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# Efficient Partial Hydrogenation of 2-Butyne-1,4-diol and other Alkynes under Microwave Irradiation

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## Abstract

The microwave-assisted partial hydrogenation of 2-butyne-1,4-diol, diphenylacetylene and phenylacetylene with novel lead-free Pd/Boehmite catalysts were investigated. Obtaining high alkyne conversion and good selectivity of the product alkenes required optimization of several reaction parameters: substrate concentration, amount of catalyst, temperature, hydrogen pressure, solvent and reaction scale. Dielectric heating strongly enhanced the conversion whilst maintaining good selectivity to alkenes (over 92%). Excellent 2-butyne-1,4-diol conversions, with 100% alkene selectivity, were achieved in water (20 mL) at 90 °C at high substrate concentrations (20 wt%).

Key words: semi-hydrogenation, 2-butyne-1,4-diol, alkyne, microwaves, selectivity.

## 1. Introduction

The selective partial catalytic hydrogenation of alkynes to produce alkenes is widely applied in the fine chemical industry. (*Z*)-2-butene-1,4-diol (BeD) is an important chemical intermediate used in the production of fungicides and insecticides [1,2], vitamin B6 [3,4], and also in the paper, textile and resin industries. BeD is obtained commercially via selective hydrogenation of 2-butyne-1,4-diol (ByD) [5]. It is of high importance to obtain high selectivity in the hydrogenation of ByD [6]. The

selective hydrogenations of diphenylacetylene (DPA) and phenylacetylene (PA) to produce *Z*-stilbene and styrene respectively are common model reactions to explore the performance of metal-supported catalysts with terminal and internal triple bonds [7-9]. Due to their unique physical and chemical properties, palladium nanoparticles catalysts supported on various type of carriers (polymers [10] and active charcoal [11,12]) have been widely exploited for the selective hydrogenation of alkynes. With the aim to improve the performance of catalytic hydrogenation as well as the selectivity toward the semi-hydrogenated products, slurry reactors [5], monolith bubble column reactors [13,14] and flow capillary reactors [15,16] have been shown to be suitable reactor designs.

Nowadays, environmentally benign non-conventional enabling technologies are widely studied to foster process intensification and combine safer protocols, cost reduction and energy savings [17]. The use of modern microwave (MW) equipment affords an easy, safe, rapid, and efficient hydrogenation in the laboratory [18,19]. The catalytic hydrogenation under MW irradiation has been conducted safely and quickly in open vessels [19], sealed reaction systems [20], a quartz reactor [18] and even under 2.5 MPa of hydrogen pressure [21]. The hydrogenation of 9,10-diphenylanthracene with palladium/activated carbon (Pd/C) proceeded at much lower temperatures and hydrogen pressure under MW irradiation than those by conventional heating [22]. The MW-assisted hydrogenation of double bonds with 10% Pd/C was carried out for 3-5 min at about 110-130 °C with ammonium formate as hydrogen donor [19], the hydrogenation of alkenes [20] azide and strychnine [21], and citral (3,7-dimethylocta-2,6-dienal) [23] are easily reduced in short reaction times under moderate temperatures and pressures. However, little is known about the selective hydrogenation of alkynes under MW irradiation.

In recent decades, ultrasound- (US-) and MW-assisted protocols for preparation of catalysts have been extensively reported [24]. US has been shown to enhance the robustness, enantioselectivity and activity of the catalyst [25]. MW volumetric heating enables more homogeneous nucleation sites in the preparation of metal nanostructured particles, leading to narrow size distributions, which is an ideal condition in catalyst preparation [26].

In a previous work we reported the effects of US and MW on the preparation and performance of lead-free Pd-catalysts [27]. Thereafter we perfected a series of synthetic protocols to US-, MW- and US/MW- assisted syntheses of catalysts. This study focuses on the effect that MW irradiation has on alkyne selective semi-hydrogenation. The main reaction parameters have been investigated aiming at process intensification and scale up. These parameters include: substrate concentration, catalyst

amount, temperature, hydrogen pressure, solvent type and volume. These investigations are indispensable to the potential development of a pilot scale MW flow of this reaction.

