

## Supplementary Material

### Effects of Ni Particle Size on Hydrogen Storage of Ni-Doped High Surface Area Activated Carbon

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The amount of Ni deposited on high surface area activated carbon was determined by Optima 2000DV model Perkin-Elmer ICP-AES at a wavelength of 213.6 nm. The operating conditions and the analytical wavelength are summarized in Table S1.

Table S1

ICP-AES operating conditions and the analytical wavelength  
(Perkin Elmer, Optima 2000DV)

parameters	
Incident power / kW	1.3
Plasma gas (Ar) flow rate / L min <sup>-1</sup>	15
Auxiliary gas (Ar) flow rate / L min <sup>-1</sup>	0.5
Nebulizer gas (Ar) flow rate / L min <sup>-1</sup>	0.8
Observation height / mm	15
Integration time / s	10
Solution pump rate / ml min <sup>-1</sup>	1.0
Wavelength / nm	Ni 213.6

Calibration function for the ICP-AES spectrometer was generated using a multi-element standard with a suite of elements having concentrations ranging from 10 to 0.1 µg/mL in 1000 µg/mL nickel and 2% (v/v) sub-boiled nitric acid. Ni was measured using single elemental standard solutions having concentrations ranging from 10 to 0.1 µg/mL. The standards were prepared using dilution of 1000 µg/mL stock standard solutions (Spex Certiprep Standard s, Metuchen,

NJ). The ICP -AES operating conditions and wave lengths used are shown in Table S1. Calibration was carried out with standard solutions of the elements containing 0.25, 0.50, 1.00, 1.50, and 2.0  $\mu\text{g}/\text{mL}$ . Standard solutions for calibration were prepared by spiking a blank solution (the model matrix) with stock solutions of the elements.

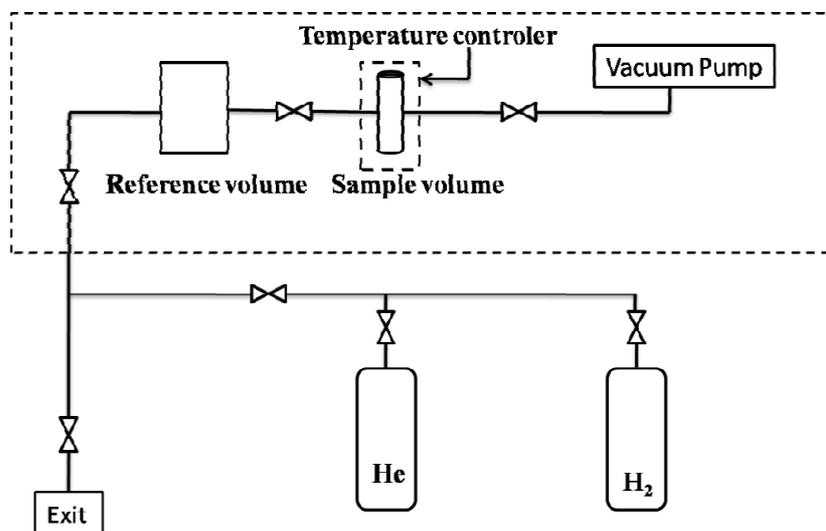


Fig. S1. Schematic diagram of the Sieverts volumetric apparatus used.

Hydrogen adsorption was measured using a static volumetric technique with a specially designed Sievert's apparatus. Schematic diagram of the Sieverts volumetric apparatus is shown in Fig. S1. The apparatus contain a central part formed by two high pressures cells interconnected by a valve, which denoted as reference cell and sample cell respectively. The volume of reference cell is  $63 \text{ cm}^3$ , while the volume of sample cell is  $24 \text{ cm}^3$ . The gas pressure in both cells was determined with digital pressure gauges. Both cells and lines were depressurized to a pressure level below  $10^{-9}$  to outgas the samples via a rotatory vacuum pump. The outgasing process was enhanced with heating. The sealing of the sample holder was carefully polished before every measurement. High pressure tests over several days showed no detectable leakage rate in the system. The volume of the system was determined by measuring accurately those of the single components using helium.

