CONVERSION OF GLYCEROL OVER GRAPHITE-NANOPLATELET CATALYST

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Introduction

The edges of nano carbon materials have been intensively studied due to varieties of properties. However, edges created on the verge of pinholes on basal plane of nano carbon attracted a little attention. Pinholes created on nano carbon materials have numerous possible applications. Lately, reduced graphite oxide with pinholes was directly observed by TEM, although the presence of pinholes was not emphasized [1]. This pinhole can be utilized as a space for coordinating metal ion. The theoretical studies of metal-coordinated carbon [2,3] and empirical studies of metal-coordinated carbon material using porphyrin [4] and wet impregnation of metal compound into carbon black [5] were reported, but the metal-coordinated at pinholes on graphite nanoplatelet has not been reported. In this work, the pinholes on graphite nanoplatelet were used as nanospace which coordinates metal ion. Especially, copper ion was adsorbed onto the graphite nanoplatelet, and the state of the adsorbed metal was determined by XPS. In other words, the pinholes on graphite nanoplatelet were utilized as ligands to coordinate copper ion planarly as shown in Fig. 1. The prepared samples were applied for catalytic reaction to convert glycerol into acetol.

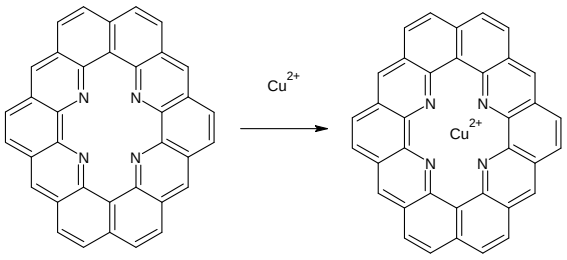

Fig. 1 An example of proposed structure of planar four-coordinated copper (II) into carbon nanoplatelet ligand.

Experimental

Highly purified graphite powder (SP270, Nippon Graphite Industries, Ltd., Japan) was oxidized by modified Staudenmaier method [6]. The graphite oxide was heated at 1050°C in air for 2 min (denote as PreO1050). The exfoliated graphite was heated in N_2 at 1000°C for 1h to remove the impurities and oxygen-containing functional groups (N1000). The powder was then heated in air at 420°C for either 3h or 9h (O420-3 or O420-9) for introducing nanopores [7]. N1000, O420-3, or O420-9 were heated in ammonia gas at 750°C for 0.5h and further heated in 750°C in N_2 for 0.5h (N1000-NH, O420-3-NH, or O420-9-NH). The resulting samples were immersed in the $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in isopropyl alcohol (IPA) at 30°C. The solution composed of nanoplatelet adsorbed Cu ion and IPA was centrifuged to separate nanoplatelet and liquid. Nanoplatelet was rinsed with IPA five times to remove excess Cu ion. Samples were further heated in N_2 at 500°C for 1h. Names of these samples are written as sample name-Cu.

Three samples were prepared as reference samples by the following preparation method. N1000 was immersed in $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in IPA. The amount of this solution was adjusted to prepare 1, 3, or 9 wt.% of Cu on N1000. The IPA was removed using evaporator at 40°C. These samples were also heated in N_2 at 500°C for 1h (R-1P, R-3P, or R-9P).

Samples were analyzed using Raman spectroscopy (NRS-2100, Jasco corp.) with 514.5 nm line of an argon ion laser at 100 mW output, XRD, and XPS (JPS-9010MX, Jeol Ltd.). Reaction of glycerol over nanoplatelet catalyst (10mg) was conducted using a fix-bed downflow reactor with inside diameter of 17 mm. 30 wt.% of glycerol dissolved into purified water was fed through the top of the reactor.

Results and Discussion

The BET surface area of as-received SP270 (250 m^2g^{-1}) was increased to 600 m^2g^{-1} after heating in N_2 at 1000°C for 1h, which corresponds to around 4 layers of graphene sheets on average. Heat treatment of PreO1050 in N_2 at 1000°C reduced 30wt.% of weight of sample, which implies some carbon and oxygen in the graphite nanoplatelet were removed by heat treatment in N_2. Raman spectra showed that heat treatment of PreO1050 (I_D/I_G=1.0) at 1000°C in N_2 significantly increased the amount of defects (I_D/I_G=1.4). It is estimated that N1000 had incredible amount of defects in the form of pinholes before heat treatment was conducted in air at 420°C.

