

Effect of Preparation Conditions on the Hydrogenation Activity and Metal Dispersion of Pt/C and Pd/C Catalysts

Sung Hwa Jung, Jin-Ho Lee, Jong-Min Lee, Ji Hye Lee, Do-Young Hong, Myong Woon Kim,[†] and Jong-San Chang^{*}

Research Center for Nanocatalysts, Korea Research Institute of Chemical Technology, P.O. Box, 107, Yusong, Daejeon 305-600, Korea. *E-mail: jschang@kRICT.re.kr

[†]DNF Solution Co., Moon Pyung Dong, Daedeok, Daejeon 306-220, Korea

Received November 30, 2004

The Pt/C and Pd/C catalysts were prepared from conventional chloride precursors by adsorption or precipitation-deposition methods. Their activities for hydrogenation reactions of cyclohexene and acetophenone were compared with those of commercial catalysts. The Pt/C and Pd/C catalysts obtained from the adsorption procedure reveal higher hydrogenation activity than commercial catalysts and the catalysts prepared by the precipitation-deposition method. Their improved performances are attributed to the decreased metal crystallite sizes of Pt or Pd formed on the active carbon support upon the adsorption of the precursors probably due to the same negative charges of the chloride precursor and the carbon support. Under the preparation conditions studied, the reduction of the supported catalysts using borohydrides in liquid phase is superior to a gas phase reduction by using hydrogen in the viewpoint of particle size, hydrogenation activity and convenience.

Key Words : Pt/C, Pd/C, Hydrogenation, Dispersion, Adsorption/Deposition

Introduction

Carbon-supported platinum group metals (PGM) such as Pt and Pd have been used as selective catalysts for organic synthesis for a long time.¹⁻³ However, most of the publications are devoted to the application rather than to the preparation or characterization.⁴ Moreover, the preparation methods of the PGM/C catalysts rely mainly on experience and tend to be predominantly empirical in nature.⁵ Only recently, a number of scientific publications on the synthesis and characterization have increasingly appeared.⁶⁻⁸

Several process conditions for the preparation of the PGM/C catalysts have been analyzed. For example, effects of pore structure of carbon support were studied by Okhloкова *et al.*⁴ They have found that the catalytic activity is not consistent with the dispersion of a metal supported on carbon. The hydrogenation activity per mass of metal reached a maximum in the range of intermediate metal dispersion. This inconsistency could be explained with the pore structure of carbon; if the pore size is too small (micropore) the entrapped PGM cannot be utilized fully as a catalyst.

The effects of reduction temperature, types of carbon and precursors and microporosity were also studied.⁵ The reduction temperature of 123 °C was optimum and types of metal precursors and carbon supports were important for the catalytic activity, whereas the pretreatment conditions of the support were not critical. Compared with a mesoporous carbon, traditional active carbon containing microporosity was not suitable as a support. Moreover, the effectiveness of the precursors for the Pd/C was in the order of $\text{PdCl}_2 < \text{Pd}(\text{OAc})_2 \sim \text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$.

Three methods such as adsorption, impregnation and

deposition have been mainly applied for the loading of the PGM on an active carbon.² Supporting by adsorption utilizes a chemical interaction between carbon and metal precursor. The incipient wetness method is usually used because the adsorption process depends on the equilibrium of the interaction. Fine metal particles can be obtained from tetraammine metal hydroxides such as $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ and $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ if the adsorbed species are reduced by hydrogen at 100-300 °C. However, the adsorption of metal chloride complexes is very complicated due to diverse mechanisms of interaction between metal chloride complexes and the carbon surface.

The PGM can also be loaded on carbon by using the impregnation method. The amount of metal loading can be high with the impregnation even though the size of the metal crystallites increases with the metal loading. In this case the pore structure is important not to cause pore blocking.

The third method to load PGM is based on the deposition by precipitation etc. There are three ways to deposit metals on carbon:

A. An alkaline solution is added to the support suspension in a Pd(II) solution.

B. A Pd(II) salt solution is added to the support suspension in an alkaline solution.

C. A solution of a Pd(II) and an alkali is contacted with carbon.

The activity of the prepared catalyst from method B is generally higher than the catalyst made by method A when the dispersion of the supported metals is similar.⁹ The method C is insensitive to the properties of the carbon support and leads to egg shell distribution.

