Effects of Pd precursors on the catalytic activity and deactivation of silica-supported Pd catalysts in liquid phase hydrogenation

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Abstract

Liquid phase hydrogenation of 1-hexene under mild conditions has been investigated on a series of silica (SiO_2 and MCM-41)-supported Pd catalysts prepared from different Pd precursors such as $Pd(NO_3)_2$, $PdCl_2$, and $Pd(OOCCH_3)_2$. For any silica support, use of $PdCl_2$ as a precursor resulted in smaller Pd particles, higher dispersion, and consequently higher hydrogenation activities. Supported Pd catalysts prepared from $PdCl_2$ showed greater metal sintering after 5-h batch reaction. However, leaching of Pd was found to occur to a significant degree for the catalysts prepared from $Pd(NO_3)_2$ and $Pd(OOCCH_3)_2$. The results suggest that deactivation of the silica-supported Pd catalysts in liquid phase hydrogenation is dependent on the palladium particle size with smaller Pd particles being more susceptible to sintering while larger particles are more likely to be leached. An optimum Pd particle size may be needed in order to minimize such loss and enhance Pd dispersion.
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1. Introduction

Silica-supported Pd catalysts are commercially attractive for liquid phase catalytic hydrogenation in many organic syntheses [1–6]. The major advantages of supported noble metal catalysts are their relatively high activity, mild process conditions, easy separation, and better handling properties. Since the catalytically active phase for hydrogenation is the metallic phase, having palladium well-dispersed and reduced is required for a catalyst to have high activity. Different preparation techniques have been tried in order to obtain catalysts with small metal particles and high metal dispersions. Recently, it has been reported that silica-supported Pd nanoparticles prepared by reduction of an organometallic precursor palladium(II) bis-dibencylidene with H_2 showed remarkable liquid phase hydrogenation activity of different organic substrates [2]. However, an increase in particle size was observed after the fourth batch of 1-hexene hydrogenation at 25 °C.

Sintering of supported metal particles 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 [7]. Despite a high number of factors potentially involved in catalyst deactivation in liquid phase organic reactions (sintering or leaching of active components, poisoning of active sites by heteroatom-containing molecules, inactive metal or metal oxide deposition, impurities in solvents and reagents, oligomeric or polymeric by-products), the mechanisms for such deactivation have not been studied very often. For example, the effects of metal dispersion and support texture and porosity on the activity and the deactivation of supported Pd catalysts in liquid phase hydrogenation remain unclear.

In this study, we investigated the activities and deactivation of Pd/MCM-41 and Pd/SiO_2 catalysts prepared

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with different Pd precursors [Pd(NO$_3$)$_2$, Pd(OOCCH$_3$)$_2$, and PdCl$_2$] for liquid phase hydrogenation of 1-hexene under mild conditions. In order to distinguish the effects of silica support structure from the effects of BET surface area and pore size, the SiO$_2$ and MCM-41 used as catalyst supports in this study possessed similar BET surface areas and narrow pore size distributions with average pore diameters of ca. 3 nm, albeit in slightly different forms of silica. The effects of Pd precursors and silica support structure were investigated in terms of metal dispersion, catalytic activity, and deactivation due to metal sintering and metal leaching.

2. Experimental

2.1. Preparation of silica-supported Pd catalysts

The two types of silica supports used in this study were pure silica MCM-41 ($S_{BET} = 921$ m^2/g, $r_p = 28$ Å, $V_p = 0.87$ cm^3/g) and high surface area chromatographic grade SiO$_2$ ($S_{BET} = 716$ m^2/g, $r_p = 22$ Å, $V_p = 0.39$ cm^3/g). MCM-41 was prepared in the manner described by Cho et al. [8] using the gel composition of CTAB:0.3NH$_3$:4SiO$_2$:-Na$_2$O:200H$_2$O, where CTAB denotes cetyltrimethyl ammonium bromide. High surface area SiO$_2$ was obtained commercially from Grace Davison Co. Ltd. The catalysts were prepared by impregnation using a slight excess of the amount of solution of different palladium precursors [Pd(NO$_3$)$_2$, PdCl$_2$, or Pd(OOCCH$_3$)$_2$ (Aldrich)] required to fill the pore volume of the supports. The catalysts were dried overnight at 110 °C and then calcined in air at 500 °C for 2 h. The final Pd loadings of the calcined catalysts were determined using atomic absorption spectroscopy (Varian Spectra A800) to be approximately 0.5 wt.% palladium content.

