

# MESOPORE FORMATION IN CARBON FROM POLYIMIDE CONTAINING NICKEL COMPOUNDS

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## Introduction

Recently, carbons complexing with diverse atoms are actively studied with a wide variety of interests concerning catalytic activity, magnetism, oxidation resistivity, etc. Carbonization of precursors containing metal compounds is one of the preparation methods of such complexes. We have already reported that Ni-carbon complex thus prepared from polyimide mixed with nickel nitrate shows the size selectivity on the catalytic hydrogenation of butene isomers [1]. In this study, we found that mesoporous structure is formed in carbonized samples by the action of nickel metal particles. It has been reported that mesopore is selectively developed by the impregnation of some kind of metal compounds and following activation [2]. However, the mesopore formation mechanism is considered to be fundamentally different from that of the Ni-carbon complex prepared in *inert* atmosphere. In the present study, the mesopore formation in the Ni-carbon complex is correlated with the growth of metal particle and the change of carbon microtexture.

## Experimental

A solution of metal compound in N,N-dimethylacetamide (DMAc) is mixed with a precursor of polyimide (PI), the DMAc solution of poly(4,4'-oxydiphenylene pyromellitic acid). Film sample containing NiCl<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> or

Table 1. Mixed ratio of metal/PI and metal content in carbonized samples, measured by X-ray fluorescence analysis.

Sample	Mixed amount of metal metal (mmol)/PI(g)	Metal content (wt%)	
		600°C	800°C
Ni-A	0.818	6.7	7.1
Ni-C	0.932	8.0	9.1
Ni-N1	0.912	8.1	9.9
Ni-N2	1.836	15.5	19.3
Cu-N	0.945	7.9	8.3

Cu(NO<sub>3</sub>)<sub>2</sub> was fabricated from the solution. The sample containing nickel acetylacetonato (NiAA) was obtained as powder, because it was difficult to make film due to the gelation of the mixed solution. The samples imidized at 200°C with the mixed ratio of metal/PI in Table 1 are shown by the abbreviation of the name of metal compounds; e.g. Ni-A for NiAA, Ni-N for Ni(NO<sub>3</sub>)<sub>2</sub>. The pristine samples were carbonized at a heating rate of 3°C/min in flowing argon. Metal content after carbonization was measured by X-ray fluorescence analysis and listed in Table 1.

X-ray diffraction profiles were given by using a Rigaku RU-300 apparatus with CuK $\alpha$ . Nitrogen adsorption isotherms were measured by using Belsorp 28SA. Total pore volume was determined from the uptake at P/P<sub>0</sub>= 0.95. Cranston-Inkley method was used to determine the pore size distribution and mesopore volume.

## Results and Discussion

It was shown by TEM observations that the fine particles of Ni metal (cubic) with a diameter of ca. 10nm are dispersed in Ni-A and Ni-N's treated at 600°C [1]. The size of Ni particles became larger up to over 100nm by heat-treatment at 800°C. On the other hand, large Ni particles with the same size as that in Ni-A and Ni-N's at 800°C are formed in Ni-C even at 600°C. The development of turbostratic carbons, clearly shown in X-ray diffraction profiles in Fig. 1, occurs at 800°C in all Ni containing carbons. It can be observed by TEM that the carbon layers windingly developed in the whole of 800°C samples, though the micro-graphitic layers are only around metal particles at lower temperatures. It is noteworthy that all Ni containing samples treated at 800°C gave the same interlayer spacing ( $d_{002}$ =0.341nm) and average crystallite size ( $L_c$ =6nm). The growth of the turbostratic carbon by the function of metals has been well investigated from the view point of catalytic graphitization. Although the turbostratic carbon layers were not developed in Cu-N even at 800°C, it can be explained by the difference in catalytic activity between Ni and Cu.

Representative curves of pore size distribution determined by CI method are shown in Fig. 2. Mesopore formation is clearly found for Ni-N2 treated

above 700°C. As summarized in Table 2, formation of mesoporous structure similarly occurs at 800°C in all Ni containing samples, though the development manner is somewhat dependent on the original salt and the content. On the other hand, mesopore is not generated in Cu-N at 800°C.

It is obvious from the present result that the formation of mesopores is related to the growth of metal particles and the change of carbon microtexture. In case of metal catalyzed activation, the mesopore is formed by the oxidation on the metal oxide surface and no turbostratic carbon layers are observed [2]. Mesopores in the Ni-carbon complexes treated at 800°C is considered to be formed by the turbostratic carbon layers windingly developed from some planes of Ni crystal.

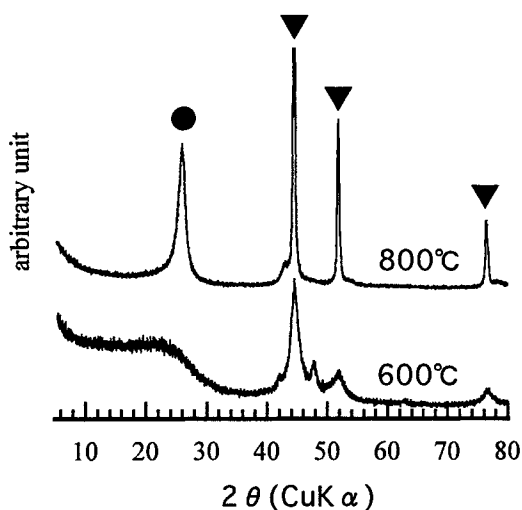


Fig. 1. X-ray diffraction profiles of Ni-N2 treated at 600°C and 800°C; ●: turbostratic carbon, ▼: Ni (cubic).

## Acknowledgments

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## References

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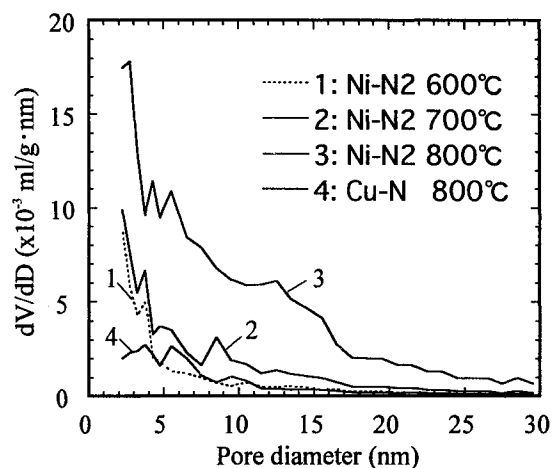


Fig. 2. Pore size distribution of carbonized samples determined by CI method.

Table 2. Change of the mesopore ratio by heat-treatment temperature; mesopore volume (cm<sup>3</sup>/g) / total pore volume (cm<sup>3</sup>/g) in parenthesis.

Samples	600°C	700°C	800°C
Ni-A	0.11 (0.025/0.221)	0.30 (0.076/0.256)	0.48 (0.096/0.200)
Ni-C	0.19 (0.045/0.238)	0.17 (0.037/0.212)	0.45 (0.106/0.237)
Ni-N1	0.12 (0.015/0.127)	0.08 (0.013/0.167)	0.73 (0.138/0.189)
Ni-N2	0.15 (0.024/0.162)	0.26 (0.042/0.161)	0.65 (0.124/0.190)
Cu-N	0.13 (0.029/0.228)	0.08 (0.017/0.205)	0.22 (0.020/0.090)