

ENHANCEMENT OF METHANE ADSORPTIVITY OF ACF WITH DISPERSED NiO CHARACTERIZED BY XAFS

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Introduction

Natural gas is a representative primary energy and has a considerable advantage over conventional fuels. The use of natural gas as a fuel has necessitated the use of high-pressure storage, because methane, which is a primary component of natural gas, is supercritical gas. The use of adsorbents is effective for an attempt to provide high density storage. Also, adsorption storage would appear to be attractive for other applications in the natural gas industry.

Activated carbon fibers (ACFs) are the hopeful adsorbent for methane, because of their characteristic adsorption properties. It is well known that their adsorption properties are mainly caused by the uniform micropores. The adsorption of vapors in micropores is enhanced by overlap of the molecular potential from opposite pore-walls [1,2]. The phenomenon is called micropore filling [3-5], which is an enhanced physical adsorption and usually a dominant process for a vapor. Therefore, the microporous solid has great adsorption capacity and adsorption rate for vapors by micropore filling. Nevertheless, micropore filling is a predominant process only for vapor and is not effective for the supercritical gas due to small molecular interactions.

The development of good adsorbent for a supercritical gas is very important in the field of the study on the energy storage materials and removal of atmospheric pollutants. Kaneko *et al.* have prepared iron oxide-dispersed ACFs

which adsorb large amount of supercritical NO at 303 K by chemisorption-assisted micropore filling [6-9]. Ultrafine iron oxides on the ACF assist the micropore filling of the supercritical NO. Also, Kaneko *et al.* have reported that the pitch-based ACFs modified with MgO and NiO fine particles give rise to a marked enhancement of methane adsorption [10,11]. These novel effects of fine metal oxide particles dispersed on ACFs are very interesting not only from industrial applications but also from scientific aspects. It is important to characterize the dispersed metal oxide state in order to elucidate the role of metal oxides in chemisorption-assisted micropore filling. In this work, we characterize the porous structures of nickel oxide-dispersed ACFs and the local structures of dispersed nickel oxide particles by means of nitrogen adsorption isotherm at 77 K, high pressure methane adsorption isotherm at 303 K, X-ray adsorption near-edge structures (XANES), and extended X-ray adsorption fine structures (EXAFS).

Experimental

The pitch-based activated carbon fibers (P20) were evacuated at 383 K for 2 h in vacuo prior to the dispersion of NiO on P20. The pre-evacuated ACFs was immersed in the 30% Ni(NO₃)₂ solution at room temperature for 15, 40, or 90 h. Then, the solution with ACF was immersed into 1 M NaOH solution. The P20 modified with Ni(OH)₂ was washed with distilled water and dried at 333

K. The Ni(OH)₂ dispersed P20 was heated at 573 K for 3 h in N₂ flow. Decomposition of the Ni(OH)₂ particles on P20 at 573 K gave NiO particles dispersed P20 (NiO-P20). The adsorption and desorption isotherms of pristine and modified P20 were measured gravimetrically using nitrogen gas as adsorbate at 77 K. Samples were pre-evacuated at 383 K and 10⁻⁵ Torr prior to measurement of N₂ adsorption. The XAFS measurements were carried out using a Technos EXAC820 with a rotating-anode X-ray source that was operated at 17 kV × 150 mA. The Ni K-edge XAFS spectra of NiO-P20, powdered NiO, and powdered Ni(OH)₂ were measured by using of the EXAC820 in transmission mode. The program FEFF8 was used for the simulation of the XANES and EXAFS spectra of NiO crystal [12]. The theoretical phases and amplitudes obtained from FEFF8 were used for curve fitting.

Results and Discussion

Figure 1 shows the adsorption isotherms of N₂ at 77 K for pristine P20 and NiO dispersed P20 prepared by immersing into 30% Ni(NO₃)₂ solution for 15, 40, and 90 h. The isotherms are of type I, suggesting that NiO dispersed samples are microporous materials. The surface modification with NiO decreases the amount of N₂ adsorption. The α_s -plot was applied to these N₂ adsorption isotherms using reference data of nonporous carbon black [13,14]. The specific surface area a_s , external surface area a_{ext} , micropore volume v_m , and micropore width w are shown in Table 1. The NiO dispersion decreases both surface area and micropore volume. On the other hand, the micropore width is almost similar to that of pristine P20. These results suggest that the NiO dispersion partially blocks the micropores. Therefore, almost NiO particles should be dispersed in the micropores.

