



Characterization of hydrogen adsorption in platinum-doped microporous carbon with varied catalytic properties

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ABSTRACT

The effect of the catalytic property of platinum (Pt) on the hydrogen adsorption of activated carbon (AC) via spillover was investigated. The catalytic effect on the hydrogen adsorption via spillover was clearly identified from both adsorption isotherms and adsorption kinetics. Factors, including Pt particle size, Pt loading content and AC nature, in the platinum-doped activated carbon (Pt/AC) were considered in this study. The hydrogen adsorption experiments were performed using a volumetric apparatus at room temperature (RT) and low pressure (~ 0.1 MPa). In this study, enhancement factors of 16–145% due to spillover were obtained for the Pt/AC samples because of the difference in the textural properties of AC receptors. The adsorption rate of spilt-over hydrogen is strongly dominated by the Pt surface sites as functions of both crystallite size and deposition type (with or without aggregation). When the Pt surface sites amounted to below 0.011 mmol/g, an insignificant spillover effect was observed in the hydrogen adsorption of Pt/AC.

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1. Introduction

High surface area and light weight structural properties are fundamental elements when choosing possible hydrogen carriers. Activated carbon is well known as one of the best adsorbents for gas storing because of its high microporous structure. In fact, the hydrogen storage capacities of carbon-based material at room temperature (RT) are not capable of meeting the Department of Energy's (DOE) target. Many investigations [1–3] have shown the hydrogen storage capacity in carbon-based materials at RT and 10 MPa is less than 1 wt.% for physisorption, strongly depending on the microporosity. Hydrogen spillover has recently been studied for increasing the hydrogen storage in carbonaceous materials at RT conditions. Hydrogen spillover is described as hydrogen molecule dissociation over the metal catalyst, followed by migration of H atoms to the support, diffusion of H atoms on the support and/or adsorption on the receptor sites.

Increasing hydrogen uptake by spillover in porous materials including nanostructured carbons, zeolites and metal–organic frameworks, has been developed in many papers [4–9]. The hydrogen uptake in different materials has been reported to increase via the spillover effect by a factor of 1.5–8 [4–9]. In fact, significant enhancement in hydrogen uptake via the spillover effect is domi-

nated by many factors involving catalytic properties [10,11], the nature of the receptor [12,13], and contact between the metal particle and the receptor [14]. In previous papers [15–17], the wide ranges of metal loading (5–45 wt.%) were considered in an attempt to obtain the maximum hydrogen adsorption via spillover. Nevertheless, a large proportion of the increase in hydrogen adsorption was contributed by the hydrogen adsorption/absorption on metal [18]. Furthermore, the catalyst size might play a critical role in hydrogen adsorption by spillover. Tsao et al. [10] claimed that Pt nanoparticles of ~ 1 nm remarkably increased the hydrogen storage capacity via spillover. Similar result was also demonstrated by Stuckert et al. [6].

For measurement, the standard volumetric system (Sievert's apparatus) has been favorably used to estimate hydrogen storage ability in materials. Furthermore, several factors involving sample weight, system volume [19] and Z value calculation [20] significantly affected the accuracy in measuring small changes of hydrogen uptake via spillover, especially high pressure conditions. In order to sensitize detecting the behavior of hydrogen adsorption by spillover, low pressure conditions (< 0.1 MPa) were favorably considered due to the unit scale. In this study, the hydrogen isotherms of the platinum-doped activated carbon (Pt/AC) were obtained using a volumetric apparatus at RT and low pressure (~ 0.1 MPa). Two synthesis methods were used to prepare the Pt/AC samples with varied catalytic properties. The catalytic properties effect was clearly measured in the hydrogen uptake via spillover in Pt/AC.

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2. Experimental

2.1. Material preparations

Three types of activated carbon (AC) receptors were used in this study: AC1 (obtained from Cape Technologies); AC2 (MAXSORB, obtained from Kansai Coke & Chemicals Company Ltd.); and AC3 (obtained from the China Steel Chemical Corporation). Prior to Pt loading, all AC samples were fully dried at 378 K in a vacuum overnight to eliminate adsorbed moisture. Two methods, including the incipient wetness impregnation and the chemical reduction method, were employed in the preparation of the Pt/AC samples. The incipient wetness impregnation procedure was similar to that reported in previous papers [7]. For incipient wetness impregnation, in order to produce different types of Pt dispersion, the synthesis parameters were adjusted in the Pt/AC preparation (e.g. Pt loading content, impregnation concentration and AC/solvent ratio).

The AC was dispersed in an acetone solution with ultrasonication (150 W, 43 kHz) for 1 h. The as-prepared acetone solution, consisting of H₂PtCl₆ (weight ratios (g/g) of Pt and AC of 0.03 and 0.06, respectively), was slowly dropped into the stirred AC solution and then magnetically stirred under RT conditions for 24 h. Finally, the Pt/AC samples were obtained by drying at 333 K overnight to remove the acetone.

