

A comparative study of liquid-phase hydrogenation on Pd/SiO₂ in organic solvents and under pressurized carbon dioxide: Activity change and metal leaching/sintering

Joongjai Panpranot^{a,*}, Kunnika Phandinthong^a, Piyasan Praserttham^a,
Masashi Hasegawa^b, Shin-ichiro Fujita^b, Masahiko Arai^b

^a Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering,
Faculty of Engineering Chulalongkorn University, Bangkok, Thailand

^b Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

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Abstract

Liquid-phase hydrogenation of cyclohexene under mild conditions on Pd/SiO₂ in different organic solvents (benzene, heptanol, and NMP), under pressurized carbon dioxide, and under solvent less condition were investigated and compared. In the cases of using organic solvents, the hydrogenation rates depended on polarity of the solvents in which the reaction rates in high polar solvents such as heptanol and NMP were lower than that in a non-polar solvent. Hydrogenation rates were much higher when the reactions were performed under high-pressure CO₂ or under solvent less condition. The use of high-pressure CO₂ can probably enhance H₂ solubility in the substrate resulting in a higher hydrogenation activity. However, metal sintering and leaching in the presence of high-pressure CO₂ were comparable to those in organic solvents.

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1. Introduction

Catalytic hydrogenation is one of the most useful, versatile, and environmentally acceptable reaction routes available for organic synthesis, and the reaction is usually carried out in a liquid-phase using batch type slurry processes and a supported noble metal (Pd, Pt, or Rh) catalyst [1–4]. The major advantages of multi-phase catalytic reactions using solid catalysts include easy separation of catalysts and products, easy recovery and catalyst recycling, and relatively mild operating conditions [5,6]. The performance of noble metal catalysts in liquid-phase hydrogenation has been found to be dependent on several factors such as liquid composition (substrate structure, solvent effect, etc.), catalyst nature (active sites composition and morphology, support effect, modifiers, etc.), and reaction conditions (temperature, pressure, etc.) [7]. Deactivation of metal catalysts in

liquid-phase reactions can occur even under mild reaction conditions because of sintering and/or leaching of active components, poisoning of active sites by heteroatom-containing molecules, inactive metal or metal oxide deposition, impurities in solvents and reagents, and oligomeric or polymeric by-products. The mechanisms for such deactivation causes, however, have not been fully understood.

Supercritical fluids particularly carbon dioxide (CO₂) as an environmentally benign reaction media offer many advantages compared to conventional organic solvents because they facilitate heat and mass transfer in the reactor and enable easy separation of the solvents from the reactants and products [8–10]. Despite numerous studies in the literature on the successful application of supercritical solvents in catalytic reactions [11–17], the performance of the catalyst in terms of both activity and deactivation in supercritical solvents has not often been compared to those performed in conventional organic solvents. Baiker and co-workers [18] showed that the rate of citral hydrogenation in carbon dioxide under single-phase conditions was about two orders of magnitude higher than in organic solvent. For

* Corresponding author. Tel.: +66 2 2186 869; fax: +66 2 2186 877.
E-mail address: joongjai.p@eng.chula.ac.th (J. Panpranot).

hydrogenation of nitrobenzene in supercritical CO₂ on Pt/C catalysts, selectivity to aniline was twice as high as that in ethanol at a similar conversion [19]. It is not clear, however, whether deactivation of supported noble metal catalyst occurred to a similar degree in high-pressure carbon dioxide compared to those in organic solvents.

In this study, we have made a comparative study of catalytic activity and metal leaching/sintering of Pd/SiO₂ catalysts during liquid-phase hydrogenation in different organic solvents, under pressurized carbon dioxide, and under solvent less condition. The metal leaching and sintering are a major cause for catalyst deactivation, which have been investigated by means of X-ray diffraction, atomic absorption spectroscopy, and CO pulse chemisorption method. Liquid-phase hydrogenation of cyclohexene under mild conditions at 0.1 MPa H₂ pressure was used as a test reaction where the rate of reaction can be studied easily.

2. Experimental

2.1. Catalyst preparation and nomenclature

Pd/SiO₂ whose Pd loading was approximately 1 wt.% was prepared by ion-exchange using Pd(NH₃)₄Cl₂ (Aldrich) and a silica gel (Aldrich, Davisil grade 646). A 20 mmol/l palladium solution was prepared by using 0.152 g of Pd(NH₃)₄Cl₂ and a certain amount of distilled water. Then 5.0 cm³ of the palladium solution was diluted with distilled water to 30 ml. Approximately 1.0 g of silica gel was immersed into the solution and the pH value was adjusted to 12 by adding 25% NH₄OH solution. The support was kept immersed in this solution at room temperature for 3 days. After filtration, the solid residue was washed with distilled water until pH 7.0 and vacuum dried over night at room temperature. The catalysts were calcined in air at 450 °C for 3 h and were denoted as “fresh catalyst” in this work. Prior to the hydrogenation reaction, the catalyst was reduced in H₂ at 25 °C for 2 h. After the reaction runs, the catalysts were re-calcined in air at 450 °C for 3 h in order to remove any carbon deposit and were denoted as “spent catalysts”.

