

Effects of the particle size of Ni- and Fe-catalyst on crystalline structure and morphologies of carbons prepared via catalytic graphitization

Katsuya Inomata, Takashi Fujimoto and Yoshinobu Otake

Department of Applied Chemistry, Meiji University,
Kawasaki, Kanagawa, Japan 214-8571

Introduction

The catalytic graphitization is a solid-state catalytic reaction of carbon. The carbonization of carbon precursor with metallic compound catalyzes the graphitization and forms the carbons composed of multi-components, e.g. amorphous component, graphite component (G-component), and turbostratic component (Ts-component). Recent studies showed that Ts-carbon, which consists predominantly of Ts-component, represented some catalytic activities, such as H_2S decomposition [1], methanol electrooxidation activity [2]. Nanoscaled morphologies, which consist of tube-like and block-like carbons etc, were found in Ts-carbon [2, 3]. There is, therefore, a growing interest in the studies relating to Ts-carbon. Moreover, Ts-carbon possesses mesoporous structure [2, 3]. We reported that the formation of mesopore in Ts-carbons is related to a unique carbon crystalline structure in Ts-component, which is partially graphitized and entangled [3]. These studies suggest that altering the crystalline structure in Ts-component possibly controls mesopore in Ts-carbons.

Oya et al. reported that heat treatment of Ts-component in Ts-carbon at elevated temperatures resulted in a formation of G-component, whereas the size of catalyst dispersed in the carbons enlarged as the temperatures of heat treatment increased [4]. This report implies that varying the catalyst size controls the carbon crystalline structure in Ts-component. However, the elevated temperature causes the sintering of catalyst and also influences the crystalline structures in Ts-component. In order to examine these two effects separately, the temperature of heat treatment was fixed at $1000^\circ C$ and altering the size of catalyst was accomplished by changing the concentration of catalyst loaded in carbon matrix. In this study, Fe and Ni were used as a catalyst, and an attempt was made to address the correlation between the particle size of catalysts and carbon crystalline structure in the Ts-component. Moreover, the discussion was made on the relation between the crystalline structure and mesoporous structure in Ts-carbons.

Experimental

Fe- and Ni-containing carbons were synthesized from phenolic resin (PF) by a following procedure described previously [3]. The catalyst content in PF was adjusted so that the sample carbonized at $1000^\circ C$ contains 0.001–1.0 mmol/g of Fe or Ni metal. The carbon samples thus obtained are named with metal content and metal species, such as 0.759 FePF and 0.082 NiPF. The crystalline structure in Ts-component and the size of doped Fe and Ni catalyst were

evaluated by X-ray diffractometer (XRD, Rigaku, Rint1200). The N_2 adsorption/desorption measurement was carried out at 77 K by Belsorp 18 plus in order to obtain pore size distribution. Scanning electron microscopy (SEM, Hitach, S-5200), and transmission electron microscopy (TEM, JEOL, JEM-2100F) were used to observe nanoscopic morphology of carbons.

Results and Discussion

The XRD measurement of the carbons carbonized at $1000^\circ C$ showed that Ts-component emerged in the carbons containing more than 0.001 mmol/g of Fe and 0.013 mmol/g of Ni. As the catalyst content increased, carbon crystal thickness (L_c) increased (Fig.1a), and interlayer spacing (d_{002}) decreased (Fig.1b) in Ts-component. These results indicate that the crystalline structure in Ts-component develops by the increase in concentration of Fe and Ni catalyst in Ts-carbon.

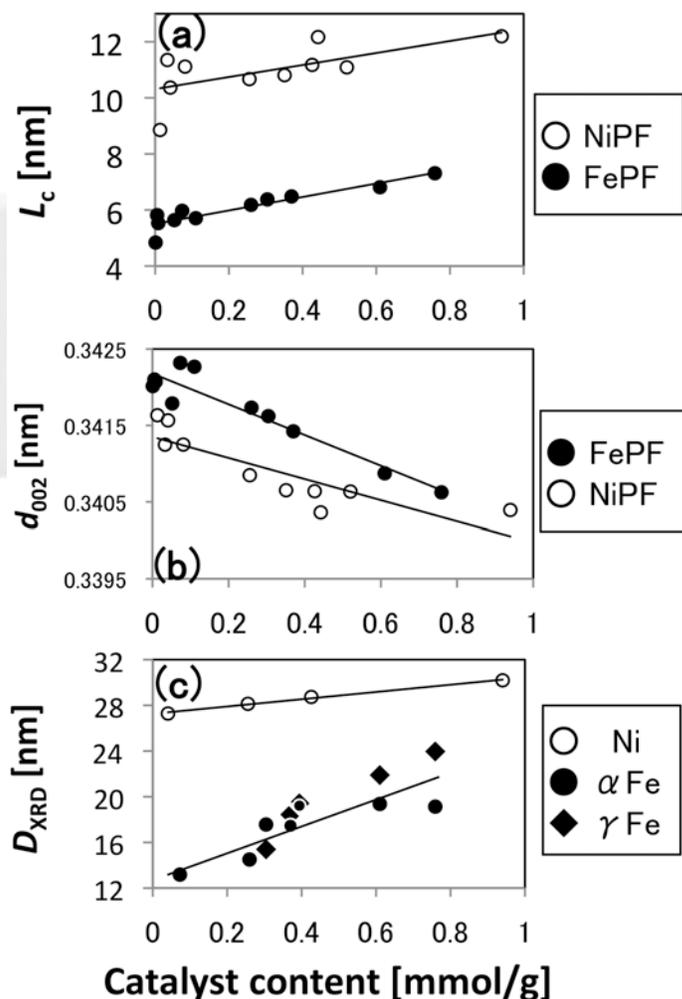


Fig.1 The change of L_c and d_{002} , and that of D_{XRD} in Ts-component as a function of metal content.

