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Preparation of carbon supported Pt-Ni alloy nanoparticle catalyst with high metal loading using cation exchange resin and its application for hydrogen production.

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Highlights

- Carbon supported Pt-Ni alloy catalysts were prepared by using a cation exchange resin.
- The prepared catalysts had high metal loading and small metal particle size.
- $Pt_{50}Ni_{50}/C$ showed similar catalytic activity for formic acid decomposition to Pt/C.

1. Introduction

Utilization of hydrogen carrier has been attracting high attentions from many researchers for fuel-cell application and biomass conversion. Carbon supported metal catalysts, usually prepared by impregnation method, are used for these applications to produce hydrogen effectively. Although it is well known that catalytic activity is enhanced by increasing metal loading and by decreasing metal particle size, the metal particle size tends to increase with increasing the metal loading for impregnation method. To overcome the dilemma between metal loading and metal particle size, the new preparation method for carbon supported metal catalyst, such as Pt/C[1] and Ni/C[2], is proposed, which uses an ion-exchange resin as an original material. In this research, we applied this method to prepare carbon supported Pt-Ni alloy catalysts to further enhance the catalytic activity of hydrogen production from formic acid.

2. Methods

Four kinds of carbon supported metal catalysts, Pt/C, $Pt_{50}Ni_{50}/C$, $Pt_{25}Ni_{75}/C$, and Ni/C, were prepared by using a cation exchange resin, WK-11 (Mitsubishi Chemical), as carbon precursor and $Ni(NO_3)_2$ and $Pt(NH_3)_4Cl_2$ as metal sources. The metal ion was loaded to the ion exchange resin by adding the metal precursor solution of the predetermined composition (Pt:Ni = 100:0, 50:50, 25:75, or 0:100) and concentration (200 mmol/L for Ni/C and 7.3 mmol/L for the others) dropwise to the ion exchange resin solution and stirring the solution at room temperature for 24 h. During the ion exchange, the pH value of the ion-exchanging solution was adjusted at 8.8 using NH_3 aqueous solution. The ion exchanged resin was collected by filtration and dried overnight at room temperature. The carbon supported metal catalyst was finally obtained by carbonizing the ion exchanged resin at 500 °C for 30 min in a nitrogen stream. The metal loading of the catalysts was estimated by combusting them at 900 °C in an air stream. The metal crystal structure and the metal surface area were respectively measured by using an X-ray diffraction spectrometer (XRD) and a CO pulsed chemisorption at 50 °C. The metal particle size was estimated by three different methods; the XRD, the CO pulsed chemisorption, and a transmission electron microscopy (TEM).

Table 1. The properties of catalysts prepared.

		Pt/C	$Pt_{50}Ni_{50}/C$	$Pt_{25}Ni_{75}/C$	Ni/C
Metal loading [wt%]		49.4	32.7	31.9	53.8
Metal surface area [m^2/g]		16.7	7.3	5.8	5.3
Metal particle size	d_{XRD} [nm]	1.8	1.8	1.9	1.8
	d_{TEM} [nm]	2.7	2.4	2.3	3.6
	d_{CO} [nm]	8.3	21.4	25.7	68.0
Accessibility* [%]		15.4	16.2	12.4	2.7

$$* \text{ Accessibility [\%]} = \frac{\text{Active metal surface area where CO adsorbed } [m^2/g]}{\text{Total metal surface area estimated using } d_{XRD} \ [m^2/g]}$$

The hydrogen production from formic acid in gas phase was employed for the catalytic activity test. The predetermined quantity of the catalyst was placed in a reactor tube and pretreated in a 10 % hydrogen containing nitrogen stream at 350 °C. The catalyst in the reactor was then cooled to the reaction temperature ranging from 100 to 200 °C and the formic acid was fed to the reactor at 1 mL-liq/h by a syringe pump with 79.2 mL/min of

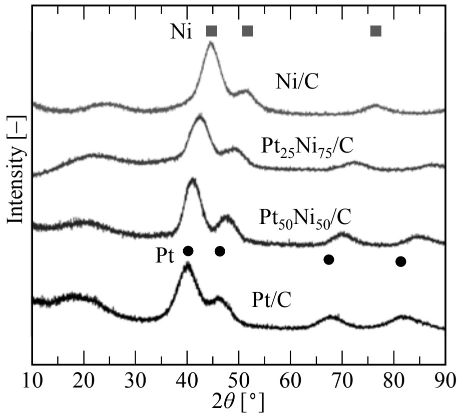

Figure 1. XRD patterns for the prepared catalysts.