2.2. Catalyst characterization

The bulk composition of palladium was determined using a Varian Spectra A800 atomic absorption spectrometer. The X-ray diffraction patterns of the catalysts were measured in a range of 2θ value between 20° and 80° using a SIEMENS D5000 X-ray diffractometer and Cu Kα radiation with a Ni filter. The number of surface palladium atoms was determined from CO chemisorption by a pulse method and the palladium dispersion was estimated from the amount of CO chemisorbed assuming a stoichiometry of CO/palladium = 1. Approximately 0.2 g of catalyst was placed in a quartz tube in a temperature-controlled oven and reduced in a flow of hydrogen (50 cm³/min) at room temperature for 2 h. Then, the sample was purged at this temperature with helium for 1 h. Carbon monoxide was pulsed at room temperature over the reduced catalyst until the TCD signal from a pulse (at the exit) became constant.

2.3. Reaction study

Liquid-phase hydrogenation in conventional organic solvents was carried out in a 100 cm³ stainless steel autoclave. The Pd/SiO₂ catalyst of 0.2 g was placed in the reactor with 20 mmol of cyclohexene (Aldrich) and 48 cm³ of solvents. For the reaction runs under high-pressure CO₂ and under solvent less condition, a 50 cm³ stainless steel autoclave was used in order to compare the reaction with a similar substrate/solvent ratio. For the application of high-pressure CO₂, the reactor was purged with CO₂ and then hydrogen was introduced to the desired pressure, followed by introduction of CO₂ to the desired pressure using a high-pressure liquid pump. Stirring was switched on to start the reaction. The products were analyzed by GC and GC–MS. Phase behavior during reaction in high-pressure CO₂ was inspected using a 10 cm³ high-pressure sapphire-windowed view cell.

3. Result and discussion

3.1. Liquid-phase hydrogenation in different solvents

Catalyst activities for liquid-phase hydrogenation of cyclohexene at 25 °C in various organic solvents, under pressurized carbon dioxide, and under solvent less condition are shown in Table 1. It is obvious that the hydrogenation rates are much higher for those performed in high-pressure CO₂ than those carried out in organic solvents. In hydrogenation reaction, H₂ solubility in common organic solvents is usually low depending on the nature of the solvent. It has been reported that hydrogenation activity decreases with increasing solvent polarity due to competitive adsorption of high polar solvent and substrate on the catalyst surface [20,21]. Similar trend was observed in this study; as the polarity of the solvent increases in the order of NMP > heptanol > benzene, the hydrogenation activity decreases in the order NMP < heptanol < benzene. Since the concentration of either cyclohexene or H₂ in high-pressure CO₂ was different from those in organic solvents, it is not easy to compare the results at 6 MPa CO₂ with those in organic solvents. However, compared to that under the solvent less condition, the hydrogenation rate increases from 93% to nearly 100% in the presence of high-pressure CO₂. A gas–liquid-phase boundary

Table 1
Catalytic activities of Pd/SiO₂ for cyclohexene hydrogenation^a in various solvents

Solvent	Polarity	Time (min)	Conversion (%)
NMP	4.09	10	15.1
Heptanol	1.33	10	27.6
Benzene	0.0	10	57.0
Cyclohexene	0.0	2	93.0
		10	96.0
CO ₂ 6 MPa	0.0	2	~100.0
		10	~100.0

Dipole moment (debye) [26]. Under solvent-less conditions. Liquid (substrate)-gas two phases (except for a solid phase of catalyst).

^a Reaction conditions: *T* = 25 °C, H₂ = 1 MPa, catalyst/substrate = 0.1 g cat./10 mmol substrate, and substrate/solvent = 1/24 (v/v).

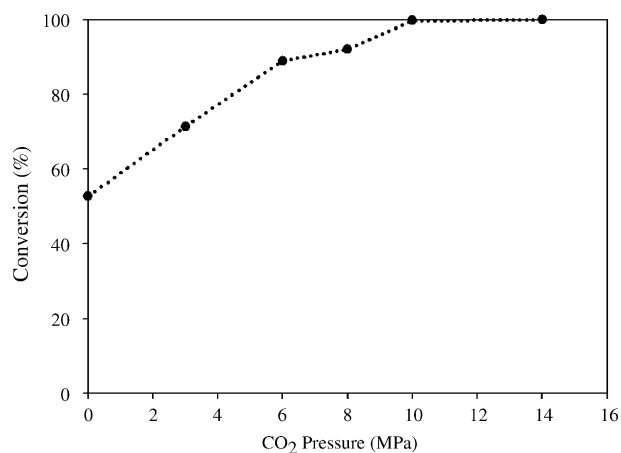


Fig. 1. Effect of CO₂ pressure on the hydrogenation activities of Pd/SiO₂ (the reaction conditions were $T = 40\text{ }^{\circ}\text{C}$, $\text{H}_2 = 5\text{ MPa}$, 0.005 g cat. , 20 mmol cyclohexene, and reaction time 3 min).