The phase of Fe and Ni in Ts-carbons was studied by XRD. The XRD profiles showed that the doped Fe and Ni exist as

metallic α -Fe, γ -Fe and Ni crystal. The mean crystal size of the metals (D_{XRD}) was determined by Scherrer equation. Fig.1c shows that the values of D_{XRD} for α -Fe, γ -Fe, and Ni increase with the metal content, possibly due to sintering effect of metals.

The values of L_c and d_{002} are plotted against D_{XRD} (Fig. 2) in order to discuss the effect of D_{XRD} on the carbon crystalline structure in Ts-component. The L_c increases and d_{002} decreases linearly in proportion to D_{XRD} for all metallic phases (α -Fe, γ -Fe, and Ni). These results indicate that the larger size of catalyst leads to the formation of more developed graphitic structure in Ts-component.

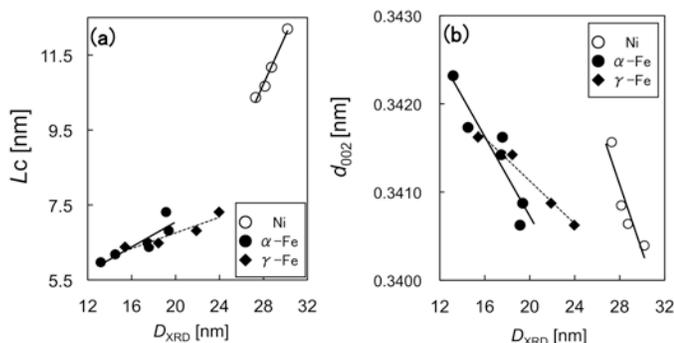


Fig. 2 Influence of D_{XRD} on (a) carbon crystal thickness, L_c , and (b) interlayer spacing, d_{002} .

Fig.3 shows pore size distribution for FePF and NiPF that contain various contents of metals in Ts-carbons. The increase in metal content resulted in the development of pores around 3-20 nm; that is, Ts-carbons with the higher catalyst contents possess the larger mesopores in size. The development of pore size in Ts-carbons is probably related to the development of graphitic structure in Ts-component.

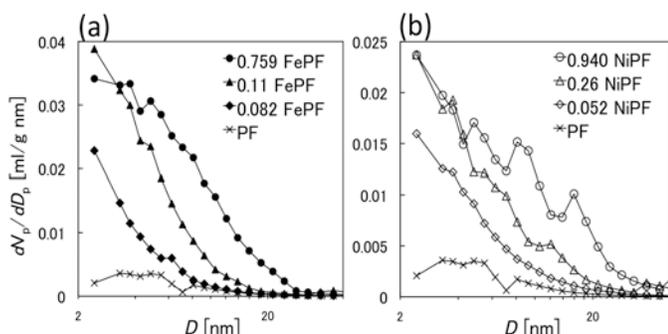


Fig. 3 Mesopore size distribution of FePF (a) and NiPF (b).

The TEM and SEM observations reveal the nanoscaled morphologies of Ts-carbons (Fig. 4). As we reported previously [3], tube-like carbon was found in FePF (Fig.4a, b), and block-like carbon in NiPF (Fig.4c, d). The length of tube-like carbon became longer with the content of Fe. Similarly, the increase in Ni content resulted in the growth of block-like carbon for the Ni catalyzed carbon. These carbons consist of

the graphitic carbon crystals in Ts-component. The growth of catalyst size might affect not only the crystalline structure but also the nanoscaled morphology in Ts-component.

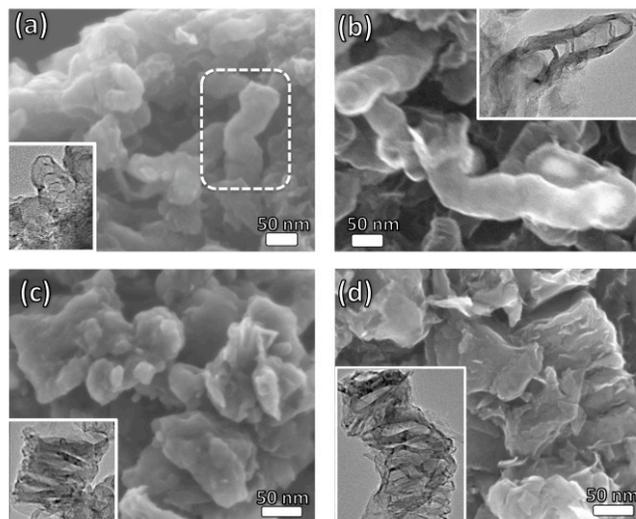


Fig. 4 The nanoscaled morphologies of FePF (a-b) and NiPF (c-d) observed by SEM and TEM (insert); (a) 0.0082 FePF, (b) 0.759 FePF, (c) 0.082 NiPF, (d) 0.940 NiPF.

Conclusions

Varying the catalyst size was accomplished by altering the content of metal loading and carbonizing under the same condition. The carbon crystalline structure in Ts-component is correlated with the size of Fe and Ni catalyst dispersed in Ts-carbon. The larger catalyst produces more graphitic carbon crystals in Ts-component. Controlling the crystalline structure in Ts-component resulted in the change in the mesoporous structure. The increase in size of catalyst might be related to the enlargement of the tube-like and block-like carbons in Ts-component.

References

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