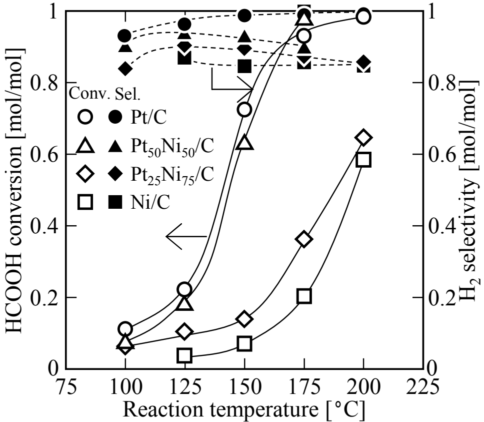

Figure 2. The catalytic activity for the prepared catalysts. (p_{HCOOH} = 12 kPa, W/F = 0.004 h g-Metal/g-HCOOH)

nitrogen stream. The W/F value was fixed at 0.004 h g-Metal/g-HCOOH. The product gas was quantified using an on-line gas chromatograph equipped with a thermal conductivity detector.

3. Results and discussion

The properties of the prepared catalysts were summarized in **Table 1**. All of the obtained carbon supported metal catalysts had spherical shape with the diameter of 200–500 μm. The metal loading was larger than 20 wt% for the all catalysts. **Figure 1** shows the XRD spectra for the obtained catalysts. For Ni/C and Pt/C, the peaks corresponding to metal were observed, indicating that the metals were loaded in metallic state. For $Pt_{50}Ni_{50}/C$ and $Pt_{25}Ni_{75}/C$, the peaks matched to neither metallic Pt nor Ni and shifted to the lower angle with increasing the proportion of Pt. This result suggests that the Pt-Ni alloy was formed during the preparation of PtNi/Cs. The metal particle sizes estimated by XRD (d_{XRD}) using Scherrer equation were smaller than 2 nm and they were almost similar to those observed by TEM (d_{TEM}), indicating that the metals in the catalysts exist as fine particles. From these results, the carbon supported metal catalysts with high metal loading and small particle size were successfully prepared. On the other hand, the metal particle sizes estimated by CO pulsed chemisorption (d_{CO}) were much larger than d_{XRD} and d_{TEM}. This difference is because that some part of metal surface was covered by carbon support during the carbonization and hence the surface area where CO could access was smaller than the geometric surface area.

Figure 2 shows the conversion of formic acid and hydrogen selectivity over the prepared catalysts at 100–200 °C. Hydrogen production proceeded above 100 °C over Pt/C and PtNi/Cs, while it proceeded above 125 °C over Ni/C. The conversion of formic acid over $Pt_{50}Ni_{50}/C$ was similar to Pt/C, suggesting that $Pt_{50}Ni_{50}/C$ could reduce Pt content without lowering its catalytic activity by forming Pt-Ni alloy.

4. Conclusions

We successfully prepared carbon supported Pt-Ni alloy catalysts with high metal loading and small metal particle size by using a cation exchange resin as an original carbon source. It was found that Pt-Ni alloy was formed during the catalyst preparation. $Pt_{50}Ni_{50}/C$ showed as high catalytic activity as Pt/C for formic acid decomposition, suggesting that Pt-Ni alloy could decrease Pt content without lowering its catalytic activity.

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References

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Keywords
Ion-exchange resin, Pt-Ni alloy, Formic acid decomposition.