However, the detailed analysis of preparation methods including hydrogenation condition has not been reported

well even though PGM/C catalysts have been used very widely. In the present study, we investigate the effects of preparation methods on the particle size and hydrogenation activity to develop commercially viable hydrogenation catalysts from conventional active carbon and inexpensive chloride precursors.

Experimental Section

Preparation and characterization of catalysts. Pt/C and Pd/C catalysts were prepared using adsorption and deposition processes, and the concentration of the PGM was fixed to 10 wt %. The adsorption process was performed by contacting active carbon (Darco G-60) to aqueous PGM solution. For deposition, aqueous PGM solution was added dropwise to the premixed carbon and Na_2CO_3 slurry. The catalysts were prepared from chloride precursors ($\text{PdCl}_2 + \text{HCl}$ or H_2PtCl_6) and the reduction after the supporting was performed in gas phase by hydrogen (~ 30 cc/min per 1 g of catalyst) at 250°C or in liquid phase using formaldehyde at 85°C or sodium borohydride at room temperature. Otherwise specified, the ratios of molar concentrations of base and liquid reductant to the metal were 4 and 3, respectively, ($\text{Na}/\text{PGM}=4$; HCOH or $\text{NaBH}_4/\text{PGM}=3$) similar to previous methods,¹⁰ and all chemicals were provided by Aldrich and used without further purification. The catalysts were denoted as Pt/C (PL), Pt/C (PG), Pt/C (AL), Pt/C (AG), Pd/C (PL) and Pd/C (AL). The notation of P, A, L, and G means precipitation-deposition, adsorption, liquid phase reduction and gas phase reduction, respectively. The detailed preparation scheme is shown in Figure 1. Commercial catalysts denoted as Pt/C(Comm-A), Pd/C (Comm-A) or Pd/C (Comm-D) were used for comparison.

The phase and crystallinity of the samples were determined with a X-ray diffractometer (Rigaku, MiniFlex, Cu

Table 1. Reaction and analysis conditions for hydrogenation of cyclohexene and acetophenone

Variable	Cyclohexene hydrogenation	Acetophenone hydrogenation
Catalyst	Pt/C or Pd/C (50 mg)	Pd/C (50 mg)
Reactant	Cyclohexene (6g)	Acetophenone (2 g)
Solvent	Methanol (94g)	n-hexane (98 g)
Reaction time	15-60 min	15-60 min
Hydrogen pressure	5 atm	10 atm
Reaction temperature	30°C	30°C
Analysis	GC (FID)	GC (FID)

$K\alpha$ radiation). The crystal size was calculated using the Scherrer equation for the XRD peak from the (111) plane. The scan speed and scan step were $0.2^\circ/\text{min}$ and 0.02° , respectively, for the two theta range of 36 – 46 . The size and morphology of PGM particles were analyzed using a high resolution transmission electron microscope (Philips CM-30). The concentration of PGM was analyzed using an inductively coupled plasma-emission spectrometer (Jobin Yvon Ultima-C).

Hydrogenation of cyclohexene and acetophenone. The prepared catalysts were evaluated with hydrogenation reactions of cyclohexene and acetophenone. The reaction was carried out using a stainless Parr reactor while stirring. The reaction temperature was maintained at 30°C using a water bath. The products, after separated from the catalyst, were analyzed with a FID-GC using an internal standard such as n-dodecane. The detailed reaction and analysis conditions are shown in Table 1.

