Nanoporosity and Chemical Activities of Pd Tailored Single Wall Carbon Nanohorn

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Introduction

The single wall carbon nanohorn (SWNH)[1] is a nanotubular material that is similar to single wall carbon nanotube (SWNT)[2]. They form unique colloidal assemblies of "Dahlia-flower"-like structure. The preceeding study[3] showed that SWNHs exhibit an excellent adsorption property even for supercritical methane. Unique chemical activities have been expected due to characteristic nanostructures. SWNHs are produced without any catalysts. Therefore, we can examine the intrinsic catalytic activity of ultrafine metal tailored SWNHs. Recently, it was shown that ultrafine Pt dispersed nanoparticles on SWNHs show larger current density than that on carbon blacks[4].

In this work, we report on the preparation of dispersed Pd nanoperticles on SWNHs, their nanoporosity, and catalytic activities for organic reaction.

Experimental

The dahlia-SWNHs was prepared by the CO_2 laser ablation of pure graphite under argon 760 Torr at room temperature without catalysts. As the capped nanohorns were opened by oxidation[5,6], we oxidized dahlia-SWNHs in oxygen by flowing O_2 at 693 K for 10 min. In a previous study[6], the SWNH thus oxidized (ox-SWNH) were opened almost completely.

Pd nanoparticles were dispersed on SWNH by the reduction of H_2PdCl_4 solution with ethanol in the presence of Poly[(2-oxopyrrolidin-1-yl)ethylene](PVP)[7]. The Pd-tailored SWNH (Pd-ox-SWNH) was obtained by the vacuum drying of the precipitates after the reduction.

Transmission electron microscopy (TEM) micrographs were obtained with a conventional transmission electron microscope (JEOL JEM-2010F) at 120 kV accelerating voltage.

The pore structures of SWNH samples were determined by nitrogen adsorption measurements at 77 K.The high-pressure hydrogen adsorption isotherm was measured at 303 K by use of a Cahn microbalance. The high purity hydrogen gas (99.99999 %, Nippon Sanso) was used after purification with a liquid nitrogen trap. The entire pretreatments prior to the adsorption measurements were performed at a pressure less than 1 mPa and a temperature at 423 K for 2 h.

The catalytic activities of the SWNH sample for Suzuki coupling was measured after preevacuation.

Results and Discussion

The TEM image of Pd-ox-SWNHs is shown in Figure 1. The tiny black spots in the figure correspond to the Pd nanoparticles. Their particle size was about 2 nm. The Pd nanoparticles are highly dispersed on SWNH assembly.

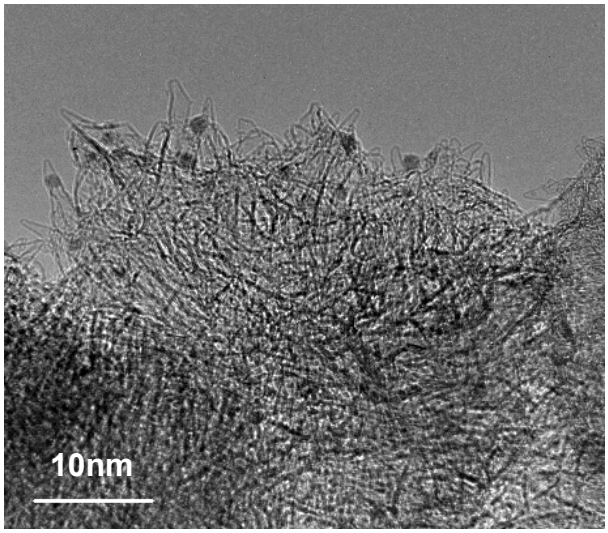


Figure 1. TEM image of Pd-ox-SWNH aggregates

The adsorption isotherms of N_2 at 77 K for ox-SWNH and Pd-ox-SWNH are shown in Figure 2. Both adsorption isotherms show presence of nanopores. The dispersion of Pd decreases the nanoporosity.

