HYDROGEN ADSORPTION BY FILAMENTOUS CARBON SYNTHESIZED FROM CARBON MONOXIDE

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Introduction

Filamentous carbons with different textures were produced by a catalytic decomposition of carbon monoxide /hydrogen mixture. By changing the feed gas composition, that is CO concentration, the crystallinity and the orientation of graphite layers along the filament axis (texture) were drastically affected. The H_2 adsorption under atmospheric pressure showed physisorptive behavior. At high pressure and temperature, the H_2 adsorption was not recognized.

Experimental

A commercial stainless steel plate (SUS304, 321) was employed as a catalyst to decompose CO and was treated by n-hexane and subsequently by (1+1) HCl solution for 15 min with ultrasonication before it is used. The filamentous carbons were produced by an open flow or a closed circulating apparatus, in which the steel plate was placed in the horizontal quartz tube and heated up to 550 ℃ in Ar flow or vacuum, respectively. When the temperature reached constant, the mixture of CO and H_2 was started to pass over the steel. The filamentous carbons obtained were examined by electron microscope (SEM and TEM) and X-ray powder diffraction. The adsorption of N_2 or H_2 was measured by a commercial automatic adsorption apparatus (BELSORP).

Results and Discussion

From 20% of CO in the feed gas, about 2 g of filamentous carbon was produced by the flow type apparatus after 50 hr of reaction. SEM and TEM photographs indicated that the filamentous carbon from 20 % of CO has the cylindrical morphology and seemed to have the conical stacking of the carbon layers along the filament axis. Audier et al. has reported quite similar morphology and texture in their filament, which was produced by the disproportionation of CO from CO and CO_2 mixture[1]. Since the initial gas mixture contained H_2 in our experiment, certain amount of water was produced during the formation of solid carbon and the formation of CO_2 was not observed. Therefore, the formation reaction of the filamentous carbon might be different from their experiment.

From 80 % of CO, about 1 g of the dense filament (without hollow at the center of filament) with the square cross section was produced by the closed circulating apparatus. TEM lattice images showed that the carbon layers stacked completely perpendicular to the filament axis.

X-ray powder patterns for two kinds of filamentous carbons are shown in figure 1. The filament from CO 20% has turbostratic structure and shows only (002) diffraction line. On the other hand, the filamentous carbon from CO 80 % showed 3-dimensional graphite structure as indicated by the appearance of (*hkl*) diffraction lines with high indices of (*00l*). Crystallographic parameters (Table 1) showed that the filamentous carbon from CO80 % has the high crystallinity with small crystallite.

Figure 2 shows the H_2 adsorption-desorption isotherms for two kinds of filamentous carbons at different temperatures. Both samples adsorbed H_2 only at liquid nitrogen temperature. From nitrogen adsorption, the BET surface areas of filamentous carbons from 20 and 80 % of CO were about 140 and 80 cm^2/g, respectively. Therefore, the difference in maximum amount of H_2 adsorption at 77K might be corresponded to their surface areas.

Conclusions

The filamentous carbons with different textures prepared from CO and H_2 mixture showed the H_2 adsorption at liquid nitrogen temperature under atmospheric pressure. Although we already conducted the H_2 adsorption experiment up to 3.3 MPa at high temperatures, the results were less reproducible and did not show an extraordinary adsorption. As mentioned by Rodriguez[2], the pretreatment of materials before the adsorption experiment might be important.

Reference

(1) M. Audier, A. Oberlin and M. Coulon, J. Cryst. Growth, 1981, **55**, 549.
(2) C. Park, C.D. Tan, R. Hidalgo, R.T.K. Baker and N.M. Rodriguez, Proc. 1998 U.S.DOE. Hydrogen Program Review, 1998, **II**, 525.

