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Research Note

Increased hydrogen spillover by gaseous impurity: The Benson–Boudart method for dispersion revisited

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ABSTRACT

A new bridge-building technique was used for facilitating H spillover on metal doped adsorbents for hydrogen storage at room temperature. By preadsorbing 1.0×10^{-3} atm of CH_4 on Pt/AX-21 (superactivated carbon), the adsorbed amount of hydrogen increased by ∼100% at 1 atm and 25 °C, attributed to the adsorbed CH_4 serving as bridges for spillover. We conclude that the Benson–Boudart method can provide a good assessment for the dispersion of metals supported on Al_2O_3 (and zeolites). For carbon and SiO_2 supports, even with pure H_2, spillover leads to overestimates of dispersion, and any small amounts of gaseous impurities could lead to much greater overestimates.

1. Introduction

The adsorption of hydrogen on nanostructured carbon materials has been studied for more than a decade [1]. Beginning with the discovery of the interesting behavior of the interaction between hydrogen and single-walled carbon nanotubes [2], carbons have been viewed as a potential solution for on-board hydrogen storage in vehicular applications [3–5]. More recently, our group has focused on using the phenomenon of hydrogen spillover to develop sorbents for ambient temperature storage [6–10]. The phenomenon of hydrogen spillover has been known for more than 4 decades [11–15]. In particular, enhanced spillover has been achieved by adsorbing a number of hydrocarbons, such as perylene and acetone, as well as undefined contamination and H_2O, which serve as bridges for spillover [13,16–18]. A simple technique has been developed involving the mixing a small amount of sugar (with the sorbent along with an H_2 dissociation catalyst) and then carbonizing the sugar into carbon bridges, which resulted in significant enhancement of spillover [9,10,19].

The Benson–Boudart method [20] has been widely used for determining the dispersion of supported metal catalysts. This method was developed when hydrogen isotherm of metal-doped support were observed to be parallel to the hydrogen isotherm of the support. This observation led to the conclusion that the difference between the two isotherms was due to monolayer coverage of H on the supported metal, and the surface of the metal becomes saturated instantaneously with exposure to hydrogen. Thus, the metal dispersion can be obtained by the amount adsorbed through extrapolation of the isotherm to zero pressure.

Here we report the significant increase in spillover by adsorbing an impurity that is commonly found in H_2 such as CH_4. Clearly, the adsorbed CH_4 molecules serve as bridges for hydrogen spillover. The results also illustrate the significant errors that can result from using the Benson–Boudart method when spillover occurs, particularly when enhanced by gas impurities.

2. Experimental

2.1. Preparation of adsorbents

All of the adsorbents used in this work were prepared by impregnating a support with chloroplatinic acid (H_2PtCl_6) (Aldrich, 99.9%).

2.1.1. Pt/AX-21

A 6.0 wt% Pt/AX-21 sample was prepared by impregnating H_2PtCl_6 on AX-21 superactivated carbon. Before doping, the AX-21 (Anderson Development Co.) was dried by degassing *in vacuo* at 120 °C for 12 h. Then 0.20 g of AX-21 was dispersed in 20 mL of acetone and was stirred for 0.5 h at room temperature. Following this, 2.0 mL of acetone solution containing 0.026 g of H_2PtCl_6 was slowly added to the above solution under vigorous stirring for 10 min, and then subjected to ultrasonication at room temperature for 1 h. The sample was then agitated at room temperature for 24 h. After being dried in an oven at 60 °C overnight to evaporate most of the acetone solvent, the impregnated AX-21 sample

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Table 1
Physical properties of different adsorbents.

Adsorbent	Pt loading (wt%)	BET surface (m^2/g)
AX-21	–	2880
Pt/AX-21	6.0	2521
SiO_2	–	552
Pt/SiO_2	1.0	550
Al_2O_3	–	148
Pt/Al_2O_3	1.0	147

was dried further in nitrogen flow at 120 °C for 2 h. Then the nitrogen flow was switched to H_2, and the temperature was raised to 300 °C and held there for 2 h. After being cooled to room temperature in H_2, the sample was purged with flowing nitrogen and then stored under nitrogen atmosphere before further measurement [10].

