

HYDROGEN STORAGE PROPERTIES OF MAGNESIUM OXIDE- AND NICKEL-TEMPLATED POROUS CARBONS

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Introduction

High density storage system of hydrogen at below 5 MPa and room temperature is required to extend the range of application for on-board system. An approach of filling the existing hydrogen storage tank for fuel cell vehicles with hydrogen storage material has been suggested for realizing higher storage density and lower charging pressure. Templated carbon proposed as hydrogen storage material has many advantages due to its light weight, low cost, non-toxic property and high specific surface area. Furthermore, for templated carbon, matrix (i.e. texture and crystallinity of pore wall) as well as pore structure which certainly has an effect on hydrogen adsorption/desorption behaviour can be controlled by synthesis conditions.

In the present study, MgO- and Ni-templated carbons were synthesized and characterized by TEM, XRD, N₂ sorption and Raman spectroscopy. An effect of the matrix structure on hydrogen storage at 298 K was discussed by comparing to commercially available materials.

Materials and Methods

The MgO-templated samples were synthesized by firing trimagnesium dicitrate nonahydrate or magnesium gluconate n-hydrate as purchased using a tube furnace at 500, 700 and 900 °C for 1 h in argon gas flow, followed by removing MgO by acid solution (CC-500, -700, -900 and GC-500, -900 (CC: carbon from citrate, GC: carbon from gluconate)). The precursors for the Ni-templated samples were prepared by evaporating the different aqueous solutions having molar ratio of citric acid monohydrate to nickel acetate tetrahydrate of 1:1 and 2:3 on a hot plate at 383 K. The Ni-templated samples was obtained by firing the precursor using a tube furnace at 500 or 1000 °C for 1 h in argon gas flow, followed by removing Ni by acid solution (C-[precursor ratio]-[firing temperature]: C-2-3-500 and C-1-1-1000). Commercially available samples, carbon fibre (CF), Ketjenblack (EC600JD), natural graphite (SNO-30), MgO-templated carbon (MPC001 and CNovel-A, -B, -C), carbon black (Fx-35) and activated carbon (AC) were also investigated.

Hydrogen adsorption/desorption curves were measured at 298 K up to 4.5 MPa using a self-build PCT apparatus based on a volumetric method (JIS H 7201).

Results and Discussion

MgO-templated sample CC-900 consists of small carbon hexagonal nets with random orientation and its dimension increased with the increase of firing temperature (**Figure 1a**). On the other hand, Ni-templated sample C-2-3-500 also consists of small carbon hexagonal nets but the nets are arranged along pore walls as a consequence of catalytic carbonization of Ni nanoparticles.

For Ni-templated sample C-1-1-1000, a growing in ab plane and a stacking along c axis of carbon hexagonal nets, i.e. catalytic graphitization effects were observed (**Figure 1b**).

The relation between carbon matrix structure and H₂ uptake was investigated by plotting the H₂ uptake on the Raman data mapping of I_D/I_G vs. I_V/I_G (I_D: D band intensity, I_V: valley intensity between D and G band, I_G: G band intensity) (**Figure 2**)¹. Carbon samples having a matrix structure in the range 0.8-1.3 of I_D/I_G and 0.2-0.5 of I_V/I_G store hydrogen from 0.09 to 0.28 wt% and these samples have a specific surface area ranged from 440 to 1900 m² g⁻¹. Among these samples, the samples C-1-1-1000 and CC-900 having 440 and 1900 m² g⁻¹ of specific surface area had distinct matrix structures and showed 0.09 and 0.20 wt% of H₂ uptake as shown in **Figures 1** and **2**. In order to evaluate an effect of matrix structure on hydrogen capacity, hydrogen uptake per unit specific surface area was calculated. Samples C-1-1-1000 and CC-900 showed 2.0×10⁻⁴ and 1.1×10⁻⁴ wt% m⁻² g of the hydrogen uptake per unit specific surface area and other samples located near the two samples on the Raman data mapping showed the value between 1.1×10⁻⁴ and 2.2×10⁻⁴ wt% m⁻² g. These results indicated that carbon sample located near each other on the Raman data mapping had almost comparable level of hydrogen storage capability at 298 K.

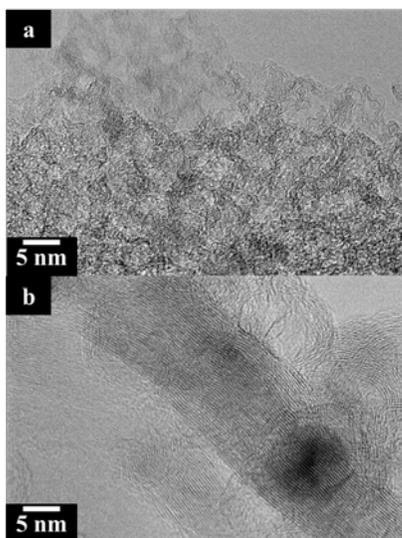


Figure 1 TEM images of MgO-templated sample CC-900 a) and Ni-templated sample C-1-1-1000 b).

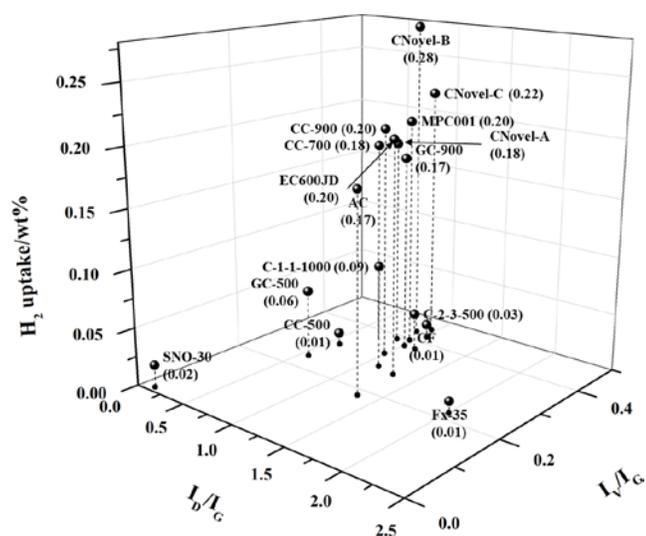


Figure 2 Plotting of the H₂ uptake of samples at 298 K on Raman data mapping of I_D/I_G vs. I_V/I_G. Numerical value depicted in bracket is the H₂ uptake in wt%.

Conclusions

Carbon samples having a matrix structure in the range 0.8-1.3 of I_D/I_G and 0.2-0.5 of I_V/I_G on Raman data mapping stored hydrogen from 0.09 to 0.28 wt%. Carbon samples having a matrix structure in the range 0.8-1.3 of I_D/I_G and 0.2-0.5 of I_V/I_G showed the value between 1.1×10⁻⁴ and 2.2×10⁻⁴ wt% m⁻² g of the hydrogen uptake per unit specific surface area. Among the synthesized samples, sample C-1-1-1000 showed the highest hydrogen storage capability per unit specific surface area of 2.0×10⁻⁴ wt% m⁻² g.

References

1. John McDonald-Wharry, Merilyn Manley-Harris, Kim Pickering (2013). Carbonisation of biomass-derived chars and the thermal reduction of graphene oxide sample studied using Raman spectroscopy. *Carbon* 59, 383-405