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Ultrasonically improved semi-hydrogenation of alkynes to (Z-)alkenes over novel lead-free Pd/Boehmite catalysts

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Keywords: semi-hydrogenation, alkynes, ultrasound, catalyst activity, catalyst selectivity.

Abstract

This paper reports the application of sonication in the semi-hydrogenation of alkynes over two novel Pd/Boehmite catalysts. The semi-hydrogenations of phenylacetylene, diphenylacetylene and 2-butyne-1,4-diol have either been investigated in an ultrasonic bath under atmospheric hydrogen pressure, or in an ultrasonic horn reactor under 0.1 - 0.5 MPa hydrogen pressure. Alkyne hydrogenation was suppressed by sonication under atmospheric hydrogen pressure, but promoted by sonication under 0.1 MPa of hydrogen pressure. Sonication increased selectivity towards the semi-hydrogenated products in both cases. Catalyst loading, hydrogen pressure, temperature and the presence of quinolone all impacted on hydrogenation rate, activity and selectivity to semi-hydrogenated products. Palladium leaching from the catalyst was evaluated in ethanol and hexane under stirring and both sonication and silent conditions.

1. Introduction

The heterogeneous catalytic semi-hydrogenation of alkynes to give alkenes is a highly desired tool in synthetic organic chemistry. This is especially true in the synthesis of natural products and biologically active compounds such as vitamins, fragrance compounds, such as linalool, and other products [1-3]. Alkenes are intermediates in the hydrogenation of alkynes meaning that highly selective semi-hydrogenations, which make use of specially developed catalysts, have been the focus of significant interest. In addition, the removal of alkynes from alkenes is mandatory if we are to avoid the poisoning of polymerization catalysts, e.g. phenylacetylene is an unwanted feedstock component in polystyrene production plants [4].

The Lindlar catalyst (palladium on calcium carbonate poisoned with lead acetate and quinoline) has played a unique role in the semi-hydrogenation of alkynes for more than 50 years [5,6]. Quinoline is thought to compete for the active sites on the catalyst. Lead, which is formed as a result of the reduction of adsorbed lead diacetate, changes palladium surface properties [5]. However, environmental concerns and lead's toxicity [7,8], mean that its use should be minimised. The design of lead-free catalysts and process intensification protocols have therefore received increasing amounts of attention [9], and research groups are continuing their extensive search for alternative modifier metals, such as Ga, Zn, [10-14] as well as for various supports, e.g. tungsten film [15], pumice [16], heterocyclic polyamides [17] and polyaniline films/membranes [18]. However, an ideal solution would be one that does not require an extra poison, be it a metal or organic compound.

Mesoporous materials are defined as having pore diameters of between 2 and 50 nm. Catalysis that is based on these materials normally provides benefits in reactions where diffusion limitations play an important role. Substantial work has been carried out on the use of silica [19] and alumina [20] in the semi-hydrogenation of alkynes in an effort to overcome diffusion resistance [21]. The hydrogenation of alkynes on solid Pd surfaces is generally structure sensitive, which is an important characteristic in the understanding of such catalytic processes [15]. Unselective hydrogenation proceeds on hydrogen-saturated β -hydride, whereas selective hydrogenation has only been possible after decoupling bulk properties from the surface events [22]. Only gas phase surface hydrogen is able to generate alkenes [23].

Although the highly selective semi-hydrogenation of alkynes using heterogeneous catalysts under mild conditions has recently been investigated [24-26], the production of fine chemicals requires new, cheaper and more environmentally sustainable technologies, which not only utilize heterogeneous catalysis but also take into account reactor engineering aspects and non-conventional energy sources. Classic catalytic hydrogenation is carried out under a hydrogen atmosphere and often at elevated temperatures in pressure resistant reactors that usually display slow heating/cooling rates. This can negatively affect selectivity and generate unwanted side reactions. The beneficial effects of ultrasound are well documented in the literature [2,27]. This non-conventional enabling technology furthers process intensification and combines safer protocols, cost reduction and energy

savings [28]. Ultrasound has been applied to the activation of heterogeneous catalytic hydrogenation since the early 1980s [29-31].

Significant enhancements in selectivity, rates and yields as well as milder reaction conditions in both homogeneous and heterogeneous systems are all recognized hallmarks of sonication [32-34], which has also been shown to enhance catalyst robustness, selectivity and activity [35-37]. It also improves organic synthesis and accelerates the hydrogenation of unsaturated hydrocarbons [29].

The chemical and physical effects of ultrasound arise from the phenomenon of cavitation which produces extreme but localized conditions. When a cavitation bubble violently collapses near a solid surface, high-speed jets of liquid are driven into particle surfaces [32]. The high-speed liquid microjets and violent cavity implosion driven shock waves grant ultrasound its significant mechanical effects, such as increasing the surface area of particles, changing surface morphology, composition and particle size as well as accelerating dissolution and/or renewing the surface of a solid reactant or catalyst [38]. Besides triggering free radical reactions, it is also known to produce high localized temperatures and pressures [39]. Catalyst activity is therefore increased by catalyst surface deformation which exposes fresh, highly active surfaces and reduces diffusion length in catalyst pores [38]. The local turbulent flow associated with acoustic streaming also improves mass transfer between the liquid phase and the surface, thus increasing observed reaction rates [40].

However, little is known about the effects of ultrasound in the semi-hydrogenation of alkynes. The excellent selective reduction results provided by sonochemical protocols in previous studies have prompted us to explore the promise of the ultrasound-assisted semi-hydrogenation of alkynes [8,41]. The aim of the present work is to investigate the influence of ultrasound on the activity and selectivity of the Pd/Boehmite-catalyzed hydrogenation of phenylacetylene (PA), diphenylacetylene (DPA) and 2-butyne-1,4-diol (ByD). Pd content, specific surface areas and other catalyst textural properties have been evaluated using ICP, nitrogen adsorption isotherms and TEM studies. This article therefore describes the effects of hydrogenation factors, such as substrate and catalyst proportions, hydrogen pressure, temperature and quinoline content on activity and selectivity. In addition, ultrasound has been shown to cause significant metal leaching when used with the standard Lindlar catalyst (Pd-Pb on calcium carbonate) [42]. We therefore also wanted to investigate whether our lead-free catalysts show higher robustness under sonication and reduced metal leaching.

2. Experimental

2.1. Catalyst preparation and characterization

Boehmite is an aluminium oxide hydroxide (γ -AlO(OH) \cdot nH₂O, 60% Al₂O₃) mineral and a component of the aluminium ore, bauxite. The microscope picture of the support particles and a double measurement of the particle

sizes show that boehmite is mainly composed of non-uniform, spheroid particles with a size range of 0.78-75 μm and a D50 of 6 μm .