2.1.2. Pt/Al_2O_3

A 1.0 wt% Pt/γ-Al_2O_3 sample was prepared by impregnating 1.0 g of γ-Al_2O_3 (Sasol North America Inc.) that was calcined in air at 595 °C for 4 h with 0.024 g of H_2PtCl_6 in an aqueous solution. The sample thus prepared was dried at 120 °C for 4 h, calcined in air at 450 °C for 3 h, reduced in hydrogen at 40 mL/min at 260 °C for 1 h and at 510 °C for 4 h, and then exposed to air [20].

2.1.3. Pt/SiO_2

SiO_2 was prepared by mixing 2 vol parts of H_2O at pH 2 (adding HCl) and 1 vol part of tetraethyl orthosilicate (TEOS) for 5 h at room temperature [21]. The resulting mixture was titrated under stirring to pH 6 with a NH_4OH solution of pH 9.5. After 16 h of gelation, the gel was dried at 130 °C for 72 h and calcined at 250 and 550 °C for, respectively, 3 and 16 h. The cake thus obtained was crushed. The 1.0 wt% Pt/SiO_2 was prepared by the same procedure as that for the preparation of 1.0 wt% Pt/Al_2O_3.

2.2. Adsorbent characterization

The BET surface areas of the samples were measured by physical adsorption of N_2 at −196 °C using a Micromeritics ASAP 2020. The results are given in Table 1.

2.3. Adsorption isotherm measurements

All isotherms were measured at 25 °C. The effect of CH_4 was measured by presorption (i.e., CH_4 was introduced before H_2). Low-pressure H_2 isotherms (0–1 atm) were measured with a standard static volumetric technique using a Micromeritics ASAP 2020. In each measurement, the sorbent was first equilibrated with CH_4 at a predetermined pressure. The adsorption gas was switched to pure H_2. Before switching, the valve connecting the sample tube and piping was closed, and then the piping containing CH_4 were evacuated and purged with H_2 twice. Hydrogen adsorption at pressures >1.0 atm and up to 100 atm was measured using a static volumetric technique with a specially designed Sievert apparatus. Before each measurement, the sample was degassed at 350 °C for at least 12 h [8]. Ultra-high-purity hydrogen (99.999%) and methane (99.97%) were used. The amounts of C_2, CO_2, N_2, H_2O, O_2, C_3 (in descending concentration), and others was <10 ppm.

3. Results and discussion

The BET surface areas of different supports and Pt-doped adsorbents are given in Table 1. The BET surface areas decreased somewhat after metal doping, depending on the amount of the supported metal.

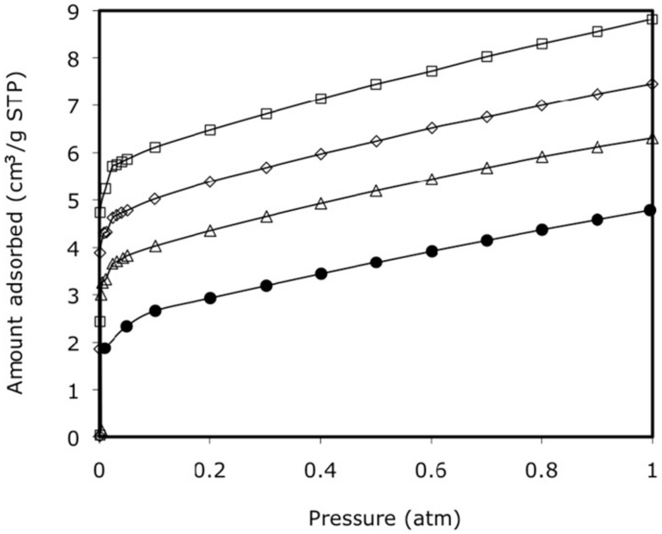

Fig. 1. Adsorption isotherm of H_2 on Pt/AX-21 at 298 K with presorbed CH_4 at $P(CH_4) = 0$ (●), 5.0×10^{-4} (◇), 1.2×10^{-3} (□) and 3.4×10^{-3} atm (△). The 3 presorbed CH_4 points fall essentially on the origin due to the large Y-axis scale.