2.2. Catalyst characterization

XRD of the catalysts was carried out from 20° to 80° 2θ using a SIEMENS D5000 X-ray diffractometer and Cu Kα radiation with a Ni filter. Relative percentages of palladium dispersion were determined by pulsing carbon monoxide over the reduced catalyst. Approximately 0.2 g of catalyst was placed in a quartz tube in a temperature-controlled oven. CO adsorption was determined by a thermal conductivity detector (TCD) at the exit. Prior to chemisorption, the catalyst was reduced in a flow of hydrogen (50 cm^3/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 each successive pulse was constant. The TPR profiles of supported palladium catalysts were obtained by temperature-programmed reduction using an in-house system and a temperature ramp of 5 °C/min from 30 to 300 °C in a flow of 5% H$_2$ in argon. Approximately 0.20 g of a calcined catalyst was placed in a quartz tube in a temperature-

controlled oven and connected to a thermal conductivity detector. The H$_2$ consumption was measured by analyzing the effluent gas with a thermal conductivity detector.

2.3. Liquid phase hydrogenation

Liquid phase hydrogenation reactions were carried out at 25 °C and 1 atm in a 100 ml stainless steel Taiatsu autoclave. Approximately 0.1 g of supported Pd catalyst was placed into the autoclave. The system was purged with nitrogen to remove the remaining air. The supported Pd catalyst was reduced in situ with hydrogen at room temperature for 2 h. The reaction mixture composed of 1 ml of 1-hexene and 7 ml ethanol was first kept in a 100 ml feed column. The reaction mixture was introduced into the reactor with nitrogen to start the reaction. The amount of hydrogen consumption was monitored every 5 min by noting the change in pressure of the hydrogen. The stirring rate used in this study was 800 rpm, sufficient to ensure that the reaction rate did not depend on the stirring rate (as determined). The liquid reactants, products, and the head space gases were analyzed by gas chromatography using a Shimazu GC-9A equipped with a FID detector. No reduction or decomposition of ethanol during the reaction was observed.

3. Results and discussion

3.1. Characteristics and catalytic behavior for 1-hexene hydrogenation

The characteristics of the catalysts based on CO chemisorption, XRD, and TEM results and their catalytic activities for 1-hexene hydrogenation are reported in Table 1. A suitable temperature for calcination of all palladium precursors was determined by thermogravimetric analysis of bulk palladium nitrate, palladium acetate, and palladium chloride (not shown). All palladium precursors appeared to be fully decomposed for calcination temperatures above 400 °C. Thus, a calcination procedure using 500 °C for 2 h was used. The presence of the palladium oxide phase (PdO) after calcination prior to reduction was confirmed by XRD results for all but the most highly dispersed catalysts prepared from PdCl$_2$ (Fig. 1). The major diffraction peak for PdO was detectable at 33.8° 2θ for the catalysts prepared from Pd(NO$_3$)$_2$ and Pd(OAc)$_2$. The average PdO crystallite sizes were calculated using the Scherrer's equation [9] with the catalysts prepared from Pd(OAc)$_2$ showed the largest PdO particle size. Supported Pd catalysts prepared from PdCl$_2$ did not exhibit any distinct XRD patterns. This suggests that the crystallite sizes of PdO prepared from PdCl$_2$ were below the lower limit for XRD detectability (3–5 nm). TEM analyses (Fig. 2) gave results in good agreement with the crystallite size inferred from XRD. The differences in PdO particle sizes on different supports can also be ascribed to differences induced by both the

Table 1
Characteristics and catalytic activities for liquid phase hydrogenation of 1-hexene

Catalyst	CO uptake[a] (molecule $CO \times 10^{18}$/g catalyst)	Pd dispersion (%)	PdO particle size[b] (nm)	PdO particle size (nm)		Rate constant $\times 10^3$ (mol/min/g catalyst)	TOF[d] (s^{-1})
				XRD	TEM		
Pd-Ac/SiO$_2$	4.1	22.0	5.1	12.0	11.5	5.0	12.1
Pd-NO$_3$/SiO$_2$	4.0	17.7	6.3	10.0	10.1	4.0	10.0
Pd-Cl/SiO$_2$	8.4	26.1	4.3	n.d.[c]	4.8	8.5	10.2
Pd-Ac/MCM-41	4.1	17.7	6.3	13.0	12.0	4.1	10.0
Pd-NO$_3$/MCM-41	3.5	18.2	6.2	11.2	10.2	4.0	11.5
Pd-Cl/MCM-41	8.0	30.2	3.7	n.d.	5.1	8.3	10.4

[a] Error of measurement = ±5%.
[b] Based on $d = 1.12/D$ (nm), where D = fractional metal dispersion [16].
[c] n.d. = not detected.
[d] Based on CO chemisorption results.

support and the Pd precursor on sintering of palladium during preparation.