## 2. Experimental

### 2.1 Catalysts preparation and characterization

Pd<sub>LV-1</sub>/Boehmite (0.78 wt.% Pd) was prepared according to a one-pot fully US-assisted protocol: Pd(OAc)<sub>2</sub> (Alfa Aesar, 99%) and Boehmite (Wako Pure Chemicals Ind., Ltd., (Al<sub>2</sub>O<sub>3</sub>) 60%) were sonicated in water in the presence of Luviquat<sup>TM</sup> (Sigma-Aldrich, 30% in water) as surfactant and reducing agent. A cavitating tube (cup-horn apparatus) operating at 19.9 kHz and 100 W was used for 30 min at 30°C.

Pd<sub>US-MW</sub>/Boehmite (0.88 wt.% Pd) was prepared according to a two-step protocol: the dispersion of Pd(OAc)<sub>2</sub> in water was performed in absence of surfactant by sonication, but the reduction of Pd was performed at 40 °C for 10 min under 1 MPa of H<sub>2</sub> as reducing agent in the SynthWave MW reactor (Milestone Srl, MLS GmbH). The catalysts were analyzed using scanning electron microscopy, transmission electron microscopy, elemental analysis as well as surface area and pore distributions studies [27]. A commercial Lindlar catalyst (5% Pd on calcium carbonate, lead-poisoned) was purchased from Alfa-Aesar and used as a reference catalyst.

### 2.2 Hydrogenations of alkynes

Catalysts were tested for the hydrogenation of 2-butyne-1,4-diol (ByD), which is a colourless, hygroscopic organic compound soluble in water and polar organic solvents. It is usually applied as a model compound for the study of the selective hydrogenation of alkynes [5,10]. The main product is *Z*-2-butene-1,4-diol (BeD) with minor amounts of the *E*-isomer (figure 1). The over-hydrogenated product is 1,4-butanediol (BaD). The hydrogenation was performed in various polar solvents, at varying H<sub>2</sub> pressures (0.5 to 3.0 MPa) and temperature (50 to 90 °C) values. The versatility of the SynthWave reactor was used to provide precise control of key reaction parameters. For reactions at room temperature the MW heating was off [18]. The hydrogenations of DPA and PA were carried out in *n*-hexane under the above-mentioned conditions.

The reaction work up entails removal of the catalyst by filtration, and evaporation of the aqueous solution under reduced pressure. The residue was then dissolved in chloroform and analyzed by GC-MS (gas chromatograph Agilent 6890, mass detector Agilent Network 5973 - Agilent Technologies,

USA) using a HP-5ms capillary column with the following characteristics: 30 m length, 0.25 mm ID and 0.25  $\mu\text{m}$  film thickness.

### 3. Results and discussion

In our previous study, the activities of Pd<sub>LV-1</sub>/Boehmite or Pd<sub>US-MW</sub>/Boehmite in DPA hydrogenation were higher than those with the Lindlar catalyst at room temperature (RT) and atmospheric hydrogen pressure with comparable selectivity to Z-stilbene. This is due to higher specific surface area (pore volume with 6.0-6.7 nm of BJH desorption average pore diameter) as well as the evenly distributed Pd nanoparticles in the prepared Pd/Boehmite catalysts [27].

#### 3.1 Comparison between Pd<sub>LV-1</sub>/Boehmite and Pd<sub>US-MW</sub>/Boehmite under MW irradiation

The hydrogenations of ByD with Pd<sub>LV-1</sub>/Boehmite and Pd<sub>US-MW</sub>/Boehmite were performed under MW irradiation in water [28]. The results are listed in Table 1.