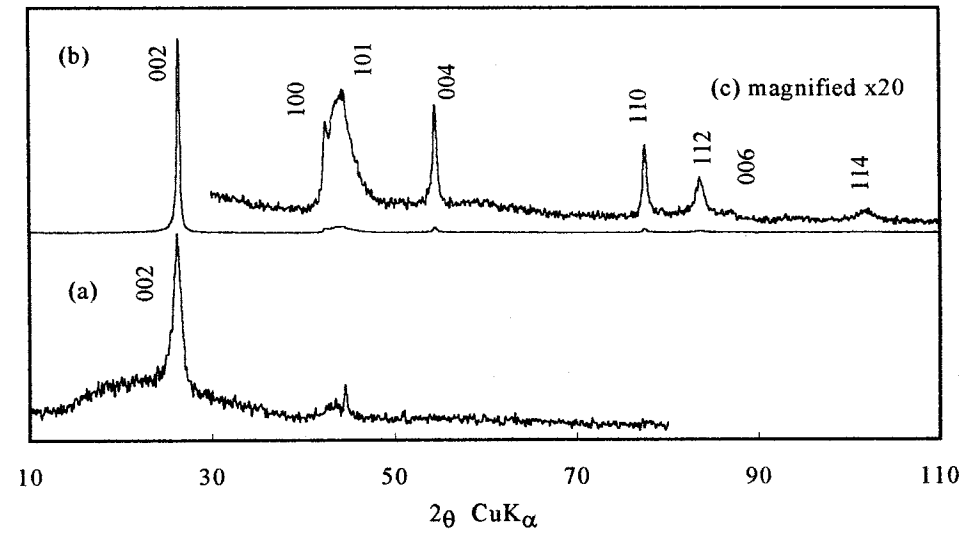

Figure 1 X-ray powder patterns of filamentous carbons prepared at 550℃;
(a) from CO 20 %, (b) from CO 80 % and (c) magnification of (b).

Table 1 Crystallographic parameters from XRD.

	$c_0/2$ nm	Lc nm	a_0 nm	La nm
filament from CO 20 %	0.339 (002)	10 (002)		
filament from CO 80 %	0.3364 (004)	39 (004)	0.2459	42

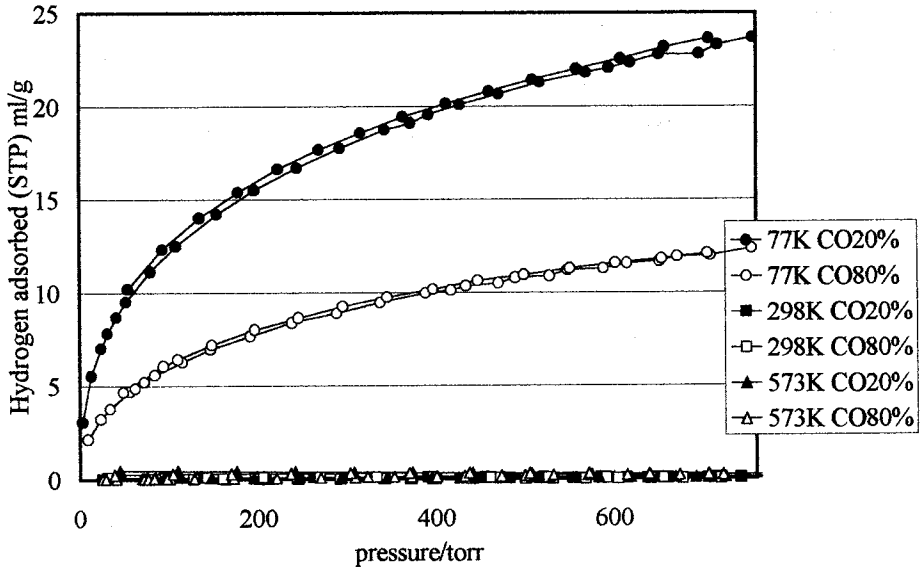

Figure 2 Hydrogen adsorption isotherms at low pressure.