Results and Discussion

Preparation and characteristics of Pt/C catalyst. Figure

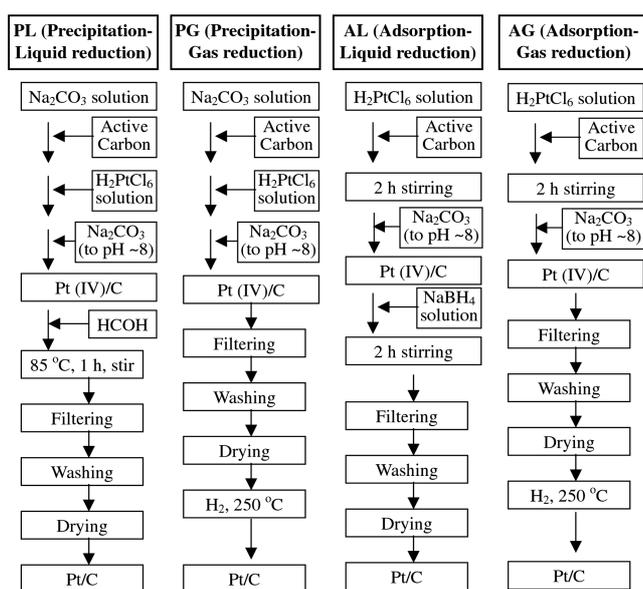


Figure 1. Preparation methods for the Pt/C catalysts. Pd/C catalysts were prepared by the same method as Pt/C.

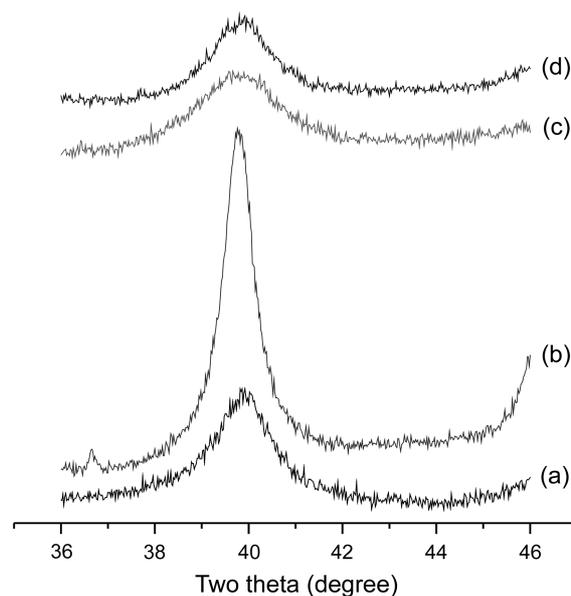


Figure 2. XRD patterns of Pt/C catalysts: (a) Pt/C (Comm-A), (b) Pt/C (PG), (c) Pt/C (AL) and (d) Pt/C (AG).

Table 2. Conversion of cyclohexene over various Pt/C catalysts

Catalyst	Pt size (nm)	Cyclohexene conversion (mol %)	
		15 min	30 min
Pt/C(Comm-A)	5.9	22	62
Pt/C(PL)	9.8	15	ND**
Pt/C(PG)	10.2	ND**	28
Pt/C(AL)	4.2	38	78
Pt/C(AG)	6.2	ND**	34
Pt/C(Colloid*)	3.1	40	61

*Pt/C catalyst prepared via black colloid made from ethylene glycol and H_2PtCl_6 .¹² **ND: not determined

2 shows the XRD patterns of prepared Pt/C catalysts and a commercial Pt/C catalyst, and the FWHM (full width at half maximum) of XRD peak from Pt (111) is in the order of Pt/C (AL) > Pt/C (Comm-A) ~ Pt/C (AG) > Pt/C (PG). The XRD pattern in wide range (data not shown) coincides well with the XRD pattern of FCC Pt.¹¹ The Pt sizes calculated from the FWHM of Pt (111) using the Scherrer equation are shown in Table 2. The Pt size of Pt/C (Colloid) prepared from black colloid using ethylene glycol¹² is smallest among the catalysts. However, this Pt/C (Colloid) is not so promising for commercial application considering the complex preparation procedure¹² and the comparable catalytic activity (see below) to the Pt/C (AL). The TEM images of Pt/C (Comm-A) and Pt/C (AL) are shown in Figure 3, clearly indicating that the particle size of Pt/C (AL) is more regular and smaller than that of the Pt/C (Comm-A). Moreover, the sizes determined with TEM agree well with the sizes calculated from XRD peak. The Pt contents of the supported catalysts determined by ICP are approximately 10 wt %, not showing any dependence on the preparation methods.