**Table 1**  
**Hydrogenations of ByD for 30 min in water.**

Entry	P <sub>H<sub>2</sub></sub> (MPa)	T (°C)	Pd <sub>LV-1</sub> /Boehmite		Pd <sub>US-MW</sub> /Boehmite	
			C <sub>ByD</sub>	S <sub>Z-BeD</sub>	C <sub>ByD</sub>	S <sub>Z-BeD</sub>
1	0.1	RT	7	100	5	100
2	0.5	RT	16	100	19	100
3	0.5	50	93	98	65	100

C<sub>ByD</sub>: ByD conversion (%); S<sub>Z-BeD</sub>: selectivity to Z-BeD; RT: room temperature (21±1 °C).

Reaction conditions: 2 mg of Pd-catalyst were added in a 2 mL of water containing 10 mg of ByD (concentration: 0.5 wt%).

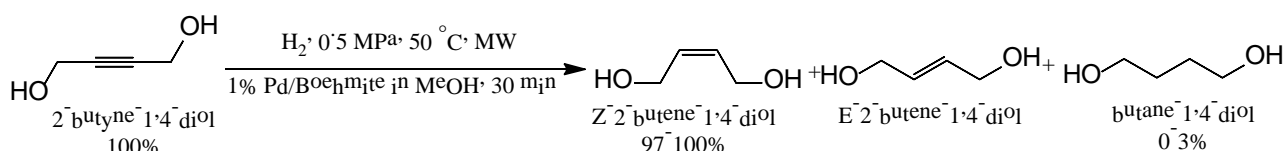


Figure 1: MW-assisted hydrogenation of 2-butyne-1,4-diol with Pd/Boehmite.

As listed in Table 1, the conversions of ByD after 30 min with both catalysts at RT under 0.1 or 0.5 MPa of H<sub>2</sub> pressure were below 20%. When the reaction was performed with the Lindlar catalyst under the same conditions, 10% conversion was similarly obtained. As green and economic solvent, water is encouraged to use in organic synthesis. In present study, the activity of ByD hydrogenation in water is quite low, but the hydrogenation could be enhanced by using MW heating. Increasing the temperature to 50 °C by MW heating (entry 3, Table 1) increased the conversion of the reaction to 93% with Pd<sub>LV-1</sub>/Boehmite and 65% with Pd<sub>US-MW</sub>/Boehmite under 0.5 MPa of H<sub>2</sub> pressure.

Meanwhile, the selectivity to Z-BeD was maintained at 98-100%. The higher activity of Pd<sub>Lv-1</sub>/Boehmite compared to Pd<sub>US-MW</sub>/Boehmite was also observed under MW irradiation.

### 3.2 Role of solvents

Alcohols such as methanol (MeOH), ethanol (EtOH), iso-propanol (iso-PrOH) as well as their mixtures with water were used as solvents to explore the effect of polar solvents on the conversion and selectivity of ByD hydrogenation under MW irradiation. The results are shown in Table 2.

**Table 2**

Hydrogenations of ByD for 30 min in H<sub>2</sub>O/alcohol (1:1) under 0.5 MPa of H<sub>2</sub> at 50 °C with MW heating

Entry	Solvent	Pd <sub>Lv-1</sub> /Boehmite		Pd <sub>US-MW</sub> /Boehmite		Lindlar	
		C <sub>ByD</sub>	S <sub>Z-BeD</sub>	C <sub>ByD</sub>	S <sub>Z-BeD</sub>	C <sub>ByD</sub>	S <sub>Z-BeD</sub>
4 <sup>a</sup>	H <sub>2</sub> O/EtOH	33	98	20	100	15	100
5	H <sub>2</sub> O/EtOH	100	74	100	95	100	93
6	EtOH	100	0	100	4	100	0
7	H <sub>2</sub> O/MeOH	85	51	60	99	73	88
8 <sup>b</sup>	H <sub>2</sub> O/MeOH	-	-	100	92	89	95
9	MeOH	100	3	100	4	100	0
10	H <sub>2</sub> O/iso-PrOH	100	78	49	100	42	98
11	iso-PrOH	100	0	100	0	100	0

C<sub>ByD</sub>: ByD conversion (%); S<sub>Z-BeD</sub>: selectivity to Z-BeD.

