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Mendeleev Commun., 2015, **25**, 367–369
Mendeleev Communications

Size effect in the liquid phase semihydrogenation of substituted alkynes over supported Pd/Al_2O_3 catalysts

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DOI: 10.1016/j.mencom.2015.09.017

The selectivity of liquid phase semihydrogenation of diphenylacetylene for *cis*-stilbene is remarkably improved by increasing Pd particle size due to different structure sensitivity of alkyne and alkene hydrogenation steps.

Alkynes are versatile reagents in organic synthesis since the terminal C≡C group can be used for the formation of a new C–C bond (*e.g.* by Sonogashira cross-coupling) retaining the triple bond. The following hydrogenation easily transforms a substituted alkyne to a corresponding *cis*-alkene *via* the stereoselective addition of H_2 over Pd catalyst.[1] This so-called semihydrogenation is an important step in industrial processes as well as in laboratory practice (Figure 1). However, minimization of over-hydrogenation and careful selectivity control are strongly required. Several factors can be used to control selectivity/activity parameters of Pd catalyst: alloying, support nature, particle size, *etc.*[2–4] This study was focused on the effect of Pd particle size for improving selectivity in liquid-phase alkyne semihydrogenation.

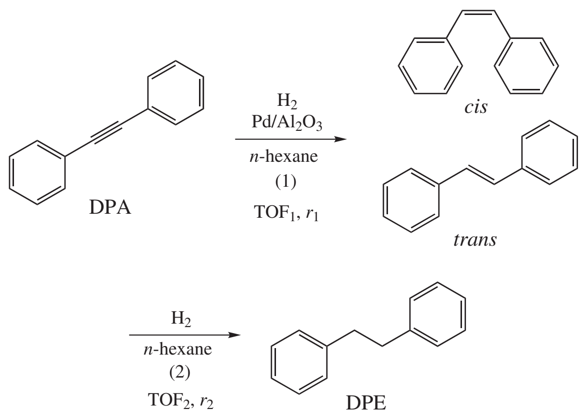

Figure 1 Schematic diagram of alkyne hydrogenation.

It was postulated by Boudart[5] that reactions over a metal surface can be categorized as structure sensitive or structure insensitive. Later, the effects of metal particle size on the performance of metal-supported catalysts have been classified by Che and Bennette into three different types, where rate, normalized per exposed metal surface atom (TOF), remains constant for structure-insensitive reactions and decreases or increases with particle size for structure-sensitive processes.[6]

In semihydrogenation the size effect has been intensively investigated and debated for gas-phase processes,[7–10] though conclusions are controversial. On the one hand, gas-phase hydrogenation of C≡C bond is argued to be structure insensitive,[9] and several facts indicate that Pd particle size does not strongly affect the selectivity of alkyne hydrogenation.[11–13] On the other hand, it was shown[13–16] that catalysts with low dispersion (and, accordingly, large Pd particle) exhibit higher selectivity in acetylene hydrogenation. Alternatively, the higher selectivity in alkyne hydrogenation over smaller Pd particles has been reported[17,18] and associated with the destabilization of a β-PdH phase as Pd particle size decreased.[19]

Despite the detailed investigation of Pd size effect for the gas phase alkyne hydrogenation, its comprehensive study for C≡C liquid phase hydrogenation is still lacking.[20] Therefore, this work was devoted to revealing a relationship between the size of Pd nanoparticles (from 1.5 to 22 nm) and the activity/selectivity of a 1% Pd/Al_2O_3 catalyst in liquid-phase diphenylacetylene (DPA) hydrogenation.