In order to increase Pt anchoring and dispersion, the functionalization of an AC surface was considered. In this study, the AC acceptor was treated with a solution of HNO₃/H₂SO₄ to create oxygen functional groups (denoted as AC-ox). The Pt/AC-ox sample was prepared by the chemical reduction procedure. Briefly, the AC-ox samples were dispersed in an ethylene glycol (EG) solution with ultrasonication for 30 min. The EG solution, consisting of H₂PtCl₆ (the weight ratio (g/g) of Pt/AC is 0.05) and a little NaHSO₃, was slowly dropped into the above solution under a strong stirring condition. Then, a 4 N NaOH solution was added to the precursor solution, adjusting the pH value of solution. The chemical reduction was carried out at 375 K for 2 h. The Pt/AC-ox products were filtered and washed with deionized water.

2.2. Characterization

The Pt metal species on the AC surface was characterized by an X-ray diffraction analyzer with Cu K α source (XRD, Bruker-D8-ADVANCE). XRD experiments were operated at 40 kV, 40 mA, over 10–60° with a constant scan rate (5 s/step). The mean crystallite size of the Pt nanoparticles was calculated by the Scherrer equation [21]:

$$D = \frac{K\lambda}{FWHM \cos \theta} \quad (1)$$

where $\lambda = 0.15406$ nm is the wavelength, D is the mean crystallite size, $K = 0.9$ is the Scherrer constant, and $FWHM$ is the full width at half maximum.

The nitrogen isotherms of Pt/AC and AC samples were measured at 77 K (Micromeritics ASAP 2020 instruments). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The total pore volume (V_{total}) was estimated from the adsorbed amount of nitrogen at relative pressure ($P/P_0 = 0.995$). The micropore volume ($V_{\text{micro-DR}}$) was calculated by application of the Dubinin–Radushkevich equation at the pressure range ($P/P_0 = 10^{-2}$ – 10^{-5}). Moreover, the mesopore volume (V_{meso}) was obtained from the difference between the total pore volume and the micropore volume. An inductively coupled plasma optical emission spectrometer (ICP-OES) was employed to determine the amount of Pt loading of Pt/AC.

2.3. Hydrogen adsorption experiments

Hydrogen adsorption isotherms were determined by a standard static volumetric apparatus at RT and low pressure (<0.1 MPa). The temperature was around 303 K \pm 1 K. Approximately 500 mg of sample were used in the experiments. Each equilibrium point was performed for over 1 h in order to observe the spillover effect. The hydrogen adsorbed amount of chemisorption on the Pt surface was obtained by the extrapolation to zero pressure from the linear adsorption isotherm at a pressure range of 0.01–0.08 MPa. The H/Pt value was expressed as:

$$\frac{H}{Pt} = \frac{Pt_s}{Pt_T} = \frac{Q_H}{W_{Pt}} \times \frac{M_{Pt}}{M_H} \quad (2)$$

where Pt_s is surface atoms of Pt particle, Pt_T is total atoms of Pt particle, Q_H is H₂ chemisorption capacity on the Pt (wt.%), W_{Pt} is Pt content in the Pt/AC (wt.%), M_{Pt} and M_H are the molecule weight of Pt and H, respectively.

Prior to measurement, the Pt/AC sample by wetness impregnation preparation was reduced to 573 K for 2 h in a hydrogen flow and then degassed at the same temperature for 5 h in a vacuum. Moreover, the Pt/AC-ox sample by chemical reduction preparation was degassed at 473 K in a vacuum for 5 h, and then activated at 423 K for 1 h in a hydrogen flow.

3. Results and discussion

3.1. Material characterization

The textural properties and the Pt catalytic properties of the Pt/AC samples were collected, as shown in Tables 1 and 2,

Table 1
Textural properties of Pt/AC samples.

Sample	BET area (m ² /g)	V_{total} (cm ³ /g)	$V_{\text{micro-DR}}$ (cm ³ /g)	V_{meso} (cm ³ /g) ^a
AC1	1836.3	0.95	0.67	0.29
Pt1/AC1	1360.0	0.70	0.48	0.22
Pt2/AC1	1640.7	0.85	0.59	0.26
Pt3/AC1	1521.4	0.78	0.54	0.24
AC2	3328.3	1.72	1.20	0.52
Pt1/AC2	3002.9	1.55	1.10	0.45
AC3	2977.9	1.46	1.09	0.37
Pt1/AC3	2444.1	1.19	0.88	0.31
AC1-ox	1003.1	0.52	0.35	0.17

Table 2
Metal characteristics of Pt/AC samples.

Sample	Pt loading (wt.%)	Surface sites of Pt (mmol/g) ^a	H/Pt _{measured} ^a	H/Pt _{calculated} ^b	d (nm) ^d	d_{XRD} (nm) ^e
Pt1/AC1	4.47	0.064	0.27	0.28	4.05	3.68
Pt2/AC1	1.81	0.032	0.34	0.23	3.19	4.50
Pt3/AC1	2.01	0.011	0.10	0.17	10.32	5.92
Pt1/AC2	3.69	0.056	0.29	0.24	3.79	4.29
Pt1/AC3	4.20	0.030	0.13	0.21	8.09	4.67
Pt2/AC3	3.91	0.099	0.47	0.33	2.27	3.04
Pt1/AC1-ox	0.79	~0.041 ^c	1.70	–	0.63	N.D.

^a The value was measured by hydrogen adsorption experiments.

^b The value was calculated by Freil's approach [22].

^c The value was approximative, due to the H/Pt_{measured} value >1.

^d Calculated from $d = 1.08/D$, D : dispersion (H/Pt) [26].

^e Calculated by Scherrer's equation [21].

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