<sup>a</sup> Room temperature; <sup>b</sup> Reaction time: 45 min. Reaction conditions: 2 mg of Pd-catalyst were added in a 2 mL of water containing 10 mg of ByD (concentration: 0.5 wt%).

In order to understand the solvent effect on the activity and selectivity of ByD hydrogenation, reactions were carried out at same conditions. Clearly, the use of alcohol accelerated the reaction but decreased the selectivity to Z-BeD, as shown in entries 6, 9, 11 of Table 2. When the reaction was performed in pure alcohol, complete hydrogenation of ByD occurred in 30 min, producing only alkane with both of the prepared Pd/Boehmite catalysts, indicating activity in alcohol is higher than that in water.

At room temperature the conversions (above 20%) with both of the prepared Pd/Boehmite catalysts were slightly higher in the mixture EtOH-water than in pure water (entry 2, Table 1 and entry 4, Table 2). At 50 °C with MW heating, full conversion was achieved with both of catalysts in a mixture of EtOH and water. The selectivity of Z-BeD was maintained at a high level (95%) with Pd<sub>US-MW</sub>/Boehmite (entry 5, Table 2). A similar results were observed with water-MeOH mixtures (entries 7-8, Table 2), but the results were inferior to those in water-EtOH. By extending the reaction time, complete conversion and 92% of selectivity to Z-BeD was obtained after 45 min with Pd<sub>US-MW</sub>/Boehmite in the mixture of water and MeOH (entry 8, Table 2). When iso-PrOH-water mixtures were used, 78% of selectivity to Z-BeD were obtained after 30 min with Pd<sub>Lv-1</sub>/Boehmite at complete

conversion of ByD; while the low activity of Pd<sub>US-MW</sub>/Boehmite (49% of ByD conversion in 30 min) was observed (entry 10, Table 2).

With the Lindlar catalyst a similar trend was obtained: the reaction was faster in alcohol-water compared to water. In pure alcohol it was so rapid that we only got BaD by the full hydrogenation in 30 minutes at 50 °C with MW heating.

### 3.3 Effect of catalyst amount

By using MeOH as co-solvent or solvent we studied the effect of catalyst amount. The results are reported in Table 3. Under the same conditions as previously (0.5 MPa of H<sub>2</sub> pressure at 50 °C with MW heating in 30 minutes) but using 10% of catalyst (1 mg) based to ByD (entry 12, Table 3) instead of 20% (2 mg, entry 7 in Table 2); a significantly better selectivity to Z-BeD (90 vs 51%) was achieved with slightly lower conversion (80 vs 85%) with Pd<sub>LV-1</sub>/Boehmite. Due to the lower activity, the hydrogenations of ByD in mixtures of water-MeOH with 1 or 2 mg of Pd<sub>US-MW</sub>/Boehmite were extended to 45 min, resulting in higher conversion and selectivity (entries 13-14, Table 3).

In pure MeOH (entries 15-17, Table 3), 0.5 mg of 5 wt.% of either catalyst (based on ByD amount) was the optimum for the conversion and selectivity to Z-BeD (entry 16, Table 3). Excessive amount of the Lindlar catalyst also led to over-hydrogenation of ByD under MW irradiation. The optimal amount of Lindlar catalyst was 1 weight % with respect to the ByD amount, due to the higher Pd content (> 4%).

The hydrogen pressure clearly influenced the ByD conversion with low amounts of catalyst. Under 0.1 MPa instead of 0.5 MPa, no conversion of ByD was obtained with 0.5 mg of Pd<sub>LV-1</sub>/Boehmite for 30 and 60 min (entry 18, Table 3).