Pd/Boehmite catalyst preparation is improved by the reduction-deposition method which sees a metal initially reduced in solution, in the presence of a stabilizer, before it is deposited on a heterogeneous support [43]. The Pd_{L_V-us}/Boehmite catalyst was prepared via the ultrasound-assisted, one-pot dispersion and reduction of Pd(OAc)₂ within a LuviquatTM aqueous solution. The Pd_{US-MW}/Boehmite catalyst was prepared using ultrasound-assisted dispersion and the MW-assisted reduction of Pd(OAc)₂ in water at 1 MPa H₂. The details of catalyst preparation methods and characterization are described elsewhere [44].

2.2. Catalyst Testing

Hydrogenation under atmospheric hydrogen pressure in an ultrasonic bath

Alkynes (Alfa Aesar, 98%) were hydrogenated over the prepared Pd-catalysts at room temperature (RT, 25 \pm 1 $^{\circ}\text{C}$) and under atmospheric hydrogen pressure (AHP, H₂ balloon). 5 mg of Pd-catalyst was added to either 50 mL of hexane (Sigma-Aldrich, \cong 99%), or ethanol (Fluka, 96%), containing 0.58 mmol of the alkyne. The reactor was evacuated to 0.02 MPa using a vacuum pump and then flushed with nitrogen (Sapio, grade 6.0), before the reaction. The reactor was then evacuated to 0.02 MPa once more and filled with hydrogen (Sapio, grade 4.5) via a connected H₂ balloon. The reaction was performed in an ultrasonic bath (Elma, Transsonic 460, 35 kHz, 85 W) filled with 1.5 L water while liquid temperature was controlled by adding ice. Aliquots (100 μl) of the solution were periodically extracted from the reaction system using an airtight syringe. These were then diluted with 900 μl cyclohexane (Alfa Aesar, 99.9%) and analyzed using GC/MS (Agilent Technologies 6850 Network GC system equipped with a 5973 Network Mass Selective Detector and an HP-5MS capillary column).

The same reaction media were placed in a water bath and the reaction was performed without sonication under stirring at 500 rpm. This was done in order to provide a basis for valid comparison.

Hydrogenation under 0.1-0.5 MPa of hydrogen pressure in an ultrasonic horn reactor

A 100 mL stainless steel autoclave, which was equipped with double-wall cooling water, a temperature sensor and monitor, was charged with 5 mg of prepared catalyst and 50 mL of either hexane or ethanol containing 0.58 mmol of alkyne. The ultrasonic horn was tightly fixed to the reactor vessel and then the closed system was flushed with hydrogen and pressurized, without stirring. Alkynes were hydrogenated at RT (25 \pm 1 $^{\circ}\text{C}$) and 0.1-0.5 MPa of hydrogen pressure. The ultrasonic horn reactor was homemade (20 kHz, 70 W, Fig. 1) and the reaction temperature was controlled using cooling water. Aliquots (100 μl) of the solution were periodically extracted from the reaction system using airtight syringes, diluted with 900 μl cyclohexane or chloroform and analyzed using GC/MS.

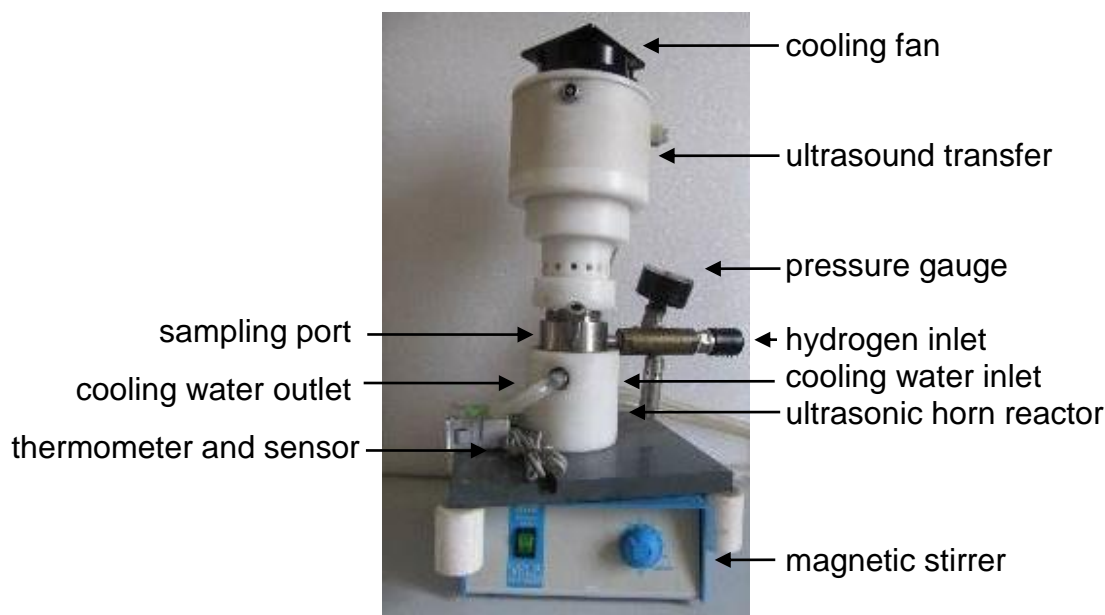


Fig. 1. Ultrasonic horn reactor for hydrogenation.

In order to provide a valid comparison, the same reaction media were set in the ultrasonic horn reactor (Fig. 1) and the reaction was performed without sonication at given hydrogen pressures and stirred at 500 rpm.

2.3. Leaching test with sonication or stirring

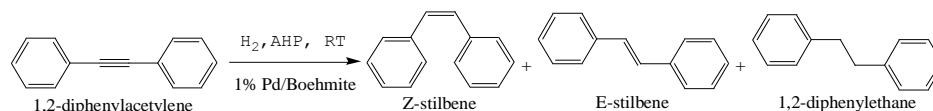
50 mL of either hexane or ethanol and 200 mg of Pd/Boehmite catalyst were added to the ultrasonic horn reactor. The mixture was either stirred for 35 min with an oval magnetic stirring bar (12.6 g) at 500 rpm or sonicated for 35 min at 20 kHz and 70 W ultrasound under an air atmosphere at 25 ± 1 °C. After treatment, samples were centrifuged for 5 min at 5000 rpm (Hermle Z320, Berthold Hermie GmbH & Co, Germany). After liquid and solid separation, the solid catalysts were naturally dried at room temperature and liquids were completely evaporated.