The conversion of cyclohexene at 15 min and 30 min over the various Pt/C catalysts are presented in Table 2. It can be presumed that the hydrogenation activity decreases with increasing the Pt size as the dependence of cyclohexene conversion on the particle size of Pt is plotted in Figure 4. The activity decreases gradually with increasing the Pt size from 6 nm and the activity increases sharply below about 4 nm.

From the particle size and activity (Table 2), it can be

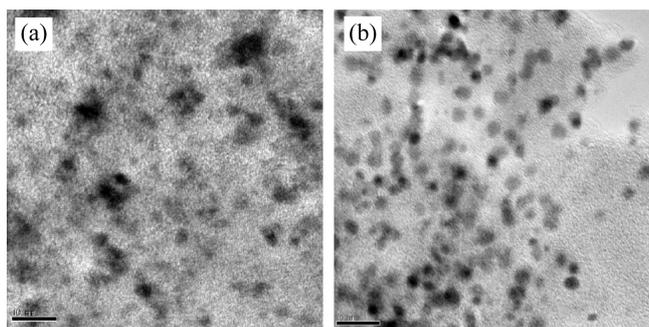


Figure 3. TEM images of Pt/C catalysts: (a) Pt/C (Comm-A) and (b) Pt/C (AL). Scale bar corresponds to 10 nm.

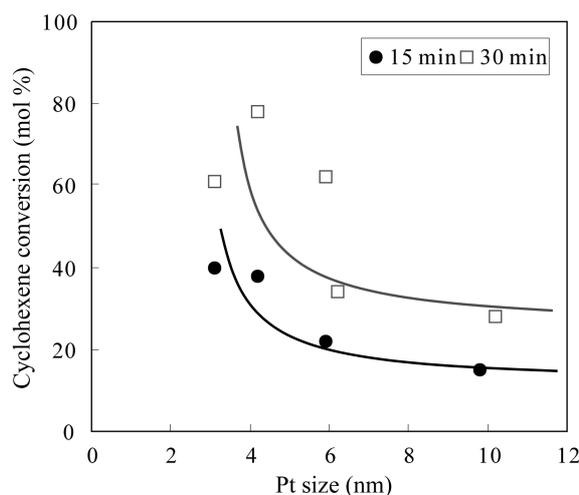


Figure 4. Dependence of cyclohexene conversion on the Pt crystallite size in Pt/C catalysts.

concluded that the preparation method of adsorption is superior to the deposition via precipitation. The zeta-potential of the surface of a carbon is negative in an alkaline condition.¹³ The chloride precursor exists in an anionic form different from the neutral species such as acetate compounds or cationic species such as ammine compounds.⁵ So, the interaction between carbon and the chloride precursor is very weak and the adsorption process is so slow to form well dispersed fine particles. The deposition via precipitation will be fast to cause the size of adsorbed species to be large. The slow adsorption and formation of fine particles (even though the loading is decreased) from the interaction between species with the same negative charge have been recently reported in the preparation of supported gold catalysts.¹⁴ It has been reported that gold exists in a highly dispersed state if the precursor Au complex is adsorbed with an anionic form.¹⁴

As shown in Figure 2 and Table 2, the reduction using liquid phase reaction exhibits better results compared with the gas phase reduction using hydrogen. Traditionally, gas phase reduction of PGM precursors has been used especially for large scale production even though liquid phase reduction using reductant such as formaldehyde, hydrazine, sodium formate and sodium borohydride is also common.³ It has been reported that the performances of the PGM/C catalyst prepared by the reduction with hydrogen rely on the reduction temperature^{4,5} and the residual moisture in the hydrogenation shows very detrimental effects.⁴ It seems that the effects of reduction temperature are not agreed on by various research groups. For example, the optimum temperatures for Pd/C and Pt/C for hydrogenation activity are reported to be about 250 and 350 °C, respectively.⁴ Gurrath *et al.*⁵ have found that the reduction temperature of 123 °C is optimum for Pd/C. Semikonelov *et al.*¹⁵ have reported that effect of temperature on the metal particle size is rather small if the treatments are performed below 223-323 °C. Therefore, the poor performance of the Pt/C (AG) and Pt/C (PG) prepared using gas phase reduction might be related