**Table 3**

Effect of Pd/Boehmite catalysts amount on hydrogenations of ByD under 0.5 MPa of H<sub>2</sub> and 50 °C with MW heating in H<sub>2</sub>O/MeOH (1:1).

Entry	solvent	t	M <sub>cat.</sub>	R <sub>cat.</sub>	Pd <sub>LV-1</sub> /Boehmite		Pd <sub>US-MW</sub> /Boehmite	
					C <sub>ByD</sub>	S <sub>Z-BeD</sub>	C <sub>ByD</sub>	S <sub>Z-BeD</sub>
12 <sup>a</sup>	H <sub>2</sub> O/MeOH	30	1.0	10%	80	90	70	100
13	H <sub>2</sub> O/MeOH	45	2.0	20%	-	-	100	92
14	H <sub>2</sub> O/MeOH	45	1.0	10%	-	-	91	100
15	MeOH	30	1.0	10%	100	42	99	81
16	MeOH	30	0.5	5%	100	97	99	100
17	MeOH	30	1.0	1%	45	98	20	100
18 <sup>b</sup>	MeOH	30	0.5	5%	mainly alkyne	-	-	-

<sup>a</sup> room temperature; <sup>b</sup> 0.1 MPa; t: reaction time (min); M<sub>cat.</sub>: catalyst amount (mg); R<sub>cat.</sub>: Catalyst ratio to the substrate; C<sub>ByD</sub>: ByD conversion (%); S<sub>Z-BeD</sub>: selectivity to Z-BeD.

Reaction conditions: Pd-catalyst were added in a 2 mL of water containing 10 mg of ByD (0.116 mmol).



### 3.4 Effect of temperature, ByD concentration and solution volume

MW irradiation produces efficient volumetric heating [29]. Depending on the microwave power applied and the desired temperature set-point, it can operate in a discontinuous (lower temperatures) or continuous (higher temperatures) mode. The combined effects of temperature and MW irradiation on the semi-hydrogenation of ByD were tested at 70 and 90 °C. As shown in Table 4, complete ByD conversion, at high selectivity (BeD 92-99%), was achieved at relatively low ByD concentrations (0.5 wt%) (entries 19-20, Table 4). Both conversion and selectivity (96% and 100% respectively) remain excellent (entry 21, Table 4) even when ByD concentration was increased 10 fold. This means that the selectivity of MW-assisted, polar ByD hydrogenation is preserved even at high temperature. Alkyne hydrogenation with a heterogeneous catalyst is generally favoured on terraces, while alkene hydrogenation and isomerization are favoured on surface defect sites, such as corners or edges [30]. It is now known that the action of MW in organic synthesis is a combination of thermal effects, such as superheating and “hot spots” that arise from the heating rate, and the selective absorption of radiation by polar substances. MW can therefore drive catalytic reactions that do not occur under conventional heating and can even improve selectivity (chemo-, regio- and stereoselectivity) [31]. The increase in selectivity can be due to a number of factors including selective MW heating of part of the molecule or the catalyst surface, or by altering the adsorption-dissociation to/from the catalyst surface. It is known that in semi-hydrogenations, the dissociation of the product alkene is a key parameter in obtaining high conversions [32, 33]. A full investigation is beyond the scope of this investigation.

**Table 4**

Effect of temperature, ByD concentration and reaction volume on the hydrogenations of ByD with Pd<sub>Lv-1</sub>/Boehmite in water.