The Pd-content in solid samples was measured on a ContrAA300 FI-AAS device (244.791 nm, C₂H₂/Air). The samples were treated as follows: 30 mg of the substance was treated with HCl (32%, 2 mL)/HNO₃ (69%, 3 mL) and placed in an ultrasonic-bath at 60 °C for 30 min. The samples were then digested in a TurboWAVE® (Microwaves device, MLS GmbH). H₂O and Schinkel-Buffer (2 mL) were added and the solution was diluted with H₂O to a final volume of 100 mL.

After sample liquid evaporation, the residue was dissolved in 2 ml of concentrated HNO₃ in a round flask. After four days of contact, each solution was diluted to 7 ml with high purity water and analysed using ICP-OES ($\lambda_{\text{Pd}} = 340.458$ nm).

3. Results and Discussion

The novel lead-free, palladium-based, boehmite supported catalysts were prepared using ultrasound and microwave irradiation. The prepared Pd/Boehmite catalysts were screened using DPA hydrogenation (Scheme 1) at RT and AHP in the stirring system. The prepared catalysts have the palladium loading of 0.78–0.88 wt%. The textural properties of catalysts and DPA hydrogenation performance were reported in our previous study [44].



Scheme 1

The ultrasonic-assisted catalyst (Pd_{L_V-us}/Boehmite) showed much higher initial DPA hydrogenation activity than the Lindlar catalyst, and comparable selectivity to Z-stilbene. It was found to give better catalytic performance than Pd_{US-MW}/Boehmite [44], and the hydrogenation performances was also comparable to the NanoSelect catalyst produced by BASF [45]. It is attributed to the synergistic effect between surfactant and ultrasound. Under sonication, the boehmite support for Pd_{L_V-us}/Boehmite (Fig.2a) was cracked into finer and more uniform particle sizes than Pd_{US-MW}/Boehmite (Fig.2b).

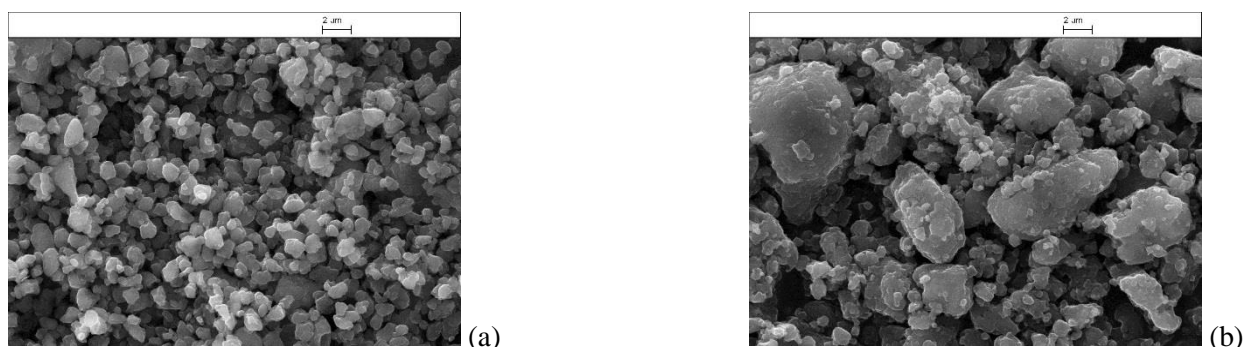


Fig. 2. SEM micrograph of Pd_{L_V-us}/Boehmite catalyst (a) and Pd_{US-MW}/Boehmite catalyst (b)

3.1. Comparison of ultrasonic hydrogenation of PA over various catalysts.

The ultrasound-assisted hydrogenations of PA over Pd_{L_V-us}/Boehmite and Pd_{US-MW}/Boehmite catalysts have been compared in this study. As listed in Table 1, the ultrasound-assisted hydrogenation activity and rate over Pd_{L_V-us}/Boehmite are more than 3-times higher than those over Pd_{US-MW}/Boehmite, in both the ultrasonic bath and horn reactor. The very low activity of Pd_{US-MW}/Boehmite and low PA conversion make it meaningless to compare selectivity to the target product.

Table 1 Comparison of PA hydrogenation conversion, rate, activity, selectivity and yield over Pd_{Lv-us}/Boehmite and Pd_{US-MW}/Boehmite in the ultrasonic reactors (5 mg of catalyst; 50 mL of hexane containing 0.58 mmol of PA; 25±1 °C; AHP in ultrasonic bath reactor (within 1.5 L of water at 35 kHz, 85 W), 0.1 MPa of H₂, 20.2 kHz, 70 W).

Test	Catalyst	T _R (min)	X (%)	S (%)	Y _{max} (%)	A (mmol mg ⁻¹ Pd min ⁻¹)	k (mM min ⁻¹)	R ²
US-bath-1	Pd _{Lv-us} /Boehmite	70	94.3	90.1	85.0	0.190	0.151	0.9811
US-bath-3	Pd _{US-MW} /Boehmite	60	26.6	90.7	24.1	0.057	0.0444	0.9128
US-horn-1	Pd _{Lv-us} /Boehmite	10	98.9	83.0	82.0	1.547	1.207	0.9891
US-horn-3	Pd _{US-MW} /Boehmite	10	39.2	94.2	36.9	0.496	0.4103	0.9524

Note: T_R: reaction time; X: PA conversion rate; S: selectivity to styrene; Y_{max}: maximal yield of styrene; A: catalyst hydrogenation activity; k: reaction rate or rate constant; R²: correlation coefficient.

The ultrasonic pre-treatment of supported catalysts has been reported to be highly beneficial, as it has improved both catalytic activity and selectivity in the hydrogenation of ethyl pyruvate and cinnamyl alcohol [46-48]. Furthermore, the catalyst surface becomes homogeneous and active centre coverage is decreased correspondingly [49,50]. Firstly, the agglomeration can be inhibited and/or boehmite particles broken up by sonication, resulting in smaller Pd particle sizes and more active centres [44]. Pd_{Lv-us}/Boehmite contains Pd nanoparticles that are 2.4±0.7 nm in average diameter and that the nanoparticles are quite evenly distributed over the catalyst support surface, due to nanoparticle stabilization with LuviquatTM and the effect of sonication in the one-pot procedure [44]. By contrast, huge palladium particle clusters are seen in a relatively broad distribution, of ~50-100 nm in Pd_{US-MW}/Boehmite, while no particles could be found in other areas. Witte et al. have reported that the metal crystallite size of the formed nanoparticles is 4–8 nm and large agglomerates of Pd(0) particles are formed using HHDMA (hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogenphosphate) which is sufficient for the full reduction of Pd(II) to Pd(0), but not for Pd nanoparticle stabilization [43]. They also considered the effect of metal crystallite size on catalytic properties [45]. There is a decrease in overall activity with increasing size, 5 > 15 > 25 nm Pd, because of the lower metal surface area available for hydrogenation. This indicates that smaller Pd sizes are not only more active but also more selective. We achieved similar results using PA hydrogenation over Pd_{Lv-us}/Boehmite and Pd_{US-MW}/Boehmite catalysts even under sonication.

