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Author(s)	Jiang, Chuanxia; Hara, Kenji; Namba, Kotaro; Kobayashi, Hirokazu; Ittisanronnachai, Somlak; Nishihara, Hirotomo; Kyotani, Takashi; Fukuoka, Atsushi
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Preparation of Highly Dispersed Pt Nanoparticles Supported on Zeolite-templated Carbon and Catalytic Application in Hydrogenation Reaction

Chuanxia Jiang,^{1,2} Kenji Hara,¹ Kotaro Namba,^{1,2} Hirokazu Kobayashi,¹ Somlak Ittisanronnachai,³ Hiroto Nishihara,³ Takashi Kyotani³ and Atsushi Fukuoka^{*1}

¹ Catalysis Research Center, Hokkaido University, Sapporo 001-0021

² Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628

³ Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577

(Received <Month> <Date>, <Year>; CL-<No>; E-mail: <fukuoka@cat.hokudai.ac.jp>)

Zeolite-templated carbon (ZTC) was utilized to prepare Pt nanoparticles as a support by using a simple impregnation method. The choice of a cationic Pt precursor led to the formation of highly and uniformly dispersed Pt nanoparticles on ZTC, which afforded a high conversion in catalytic hydrogenation of phenylacetylene.

In heterogeneous metal-catalyzed reaction, support materials play a key role in modifying catalytic activity and selectivity. Various metal nanoparticles have been prepared on numbers of metal oxides and carbons for a wide variety of catalytic application. Novel catalytic performance can be expected with a catalyst prepared on a new type of support material. Zeolite-templated carbon (ZTC)¹ is a potentially promising support, because ZTC is a carbon replica obtained from a zeolite as a template, giving ordered three-dimensional micropores consisting of nano-sized graphene units. Although ZTC has been extensively studied as attractive materials for storage of hydrogen,^{2,3} electrochemical capacitors³ and lithium-ion batteries,³ its application in catalysis has been limited to the studies related with fuel cell.⁴ In addition, the metal nanoparticles incorporated in zeolite for fuel cell applications were prepared using Pt-incorporated zeolite. We thus envisioned further utilization of ZTC as a catalyst support by using a simple impregnation method. Herein we report the preparation of Pt nanoparticles on ZTC and their catalytic performance in hydrogenation of phenylacetylene.

Many inorganic and organic materials such as SiO₂,⁵ γ -Al₂O₃,^{6,8} pumice,⁸ zeolites,⁹ polymers,⁹ organic matrices,¹⁰ clays,¹¹ mesostructured silica^{8,12} and TiO₂¹³ have been already employed as supports for Pt, Pd, Ni and Cu catalysts in the hydrogenation of phenylacetylene. As recent examples of supported metal catalysts on carbon materials, Pd, Pt, Ru and Pt-Ru on carbon nanotube were used for this reaction,¹⁴ whereas metal catalysts supported on ZTC have not been applied. ZTC was obtained by the reported method using zeolite Y as a template.^{1d} The Pt catalyst supported on ZTC (Pt/ZTC) was prepared by a typical wet impregnation method. ZTC (0.2 g) was mixed with an aqueous solution (50 mL) of diamminedinitrito-platinum(II) (Pt(NH₃)₂(NO₂)₂) with a Pt loading of 2 wt%. The mixture was stirred for 18 h, evaporated to dryness and dried under vacuum for overnight. The resulting solid was reduced in H₂ flow at 400 °C for 2 h. For comparison, commercially available carbon materials such as Ketjen Black EC-600JD (KB) and Norit SX ultra (denoted as AC) were used as supports to prepare Pt/KB and

Pt/AC, respectively. As another Pt precursor, hydrochloroplatinic acid (H₂PtCl₆·6H₂O) was used to prepare a Pt catalyst on ZTC (Pt/ZTC-Cl). The four Pt catalysts used in this study are summarized in Table 1.

Table 1. Preparation of Pt catalysts and their particle sizes.

Pt catalysts	Pt Precursor	Pt particle diameter (nm)	
		XRD	TEM
Pt/ZTC	Pt(NH ₃) ₂ (NO ₂) ₂	1.7	2.2 ± 0.8
Pt/KB	Pt(NH ₃) ₂ (NO ₂) ₂	2.5	3.5 ± 1.2
Pt/AC	Pt(NH ₃) ₂ (NO ₂) ₂	4.4	4.4 ± 1.1
Pt/ZTC-Cl	H ₂ PtCl ₆ ·6H ₂ O	17	15 ± 11

Figure 1. XRD patterns of carbon supports and supported Pt catalysts.

Figure 1 shows XRD patterns of the Pt catalysts and the carbon supports. No obvious Pt peaks were obtained for Pt/ZTC and Pt/KB, giving weak and broad peaks at 40°. In contrast, three intense peaks were found with Pt/AC and Pt/ZTC-Cl at 40, 46 and 67°, which were assigned to (111), (200) and (220) reflections of face-centered cubic (fcc) Pt crystalline (JCPDS card, No. 04-0802), indicating the formation of large Pt nanoparticles. The Pt particle sizes of Pt/ZTC, Pt/KB, Pt/AC and Pt/ZTC-Cl were estimated by the Scherrer equation with the (111) peaks to be 1.7, 2.5, 4.4 and 17 nm, respectively (Table 1).