Table 2
Results of CH_4 and H_2 adsorption on Pt/AX-21.

Initial pressure of CH_4 (atm)	Saturation amount of		Chemisorption amount of H_2 (cm^3/g, STP)[c]	Platinum dispersion (%)
	CH_4 (cm^3/g, STP)[a]	H_2 (cm^3/g, STP)[b]		
0	–	4.78	2.52	73
5.0×10^{-4}	1.5×10^{-2}	7.45	4.92	143
1.2×10^{-3}	3.7×10^{-2}	8.81	5.93	173
3.4×10^{-3}	15×10^{-2}	6.03	3.92	114

[a] The saturation amount of CH_4 was obtained at the corresponding initial equilibrium pressure of CH_4.

[b] The saturation amount of H_2 was obtained at 1.0 atm of H_2.

[c] The chemisorption amounts of H_2 adsorption was obtained at the equilibrium pressure of H_2 extrapolated to zero.

To investigate the effect of methane molecules on the spillover of hydrogen from the Pt surface to the AX-21 carbon surface, CH_4 was presorbed at predetermined pressures before H_2 isotherms were measured, as described earlier. The results are given in Fig. 1 and Table 2. Fig. 1 shows the effect of methane on hydrogen adsorption. The adsorption capacity of H_2 on Pt/AX-21 varied with the initial pressure of methane. Presorbing with methane in the range of 5.0×10^{-4} to 3.4×10^{-3} atm resulted in significantly increased H_2 adsorption. From Fig. 1 and Table 2, it can be seen that the spillover-adsorption amount of H_2 reached the highest value at an initial pressure of methane of 1.2×10^{-3} atm. At 1.2×10^{-3} atm of methane, the equilibrium adsorption amount of H_2 at 1 atm increased from 4.78 cm^3/g STP to 8.81 cm^3/g STP (i.e., nearly doubled) without methane.

There is considerable evidence showing that surface diffusion of H atoms from the metal to the support and between the support particles or domains are the rate-determining steps [22,23]. The results, shown in Fig. 1, provide strong evidence that the adsorbed CH_4 molecules play the role of a stepping-stone or bridge for spillover between Pt and AX-21, as well as between different domains/grains of carbon within a particle.

To obtain the "monolayer volume" of adsorbed hydrogen, fitting using the Langmuir isotherm has been suggested [24,25]. But our results could not be fitted by the Langmuir equation (see Figs. 1 and 2). Therefore, the original extrapolation method (to zero pressure) suggested by Benson and Boudart [20] was applied, and the last 9 points of every isotherm (see Figs. 1 and 2) were

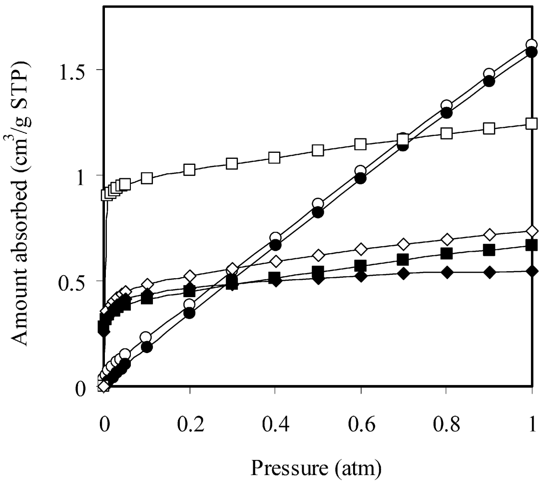

Fig. 2. Adsorption isotherm of H_2 on AX-21 (●, ○), Pt/SiO_2 (■, □) and Pt/γ-Al_2O_3 (◆, ◇) at 298 K with presorbed CH_4 at $P(CH_4) = 0$ (filled symbols) and $\sim 1.0 \times 10^{-3}$ atm (empty symbols).