Secondly, the effects of sonication and surfactant on pore size and volume can be attributed to strong surfactant molecule adsorption in the catalyst pores and to a restructuring of the boehmite structure as directed by surfactant molecules [51,52]. Boehmite is known to contain mesopores, but not micro- and macropores. This means that

there is a lower probability that Pd particles can diffuse into the pores. Thus, the intermediate immediately leaves the vicinity of the active metal after formation and cannot react further [45].

Changing the input amounts of PA or catalyst leads to very different rates and activity at different PA:Pd_{Lv-us}/Boehmite ratios, as shown in Table 2. An increase in PA:Pd_{Lv-us}/Boehmite ratio caused a linear decrease in PA hydrogenation activity, while the hydrogenation rate dropped exponentially. This means that high substrate concentrations cover the active catalyst centres, leading to a decrease in hydrogenation activity and rate, even under ultrasound. As reported, the apparent reaction rate is proportional to catalyst amount. It is proven that the performance of the catalyst under the experimental conditions is within the kinetic regime and that the reaction is free of artifacts [53]. In addition, the PA:Pd_{Lv-us}/Boehmite ratio has almost negligible impact on selectivity to styrene in the ultrasonic horn reactor (Table 2).

Table 2 PA:Pd_{Lv-us}/Boehmite ratio effects on PA hydrogenation conversion, rate, activity, selectivity and yield in the ultrasonic horn reactor (50 mL of hexane containing PA; 25±1 °C; 0.1 MPa of H₂, 20.2 kHz, 70 W).

Test	PA (mg)	Catalyst (mg)	S/C	T _R (min)	X (%)	S (%)	Y _{max} (%)	A (mmol mg ⁻¹ Pd min ⁻¹)	k (mM min ⁻¹)	R ²
US-horn-4	59	10	6	4	94.0	85.8	80.7	1.772	2.7642	0.9966
US-horn-1	59	5	12	10	98.9	83.0	82.0	1.547	1.207	0.9891
US-horn-5	120.3	5	24	20	78.7	93.2	73.4	1.160	0.9227	0.9989

Note: S/C: PA:Pd_{Lv-us}/Boehmite ratio; T_R: reaction time; X: PA conversion rate; S: selectivity to styrene; Y_{max}: maximal yield of styrene; A: hydrogenation activity of catalyst; k: reaction rate or rate constant; R²: correlation coefficient.

3.2. Ultrasonic effects on semi-hydrogenation of PA and ByD

The overall production rate is often limited by interphase mass transfer in these gas-liquid-solid reactions [13]. Ultrasound has been used to overcome this problem and is usually reported to greatly accelerate the catalytic hydrogenation of olefins [29,54], cinnamaldehyde [55,56], 3-buten-2-ol [57,58], while selectivity to target products is either unchanged or increased under mild RT and AHP conditions. This effect has been attributed to sonication's dispersion effect on the catalyst and the effect of cavitation on the hydrogenation process.

The highly active Pd_{Lv-us}/Boehmite catalyst was selected as a means to explore the ultrasonic effect on PA hydrogenation (Scheme 2) under the following conditions; an ultrasonic bath, an ultrasonic pressure reactor and only stirring being used in both reactors. The effect of sonication on PA hydrogenation was studied in hexane under mild experimental conditions (25±1 °C, AHP or 0.1 MPa H₂). PA hydrogenation experiments using the

same catalyst amounts in different ultrasonic reactors gave different activities. The results of the four typical experiments over Pd_{LV-us}/Boehmite catalyst are given in Fig. 3.

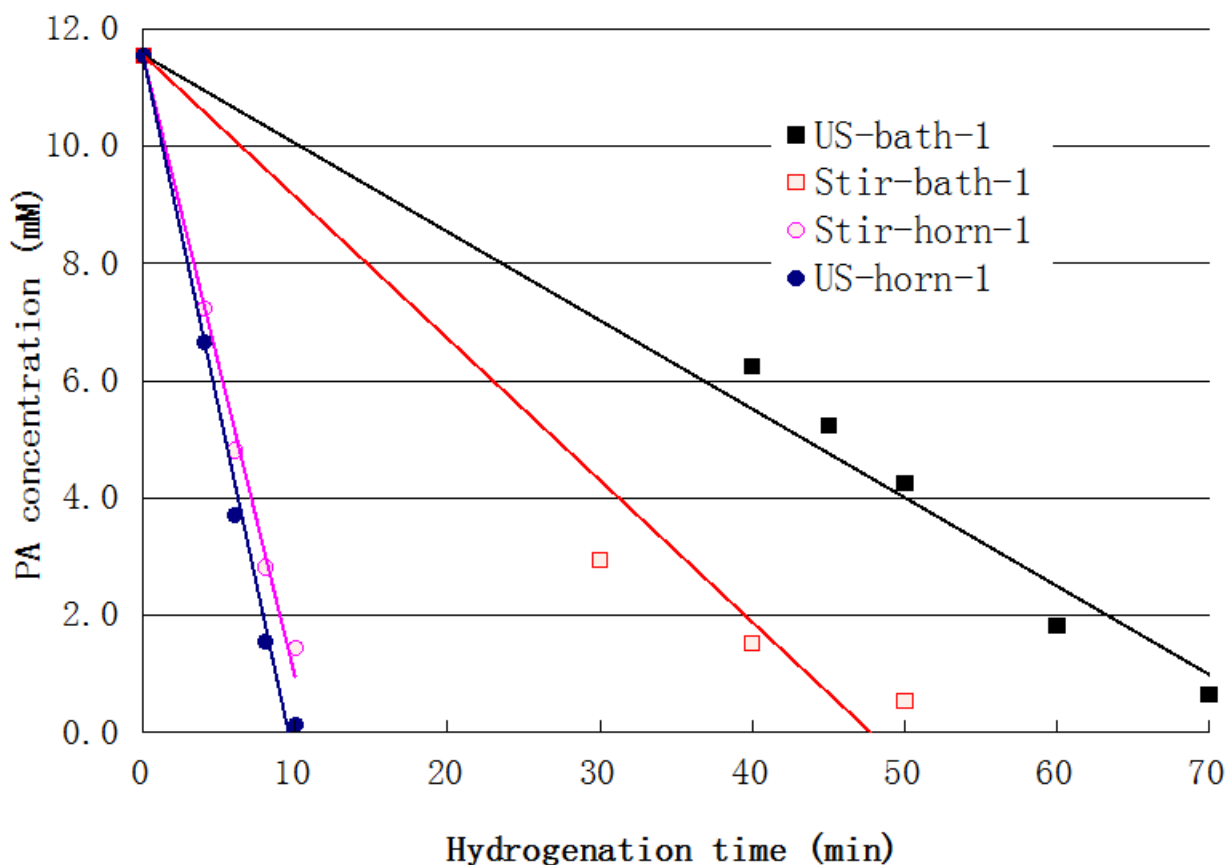
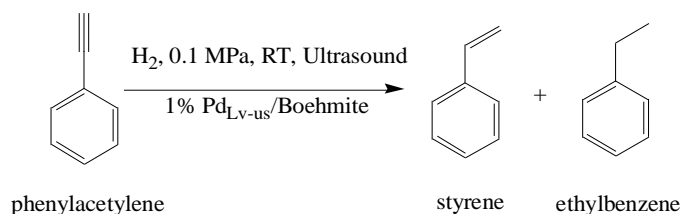


