

# STRUCTURE AND PROPERTIES OF CARBON FILMS PREPARED FROM POLYIMIDE CONTAINING METAL COMPOUNDS

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## Introduction

We have previously reported about molecular sieving carbon films obtained from Kapton-type polyimide [1,2]. The molecular sieving properties of polyimide carbons are comparable to zeolite 4A or 5A. There were some works to use molecular sieving carbon as a shape or size selective catalyst support [3,4]. In the present study, carbon-metal complexes were prepared from polyimide mixed with the metal compounds, and the micropore structure and catalytic effects of the complexes were investigated.

## Experimental

Polyimide films (PIF) containing nickel or copper were fabricated from the solution of each nitrates and polyamic acid, the precursor of polyimide, in N,N-dimethylacetamide. After imidization at 200°C, the films were carbonized at a heating rate of 3°C/min in flowing argon.

Metal content was measured by X-ray fluorescence analysis. Micropore size distribution was evaluated by adsorption (25°C) of gases with different molecular sizes, CO<sub>2</sub>, ethane, butane, isobutane, the sizes of which are 0.33, 0.40, 0.43 and 0.50nm [5], respectively. Hydrogenation reaction of butene isomers on carbon-Ni complexes was performed in continuous flow reactor.

## Results and Discussion

Nickel content in carbonized samples is listed in Table 1. TEM micrograph of the polyimide film heat-treated at 600°C for 1h (PIF-Ni-600) is shown in Fig. 1. Ni fine particles with the diameter of about 5-10nm are homogeneously dispersed in carbon. It was shown by the

Table 1. Nickel content in carbonized samples.

sample	content (wt%)
PIF-Ni-600	15
PIF-Ni-650	17
PIF-Ni-700	17
PIF-Ni-800	19

X-ray diffraction measurement that the fine particles are cubic crystal of Ni metals. The average crystallite sizes calculated by scherrer's equation was 5nm. The size of Ni particles became larger by heat-treatment at higher temperatures. The average crystallite size was 24nm in PIF-Ni-800, and some particles with the diameter over 100nm were observed by TEM. In this sample, micro-graphitic carbon with interlayer spacing ( $d_{002}$ ) of 0.341nm and average crystallite size ( $L_c$ ) of 6nm was partly developed.

Nitrogen adsorption measurement showed the PIF-Ni-600 and 650 have microporous structure with few mesopores. On the other hand, development of mesopores was found for the sample treated above 700°C. The development of mesopores is considered to be related to the growth of metal particles and the change of carbon microtexture. The limiting micropore volumes were determined for four gases with different sizes by using Dubinin-Radushkevich equation. The values are plotted against molecular sizes in Fig. 2. Molecular sieving

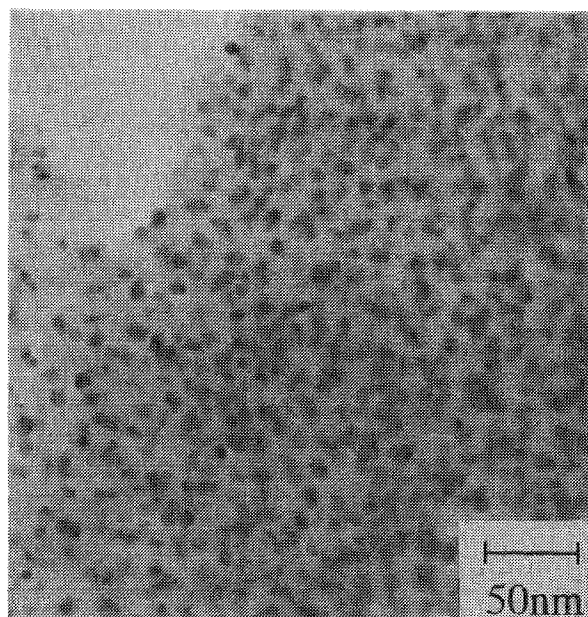


Fig. 1. TEM micrograph of PIF-Ni-600.

effect for isobutane is clear on the PIF-Ni-650. The sieving property is comparable to that of zeolite 5A.