was still observed from visual observations under the reaction conditions used, and so the hydrogenation occurs mainly in the nearly pure substrate liquid phase. The H₂ concentration in the liquid phase may be enhanced by dissolution of CO₂, resulting in the increase of the hydrogenation rate at high CO₂ pressure.

The effect of CO₂ pressure on liquid-phase hydrogenation of cyclohexene on Pd/SiO₂ catalysts was investigated for CO₂ pressure in the range between 0 and 14 MPa at 40 °C where CO₂ can be in the supercritical state. The results are shown in Fig. 1. It is seen that the hydrogenation rate increases with increasing CO₂ pressure. Phase behavior study revealed that the mixture of cyclohexene and CO₂ (without catalyst) was gas–liquid two phases at pressures up to 9 MPa but a single phase at 9.4 MPa or above. Nearly 100% cyclohexene conversions were observed under those homogeneous conditions. Arai and co-workers [22] has recently suggested that hydrogenation rate in dense carbon dioxide strongly correlates with the phase behavior of the reaction mixture. In selective hydrogenation of cinnamaldehyde using ruthenium–phosphine complex catalysts, total conversion and cinnamyl alcohol increased with increasing CO₂ pressure when the reactions were carried out in an organic solvent free two-phase system.

3.2. Metal sintering and leaching during hydrogenation

Under the reaction conditions studied, metal leaching and metal sintering were observed and for some cases were found to be in large extents. The XRD patterns of the fresh catalysts (after first calcination), after reduction in H₂ at room temperature, after reduction and re-calcination (without reaction), and after reduction and being used in hydrogenation reaction with NMP solvent are shown in Fig. 2. There was no significant change in the XRD patterns of the calcined, the reduced, and the re-calcined catalysts (without reaction) since only a broad peak for SiO₂ is observed at $2\theta = 22^{\circ}$. XRD characteristic peaks for palladium oxide (PdO) or metallic Pd⁰ are not detected, suggesting that palladium is highly dispersed on the silica sup-

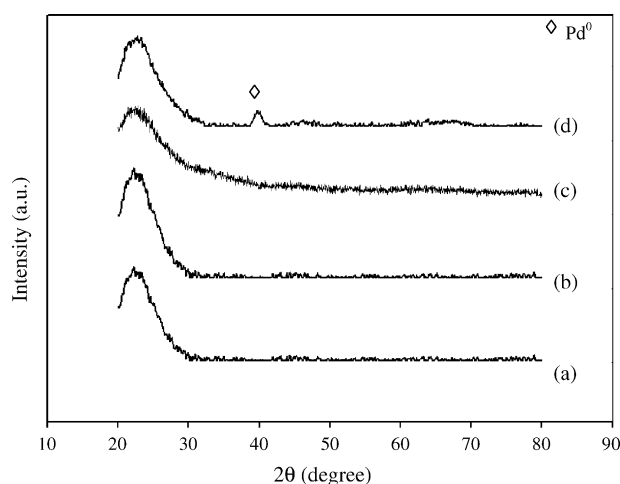


Fig. 2. XRD patterns of Pd/SiO₂ catalysts: (a) after first calcination and (b) after reduced in H₂ at room temperature; (c) after reduced and re-calcination (without reaction) and (d) after reduced and reaction in NMP.

port and its crystallite size is smaller than the XRD detectable limit. However, XRD characteristic peak for metallic Pd⁰ was observed after reduced and being used in hydrogenation reaction. Therefore, metal sintering did not occur by the reduction at ambient temperature or by thermal effects during the calcination at 450 °C. After being subjected to the hydrogenation reaction runs, the catalysts were re-calcined at 450 °C for 3 h in order to remove any carbon deposits. The XRD patterns of these so-called spent catalysts are shown in Fig. 3. The diffraction peaks for PdO are now evident at $2\theta = 33.8^{\circ}$, 42.0° , 54.8° , 60.7° and 71.4° for all the spent catalysts, showing that the metal sintering occurred during the liquid-phase hydrogenation reaction, since no XRD peak of PdO was detected over the re-calcined catalyst (Fig. 2). The PdO crystallite sizes were calculated from the full width at half maximum of the XRD peak at $2\theta = 33.8^{\circ}$ using Scherrer equation and are reported in Table 2. The crystallite sizes of PdO on the spent catalysts are in the order of solvent-less < benzene < CO₂ < heptanol < NMP.