Fig. 3 PA concentration as a function of reaction time for hydrogenation over Pd_{LV-us}/Boehmite via sonication or stirring. PA hydrogenation conditions: 5 mg of Pd_{LV-us}/Boehmite; 50 mL of hexane containing 0.58 mmol PA; 25 ± 1°C; within ultrasonic bath under AHP (US-bath-1), ultrasonic horn reactor under 0.1 MPa H₂ (US-horn-1), stirring with 500 rpm under AHP (Stir-bath-1), stirring with 500 rpm under 0.1 MPa (Stir-horn-1).



Scheme 2

In Fig. 3, sonication causes a significant decrease in PA hydrogenation rate in the ultrasonic bath at AHP and RT, due to ultrasound mechanical and degassing effects. By contrast, only slight ultrasound effects were observed

with the ultrasonic horn reactor at 0.1 MPa H₂ and RT, as compared with stirring, because the ultrasonic degassing phenomenon was weakened under pressure in the closed horn reactor. The slightly faster rate observed using ultrasound in the horn could be due to the ultrasonic cleaning effect on the catalyst surface and slightly enhanced mass transfer.

The zero order reaction rate is apparently independent of reactant concentration. This means that the rate of the reaction is equal to the rate constant (k), i.e.:

$$C_t = -kt + C_0 \quad (1)$$

where C_0 is the initial alkyne concentration, C_t is the alkyne concentration at a given time (t), and k is the reaction rate or rate constant (mM min⁻¹).

k , R^2 values, PA conversion rate, selectivity, yield to styrene and activity are listed in Table 3.

The values shown in Table 3 are consistent with pseudo-zero order kinetics whether the reactions were carried out in the ultrasonic bath or ultrasonic horn reactor. In addition, PA hydrogenation was slowed under AHP in the ultrasonic bath, but slightly accelerated under 0.1 MPa in the ultrasonic horn reactor, according to the hydrogenation activity index and rate constant. In the ultrasonic bath, the PA hydrogenation rate decreased by 38% over Pd_{L_V-us}/Boehmite, as compared to the stirring mode at AHP. However, a 14% increase in PA hydrogenation rate over Pd_{L_V-us}/Boehmite was obtained at 0.1 MPa of hydrogen pressure in the ultrasonic horn reactor.

Table 3 Ultrasonic effects on PA hydrogenation conversion, rate, activity, selectivity and yield to styrene in the ultrasonic bath and horn reactor (5 mg of Pd_{L_V-us}/Boehmite; 50 mL of hexane containing 0.58 mmol PA; 25±1 °C; AHP in ultrasonic bath reactor (within 1.5 L of water at 35 kHz, 85 W), 0.1 MPa of H₂ in ultrasonic horn reactor (20.2 kHz, 70 W)).

Test No.	Treatment	T _R (min)	X (%)	S (%)	Y _{max} (%)	A (mmol mg ⁻¹ Pd min ⁻¹)	k (mM min ⁻¹)	R^2
US-bath-1	Sonication in ultrasonic bath	70	94.3	90.1	85.0	0.190	0.151	0.9811
Stir-bath-1	Stirring in ultrasonic bath	50	95.4	85.0	81.0	0.304	0.242	0.9589
Stir-horn-1	Stirring in ultrasonic horn reactor	15	98.7	76.8	75.8	1.331	1.059	0.9929
US-horn-1	Sonication in ultrasonic horn reactor	10	98.9	83.0	82.0	1.547	1.207	0.9891

Note: T_R: reaction time; X: PA conversion rate; S: selectivity to styrene; Y_{max}: maximal yield of styrene; A: hydrogenation activity of catalyst; k : reaction rate or rate constant; R^2 : correlation coefficient.