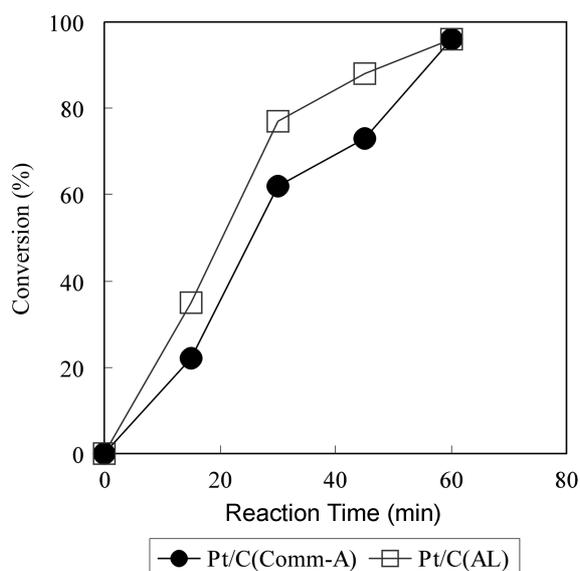


Figure 5. Comparison of conversion of cyclohexene hydrogenation over Pt/C (Comm-A) and Pt/C (AL) catalysts.

with a bit higher temperature or residual moisture. This should be explored more for further understanding.

The hydrogenation activities of Pt/C (Comm-A) and Pt/C (AL) that was produced in larger scale are compared according to the reaction time (Fig. 5). The activity of the latter is higher than that of the former in accordance with the results in Table 2. This result indicates that the catalyst prepared from the adsorption of conventional chloride precursor followed by reduction with well-known reductant in liquid phase is superior to a commercial catalyst.

Preparation and characteristics of Pd/C catalyst. The XRD patterns of prepared Pd/C catalysts and commercial ones are shown in Figure 6 and the TEM images of the Pd/C (AL) and Pd/C (Comm-D) are compared in Figure 7. Similar to the results of Pt/C, the prepared Pd/C catalysts show similar trends with preparation conditions in XRD and TEM results. The sizes of Pd crystallite determined by using the Scherrer equation are in the order of Pd/C (PL) > Pd/C (Comm-A) > Pd/C (Comm-D) > Pd/C (AL) (Table 3). The TEM images (Fig. 7) reveal that the Pd of Pd/C (AL) catalyst is more homogeneous and smaller than that of a commercial catalyst Pd/C (Comm-D) in accordance with the XRD result. Various Pd/C catalysts were also prepared with different molar ratios of $\text{Na}_2\text{CO}_3/\text{Pd}$ and NaBH_4/Pd by adsorption and deposition (via precipitation) processes (Fig. 1). The Pd/C (AL) catalysts and Pd/C (PG) catalysts do not show noticeable change in XRD patterns and TEM images with the base/Pd and reductant/Pd ratios.

The catalytic activities of cyclohexene hydrogenation for various catalysts are shown in Figure 8 and Table 3. Their activities increase with decreasing the Pd crystallite size. The catalytic activity is in the order of Pd/C (AL) > Pd/C (Comm-D) > Pd/C (PL), and this is in accordance with the reverse of Pd size (size is in the order of Pd/C (AL) < Pd/C (Comm-D) < Pd/C (PL)) determined by FWHM of a