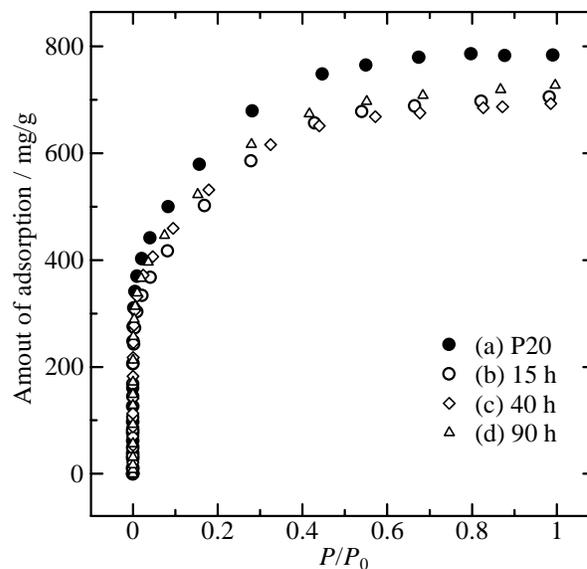


Fig. 1. The N₂ adsorption isotherms of (a) P20 and of NiO dispersed P20 prepared by immersing into Ni(NO₃)₂ solution for (b)15, (c) 40, and (d) 90 h.

Table 1. Micropre structural parameters of P20 and of NiO dispersed P20 prepared by immersing into Ni(NO₃)₂ solution for 15, 40, and 90 h.

Sample name	a_s m ² /g	a_{ext} m ² /g	v_m ml/g	w nm
P20	1658	28.2	0.937	1.15
P20-15h	1397	52.8	0.808	1.20
P20-40h	1496	41.2	0.806	1.11
P20-90h	1519	56.8	0.828	1.13

Figure 2 shows the high-pressure adsorption isotherms for P20 and NiO dispersed P20. All isotherms are of Langmuire type, indicating the presence of the micropore in which supercritical methane gas can be filled. Table 2 shows the amount of methane adsorption for P20 and NiO dispersed P20 at 3.5 MPa. The amount of methane adsorption for P20-15h is greater than that of pristine P20, indicating that the NiO dispersion enhances the amount of

methane adsorption. The Nickel-based catalysts are usually used as a catalyst for the decomposition of hydrocarbons, because they have the potential for providing the dehydrogenation particularly at high temperature [15,16]. Therefore, a weak chemisorption interaction of the dispersed NiO with methane gas should be associated with the enhancement of methane adsorptivity.

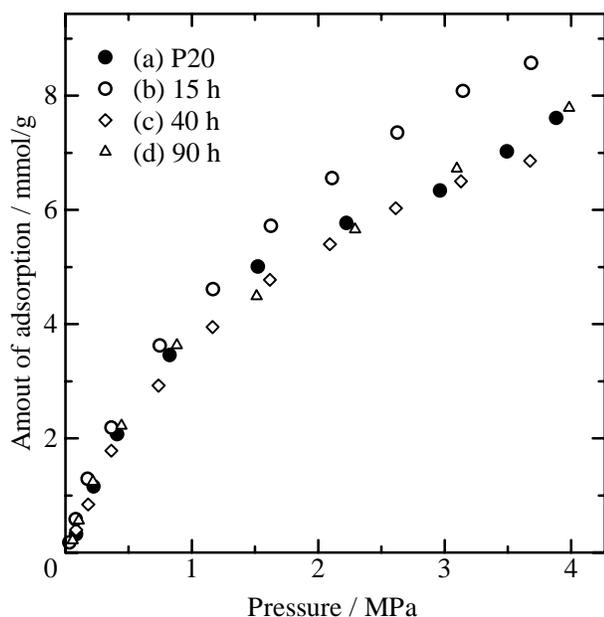


Fig. 2. The high pressure methane adsorption isotherms of (a) P20 and of NiO dispersed P20 prepared by immersing into $\text{Ni}(\text{NO}_3)_2$ solution for (b)15, (c) 40, and (d) 90 h.

Table 2. The amount of methane adsorption for P20 and for NiO dispersed P20 prepared by immersing into $\text{Ni}(\text{NO}_3)_2$ solution for 15, 40, and 90 h.