Table 3
Results of CH_4 and H_2 adsorption on different adsorbents.

Adsorbent	Initial pressure of CH_4 (atm)	Saturation amount of CH_4 (cm^3/g, STP)	Chemisorption amount of H_2 (cm^3/g, STP)[a]	Platinum dispersion (%)
AX-21	–	–	0.04	–
	1.1×10^{-3}	3.7×10^{-2}	0.05	–
Pt/SiO_2	–	–	0.40	69
	1.2×10^{-3}	1.8×10^{-3}	0.96	168
Pt/Al_2O_3	–	–	0.45	80
	1.2×10^{-3}	8.0×10^{-4}	0.49	84

[a] The chemisorption amounts of H_2 adsorption on adsorbents at the equilibrium pressure extrapolated at zero.

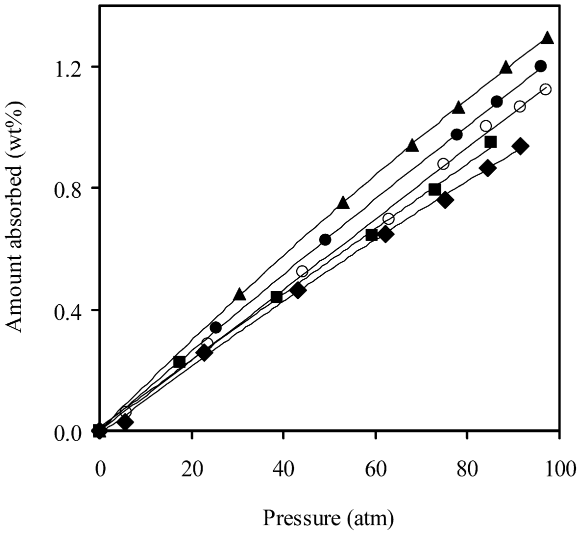

Fig. 3. Adsorption isotherm of H_2 on Pt/AX-21 at 298 K with presorbed CH_4 at $P(CH_4) = 0$ (○), 1.0×10^{-3} (●), 5.0×10^{-3} (▲), 1.0×10^{-2} (■), and 0.1 atm (◆).

used to plot the trendline. On every trendline, the R^2 value was >0.99, which indicated good fitting. From the adsorbed amount of hydrogen extrapolated to zero pressure, the dispersion of Pt metal on AX-21 could be calculated according to the method of Benson–Boudart [20]. The adsorption of pure hydrogen on AX-21 occurred through physical adsorption, because the adsorption capacity at zero pressure, determined by extrapolating the isotherm, was ~ 0 cm^3/g STP (see Fig. 2). The chemisorption amount at zero pressure on Pt/AX-21 was 2.52 cm^3 STP/g (see Fig. 1 and Table 2). Using the assumption of 1 H per surface Pt atom, the dispersion using pure H_2 was 73% [26]. But the dispersion exceeded 100% when H_2 contained a small amount of CH_4 (see Table 2). At 1.2×10^{-3} atm of CH_4, the dispersion reached 173% because of the enhanced spillover over CH_4 bridges. Likewise, the dispersion reached 143% at an initial pressure of methane of 5.0×10^{-4} and 114% at an initial pressure of methane of 3.4×10^{-3} atm. At still higher pressures of CH_4, competitive adsorption between H and CH_4 occurred, that is, competition for the most energetic sites, as is the case in all binary mixture adsorption. Such was the case for CH_4 at a pressure of 3.4×10^{-3} atm. For the pure AX-21, no hydrogen spillover or promotion effect of CH_4 on hydrogen adsorption was found (see Fig. 2).