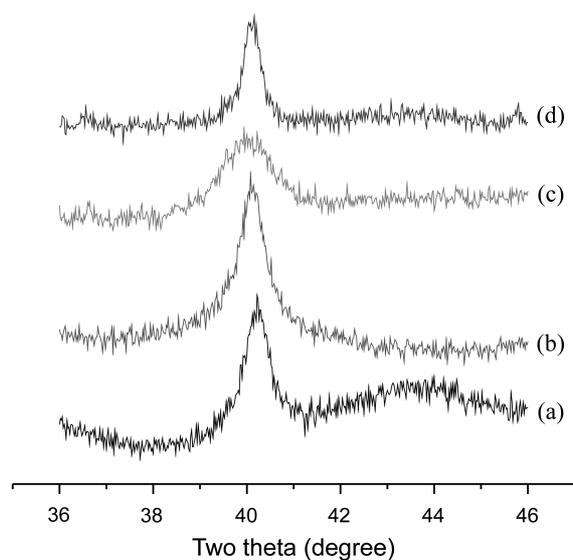


Figure 6. XRD patterns of Pd/C catalysts: (a) Pd/C (Comm-A), (b) Pd/C (Comm-D), (c) Pd/C (AL) and (d) Pd/C (PL).

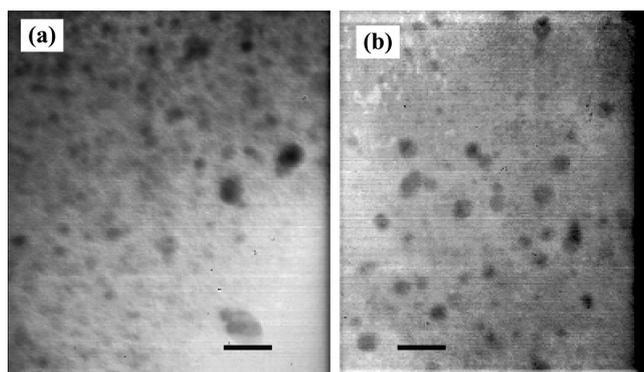


Figure 7. TEM images of Pd/C catalysts: (a) Pd/C (Comm-D) and (b) Pd/C (AL). Scale bar corresponds to 20 nm.

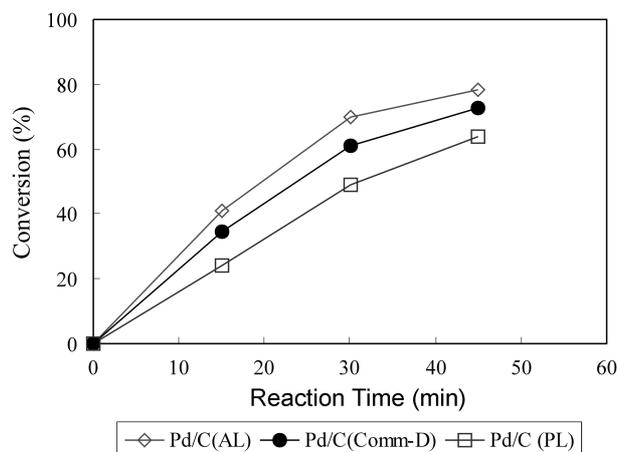


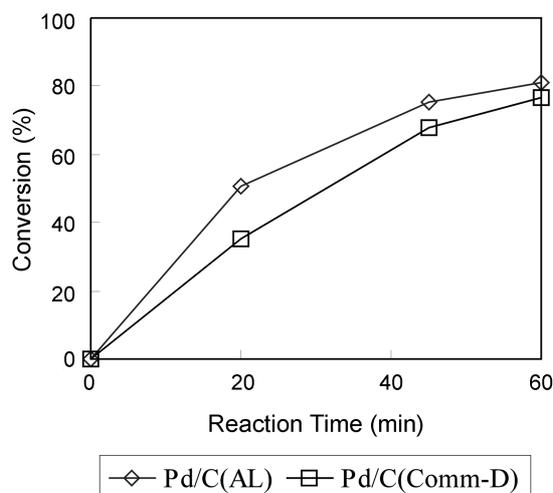
Figure 8. Comparison of conversion of cyclohexene hydrogenation over Pd/C (Comm-D), Pd/C (AL), and Pd/C (PL) catalysts.

diffraction peak from (111) plane. Figure 9 and Figure 10 show the activity and selectivity of hydrogenation of acetophenone over the two catalysts. Similar to the results of