Entry	P <sub>H2</sub> (MPa)	T (°C)	t (min)	ByD (wt%)	C <sub>ByD</sub>	S <sub>Z-BeD</sub>
3	0.5	50	30	0.5	93	98
19	0.5	70	30	0.5	100	99
20	0.5	90	30	0.5	100	92
21 <sup>a</sup>	0.5	90	30	5	96	100
22 <sup>b</sup>	0.5	90	60	10	75	99
23 <sup>c</sup>	0.5	90	60	20	52	97
24 <sup>d</sup>	3.0	90	90	5	82	100
25 <sup>d</sup>	5.0	90	90	5	100	95

C<sub>ByD</sub>: ByD conversion (%); S<sub>Z-BeD</sub>: selectivity to Z-BeD;

Reaction conditions: Without special note: 2 mg of Pd-catalyst were added to 2 mL of water containing 10 mg of ByD (0.5 wt%); <sup>a</sup>20 mg of Pd-catalyst were added to 2 mL of water containing 100 mg of ByD (5 wt%); <sup>b</sup> 40 mg of Pd-catalyst were added to 2 mL of water containing 200 mg of ByD (10 wt%); <sup>c</sup> 80 mg of Pd-catalyst were added to 2 mL of water containing 400 mg of ByD (20 wt%); <sup>d</sup> 200 mg of Pd-catalyst were added to 20 mL of water containing 1 g of ByD (5 wt%).

Catalytic conversions at low ByD concentrations (<10 wt%) generally suffered from high energy consumption and difficult product recovery. Increasing substrate concentration is thus highly desirable as it enhances production capacity and saves energy [34]. As shown in entries 21-23 (Table 4), increasing the ByD concentration to 5 wt% results in similar performance. At 10 wt% the selectivity remains high (99%), however the conversion decreases (75% after 60 min compared with 96% after 30 min). At 20 wt% ByD concentration, the conversion decreases further (entry 23). The maximum reaction tube volume (ByD 5 wt%) was also scaled up 10-fold, from 2 to 20 mL. As shown in entry 24 (Table 4), 82% ByD conversion and 100% selectivity to BeD were achieved on this larger scale (3 MPa H<sub>2</sub>, 90 °C, 90 min), which clearly shows that further scale-up is feasible.

### 3.5 Hydrogenation of DPA and PA

2 mg of Pd-catalyst was added in a 2 mL of n-hexane containing 0.116 mmol of DPA or PA. The hydrogenation process was performed for 30 min under 0.5 MPa of H<sub>2</sub> pressure exploiting the versatility of the Synthwave<sup>TM</sup> reactor (Milestone) (Figure 2 and 3). The results are listed in Table 5.

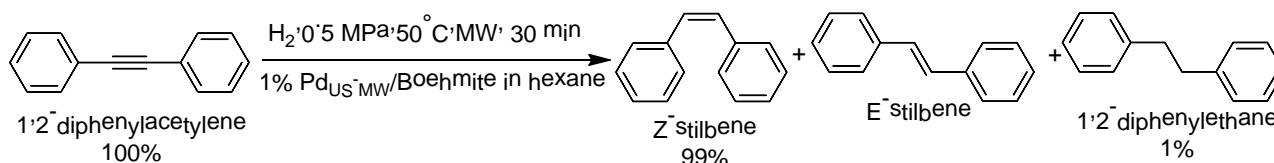


Figure 2: Hydrogenation of diphenylacetylene with Pd/Boehmite under MW heating

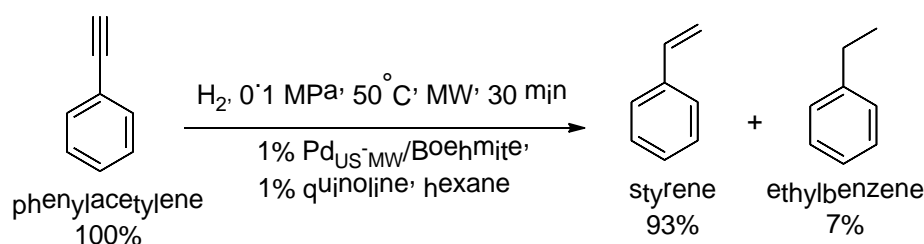


Figure 3: Hydrogenation of phenylacetylene with Pd/Boehmite under MW heating

As listed in Table 5, the full conversion of DPA with Pd<sub>LV-1</sub>/Boehmite was achieved in 30 min at room temperature and 0.5 MPa of hydrogen pressure, with 95% selectivity to Z-stilbene. Due to the lower activity of Pd<sub>US-MW</sub>/Boehmite, the temperature was increased to 50 °C with MW heating; the

DPA conversion reached 100% after 30 min at 0.5 MPa hydrogen pressure with 99% *Z*-stilbene selectivity.