A series of monodisperse Pd/Al_2O_3 catalysts was prepared by the incipient wetness impregnation of acetic acid pretreated γ-alumina (Sasol TKA-432, BET specific surface area of 215 $m^2\ g^{-1}$) with an aqueous solution of trinuclear Pd acetate acidified with nitric acid. Impregnated products were air calcined at 400–600 °C for 2 h and reduced in a flow of H_2 at 400 °C for 3 h followed by cooling in an Ar flow to finalize the preparation procedure. Variation of Pd/NO_3^- ratio during impregnation and the calcination temperature enabled the preparation of three samples having average Pd particle sizes of 1.5, 5.7 and 22 nm with a narrow particle size distribution (Figures 2, 3). According to inductively coupled plasma atomic emission spectroscopy (ICP-AES; Baird

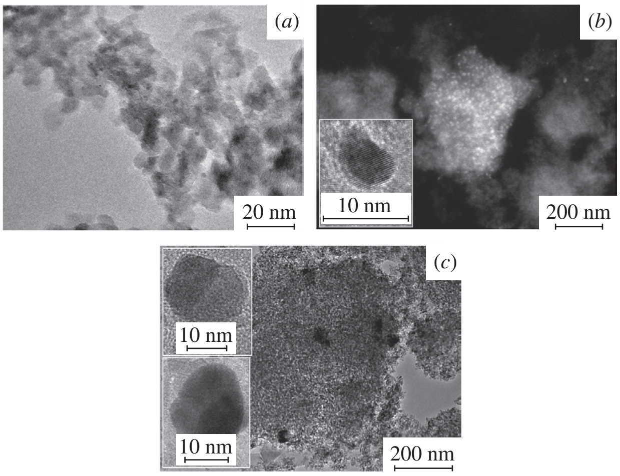

Figure 2 TEM images for Pd/Al_2O_3 catalyst with average particle sizes of (*a*) 1.5, (*b*) 5.7 and (*c*) 22 nm.

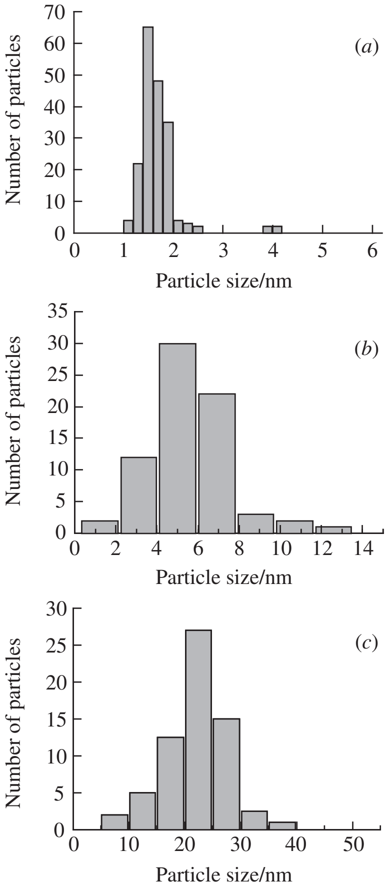

Figure 3 Particle size distribution diagrams for Pd/Al_2O_3 catalyst with average particle sizes of (*a*) 1.5, (*b*) 5.7 and (*c*) 22 nm.

Table 1 Performance of Pd/Al_2O_3 catalysts with different particle sizes in DPA hydrogenation.

Pd particle size/nm	r_1/ μmol min^{-1} mg$_{cat}^{-1}$	r_2/ μmol min^{-1} mg$_{cat}^{-1}$	TOF$_1$/s^{-1}	TOF$_2$/s^{-1}	r_1/r_2
1.5	17.43	6.75	5.2	2.0	2.6
5.7	9.88	2.36	11.1	2.7	4.2
22.0	4.56	0.45	19.9	2.0	10.1