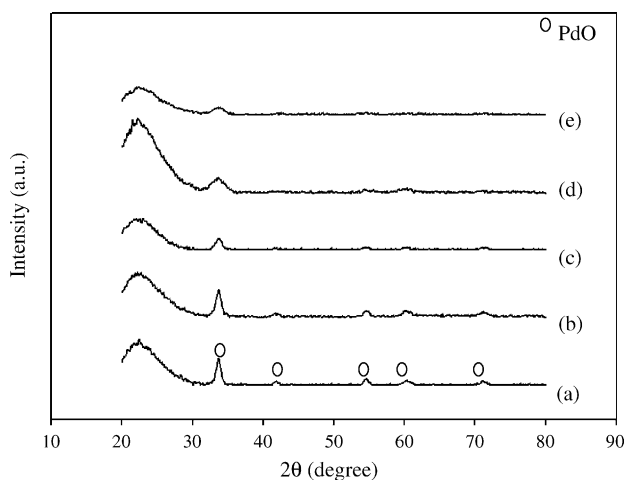


Fig. 3. XRD patterns of re-calcined spent Pd/SiO₂ catalysts after hydrogenation reaction in various solvents: (a) NMP, (b) heptanol, (c) CO₂ 6 MPa, (d) solvent less and (e) benzene.

Table 2
Characteristic of fresh and spent^a Pd/SiO₂ catalysts

Catalyst	PdO particle size ^c (nm)	Amount of Pd ^b (wt.%)	Pd leached (%)	Amount of CO chemisorbed ^d × 10 ¹⁹ (molecule/g cat.)	Pd dispersion ^e (%)
Fresh	n.d. ^f	0.97	–	2.43	44.3
Spent-benzene	3.9	0.86	11.3	1.00	20.6
Spent-CO ₂ 6 MPa	7.6	0.77	20.6	0.61	14.0
Spent-solvent less	3.5	0.85	12.4	0.38	6.9
Spent-heptanol	10.3	0.82	15.5	0.18	3.9
Spent-NMP	11.0	0.76	21.6	0.16	3.8

^a Reaction conditions: *T*, 25 °C; H₂ pressure, 1 MPa; catalyst, 0.1 g; substrate, 10 mmol; substrate/solvent, 1/24 (v/v), reaction time = 10 min.

^b Determined by atomic absorption spectroscopy. Error of measurements = ±5%.

^c Based on XRD results.

^d Error of measurements = ±5%.

^e Based on total amount of palladium determined by atomic absorption spectroscopy.

^f Not detected.

The actual amounts of palladium loading determined by atomic absorption spectroscopy and the CO chemisorption results for all the catalysts are also given in Table 2. The palladium loading on the fresh catalyst is 0.97 wt.% and those on the spent catalysts are always lower than that on the fresh catalyst, meaning that palladium was leached in the course of the reaction. Leaching of active metal is another main cause of catalyst deactivation in liquid-phase reaction. In general, it depends upon the reaction medium (pH, oxidation potential, chelating properties of molecules) and upon bulk and surface properties of the metal [23]. In this study, the percentages of the leaching are between 11 and 22% and there is no correlation between the amount of metal leached and the polarity of solvent employed (see Table 1). The amount of CO chemisorbed, i.e. the number of surface Pd atoms, significantly decreased by 60% or more for all the spent catalysts. The decreases in the amount of CO adsorbed are much more than those expected from the results for the Pd leaching. This would be caused by the Pd sintering. The Pd dispersions determined for the spent catalysts are below 50% of for the fresh catalyst. The extent of the Pd sintering depends on the solvent employed for the reaction and is significant in heptanol and NMP. The Pd dispersions of the spent catalysts used in these polar solvents are below 10% of that of the fresh catalyst.

Sintering of supported metal particles in liquid-phase reactions is typically irreversible and can occur even at ambient temperature because of atomic migration processes involving the extraction and transport of surface metal atoms by chelating molecules [23]. The use of high polar solvents such as NMP and heptanol appeared to promote such processes. Some of the leached metal species probably re-deposited on surfaces of the support and/or the Pd particles remaining on the catalysts, causing the sintering as suggested earlier by Arai and co-workers for sintering of Pd/C during Heck coupling reaction [24,25].

4. Conclusions

The study provides a cautionary note for selection of a solvent used in liquid-phase hydrogenation. The use of high polar organic solvents can result in low hydrogenation activities as

well as significant metal sintering and metal leaching during reaction. Compared to the use of organic solvents or solvent less, the use of high-pressure CO₂ enhanced the hydrogenation activity of Pd/SiO₂ catalyst. However, metal sintering and leaching in the presence of high-pressure CO₂ were comparable to those in organic solvents.

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