	P20	15h	40h	90h
Amount of adsorption (mmol/g)	7.00	8.49	6.74	7.40

X-ray absorption spectroscopic technique was applied to characterize NiO dispersed on P20. Figure 3 shows the XANES spectra of powdered NiO, NiO-P20, and simulated by FEFF8. All spectra show a weak pre-edge peak (A), which arises from the $1s-3d$ forbidden transition in the case of the O_h symmetry around a Ni atom. The intensity of this peak is so weak that O_h symmetry is almost maintained irrespective of dispersion on P20. The peaks B and C are assigned to the $1s-4p$ transition. The fact that the spectra of NiO-P20 are almost similar to the spectrum simulated by FEFF8 with atomic position of NiO crystal, indicates the formation of NiO-like substances on P20.

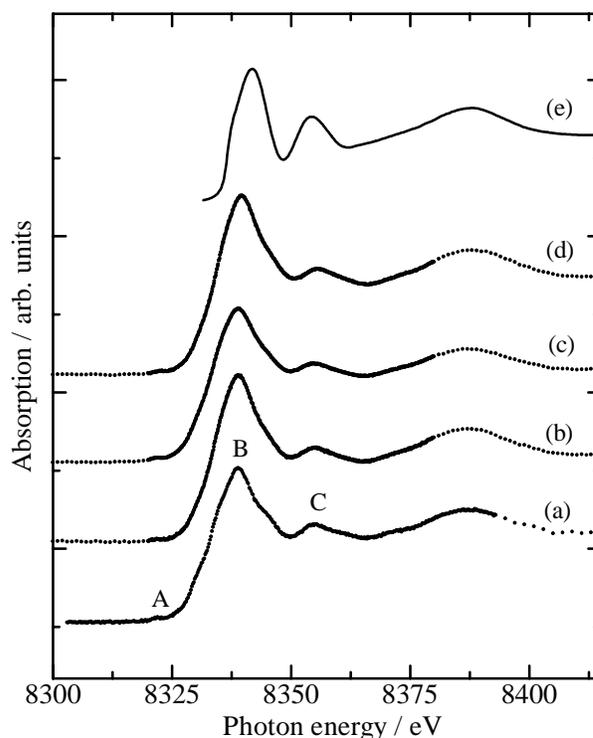


Fig. 3. The XANES spectra of (a) NiO and of NiO dispersed P20 prepared by immersing into $\text{Ni}(\text{NO}_3)_2$ solution for (b)15, (c) 40, and (d) 90 h. The spectrum (e) is that simulated by FEFF8 program code with atomic position of NiO crystal.

Figure 4 shows the Ni *K*-edge EXAFS spectra of powdered NiO, NiO-P20, and simulated by FEFF8. The edge-jump of the Ni *K*-edge is clearly observed and the EXAFS signal is well observed up to $k = 12 \text{ \AA}^{-1}$. Figure 5 shows the k^3 weighted Fourier transforms (without phase-shift correction) of $\chi(k)$ extracted the EXAFS spectra for powdered NiO, NiO-P20, and simulated by FEFF8. There are 5 peaks (A-E) which are ascribed to Ni-O (A), Ni-Ni (B), Ni-O (C), Ni-Ni (D), and Ni-O (E) distances, respectively. All Fourier transforms for NiO-P20 have similar feature of that by NiO and are in agreement with that by FEFF8, suggesting the formation of NiO-like substance on the P20.