For the first, the whole system was gradually depressurized for several hours to a pressure level below  $10^{-9}$  bar while the sample cell was heated at 473 K. Then, the valve connecting the two high pressures cells was closed. The hydrogen adsorption of carbon materials was measured at a series of hydrogen pressures (eg. 2,3,4,..10, 12,14,...,26,and 30 bar). At the beginning of each measurement, the referent cell was filled with hydrogen at the given pressure respectively (eg. 2,3,4,..10, 12,14,...,26,and 30 bar). After 30 min, the whole system was considered to be in thermal equilibrium. Finally, the valve of the sample cell was opened and when pressure equilibrium was reached, this valve was closed. Due to the expansion of the hydrogen gas into the sample cell volume, the pressure in the sample cell increased whereas the pressure in the reference cell decreased. Thereby, the initial value of pressure the in sample cells was 2,3,4,..10, 12,14,...,26,and 30 bar, respectively. The hydrogen adsorption was calculated using the van der Waals (1) and Soave- Redlich-Kwong Eq.(2):

$$\left( P + \frac{a \cdot n^2}{V^2} \right) \cdot (V - b \cdot n) = n \cdot R \cdot T \quad (1)$$

Where  $p$  and  $T$  are the actual pressure and temperature of the hydrogen gas,  $R$  is the gas constant, equal to  $83.145 \text{ cm}^3 \cdot \text{bar} / \text{mol} \cdot \text{K}$ ;  $a$  and  $b$  are the van der Waals constants, depending on the gas, which were taken from the literature :  $a = 247600(\text{cm}^3)^2 \cdot \text{atm} / \text{mol}^2$  and  $b = 26.61 \text{ cm}^3 / \text{mol}$  ;  $n$  is the amount of hydrogen gas (in mol); and  $V$  is the volume of the sample cell.

$$p = \frac{R \cdot T}{V_m - b} - \frac{a \cdot \alpha}{V_m \cdot (V_m + b)} \quad (2)$$

Where  $p$  and  $T$  are the actual pressure and temperature of the hydrogen gas,  $R = 83.145 \text{ cm}^3 \cdot \text{bar} / \text{mol} \cdot \text{K}$ ,  $a = 0.42747 \cdot R^2 T_c^2 / P_c = 20419.61 (\text{cm}^3)^2 \cdot \text{atm} / \text{mol}^2$  ( $T_c = 33.2 \text{ K}$  and  $P_c = 1.28 \text{ MPa}^{[1]}$ ) and  $b = 0.08664 \cdot R \cdot T_c / P_c = 18.94 \text{ cm}^3 / \text{mol}$ .  $\alpha = (1 + (0.48508 + 1.55171 \cdot \omega - 0.15613 \cdot \omega^2) \cdot (1 - T_r^{0.5}))^2$ ,  $\omega = -0.212$  for hydrogen [48] and  $T_r = T / T_c$ . Finally,  $V_m$  is the molar volume of the sample cell.

At each experiment, the volume of the sample cell was corrected for the displaced volume of the carbon sample (0.3 g of carbon material). This volume was determined using helium at different pressures<sup>[2]</sup>. According to Eq. (2) or (3), the amount of hydrogen,  $n_1$ , after opening the valve (between the reference and sample cells) and once the equilibrium was reached (the valve was closed), was calculated at the appropriate pressure and temperature ( $p_1$  and  $T_1$ ). Similarly, the amount of hydrogen gas,  $n_2$ , after saturation of the carbon materials, was calculated with  $p_2$  and  $T_2$ . The difference  $n_1 - n_2$  directly yields the amount of gas adsorbed<sup>[3]</sup>.

### Reference

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**Table S2** Hydrogen sorption of samples and hydrogen spillover activity of nickel

Samples	H <sub>2</sub> sorption (wt%) at 77 K, 10 bar	H <sub>2</sub> sorption (wt%) at 298 K, 30 bar	Mean Ni particle size (nm)	Metal surface area (m <sup>2</sup> g <sup>-1</sup> <sub>Ni</sub> )	H <sub>2</sub> sorption (wt%) at 298 K, 30 bar / nickel content (%)
hsAC	4.88	0.27	/	/	/
hsAC0.13%Ni	3.90	0.79	12	5.62	6.07
hsAC0.35%Ni	4.84	0.72	25	2.70	2.06
hsAC0.53%Ni	4.73	0.49	35	1.93	0.92
hsAC0.78%Ni	4.56	0.44	95	0.66	0.56