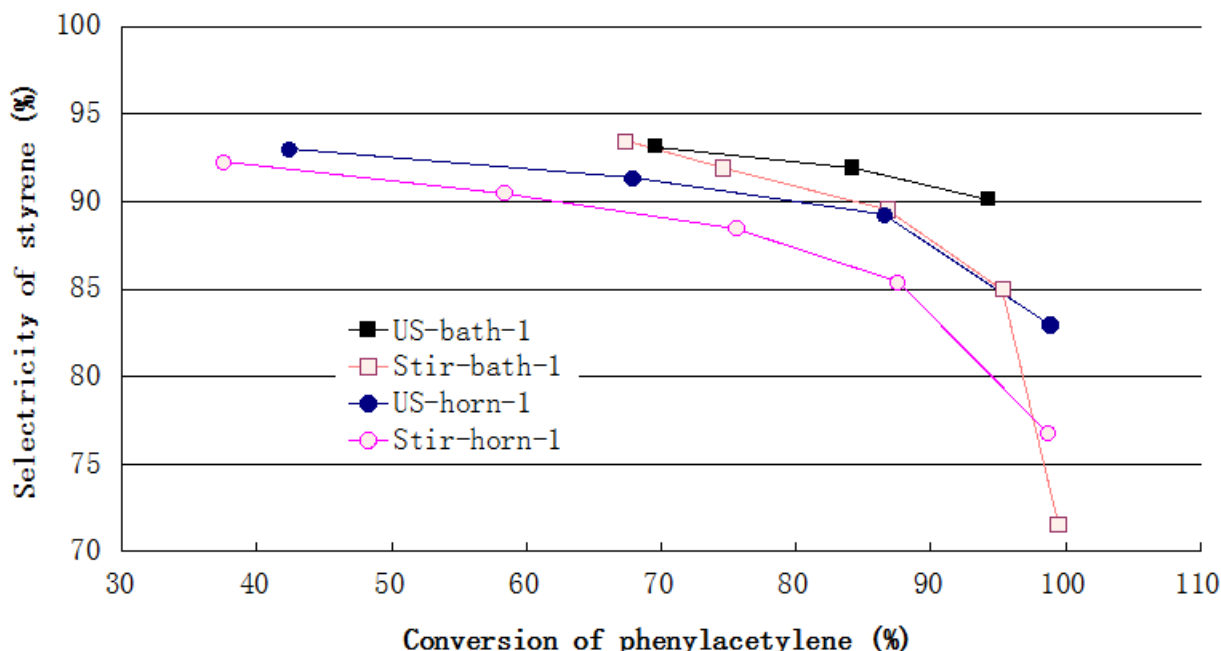


Fig. 4 Selectivity to styrene as a function of PA conversion over Pd_{L_V-us}/Boehmite by sonication or stirring. PA hydrogenation conditions: 5 mg of Pd_{L_V-us}/Boehmite; 50 mL of hexane containing 0.58 mmol PA; 25 ± 1°C; within ultrasonic bath under AHP (US-bath-1), ultrasonic horn reactor under 0.1 MPa of H₂ (US-horn-1), stirring with 500 rpm under AHP (Stir-bath-1), stirring with 500 rpm under 0.1 MPa of H₂ (Stir-horn-1).

As expected, sonication allows the maximal yield of Z-2-butene-1,4-diol to increase by 13% in the hydrogenation of 2-butyne-1,4-diol (Table 4). Surprisingly, the selectivity of 2-butene-1,4-diol was increased to approx. 95% under ByD hydrogenation sonication enhancement, while alkene selectivity of 89% was achieved without sonication in the stirring system.

Furthermore, selectivity toward the target product is higher in the ultrasonic bath than in the ultrasonic horn reactor, due to the degassing effect under atmospheric hydrogen pressure. The influence of hydrogen pressure on selectivity to the target product will be discussed hereafter.

3.3. Pressure effect on PA semi-hydrogenation

In general, linear reaction rate dependence on hydrogen pressure occurs up to a conversion of 95% [13]. At higher pressure, alkanes formed via over-hydrogenation are easily the major product. At lower pressures, hydrogenation is much slower, but is almost totally selective to alkenes [23]. In this study, the role of pressure on PA hydrogenation has been studied under AHP to 0.5 MPa of H₂. Table 5 shows the influence of hydrogen pressure in the ultrasonic horn reactor on the conversion, selectivity, activity and rate of PA hydrogenation over the weaker catalyst Pd_{US-MW}/Boehmite.

Table 5 Conversion, selectivity, activity and PA hydrogenation rate as a function of hydrogen pressure under sonication (5 mg of Pd_{US-MW}/Boehmite; 50 mL of hexane containing 0.58 mmol of PA; 25±1 °C; AHP in ultrasonic bath reactor (within 1.5 L of water at 35 kHz, 85 W), 0.1-0.5 MPa in ultrasonic horn reactor (20.2 kHz, 70 W)).

Test	Pressure (MPa)	T _R (min)	X (%)	S (%)	Y _{max} (%)	A (mmol mg ⁻¹ Pd min ⁻¹)	k (mM min ⁻¹)	R ²
US-bath-3	AHP	60	26.6	90.7	24.1	0.057	0.0444	0.9128
US-horn-3	0.1	10	39.2	94.2	36.9	0.496	0.4103	0.9524
US-horn-7	0.3	30	92.7	91.1	84.5	0.425	0.3737	0.989
US-horn-6	0.5	20	91.1	90.3	82.3	0.613	0.5393	0.9766

Note: T_R: reaction time; X: PA conversion rate; S: selectivity to styrene; Y_{max}: maximal yield of styrene; A: hydrogenation activity of catalyst; k: reaction rate or rate constant; R²: correlation coefficient.

In Table 5, both PA hydrogenation activity and rate linearly increase with hydrogen pressure, except at 0.3 MPa. The catalytic PA hydrogenation activity of Pd_{US-MW}/Boehmite at 0.3 and 0.5 MPa is over 7 and 10 times higher, respectively, than that at atmospheric hydrogen pressure. It also maintains high selectivities to styrene of 91.1 and 90.3%, respectively, at over 90% PA conversion.

3.4. Temperature effects on semi-hydrogenation of PA and ByD

The hydrogenation of alkynes over Pd-supported catalysts was generally performed at RT or under 40 °C, due to their higher activity [59]. The non-palladium catalysts, such as ternary Cu-Ni-Fe systems, require higher operating temperatures [60]. Hydrogenation activity to alkene increases with temperature; however, the influence of temperature on selectivity was found to be far less decisive than pressure [13].

Table 6 shows the influence of reaction temperature on PA and ByD hydrogenation activity and rate over the weaker Pd_{US-MW}/Boehmite catalyst in the ultrasonic horn reactor.

As seen in Table 6, hydrogenation rate and activity synchronously increase as temperature rises from room temperature to 40 °C. PA and ByD hydrogenation rate increased by 112.7% and 27.9%, respectively. Meanwhile, the hydrogenation activity of PA and ByD increased by 111.6% and 35.5 %, respectively. The selectivity of ByD hydrogenation to Z-2-butene-1,4-diol decreased from 94.6 to 87.7% at 100% ByD conversion. PA hydrogenation styrene selectivity was only slightly lower at 40 °C than at 25 °C, at approximately 95% PA conversion, leading to very similar alkene yields. Reaction temperature can therefore obviously increase alkyne hydrogenation rate and Pd catalyst activity, but slightly influences alkene selectivity.

Table 6 Temperature effects on the conversion, selectivity, activity and rate of PA and ByD hydrogenation under sonication (5 mg of Pd_{US-MW}/Boehmite; 50 mL of hexane containing 0.58 mmol of PA or ByD; PA hydrogenation at 0.3 MPa and ByD hydrogenation at 0.5 MPa in ultrasonic horn reactor (20.2 kHz, 70 W)).

