343 K for 2 h, the mixtures were individually slowly dropped into the CAC-EG mixture by creeping pump under stirring. This mixture was ultrasonicated and stirred for 2 h. The 2 M NaOH solution was added into this mixed solution to acquired pH value about 12, and the mixture was stirred and refluxed at a temperature of 403 K for 4 h, then cooled to room temperature. The resultant powders were filtered, washed, and then dried in a vacuum oven. Finally, the as-obtained samples were reduced by H$_2$ at 523 K for 2 h in a tube furnace under flowing H$_2$. According to the above procedures 5 wt%Pt, 10 wt%Pt, 5 wt%Pd and the mixture of 2.5 wt%Pt and 2.5 wt%Pd were respectively doped onto corncob-derived activated carbon. They are denoted as 5Pt/CAC, 10Pt/CAC, 5Pd/CAC and 2.5Pt2.5Pd/CAC, respectively.

Material characterization and analysis methods

The textual properties of the samples were studied by N$_2$-sorption at 77 K with automatic instrument (ASAP2020,