In the TEM observation (Figure 2), the Pt particles on Pt/ZTC were highly and uniformly dispersed on ZTC with a mean diameter of 2.2 ± 0.8 nm based on 100 particles in random regions (Figure 2a). Larger Pt particles were observed in Pt/KB and Pt/AC with mean sizes of 3.5 ± 1.2 nm and 4.4 ±

1.1 nm, respectively, as shown in Figure 2b and c. In contrast, Pt/ZTC-Cl catalyst had a relatively larger size and broader distribution with 15 ± 11 nm (Figure 2d). The Pt particle sizes analyzed by TEM were in good accordance with the results estimated by XRD (Table 1).

Figure 2. TEM images (left) and particle size distributions (right) of the (a) Pt/ZTC, (b) Pt/KB, (c) Pt/AC and (d) Pt/ZTC-Cl.

The uniformly dispersed smaller Pt particles observed in Pt/ZTC can be attributed to extremely high specific surface area of ZTC (ca. $4000 \text{ m}^2\text{g}^{-1}$) compared to KB (ca. $800 \text{ m}^2\text{g}^{-1}$) and AC (ca. $1200 \text{ m}^2\text{g}^{-1}$). In addition, the high dispersion of Pt particles might be due to the presence of higher amount of surface functional groups on ZTC surface. ZTC has a uniquely high oxygen content (9wt%) and proposed oxygen functional groups are mainly ether groups together with minor functionalities such as phenol and acid anhydride.^{1d} The cationic Pt precursor to prepare Pt/ZTC, $\text{Pt}(\text{NH}_3)_2^{2+}$, possibly has a strong attractive interaction with such oxygen-containing functional groups on ZTC. In contrast, the anionic Pt precursor, PtCl_6^{2-} , can have a repulsive interaction with the surface functional groups¹⁵ on ZTC, which may enhance the aggregation of the Pt nanoparticles in Pt/ZTC-Cl.

Hydrogenation of phenylacetylene was carried out with 0.50 mL of phenylacetylene, 5.0 mg of the catalyst and 4.5 mL of ethanol in a 50 mL autoclave under controlled H_2 pressures and temperatures. The molar ratio of

phenylacetylene/Pt(bulk) was 8900. The products were analyzed by a Shimadzu GC-14B gas chromatograph using an FID detector with a capillary column (HR-1, $0.25 \text{ mm} \times 50 \text{ m}$). A known amount of *n*-dodecane was added to the reaction mixture as an internal standard.

Figure 3 shows the conversion and selectivity for styrene by the Pt catalysts under the conditions of 0.40 MPa H_2 at 50 °C. Pt/ZTC catalyst afforded 63% conversion in 60 min, which was apparently the best among the tested catalysts. Pt/KB and Pt/AC gave conversions of 53 and 25%, respectively. Pt/ZTC-Cl resulted only in 3% conversion. The striking difference in conversion among the tested catalysts can be attributed to the difference in Pt particle size. The high dispersion of Pt nanoparticles on ZTC probably afforded the high conversion due to the more available Pt surface area for the reaction. This attribution can be supported by the fact that the conversions increase in almost direct proportion to the Pt surface areas estimated from the Pt particle diameters (Table 1).

Figure 3. Hydrogenation of phenylacetylene over the different Pt catalysts supported on carbon. Reaction conditions: 0.4 MPa H_2 , 50 °C

Pt/ZTC catalyst was further utilized to investigate the influence of H_2 pressure (Figure 4) and reaction temperature (Figure 5) on hydrogenation of phenylacetylene. As shown in Figure 4, the higher H_2 pressure afforded the higher conversion of phenylacetylene, but the selectivity to styrene dramatically dropped under 0.70 MPa H_2 . Figure 5 indicates that elevated reaction temperature increases the phenylacetylene conversion while the styrene selectivity gradually decreases. The optimized conditions are 0.4-0.5 MPa and 60-80 °C, giving 75-78% yields of styrene in 60 min.

Figure 4. H₂ pressure effect on hydrogenation of phenylacetylene over the Pt/ZTC catalyst. Reaction conditions: 0.2-0.7 MPa H₂, 50 °C, 60 min

Figure 5. Reaction temperature effect on hydrogenation of phenylacetylene over the Pt/ZTC catalyst. Reaction conditions: 0.4 MPa H₂, 40-80 °C, 60 min

In order to confirm the durability of the Pt nanoparticles supported on ZTC, recycle use of Pt/ZTC for the catalytic reaction was conducted. As shown in Figure 6, the similar catalytic performance was obtained for three successive recycle runs. The heterogeneity of the catalyst was confirmed by observation of no further conversion after removing the catalyst from the reaction mixture. In addition, the TEM observation of Pt/ZTC after the catalytic hydrogenation reaction showed almost no change in the narrow Pt particle size distribution (2.2 ± 0.8 nm), which suggests the stability of the Pt nanoparticles on supported on ZTC during the reaction conditions.

Figure 6. Recycle use of Pt/ZTC for hydrogenation of phenylacetylene. Reaction conditions: 0.4 MPa H₂, 50 °C, 60 min

Although the selectivity to styrene with Pt/ZTC were not extremely high (85-90%) even in a shortened reaction time (15 min) leading to a lower conversion (Figure 3), high conversions were obtained with a relatively low catalyst amount compared to a recently reported catalyst with Pt nanoparticles of 1.8 nm size (average size by TEM) supported on surface-oxidized carbon nanotube.^{14c} The remaining by-product was only ethylbenzene with the all Pt catalysts examined in this study.

In summary, Pt catalysts supported on zeolite-templated carbon (ZTC) were prepared by using a simple impregnation method and applied to hydrogenation of phenylacetylene. The utilization of ZTC as a catalyst support with a cationic Pt

precursor gave highly and uniformly dispersed Pt nanoparticles and led to the highest conversion in catalytic hydrogenation of phenylacetylene among the Pt catalysts prepared in this study.

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