Temperature-programmed reduction is a powerful tool to investigate the reducibility of the catalyst as a function of temperature. TPR profiles of all the catalyst samples are shown in Fig. 3. It was found that the catalysts reduced readily to PdH$_2$ once hydrogen was introduced to the system, which is typical for supported Pd catalysts [10]. For the
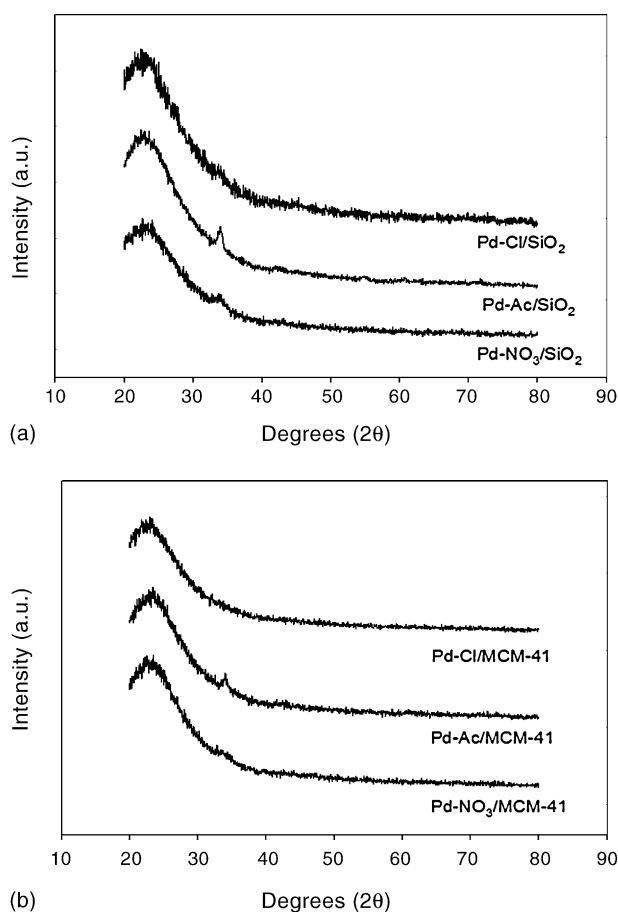

(a)

(b)

Fig. 1. XRD patterns of various supported Pd catalysts prepared from different Pd precursors: (a) SiO$_2$-supported Pd catalysts and (b) MCM-41-supported Pd catalysts (after calcinations at 500 °C for 2 h).

MCM-41 supported catalysts, a small reduction peak at ca. 65 °C was observed for all the catalysts prepared with different Pd precursors. This peak has been attributed to a portion of the PdO that could not be reduced at ambient temperature [11,12]. It should, however, be noted that the reduction of the catalysts measured after 2 h hydrogen flow maybe different from that under 5% H$_2$/Ar in the TPR conditions. Temperature-programmed study (TPO) revealed that a minimal amount (<10%) of PdO was not reduced at room temperature after 2 h exposure to hydrogen (results not shown). A significant negative peak at ca. 85 °C was observed for all the catalysts, this peak can be attributed to the decomposition of PdH$_2$ [13].

Although the MCM-41 possessed higher BET surface area and pore volume than the SiO$_2$, the catalysts prepared on both supports showed similar Pd dispersions and hydrogenation activities. For a given type of silica support, the activities of the catalysts were found to be in the order: Pd-Cl ≫ Pd-NO$_3$ ≈ Pd-Ac. The turnover frequencies were calculated using the number of surface metal atoms measured by CO chemisorption. Since the TOFs were not significantly different for any of the catalysts, the internal resistance due to diffusion within the pores of the reactant species probably did not have any influence on the catalytic activity of the catalysts. The overall catalyst activities were, thus, merely dependent on the Pd dispersion based on CO chemisorption results (as seen by the similar TOFs).