High-resolution TEM images of the Pt/AX-21 sample showed that the metal particle sizes were approximately 2–3 nm, which translated to dispersions of approximately <50%, lower than the 73% estimated by the Benson–Boudart method.

The kinetics of spillover on Pt/AX-21 carbon was studied previously [10]. Spillover was found to be a fast process at temperatures as low as 25 °C and was essentially completed in 1 sec. Thus, when using the Benson–Boudart method, the spillover amounts also are included, which can lead to large errors, even without the adsorbed CH_4 bridges.

To investigate the effects of CH_4 on hydrogen adsorption on different supports, isotherms of H_2 on Pt/SiO_2 or Pt/Al_2O_3 were measured with $\sim 1.0 \times 10^{-3}$ atm of CH_4 presorption. The results, given in Fig. 2 and Table 3, show that the adsorption capacity of hydrogen on Pt/SiO_2 was enhanced substantially by adsorbed CH_4. The Benson–Boudart dispersion of Pt on Pt/SiO_2 was 69% based on the adsorption of pure hydrogen and 168% as obtained from the adsorption of hydrogen with presorption of CH_4. For the adsorption of H_2 on Pt/Al_2O_3, the CH_4 molecules showed no clear effect on the adsorption of hydrogen (see Fig. 2 and Table 3).

The rates of spillover on SiO_2 and Al_2O_3 have been studied by various groups [22,27,28]. The rates were characterized by surface diffusivities (SDs), which were approximately 9×10^{-15} cm^2/s at 400 °C for spillover on Al_2O_3 [28] and were in the range of $1 \times 10^{-3} - 1 \times 10^{-5}$ cm^2/s at 140–200 °C for spillover on SiO_2 [22]. Thus, spillover was much faster on SiO_2 than on Al_2O_3, and it did not proceed on Al_2O_3 at near ambient temperature. This explains the result shown in Fig. 2. Zeolites also are used as catalyst supports. Although not included in this study, the spillover rates on zeolites have been reported previously [22]. The spillover rates on zeolites were similar to those on Al_2O_3. Thus, it is reasonable to conclude that H spillover does not proceed readily on zeolites at 25 °C.

We can safely conclude that the Benson–Boudart method would give a good assessment for the dispersion of metals supported on Al_2O_3 (and zeolites). For carbon and SiO_2 supports, even with pure H_2, spillover would lead to overestimates, and the presence of gaseous impurities would lead to much larger overestimates.

For our interest in H_2 storage, high-pressure isotherms also were measured. The results, given in Fig. 3, show that the capacity of pure hydrogen on Pt/AX-21 was 1.20 wt% at 25 °C and 100 atm, which was the same as we reported in previous work [10]. The effect of methane on H_2 storage at high pressures was similar to that at <1 atm. The greatest H_2 storage on Pt/AX-21 occurred at 5.0×10^{-3} atm of the initial CH_4 pressure. Increasing or decreasing the initial pressure of methane decreased hydrogen adsorption. When the pressure of methane was at 5.0×10^{-3} atm, H_2 storage reached 1.38 wt%, $\sim$15% higher than that of pure H_2 adsorption. Taking the area per surface carbon atom as 8.2 Å^2, 0.21 H atom was adsorbed per C atom at 100 atm without CH_4 impurities. By preadsorbing CH_4, the density increased to 0.24 H/C.