Test	Temp (°C)	P (MPa)	Substrate	T _R (min)	X (%)	S (%)	Y _{max} (%)	A (mmol mg ⁻¹ Pd min ⁻¹)	k (mM min ⁻¹)	R ²
US-horn-7	25	0.3	PA	30	92.7	91.1	84.5	0.425	0.3737	0.989
US-horn-8	40	0.3	PA	15	96.6	88.8	85.7	0.903	0.7949	0.9824
US-horn-2	25	0.5	ByD	20	100.0	94.6	94.6	0.633	0.602	0.9941
US-horn-9	40	0.5	ByD	15	100.0	87.7	87.7	0.858	0.77	0.999

Note: Temp: Temperature; P: pressure; T_R: reaction time; X: PA or ByD conversion rate; S: selectivity to alkene; Y_{max}: maximal yield of styrene; A: hydrogenation activity of catalyst; k: reaction rate or rate constant; R²: correlation coefficient.

3.5. Quinoline effect on semi-hydrogenation of PA and DPA

The commercial Lindlar catalyst is a commonly used catalyst for the semi-hydrogenation of alkynes. It is calcium carbonate-supported palladium, modified by the addition of lead, while organic bases (e.g., quinoline) are often added to improve selectivity [6]. Higher selectivity to alkene was achieved using electron-donor compounds, such as N-bases (quinoline, pyridine, and ammonia) or via the addition of electron-donor compounds (Pb, Zn) to the Pd nanoparticles [13,45]. In this study, various amounts of quinoline have been added to the hydrogenation of DPA and PA in the ultrasonic horn reactor. DPA and PA hydrogenations were performed under 0.5 MPa at 25°C and 0.3 MPa at 40°C, respectively. Table 7 shows the influence of quinoline on the hydrogenation activity and rate of DPA. Fig. 5 shows the influence of quinoline on selectivity to Z-stilbene during the DPA hydrogenation.

As seen in Table 7, the addition of quinoline causes ultrasonic hydrogenation activity and DPA rate to decrease under 0.5 MPa at room temperature. PA hydrogenation activity was reduced from 0.90 to 0.73 mol g⁻¹Pd min⁻¹, and the rate decreased from 0.79 to 0.68 mM min⁻¹, respectively.

Table 7 Quinoline effects on the conversion, selectivity, activity and rate of PA and DPA hydrogenation in the ultrasonic horn reactor (5 mg of Pd_{US-MW}/Boehmite; 50 mL of hexane containing 0.58 mmol of PA or DPA; PA hydrogenation at 0.3 MPa and 40±1 °C and DPA hydrogenation at 0.5 MPa and 25±1 °C; 20.2 kHz, 70 W).

Test	Substrate	Quinoline (μl)	T _R (min)	X (%)	S (%)	Y _{max} (%)	A (mmol mg ⁻¹ Pd min ⁻¹)	k (mM min ⁻¹)	R ²
US-horn-8	PA	0.0	15	99.9	84.5	84.4	0.90	0.79	0.9824
US-horn-10	PA	2.5	18	99.1	90.5	89.6	0.73	0.68	0.9862
US-horn-11	DPA	0.0	24	88.7	88.3	78.3	0.47	0.41	0.987
US-horn-12	DPA	1.0	35	89.4	91.6	82.0	0.35	0.30	0.997
US-horn-13	DPA	2.5	38	89.7	92.0	82.5	0.30	0.27	0.996

Note: T_R: reaction time; X: PA or DPA conversion rate; S: selectivity to alkene; Y_{max}: maximal yield of alkene; A: hydrogenation activity of catalyst; k: reaction rate or rate constant; R²: correlation coefficient.

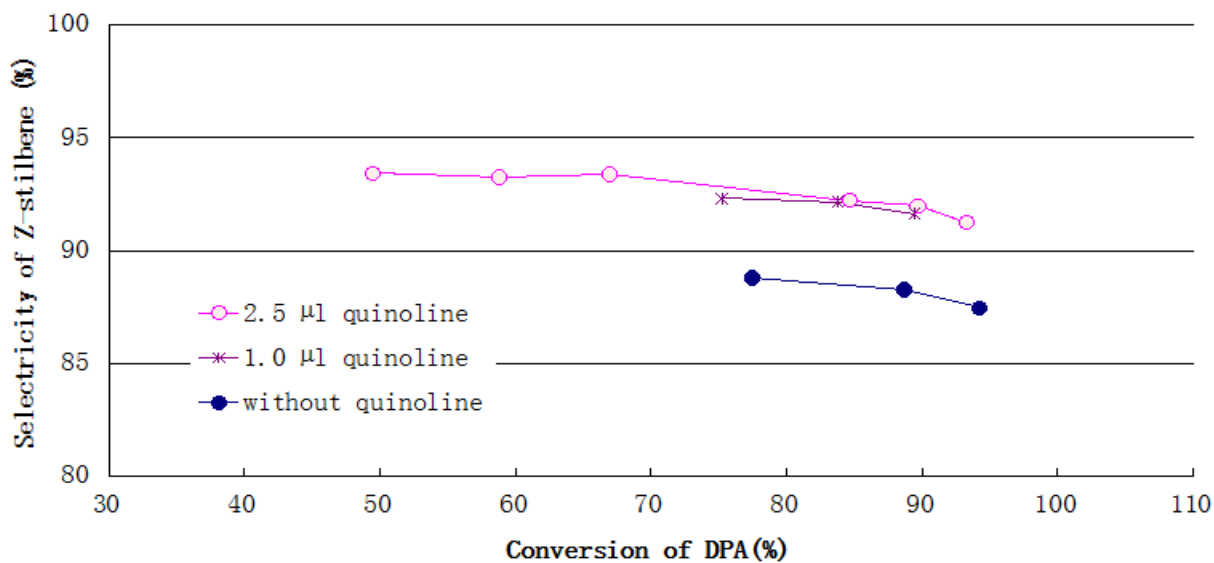


Fig. 5 Selectivity to Z-stilbene as a function of DPA conversion over Pd_{US-MW}/Boehmite with various additions of quinoline. DPA hydrogenation conditions: 5 mg of Pd_{US-MW}/Boehmite; 50 mL of hexane containing 0.58 mmol of DPA; DPA hydrogenation at 0.5 MPa of H₂ and 25±1 °C; 20.2 kHz, 70 W).