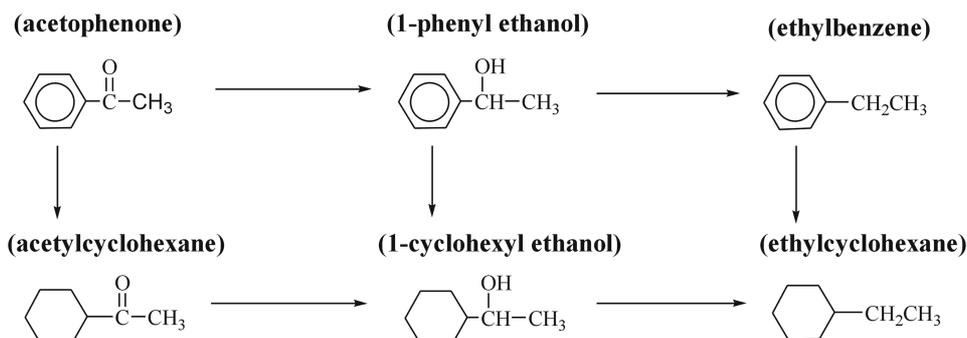
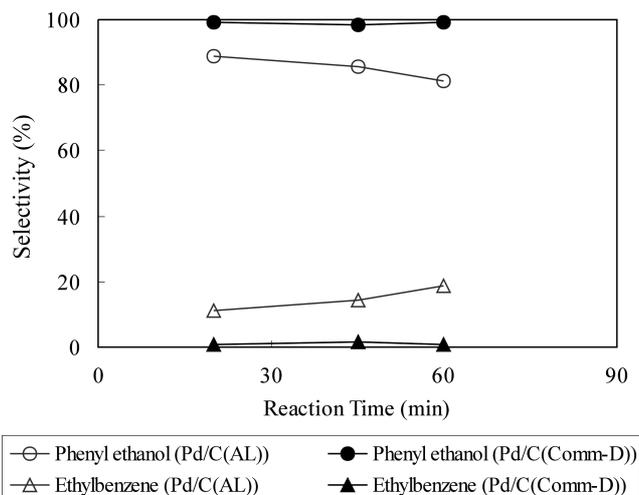
Table 3. Conversion of cyclohexene and acetophenone over various Pd/C catalysts

Catalyst	Pd size (nm)	Cyclohexene conversion (mol %)		Acetophenone conversion (mol %)	
		15 min	30 min	20 min	45 min
Pd/C (Comm-A)	12.7	31	61	ND*	ND*
Pd/C (Comm-D)	11.5	35	61	35	68
Pd/C (AL)	6.4	41	70	51	76
Pd/C (PL)	16.9	24	49	ND*	ND*

*ND: not determined

**Figure 9.** Comparison of conversion of acetophenone hydrogenation over Pd/C (Comm-D) and Pd/C (AL) catalysts.

cyclohexene hydrogenation, the activity of Pd/C (AL) is higher than that of a commercial catalyst (Pd/C (Comm-D)). However, the selectivity of ethylbenzene over the Pd/C (AL) is very high compared with the selectivity over the commercial catalyst. This might be related to the increased activity of the Pd/C (AL) considering the consecutive hydrogenation of acetophenone to phenylethanol and phenylethanol to ethylbenzene as shown in Scheme 1.¹⁶ Other products that can be obtained from ring hydrogenation are negligible over both catalysts. Similar to the results on Pt/C catalysts, the

**Scheme 1.** Reaction pathways of acetophenone hydrogenation.**Figure 10.** Comparison of selectivity of acetophenone hydrogenation over Pd/C (Comm-D) and Pd/C (AL) catalysts.

Pd/C catalyst prepared from adsorption of PdCl₂ (dissolved in aqueous HCl) and consecutive reduction by sodium borohydride in liquid phase shows improved activity compared with commercial catalysts.

Conclusions

The Pt/C or Pd/C catalyst prepared by adsorption of conventional chloride precursors and liquid phase hydrogenation shows increased hydrogenation activity compared with commercial Pt/C or Pd/C catalyst. The increased activities of the prepared catalysts are attributed to the decreased particle size of precious metals probably due to the same negative charge of the chloride precursors and active carbon support at the preparation condition. The Pt/C or Pd/C catalyst prepared by deposition *via* precipitation using alkali shows coarse particle size and decreased hydrogenation activity. In the reaction conditions studied, the reduction using borohydride in liquid phase is superior to a gas phase reduction by using hydrogen because of the smaller particle size, increased activity and convenience.