The effects of Pd precursors on the catalyst activity in hydrogenation reactions have been reported by many groups [10,14–18]. Pd catalysts supported on CeO$_2$ [14], SiO$_2$ or Al$_2$O$_3$ [15] prepared from PdCl$_2$ showed higher activities than those prepared from Pd(NO$_3$)$_2$ for CO hydrogenation. Mahata and Vishwanathan [16] reported that Pd(OOCCH$_3$)$_2$ offered better dispersion of Pd on alumina than PdCl$_2$ or Pd(NH$_3$)$_4$Cl$_2$. Phenol hydrogenation activity over these catalysts was found to be a direct function of available palladium surface area. Recently, in a study of the catalytic reduction of NO to N$_2$ over supported Pd catalysts, Pd catalysts supported on EDTA-activated γ-Al$_2$O$_3$ prepared from Pd(NO$_3$)$_2$ were found to exhibit higher activities than those prepared from PdCl$_2$ [18]. The contradiction of the
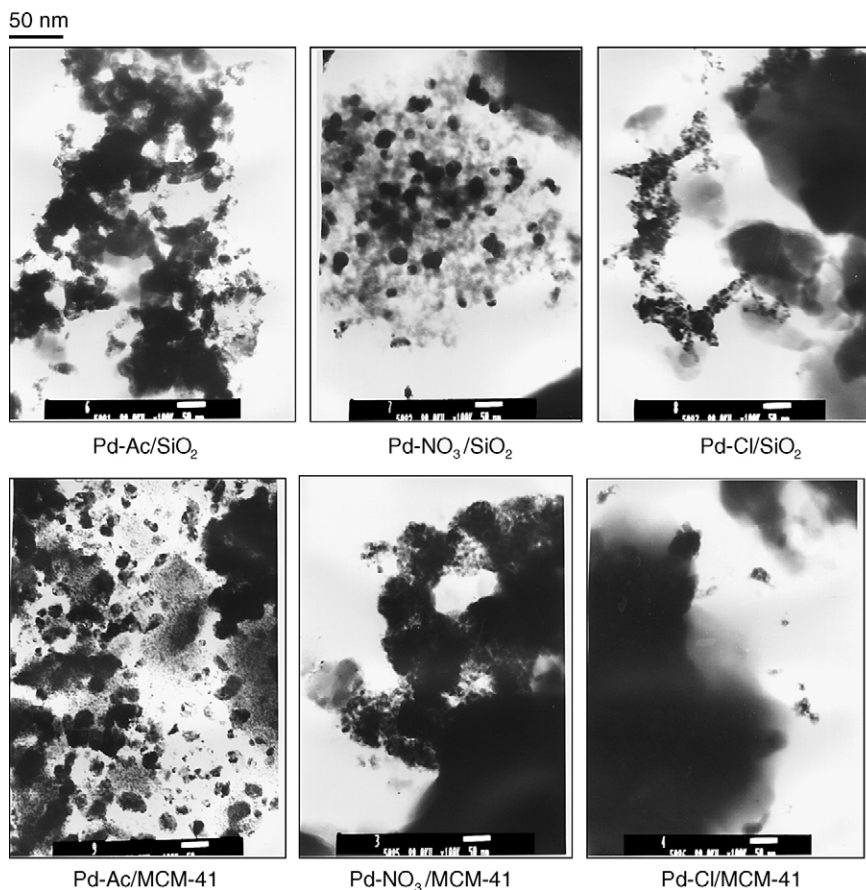
50 nm

Fig. 2. TEM images of various supported Pd catalysts (after calcinations at 500 °C for 2 h).

influence of palladium precursors on activities of supported Pd catalysts in the literature suggests that, besides Pd metal particle size and Pd dispersion, the precursor- or the metal-support interaction may also play an important role in determining the catalytic properties of the catalysts.

It should be noted that, when chloride-containing compounds were used as the catalyst precursor, the presence of residual chloride has been found occasionally in supported metal catalysts [19,20] and then the catalyst activity has decreased. However, in this work the catalysts prepared from PdCl$_2$ were found to exhibit higher hydrogenation activities than the ones prepared from Pd(NO$_3$)$_2$ or Pd(OOCCH$_3$)$_2$; thus we conclude that there was probably no residual chloride blocking the palladium sites. Most of the residual chloride can be significantly removed during the reduction procedure, especially when water vapor is produced.