Table 1. Contents of elements in graphite nanoplatelet-catalyst measured by XPS

Sample name	C 1s	O 1s	N 1s	Cu $2p_{3/2}$
R-3P	94	5	0.0	0.13
N1000-Cu	91	9	0.1	0.06
O420-9-Cu	89	10	0.2	0.19
N1000-NH-Cu	92	6	1.6	0.55
O420-9-NH-Cu	90	8	1.7	0.55

Table 1 shows that the amount of N and Cu is increased by treating in ammonia gas, but Fig. 2 shows that the peaks of CuO of R-3P at 35.4 and 38.6 degree is the largest among all analyzed samples, implying that the crystal size of CuO on R-3P was the largest among samples. Especially, in spite of five times of Cu content of R-3P, N1000-NH-Cu and O420-9-NH-Cu shows small peaks. This phenomenon can be explained by the results of XPS shown in Fig. 3. A peak at 935 eV indicated CuO was present on R-3P, N1000, and O420-9, but the peak of nanoplatelet treated by ammonia clearly shifted its peak to lower binding energy (932.8 eV), which indicates Cu ion is coordinated to ligand [8]. In addition, N1s peaks shows that

pyridine is dominant for ammonia-treated samples (N1000-NH and O420-9-NH), and the content of quartenary amine is negligible. From these results, it is clear that nitrogen is effectively doped at the edge of the nanoplatelet and worked as the effective functional group for coordination as shown in Fig. 1.

Fig. 4 shows the selectivity of glycerol into acetol. Various treatments gave different trend of catalytic activity. R-series shows high selectivity at 250°C and maintains at 300°C. Samples other than R-series shows low selectivity at 250°C, probably due to the presence of remaining oxygen-containing functional groups. However, catalysts including nitrogen increase its activity at 300°C, and show the highest among tested catalysts.

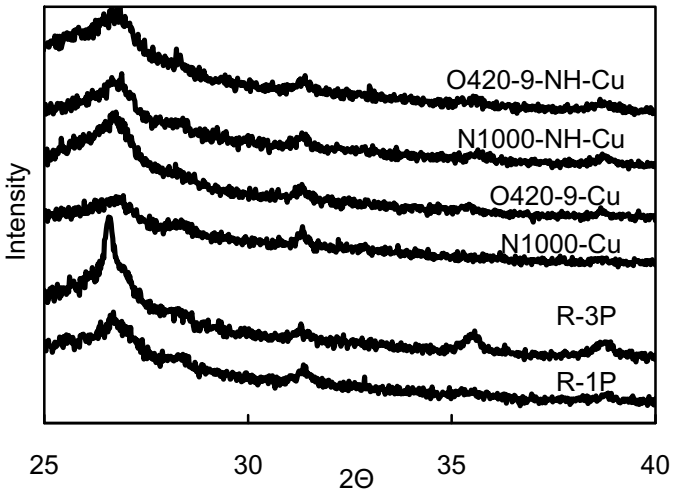

Fig. 2 Diffraction curves of graphite-nanoplatelet catalysts analyzed by XRD

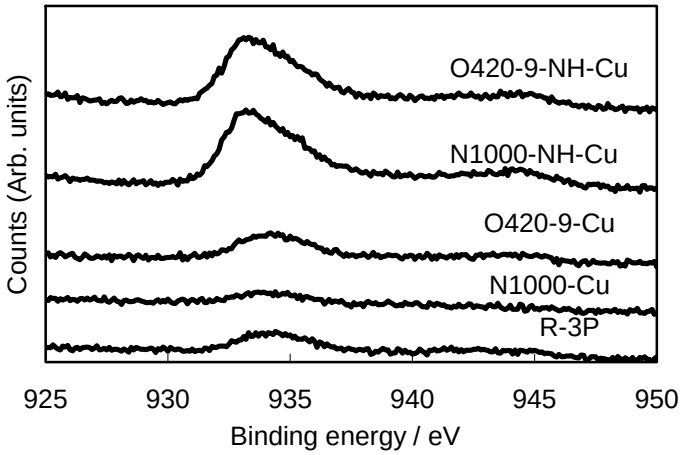

Fig. 3 Cu $2p_{3/2}$ spectra of graphite-nanoplatelet catalysts analyzed by XPS

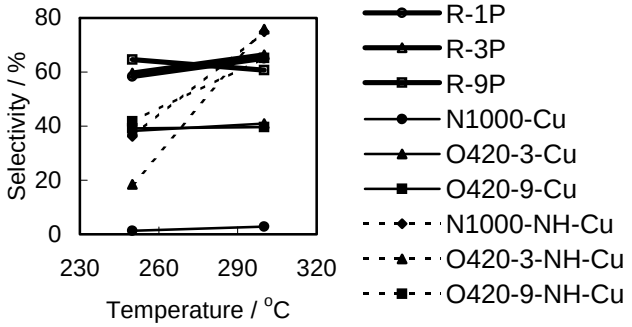

Fig. 4 Selectivity of glycerol into acetol over graphite nanplatelet catalyst

Conclusions

Nitrogen was successfully introduced at the edge of the pinholes as mainly pyridine. This carbon material was worked as a ligand to coordinate Cu ion. Preparation method significantly affects the selectivity of glycerol into acetol. The highest selectivity was obtained by reacting glycerol over the ammonia-treated nanoplatelet with coordinated Cu at 300°C.

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References

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