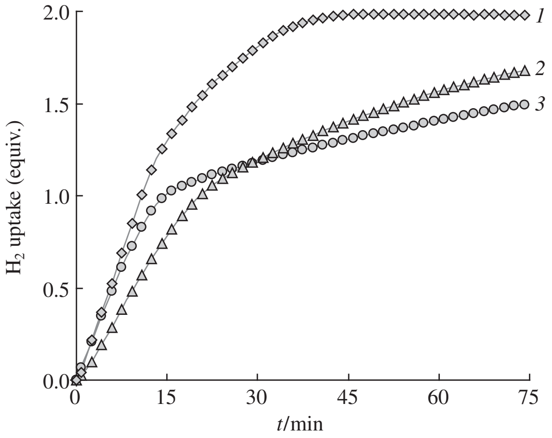

Figure 4 Effect of particle size on the performance of Pd/Al_2O_3 catalysts in the liquid-phase hydrogenation of DPA. Pd particle sizes are (*1*) 1.5, (*2*) 5.7 and (*3*) 22 nm. Reaction conditions: P_{H_2} = 5 bar; T_{react} = 25 °C; [DPA]/Pd ~ 4000; solvent, *n*-hexane. Catalyst amount: 2.5 mg for (*1*) and (*2*), and 7.5 mg for (*3*).

Plasma Spectrovac PS-6), the synthesized samples contained 1.0 ± 0.08 wt% Pd.

Transmission electron microscopy (JEM-2010, Jeol Co.) was used to characterize the Pd particle size distribution on the support surface and to define the mean particle sizes and Pd dispersion for each synthesized sample. All TEM measurements were performed at 200 kV and a line-in-line resolution of 0.14 nm. The size distribution of palladium crystallites was determined by measuring 200–700 particles for each sample.

In addition to TEM measurements, the chemisorption characteristics of the samples were measured using an Autosorb-1-C-MS/TCD automated adsorption analyzer (Quantachrome Instruments, the United States). The filled volume was determined by a volumetric helium method. The degree of dispersion (*D*) of both metals was determined by the irreversible chemisorption of hydrogen using a double isotherm method, assuming H/Pt(Pd) = 1/1 stoichiometry. The data of the both methods were found consistent.

Hydrogenation was carried out in a stainless-steel autoclave at 5 atm of H_2 and room temperature in *n*-hexane (98%, Merck) as a solvent. The DPA/Pd ratio was about 4000. The reaction rates were measured by the rate of H_2 uptake at the first and the second hydrogenation steps (r_1 and r_2, respectively) by monitoring hydrogen pressure. The hydrogenation of individual *cis*-stilbene (96%, Sigma-Aldrich) was also performed under the same conditions. The reaction rates were found identical to the rates at the second stage of DPA hydrogenation (r_2). Specific catalytic activity was evaluated by the turnover frequencies at the first (TOF$_1$) and the second (TOF$_2$) steps of the reaction (see Figure 1) calculated as the ratio of converted substrate molecules (DPA or DPE, respectively) to the surface Pd atoms in the catalyst per second. The number of surface atoms was calculated based on TEM results and chemisorption data using a published approximation procedure.[21] Other details of the catalyst preparation and characterization can be seen elsewhere.[22]

Kinetic selectivity of the process was characterized by the r_1/r_2 ratio.[23,24] In addition to the kinetic parameter, selectivity for stilbene (diphenylethylene) and the *cis*/*trans* isomer ratio were determined using ^{1}H NMR data obtained on a Bruker AM-300 spectrometer. Samples for ^{1}H NMR analysis were taken after hydrogen uptake corresponding to the complete half-hydrogenation step (mole H_2/mole DPA = 1).

The kinetics of hydrogenation was followed by the hydrogen uptake as a function of reaction time and reported in Figure 4 for the conversion of DPA over Pd/Al_2O_3 having different Pd dispersion. The data on the reaction rates and TOF values are summarized in Table 1.

The decrease in the overall reaction rate was observed, as the size of Pd particle increases (Figure 4, Table 1). On the other hand, the data revealed a four-time increase in turnover frequency TOF$_1$ from 5.2 to 19.9 s^{-1}, as Pd particle size increased from 1.5 to 22 nm (Table 1). The strong increase in TOF$_1$ with increasing Pd particle size indicates the structure sensitivity of triple bond hydrogenation (Figure 1, reaction 1). The observed relationship can be explained by the strong adsorption of a bulky DPA molecule on low-coordinated corner and edge Pd atoms of small nanoparticles, thus competing with hydrogen adsorption. As Pd particle size grows, the percentage of low-coordinated palladium surface atoms rapidly decreases thus increasing TOF$_1$.