Finally, we discuss the possible effects or roles of dissociated CH_4 species on Pt. At 300 K, at 1 Torr, CH_4 can dissociate on Pt(111) to form CH_3, C, and H [29]. The dissociation probability over 60 s was 1×10^{-8}. The time for the first data point shown in Fig. 1 (at the high "knee" point) was <1 h. Thus, the dissociation probability for the case with 1.2×10^{-3} atm CH_4 was $\sim 6 \times 10^{-7}$. In other words, only a negligible amount of CH_4 molecules were dissociated into CH_3, C, and H atoms on Pt. In contrast, the amount of adsorbed CH_4 molecules on the carbon surfaces was significant. Thus, the role of bridges most likely was played by adsorbed CH_4 on carbon. The role of the dissociated species on spillover merits further investigation, however.

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References

[1] J.S. Noh, R.K. Agarwal, J.A. Schwarz, Int. J. Hydrogen Energy 12 (1987) 693.
[2] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[3] C.K. Back, G. Sandí, J. Prakash, J. Hranisavljevic, J. Phys. Chem. B 110 (2006) 16225.
[4] H.S. Kim, H. Lee, K.S. Han, J.H. Kim, M.S. Song, M.S. Park, J.Y. Lee, J.K. Kang, J. Phys. Chem. B 109 (2005) 8983.
[5] A. Ansón, E. Lafuente, E. Urriolabeitia, R. Navarro, A.M. Benito, W.K. Maser, M.T. Martinez, J. Phys. Chem. B 110 (2006) 6643.
[6] F.H. Yang, R.T. Yang, Carbon 40 (2002) 437.
[7] A.D. Lueking, R.T. Yang, J. Catal. 206 (2002) 165.
[8] Y.W. Li, R.T. Yang, J. Am. Chem. Soc. 128 (2006) 726.
[9] Y.W. Li, R.T. Yang, J. Am. Chem. Soc. 128 (2006) 8136.
[10] Y.W. Li, R.T. Yang, J. Phys. Chem. C 111 (2007) 11086.
[11] S. Khoobiar, J. Phys. Chem. 68 (1964) 411.
[12] M. Boudart, M.A. Vannice, J.E. Benson, Z. Phys. Chem. 64 (1969) 171.
[13] M. Boudart, A.W. Aldag, M.A. Vannice, J. Catal. 18 (1970) 46.
[14] A.J. Robell, E.V. Ballou, M. Boudart, J. Phys. Chem. 68 (1964) 2748.
[15] H. Taylor, Ann. Rev. Phys. Chem. 12 (1961) 127.
[16] W.C. Neikam, M.A. Vannice, J. Catal. 27 (1972) 207.
[17] W.C. Neikam, M.A. Vannice, in: Proc. 5th Int. Congr. Catal. Amsterdam, vol. 1, North-Holland, Amsterdam, 1973, p. 609.
[18] G.C. Bond, T. Mallat, J. Chem. Soc. Faraday Trans. I 77 (1981) 1743.
[19] R.T. Yang, Y.W. Li, G.S. Qi, A.J. Lachawiec, US Patent Application US2007-0082816A1 (2005).
[20] J.E. Benson, M. Boudart, J. Catal. 4 (1965) 704.
[21] B.M. Weckbuysen, L.M. De Ridder, R.A. Schoonheydt, J. Phys. Chem. 97 (1993) 4756.
[22] W.C. Connor Jr., J.L. Falconer, Chem. Rev. 95 (1995) 759.
[23] G.C. Bond, Stud. Surf. Sci. 17 (1983) 1.
[24] G.C. Bond, H. Lou, J. Catal. 147 (1994) 346.
[25] G.C. Bond, in: M.V. Twigg, M.S. Spencer (Eds.), Metal-Catalysed Reactions of Hydrocarbons, Springer, New York, 2005, p. 118.
[26] J. Freel, J. Catal. 25 (1972) 149.
[27] B. Chen, J.L. Falconer, J. Catal. 134 (1992) 737.
[28] R. Kramer, M. Andre, J. Catal. 58 (1979) 287.
[29] A.L. Marsh, K.A. Becraft, G.A. Somorjai, J. Phys. Chem. B 109 (2005) 13619.