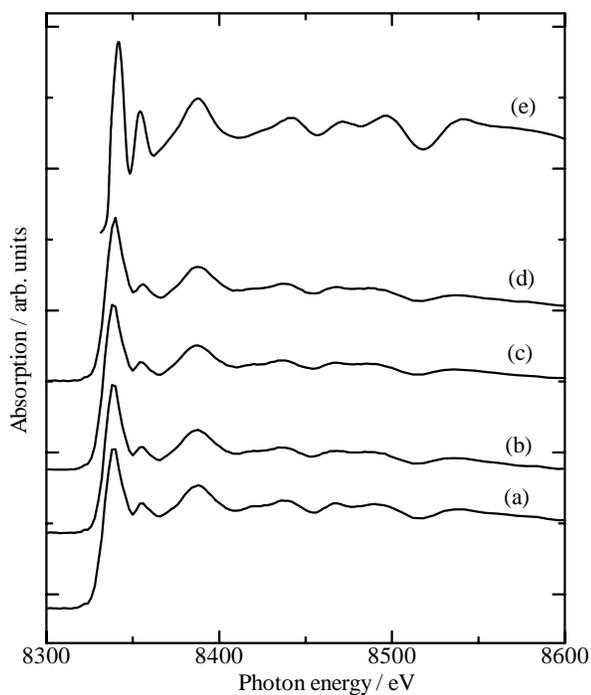


Fig. 4. The EXAFS spectrum of (a) NiO and of NiO dispersed P20 prepared by immersing into $\text{Ni}(\text{NO}_3)_2$ solution for (b)15, (c) 40, and (d) 90 h. The spectrum (e) is that simulated by FEFF program code with atomic position of NiO crystal.

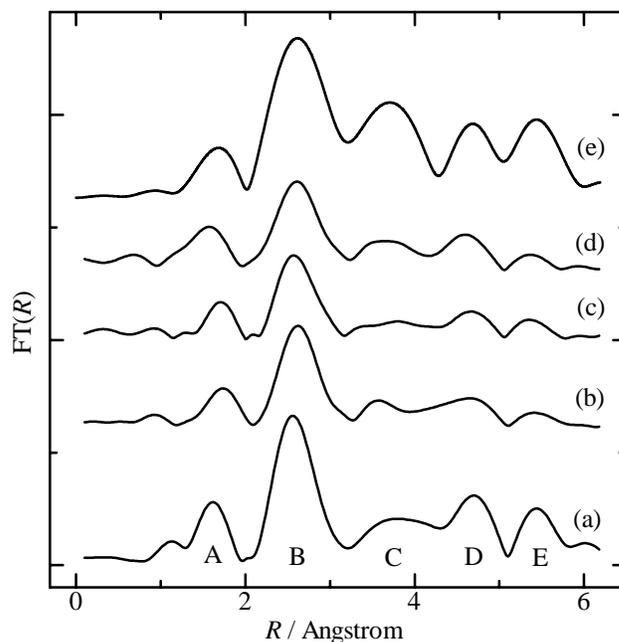


Fig. 5. The k^3 weighted Fourier transforms of $\chi(k)$ extracted the EXAFS spectra of (a) NiO and of NiO dispersed P20 prepared by immersing into $\text{Ni}(\text{NO}_3)_2$ solution for (b)15, (c) 40, and (d) 90 h. The spectrum (e) is that simulated by FEFF program code with atomic position of NiO crystal.

Table 3. First and second nearest-neighbor interatomic distances of powdered NiO and NiO dispersed P20 prepared by immersing into into $\text{Ni}(\text{NO}_3)_2$ solution for 15, 40, and 90 h. The values of bond distances for NiO* are from JCPDS card data

	Ni-O (\AA)	Ni-Ni (\AA)
NiO	2.10	2.94
P20-15h	2.22	2.99
P20-40h	2.14	2.98
P20-90h	2.08	2.98
NiO*	2.09	2.95

However, the distance of peak A for sample (b) and (c) is somewhat larger than that of powdered NiO. In order to determine the accurate structural parameters, we used the r space method to curve fit the Fourier transform data. The results of best fits data for first and second shells are tabulated in Table 3. The Ni-O and Ni-Ni bond distances for NiO calculated from X-ray diffraction data are 2.09 and 2.95 Å, respectively. The bond distances for powdered NiO correspond to those calculated by x-ray diffraction data. On the other hand, the bond distances for NiO-P20 slightly larger than those of powdered NiO, and decrease with increase in the immersion time in Ni(NO₃)₂ solution. The differences in the local structures of the NiO particles on P20 will become the first step to find a clue to clear up the reason for the enhancement of adsorptivity on the methane gas.

Conclusions

The micropore structures of NiO dispersed activated carbon fibers (P20) were characterized by N₂ adsorption isotherm. All the adsorption isotherms for NiO-P20 are of type I isotherm, suggesting the presence of micropores. The adsorptive properties for methane gas were improved by the surface modification with NiO. The Ni K-edge XANES and EXAFS spectra of NiO-P20 supported the formation of fine NiO particles in micropores of P20, although the local structure of NiO particles in the micropores is slightly different from that of powdered NiO.

Acknowledgements

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