Table 2 DPA conversion (X_{DPA}) and selectivity for stilbene ($S_{stilbene}$) calculated based on ^{1}H NMR data[a] for Pd/Al_2O_3 catalysts with different particle sizes.

Pd particle size/nm	H_2 uptake (equiv.)	X_{DPA} (%)	$S_{stilbene}$ (%)
1.5	1.07	93	71
5.7	1.02	94	75
22.0	1.02	92	87

[a] Sampling point for ^{1}H NMR analysis is 1 equiv. of H_2 uptake after subtracting of 0.1 equiv. of H_2 absorbed by the solvent.

Remarkably, the selectivity in DPA hydrogenation was distinctly improved when Pd particle size increases. This is evident from the change of the shape of H_2 uptake curves (Figure 4) and from a significant increase in the r_1/r_2 ratio (Table 2). Kinetic measurements indicate that the r_1/r_2 ratio rises from 2.6 (for 1.5 nm Pd particles) to 10.1 (for 22 nm Pd particles). The increase in selectivity is also confirmed by NMR data for the reaction products (Table 2).

Detailed kinetic analysis of the relationship between TOF_1, TOF_2 and the particle size suggests that the observed improvement of the reaction selectivity stems from the fact that TOF_1 increases as Pd particles become bigger, while TOF_2 of double bond hydrogenation (Figure 1, reaction 2) remains essentially independent of Pd particle size (Table 1). Due to this fact, the increase in Pd particle size within a range of 1.5–22 nm leads to the improvement of the process selectivity, as manifested by an increase in the r_1/r_2 ratio from 2.6 to 10.1.

This is in a good agreement with published data indicating that, in olefin hydrogenation, in contrast to alkyne hydrogenation, specific catalytic activity is not strongly correlated with Pd particle size. In most cases for olefin hydrogenation specific catalytic activity changes less than 2–3 times as particle size changes within a range of 1–10 nm[25,26] implying lower structure sensitivity of double bond hydrogenation. The recent data by Quek *et al*.[27] showed that the catalytic activity in phenylacetylene hydrogenation increases with Pd particle size, whereas the activity remains constant for 1-octene, which testifies that the hydrogenation of phenylacetylene is more structure sensitive as compared with 1-octene.[27]

However, these results were obtained in the hydrogenation of individual alkyne and alkene molecules. In our study we showed that a similar effect can be observed in the course of the consecutive hydrogenation of the same molecule, which leads to a significant improvement of the selectivity of semihydrogenation.

Tentatively, the different structure sensitivity of the first and second hydrogenation steps can be interpreted using the model proposed by Van Santen *et al*.[9,10] The most significant factor influencing the structure sensitivity of the process for each reaction stage is the difference in the rate-limiting step. Generally, the hydrogenation is usually described as the sequential addition of hydrogen to the adsorbed alkyne or alkene molecule.[9] This reaction pathway is known as the Horiuti–Polanyi mechanism, and it includes the adsorption of alkyne or alkene molecule onto the catalytic surface, the activation of the unsaturated C–C bond and the stepwise addition of hydrogen atoms to the adsorbed molecule followed by desorption of the hydrogenated product.[27] For the first step of DPA hydrogenation, the increase in the reaction rate with particle size suggests that the rate-limiting step is the activation of triple C≡C bond through multiple contacts with several surface atoms. Therefore, this step proceeds faster on larger particles. On the other hand, for next step of double bond hydrogenation formation of C–H σ-bond seems to be a rate-limiting step,[9] which proceeds over a single metal atom. This makes TOF_2 essentially independent of the size of Pd particles.

Thus, we found that the variation of Pd particle size provides an effective tool for tuning activity–selectivity parameters in the selective semihydrogenation of substituted alkynes due to different structure sensitivities of the first and second hydrogenation steps.

This study was supported by the Russian Science Foundation (grant no. 14-50-00126).

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Received: 24th April 2015; Com. 15/4609