In Fig.5, Z-stilbene selectivity clearly increases when quinoline is added at room temperature, under sonication and at 0.5 MPa of hydrogen pressure, leading to the Z-stilbene yield increasing by 3.3%. Similarly, selectivity to styrene increased from 84.5 to 90.5% at greater than 99% conversion at 40 °C and 0.3 MPa of hydrogen pressure, leading to the styrene yield increasing by 6.1%.

3.6. Pd Leaching test and effect of sonication on boehmite particles

Bulk metal contents in the initial and recovered catalysts were compared in order to study the effect of US treatment on the catalysts. The Pd content in the original Pd/Boehmite catalyst was measured to be 0.88% and the Pd mass in 200 mg sample was calculated to be 1760 µg. As listed in Table 8, the Pd contents in catalysts recovered after stirring or sonication were very similar. This indicates that no metal leached from the catalysts during sonication. As a confirmation of this, the palladium content in the liquid samples was also measured. For the experiments in hexane, only traces of metal were found in solutions. However, some palladium was observed in the experiments performed in ethanol and a significant amount was observed in those that had undergone sonication (Fig 6). One possible reason is the fact that boehmite particles were cracked into finer particles by sonication.

Table 8 Pd contents in solid and liquid phase for leaching tests (200 mg catalyst each sample in 50 mL hexane or ethanol).

Sample	Treatment mode	Solvent	Content in solid phase (%)	Solid phase		Concentration (mg L ⁻¹)	Liquid phase		Pd lost (%)
				Pd mass in 200 mg sample (µg)	Mean (µg)		Pd mass in 50 mL solvent (µg)	Mean	
Original sample	Before leaching test		0.88		1760				
Test 1	Stirring	hexane	0.84	1680	1730±50	0.02	1.0	1.5±0.5	0.1
Test 2	stirring	hexane	0.89	1780		0.04	2.0		
Test 3	sonication	hexane	0.85	1700	1770±70	0.04	2.0	1.5±0.5	0.1
Test 4	sonication	hexane	0.92	1840		0.02	1.0		
Test 5	stirring	ethanol	0.93	1860	1790±70	0.62	31.0	23.5±7.5	1.3
Test 6	stirring	ethanol	0.86	1720		0.32	16.0		
Test 7	sonication	ethanol	0.84	1680	1720±40	5.11	255.5	228±27.5	13.0
Test 8	sonication	ethanol	0.88	1760		4.01	200.5		

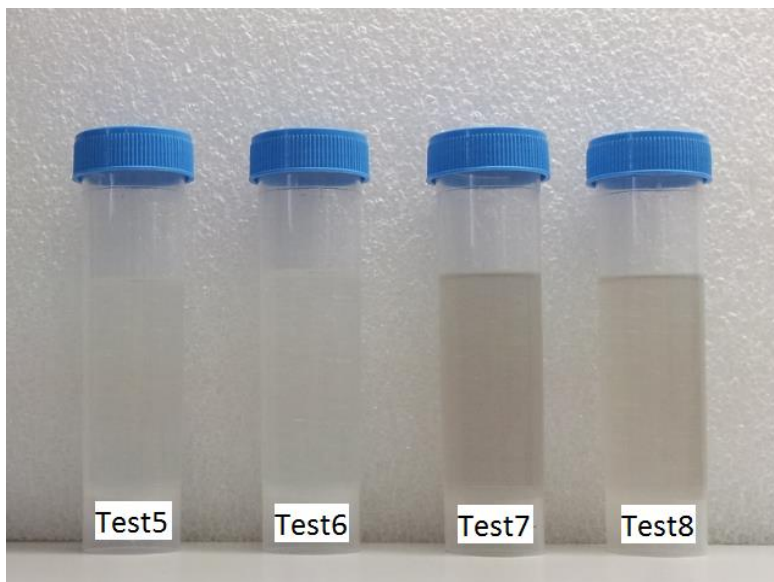


Fig. 6 Pd/Boehmite suspensions standing in ethanol for 7 days after centrifugation (Test 5 and 6 were agitated for 35 min in ethanol and Test 7 and 8 were sonicated for 35 min in ethanol)

The fact that Pd was lost in alcoholic solvents after ultrasonic treatment is in agreement with a previous study performed with the Lindlar catalyst in methanol [42]. Metal removal from the catalysts during sonication is due to fragmentation that was caused by the implosion of cavitation bubbles near the surface, possibly forming nanoparticles, rather than leaching through the formation of soluble metal compounds. However, leaching can be considerably reduced using the new Pd/Boehmite catalysts by avoiding ultrasonication and almost completely eliminated by changing the solvent to hexane (even using ultrasound). This is a significant improvement upon the traditional Lindlar catalyst.

4. Conclusions

Novel Pd/Boehmite catalysts have been tested in the ultrasound-assisted semi-hydrogenation of alkynes. The Pd_{LV-US}/Boehmite catalyst exhibited much higher activity than the Pd_{US-MW}/Boehmite and Lindlar catalysts in PA hydrogenation. The ultrasonic bath was used under atmospheric pressure and the ultrasonic horn reactor under 0.1-0.5 MPa hydrogen pressure and both were tested for DPA and PA hydrogenation in hexane as well as ByD in ethanol. Under atmospheric pressure, the PA hydrogenation rate and activity over Pd_{LV-US}/Boehmite with sonication was lower than with stirring; however, selectivity to the semi-hydrogenated product was higher with sonication than with stirring. Under 0.1 MPa of hydrogen pressure, the PA hydrogenation rate and activity was higher under sonication than stirring. Meanwhile, selectivity to the semi-hydrogenated product was also higher under sonication than stirring.

In the ultrasonic horn reactor, the catalytic activity of Pd_{US-MW}/Boehmite catalyst at 0.3 or 0.5 MPa of H₂ is 7 to 10 times higher than that at atmospheric hydrogen pressure, while the high selectivity of 91.1 and 90.3% at over 90% PA conversion was preserved. Under sonication, the hydrogenation rate and activity of ByD synchronously increased by about 27.9-35.5% as temperature rose from 25 to 40 °C at 0.5 MPa. PA hydrogenation rate and activity increased 1-fold with rising temperature from 25 to 40 °C at 0.3 MPa. Selectivity to the ByD semi-hydrogenated product decreased from 94.6 to 87.7% at 100% ByD conversion, but PA hydrogenation styrene selectivity was almost equal at 25 °C or 40 °C, at about 95% PA conversion.

The addition of quinoline caused DPA and PA hydrogenation activity and rate to decrease slightly under sonication. Selectivity to DPA and PA semi-hydrogenated products clearly increased upon adding quinoline under sonication.

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