3.2. Catalyst deactivation during liquid phase hydrogenation

After 5 h of batch reaction, the catalysts were collected by simple filtration. Catalyst deactivation processes by metal sintering and by metal leaching were investigated. The results are reported in Table 2. From the CO chemisorption

results, it was found that the active Pd surface of the spent catalysts decreased by half of those of the fresh catalysts. It was found that the catalysts prepared from PdCl$_2$ and having small PdO particles exhibited greater Pd sintering. The particle sizes of Pd-Cl catalysts increased by 100–124% (from 4.8 to 5.1 nm to 9.6 to 11.4 nm), while those of Pd-NO$_3$ and Pd-Ac were not significantly changed. We wanted to avoid the influence of carbon deposits on the pore structure and on the contrast of the TEM images; after being

Table 2

Deactivation of various supported Pd catalysts during liquid phase hydrogenation of 1-hexene[a]

Catalysts	CO chemisorption of the spent catalysts (molecule CO $\times 10^{18}$/g catalyst)	Increase of PdO particle size[b] (%)	Pd loss[c] (%)
Pd-Ac/SiO$_2$	2.5	7.8	36.4
Pd-NO$_3$/SiO$_2$	2.5	18.8	40.9
Pd-Cl/SiO$_2$	5.4	100	1.8
Pd-Ac/MCM-41	2.7	9.2	34.1
Pd-NO$_3$/MCM-41	1.7	24.5	41.2
Pd-Cl/MCM-41	3.8	123.5	2.1

[a] After 5-h batch hydrogenation reaction of 1-hexene at 25 °C and 1 atm.

[b] Based on XRD results.

[c] Determined from atomic absorption spectroscopy. Error of measurement = ±10%.
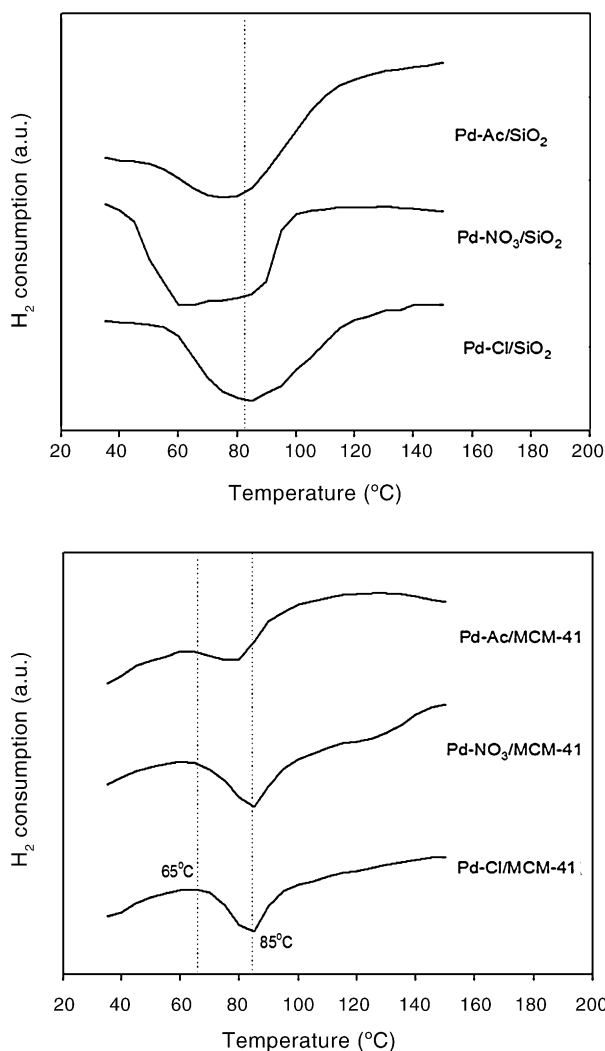
Fig. 3. TPR profiles of various SiO_2 and MCM-41-supported Pd catalysts (after calcinations at 500 °C for 2 h).

taken out from the reactor and dried at room temperature, the catalysts were thus re-calcined in air at 500 °C for 2 h to remove any carbon deposits before characterization. The TEM micrographs of Pd-Cl/SiO₂ and Pd-Cl/MCM-41 catalysts after reaction and re-calcination are shown in Fig. 4, larger PdO particle sizes were evident. The sintering probability can be higher when a metal particle is located closer to other particles. It is known that temperature, atmosphere, metal type and metal dispersion, promoters/impurities, and support surface area, texture and porosity are the principal parameters affecting rates of sintering [21]. However, the mechanism of metal sintering in liquid phase reactions has not been well-investigated so far. Arai and co-workers have proposed that sintering occurs through transport of Pd metal between support and solvent as well as through transport on the support during Heck coupling reactions [22].

