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Nitrogen-doped porous carbons with high performance for hydrogen storage

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ABSTRACT

Hydrothermally carbonized chitosan has been successfully used as a carbon source for the preparation of highly porous carbons via chemical activation. The porous carbons with different nitrogen contents (0.56–6.53 wt%) have high surface area (1362–3009 m² g⁻¹) and large pore volume (0.670–1.497 cm³ g⁻¹). These properties can be varied from modifying the activation parameters (*i.e.*, amount of activation agent and activation temperature). We observed hydrogen storage capacity of up to 2.71 wt% at 77 K and 1 bar, and 6.77 wt% at 20 bar, for PC-2-800 porous carbons. This result indicates that the hydrogen uptake of porous carbons mainly depends on the high micropore surface area related to optimum pore size. Furthermore, one found that high N-doping is beneficial for hydrogen storage at low pressure but it is detrimental at high pressure according to the analysis of hydrogen uptake isotherms.

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Introduction

To meet the increasing energy demands of the world, high-performance energy storage systems have been extensively investigated for recent decades. Hydrogen storage is one of the

most important technologies in energy storage. Recently, abundant researches on porous materials, including carbon materials [1–4], zeolite [5,6], metal-organic frameworks (MOFs) [7–9], and covalent organic frameworks (COFs) [10,11] have been widely investigated. Among them, carbon materials as a candidate for hydrogen storage have been

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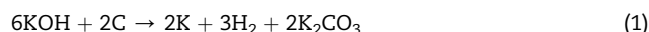
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extensively studied due to their high surface area, well-developed pore structure, low cost, low mass density, and good chemical stability. In generally, high surface area and large micropore volume are essential for enhancing the hydrogen uptake [12,13]. In this respect, template carbonization was applied to prepare porous carbons with tunable porous structure for hydrogen storage. It has been demonstrated that zeolites are appropriate templates to fabricate microporous carbons with uniform micropores (<1 nm) [14]. Hydrogen test exhibited that zeolite-template carbons had a hydrogen uptake of 5.4 wt% at 77 K and 20 bar. However, the template technology is costly and requires complicated processes, which impedes its industrial applications. On the other hand, carbide-derived carbons (CDCs) with well-developed pore structure have been considered as effective hydrogen adsorption materials [15–18]. A maximum hydrogen storage capacity of ca. 4.4 wt% (at 77 K and 60 bar) has been reported for this type of CDCs [19]. However, the surface area and micropore volume of the CDCs are smaller than that of the zeolite-templated carbons, which limited their application in hydrogen storage.

It is noteworthy that chemical activation of carbonaceous precursors (i.e., coal, batch, biomass-derived product, etc) improves a feasible route to fabricate porous carbons with high surface area and large micropore volume [20]. In general, there were several chemical agents, such as KOH, ZnCl₂, H₃PO₄, for the preparation of porous carbons [21,22]. Among them, porous carbons prepared using KOH as activation agent exhibit attractive properties. The prominent reaction of KOH activation as follows [23]:



The carbon matrix is etched to generate pores due to the redox reaction between potassium hydroxide and carbons to release volatiles. Furthermore, the production of CO₂ from the decomposition of K₂CO₃ at activation temperature greater than 700 °C results in opening up closed pores and enlarging further porosity [24]. According to these reasons, the preparation of porous carbons via KOH activation for hydrogen storage has been extensively investigated. However, only moderate hydrogen storage capacity (3.3–6.2 wt% at 77 K and 20 bar) has been achieved for KOH activated porous carbons [25–28]. Therefore, the synthesis of highly porous carbons with large hydrogen uptake remains an important challenge.

Several studies show that cryogenic hydrogen storage capacity of porous materials mainly depend on surface area, pore volume, and pore size, specially rely on narrow micropores (<0.7 nm) [29]. Therefore, in order to improve the hydrogen storage capacity, carbon materials with high surface area and narrow micropores are required. However, there are only few experimental studies on the effect of the hetero atoms within the carbon frameworks on hydrogen storage performance. Several theoretical studies demonstrated the changes in hydrogen uptakes of porous carbons due to nitrogen incorporation into carbon [30,31]. Therefore, it is of importance to experimentally investigate the effect of nitrogen doping on the hydrogen storage capacity of carbons. In order to explore the relationship among porosity, nitrogen

species and hydrogen storage, we select chitosan as a candidate for preparing the highly porous carbons with different nitrogen contents. Hydrothermally carbonized chitosan was subjected to chemical activation with KOH. The textural and chemical characteristics of the porous carbons were controlled by modifying the amount of activation agent (KOH/HC ratio) and the activation temperature. The work focuses not only on the impact of pore structure on the hydrogen uptake but also on the relationship between the N-doping of the carbons and their hydrogen storage capacity.

Experimental

Samples synthesis

Highly porous carbons were prepared through chemical activation with hydrochar materials. In a typical synthesis, 3.0 g chitosan and 18.0 g deionized water were mixed and sealed into a steel vial inside a PTFE inlets autoclave, followed by hydrothermal treatment at 220 °C for 12 h. The formed black solid powder was separated by filtration and washed with abundant distilled water and dried, which was denoted as HC. The powder was activated with KOH (KOH/HC at a weight ratio of 2 or 4) under Ar up to a temperature in the 600–800 °C range (heating rate: 3 °C/min, holding time: 1 h). The samples were washed two times with HCl (10 wt%) to remove inorganic salts and then thoroughly washed with distilled water until neutral pH and dried in an oven at 105 °C. The carbon materials are denoted as PC-x-y, where x is the weight ratio of KOH/HC and y is the activation temperature in °C. For the purpose of comparison, porous carbons (PC) without any nitrogen groups were prepared via the same method, which has a similar porous structure with the sample PC-2-600.

Characterization

The morphology and structure of porous carbon was examined by using scanning electron microscopy (SEM, JSM-6360LV, JEOL Ltd., Japan) and high resolution transmission electron microscopy (HRTEM, TecnaiG2 F20 S-Twin). Nitrogen sorption isotherms and textural properties of the porous carbons were determined at 77 K using N₂ in a conventional volumetric technique by a Quantachrome Autosorb-1 sorptometer. Before analysis, the samples were evacuated for 12 h at 250 °C under vacuum. The surface area was calculated using BET method based on adsorption data in the relative pressure of 0.01–0.2, and total pore volume was determined from the amount of nitrogen adsorbed at the highest relative pressure (ca. 0.995). The micropore surface area and the micropore volume were obtained via t-plot analysis. The pore size distributions (PSDs) were determined via a non-local density functional theory (NLDFT) method using a slit pore model with nitrogen adsorption data. Elemental analysis was obtained on a Vario III elemental analyzer.

Hydrogen storage

The low hydrogen sorption isotherms (1 bar) of the carbons was measured by a volumetric method with a Quantachrome

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