Synthesis of Ni-Pt alloy carbon catalysts with high metal loading using cation-exchange resin for hydrogen production via formic acid decomposition

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Abstract: The dilemma between high metal loading and small metal particle size, typically occurred with high metal loading carbon catalyst prepared by impregnation method, could be overcome by using the ion-exchange resin technique. The carbon supported Ni-Pt alloy metal catalyst at high metal loading with fine particle was successfully prepared by using cation-exchange resin as a carbon support precursor. The catalytic activity of $Pt_{75}Ni_{25}/C$ resembled that of Pt/C toward formic acid decomposition, indicating Ni-Pt alloy could decrease Pt content without lowering its catalytic activity.

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

1. Introduction

The carbon supported metal catalyst, conventionally prepared by impregnation method, has been typically used for effective hydrogen production via formic acid decomposition. Generally, catalyst with metal loading and fine metal particle size are preferable to yield high catalytic activity. Although impregnation method is well known and straightforward, it has low capability to support large amount of metal in highly dispersed state due to an agglomeration of adjacent active metals. During preparation to overcome this dilemma condition of high metal loading and small metal particle size, the new preparation technique for carbon supported metal catalyst using ion-exchange resin as a precursor has been developed[1],[2]. In this research, the technique of using ion-exchange resin as a carbon precursor has been selected for synthesis of high metal loading Ni-Pt alloy catalyst with highly dispersed metal to further enhance the catalytic activity of hydrogen production via formic acid decomposition reaction.

2. Experimental

Four types of carbon supported metal catalysts, Pt/C, $Pt_{75}Ni_{25}/C$, $Pt_{25}Ni_{75}/C$, and Ni/C, which were prepared by using a cation-exchange resin, WK-11 (Mitsubishi Chemical), as a starting material. $Pt(NH_3)_4Cl_2$ and $Ni(NO_3)_2$ were used as Pt and Ni metal precursors. The metal cation in aqueous solution, corresponding to the predetermined compositions (Ni:Pt = 100:0, 75:25, 25:75, 0:100), was added into ion-exchange resin solution in dropwise to perform ion-exchange process. The molar ratio of metal to ion-exchange site and concentration of metal solution during ion-exchange process was fixed as 0.25 and 0.0075 M, respectively, for all samples except for Ni/C in which the metal solution concentration was 0.2 M., continually stirring at room temperature for 24 h. Simultaneously, pH value was adjusted at 8.8 by NH_3 aqueous solution. The metal loaded resin was collected and dried overnight at room temperature, followed by carbonization at 500 ºC for 30 min in N_2 atmosphere. The metal loading was estimated by combustion at 900 ºC in an air stream. An X-ray diffraction spectrometer (XRD) and a CO pulsed chemisorption at 50 ºC were used for metal crystal structure and metal surface area analyses. The metal particle size was estimated by three different methods; the XRD, the CO pulsed chemisorption, and a

Table 1. The properties of catalysts prepared.

		Pt/C	$Pt_{75}Ni_{25}/C$	$Pt_{25}Ni_{75}/C$	Ni/C
Metal loading [wt%]		49.4	42.8	31.9	53.8
Metal surface area [m^2/g]		16.7	10.3	5.8	5.3
Metal particle size	d_{XRD} [nm]	1.8	1.6	1.9	1.8
	d_{TEM} [nm]	2.7	2.4	2.3	3.6
	d_{CO} [nm]	8.3	12.6	25.7	68.0
Accessibility* [%]		15.4	12.5	12.4	2.7