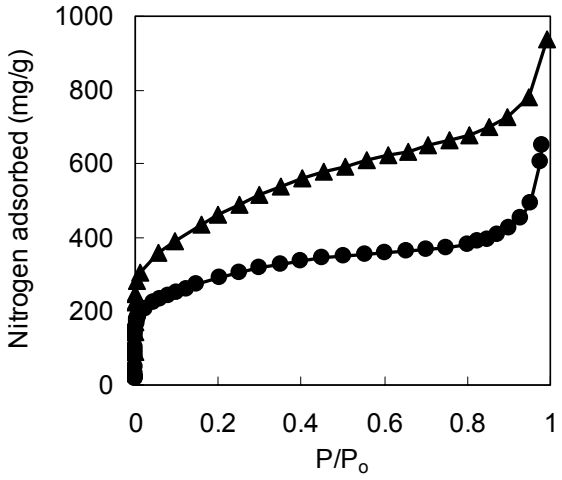


Figure 2. Nitrogen adsorption isotherms of ox-SWNH (triangles) and Pd-ox-SWNH (circles) at 77 K

Figure 3 illustrates the hydrogen adsorption isotherms of ox-SWNH and Pd-ox-SWNH at 303 K. The adsorption isotherm of ox-SWNH is of Henry type and thereby all of adsorption sites are too weak to adsorb supercritical hydrogen at 303 K. On the contrary, the adsorption isotherm of H_2 on Pd-ox-SWNH is Langmurian, indicating the strong interaction of H_2 molecules with the Pd-ox-SWNH. Therefore, the Pd-ox-SWNH is expected to show characteristic chemical activities.

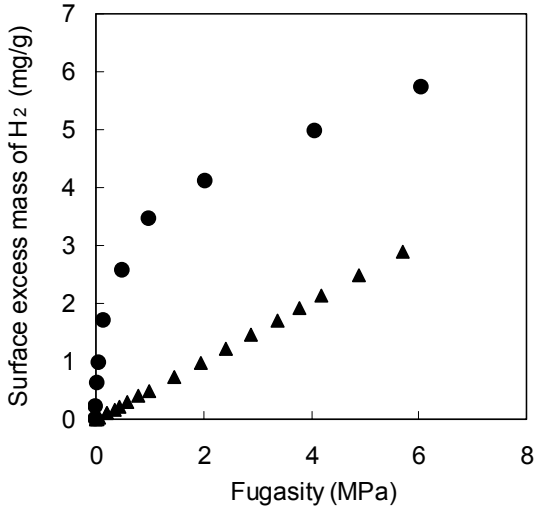
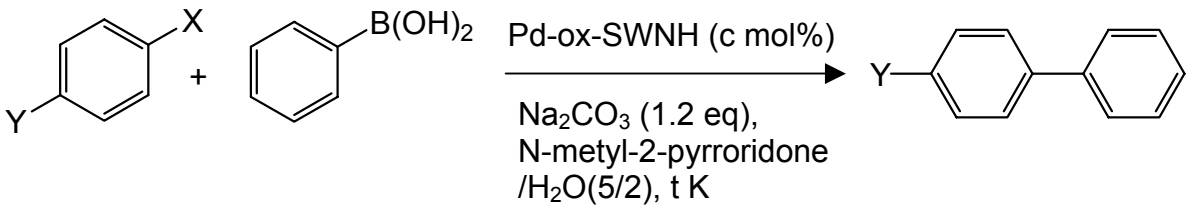


Figure 3. Hydrogen adsorption isotherms at 303 K of ox-SWNH (triangles) and Pd-ox-SWNH (circles)

The chemical reactivity of Pd-ox-SWNH for Suzuki coupling was summarized in Table 1. The yield obtained by use of the established Pd catalyst (1-2 mol%) is 80-100 %. The Pd-ox-SWNH shows similar yield irrespective of much small amount of Pd (0.0375 mol%). Thus, Pd-ox-SWNH shows an excellent catalysis for Suzuki coupling.

Table 1. Suzuki coupling of halogenarenes with phenylboronic acid



X	Y	c	t	Time (h)	Yield (%)
Br	OCH_3	0.0375	393	1	74
Br	H	0.05	373	1	75
I	OCH_3	0.05	373	2	92
I	H	0.05	373	1	92

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