The percentages of palladium before and after 5 h of batch reaction were determined by atomic absorption spectroscopy. Palladium leaching occurred to a significant degree (30–40%) for the catalysts prepared from palladium nitrate and palladium acetate, whereas for the catalysts prepared from palladium chloride almost no Pd leaching was found. Pd leaching was little affected by the silica support structure (SiO₂ and MCM-41). The mechanism of metal leaching usually involves metal compounds that are formed and are soluble in the reaction mixture. Since it is unlikely that 1-hexene forms a compound with Pd at room temperature, unless it is some hydrido–organic complex, it is likely that Pd hydride formation is the cause of metal loss. It is well known that Pd particles are able to absorb hydrogen within their structure to form a Pd-β-hydride phase. A number of publications [23,24] have reported that the formation of Pd hydride depends on the particle size of palladium; larger Pd particles more easily form Pd hydride, whereas smaller Pd particles may be unable to form the Pd-β-hydride phase. Under certain conditions, the Pd-β-hydride
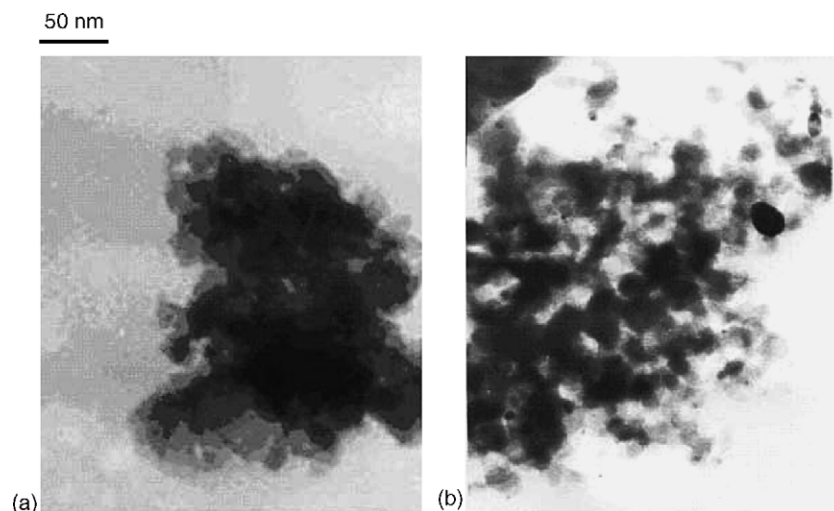

Fig. 4. TEM micrographs of the (a) Pd-Cl/SiO₂ and (b) Pd-Cl/MCM-41 catalysts after reaction and re-calcination.

phase can appear as a soft material with higher mechanical abrasion [25]. This may be one reason why larger Pd particles form a Pd-β-hydride phase that is lost (leached) from the catalysts. The results were found to be in agreement with the previous work reported by our group that large Pd particles on silica supports result in Pd being leached during liquid phase hydrogenation reaction [12,26]. Recently, Mastalir et al. [27] showed that the Pd-β-hydride phase is catalytically inactive for hydrogenation reactions. Keeping palladium crystallites in a well-reduced, metallic state has also been suggested in order to prevent formation of soluble complex compounds during liquid phase hydrogenation reactions [28]. The results of this study emphasize the need for an optimum Pd particle size to maximize the surface area of Pd while minimizing metal deactivation by sintering and leaching.

4. Conclusions

In this research, we have studied the activity and deactivation of Pd/SiO$_2$ and Pd/MCM-41 catalysts prepared with different Pd precursors in liquid phase hydrogenation under mild conditions. Pd/MCM-41 showed similar Pd dispersion and catalytic activities for liquid phase hydrogenation of 1-hexene as Pd/SiO$_2$. Use of PdCl$_2$ as the Pd precursor for catalyst preparation resulted in smaller Pd particle sizes, greater Pd surface area, and, hence, higher hydrogenation activities. However, catalysts with smaller Pd particles (from PdCl$_2$) were found to exhibit also greater metal sintering during liquid phase reaction. Significant Pd leaching occurred for those catalysts with larger particles [prepared from Pd(NO$_3$)$_2$ and Pd(OOCCH$_3$)$_2$] due probably to formation of palladium hydride, which is known to form more easily on large Pd particles.

Acknowledgements

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