Acknowledgement. This work was supported by the Korea Ministry of Commerce, Industry and Energy (KN-

0479, TS-0371) and Institutional Research Program. The authors thank Dr. Y. K. Hwang and Miss H. K. Kim for their beneficial contribution.

References

1. Seldon, R. A.; van Bekkum, H. *Fine Chemicals through Heterogeneous Catalysis*; Wiley-VCH: Weinheim, 2001.
 2. Simonov, P. A.; Likholobov, V. A. In *Catalysis and Electrocatalysis at Nanoparticle Surfaces*; Wieckowski, A.; Savinova, E. R.; Vayenas, C. G., Eds.; Marcel Dekker: New York, 2003; pp 409-454.
 3. (a) Auer, E.; Freund, A.; Pietsch, J.; Tacke, T. *Appl. Catal. A* **1998**, 173, 259; (b) Shen, K.; Li, S.; Choi, D. H. *Bull. Kor. Chem. Soc.* **2002**, 23, 1785.
 4. Okhlopko, L. B.; Lisitsyn, A. S.; Likholobov, V. A.; Gurrath, M.; Boehm, H. P. *Appl. Catal. A* **2000**, 204, 229.
 5. Gurrath, M.; Kuretzky, T.; Boehm, H. P.; Okhlopko, L. B.; Lisitsyn, A. S.; Likholobov, V. A. *Carbon* **2000**, 38, 1241.
 6. Rodriguez-Reinoso, F. *Carbon* **1998**, 36, 159.
 7. (a) Kim, S.-C.; Park, H.-H.; Lee, D.-K. *Catal. Today* **2003**, 87, 51; (b) Noh, J.; Yang, O.-B.; Kim, D. H.; Woo, S. I. *Catal. Today* **1999**, 53, 575; (c) Kim, W. B.; Park, E. D.; Lee, J. S. *Appl. Catal. A* **2003**, 242, 335; (d) Kim, W. B.; Park, E. D.; Lee, C. W.; Lee, J. S. *J. Catal.* **2003**, 218, 334.
 8. (a) Jhung, S. H.; Romanenko, A. V.; Lee, K. H.; Park, Y.-S.; Moroz, E. A.; Likholobov, V. A. *Appl. Catal. A* **2002**, 225, 131; (b) Romanenko, A. V.; Tyschishin, E. A.; Moroz, E. A.; Likholobov, V. A.; Zaikovskii, V. I.; Jhung, S. H.; Park, Y.-S. *Appl. Catal. A* **2002**, 227, 117; (c) Jhung, S. H.; Park, Y.-S. *J. Korean Chem. Soc.* **2002**, 46, 57.
 9. Suh, D. J.; Park, T.-J.; Ihm, S.-K. *Ind. Eng. Chem. Res.* **1992**, 31, 1849.
 10. Romanenko, A. V.; Likholobov, V. A.; Timofeeva, M. N.; Jhung, S. H.; Park, Y.-S. *US Patent* **2004**, 6 753 290.
 11. Prabhuram, J.; Zhao, T. S.; Wong, C. W.; Guo, J. W. *J. Power Sources* **2004**, 134, 1.
 12. Mao, S. S.; Mao, G. *US Patent* **2004**, 6 686 308.
 13. Wu, S. F.; Yanagisawa, K.; Nishizawa, T. *Carbon* **2001**, 39, 1537.
 14. Kung, H. H.; Kung, M. C.; Costello, C. K. *J. Catal.* **2003**, 216, 425.
 15. Semikolenov, V. A.; Lavrenko, S. P.; Zaikovskii, V. I. *React. Kinet. Catal. Lett.* **1993**, 51, 507.
 16. Chen, C.-S.; Chen, H.-W.; Cheng, W.-H. *Appl. Catal. A* **2003**, 248, 117.
-