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

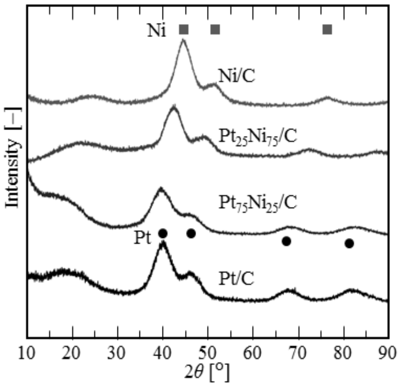

Figure 1. XRD patterns of the prepared catalysts

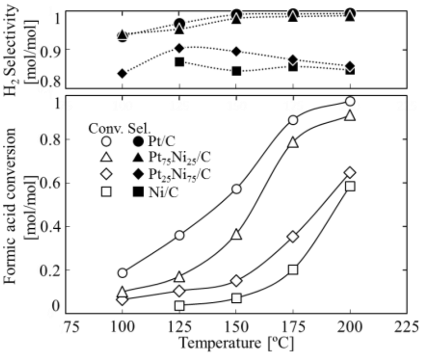

Figure 2. The catalytic activity of the prepared catalysts. (p_{HCOOH} = 12 kPa, W/F = 0.004 h g-Metal/g-HCOOH)

transmission electron microscopy (TEM). The catalytic activity test for H_2 production via formic acid decomposition was conducted in a flow reactor after 1 h of catalyst pretreatment in 10 % H_2/N_2 stream at 350 ºC. The catalyst in the reactor then was cooled to the reaction temperature ranging from 100 to 200 ºC. Formic acid was fed into reactor at 1 mL-liq/h with 79.2 mL/min of N_2. The W/F was controlled at 0.004 h g-Metal/g-HCOOH. The product gas was quantitatively analyzed by an on-line gas chromatography equipped with a thermal conductivity detector.

3. Results and discussion

The results, according to **Table 1,** show that the metal loading of all prepared catalyst was higher than 30 wt%. According to **Figure 1**, the XRD pattern shows that the observed peak of Pt/C and Ni/C were consistent with the characteristic peak of Pt and Ni, respectively, indicating the metals were loaded in metallic state. On the other hand, the observed peak of $Pt_{75}Ni_{25}/C$ and $Pt_{25}Ni_{75}/C$ were corresponding to neither Pt nor Ni characteristic peak and shifted to the higher angle with increasing the Ni composition. This result can be claimed that the Ni-Pt alloy was formed during NiPt/Cs preparation. The metal particle size estimated from XRD (d_{XRD}) using Scherrer's equation and by TEM (d_{TEM}) were almost similar at approximately 2 nm, indicating the metal particles were in highly dispersed state. These results confirm that carbon supported Ni-Pt alloy metal catalyst at high metal loading with fine particle can be obtained by using the ion-exchange resin as a carbon support precursor. Nevertheless, the metal particle size which estimated from CO chemisorption metal surface area (d_{CO}) was significantly larger than d_{XRD} and d_{TEM}. The result could be attributed to the difference between the metal surface area which can be accessed by CO and the geometric surface area. It is indicated that most of the metal particles were embedded in the carbon support layer. **Figure 2** shows that formic acid conversion considerably increased with the Pt composition whereas H_2 selectivity was slightly increased. The TOF of $Pt_{75}Ni_{25}/C$ was similar to that of Pt/C at temperatures below 150 ºC while the TOF of $Pt_{75}Ni_{25}/C$ at 175 ºC (2.12 s^{-1}) was larger than that of Pt/C (1.99 s^{-1}). The result indicates that the reduction in Pt content can be performed by $Pt_{75}Ni_{25}/C$ without decreasing the catalytic activity due to the alloy formation.

4. Conclusions

The carbon supported Ni-Pt alloy metal catalyst at high metal loading (>30 wt%) with fine particle (≈2 nm) was successfully prepared by using cation-exchange resin as a carbon support precursor. All of the catalysts show catalytic activity of H_2 production via formic acid decomposition above 125 ºC. The catalytic activity of $Pt_{75}Ni_{25}/C$ was similar to that of Pt/C, indicating the ability of reducing Pt content without lowing the catalytic activity of Ni-Pt alloy catalyst.

References

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