The catalytic hydrogenation of butene isomers on this carbon-nickel complexes was tested using mixed gas containing 1vol% of butane, isobutane, 1-butene, trans-2-butene, cis-2-butene and isobutene with 5vol% of hydrogen. Isobutene, as well as the other butene isomers, was hydrogenated on Ni powder without carbon complexing. The conversion ratio between 1-butene and isobutene on PIF-Ni-600 was higher than that on nickel powder (Fig. 3). Further, quite high selectivity on PIF-Ni-650 is remarkable. The results indicate that hydrogenation occurs on the surface of Ni fine particles covered with polyimide carbon. In other words, micropores in polyimide carbon are the place where the reaction takes place. It was proved by the adsorption measurements that all butene isomers are accessible in micropores of PIF-Ni-650. Therefore the selectivity is due to the size of isobutane, the hydrogenation product of isobutene, which is not containable in the micropores. Undoubtedly the reactant, introduced into micropore, is not able to lead to the product larger than the free space in micropore. As for the samples treated above 700°C, the selectivity is similar to that of Ni powder. It is in agreement with the low molecular sieving effect for isobutane. The reaction can be also regarded as taking place on nickel surface standing out of polyimide carbon microtexture, because mesopores and large size of Ni particles are developed above 700°C.

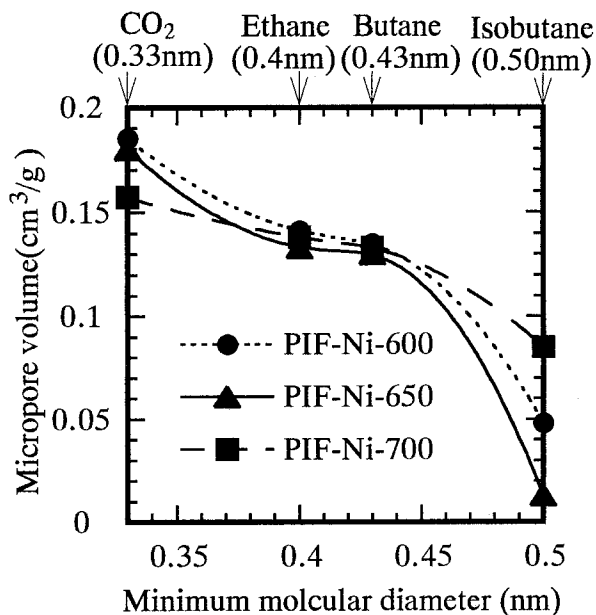


Fig. 2. Cumulative curves of micropore size distribution in carbon-Ni complexes.

Polyimide containing copper nitrate gave carbon-Cu complexes in which Cu fine particles with the average crystallite size of 12nm are homogeneously dispersed in carbon. In case of carbon-Cu complex, however, the change of carbon microtexture was not observed even at a heat-treatment temperature of 800°C. PIF-Cu-800 has molecular sieving property similar to that of zeolite 4A.

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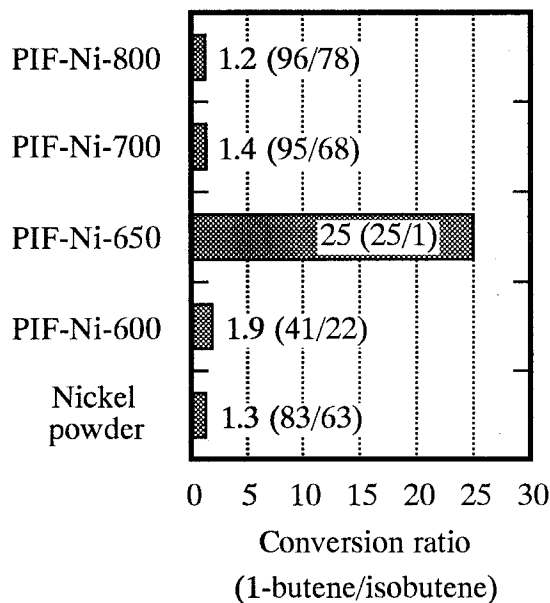


Fig. 3. The conversion ratio between 1-butene and isobutene.