The conversion of PA with Pd<sub>LV-1</sub>/Boehmite was 96% after 30 min at room temperature and 0.1 MPa of hydrogen pressure, with 91% of selectivity to styrene. However, the conversion of PA with Pd<sub>US-MW</sub>/Boehmite was only 5% under the same conditions (entry 27, Table 5). When the hydrogen pressure was raised to 0.5 MPa at RT, the over hydrogenation of PA was seen with Pd<sub>LV-1</sub>/Boehmite. Using Pd<sub>US-MW</sub> the conversion of PA was increased to 93% with 83% selectivity of styrene (entry 28, Table 5). In order to increase the selectivity of styrene, 1% of quinoline was added into the reaction system, leading to reduction in the PA conversion (entry 29, Table 5). Extending the reaction time to 45 min, resulted in higher PA conversion (93%) and good styrene selectivity (92%, entry 30, Table 5).

Similarly, MW heating can also enhance the PA conversion with the weaker catalyst (Pd<sub>US-MW</sub>/Boehmite). The over hydrogenation of PA was observed for 30 min at 0.1 MPa and 50 °C with MW heating (entry 31, Table 5), leading to lower selectivity of styrene. In order to raise the selectivity to styrene, 1% of quinoline was therefore added into the reaction system, resulting in the complete conversion of PA with 93% of selectivity to styrene under MW irradiation (entry 32, Table 5).

**Table 5**  
MW-assisted hydrogenations of DPA and PA for 30 min in *n*-hexane.

Entry	Alkyne	P <sub>H<sub>2</sub></sub> (MPa)	T (°C)	Pd <sub>LV-1</sub> /Boehmite		Pd <sub>US-MW</sub> /Boehmite	
				C <sub>alkyne</sub>	S <sub>(Z)-alkene</sub>	C <sub>alkyne</sub>	S <sub>(Z)-alkene</sub>
25	DPA	0.5	RT	100	95	76	95
26	DPA	0.5	50	-	-	100	99
27	PA	0.1	RT	96	91	4.5	100
28	PA	0.5	RT	100	48	93	83
29 <sup>a</sup>	PA	0.5	RT	-	-	57	92
30 <sup>b</sup>	PA	0.5	RT	-	-	93	92
31	PA	0.1	50	-	-	100	69
32 <sup>a</sup>	PA	0.1	50	-	-	100	93

<sup>a</sup> With 1% quinoline; <sup>b</sup> 45 min of reaction time with 1% quinoline.

P<sub>H<sub>2</sub></sub>: Hydrogen pressure (MPa); T: solvent temperature (°C); C<sub>alkyne</sub>: alkyne conversion (%); S<sub>(Z)-alkene</sub>: selectivity to (*Z*)-alkene; RT: room temperature (21±1 °C).

Reaction conditions: 2 mg of Pd-catalyst were added in a 2 mL of water containing 0.116 mmol of DPA or PA.

## Conclusion

The partial hydrogenations of 2-butyne-1,4-diol, diphenylacetylene or phenylacetylene have been studied with the novel Pd/Boehmite catalysts at 0.1-0.5 MPa hydrogen pressure and 50 °C with MW

heating. With ultrasonically prepared 0.78% Pd/Boehmite ( $\text{Pd}_{\text{LV-1}}$ / Boehmite), the conversion of 2-butyne-1,4-diol reached 93% with 98% selectivity to 2-butene-1,4-diol in 30 min of hydrogenation at 0.5 MPa in water, while with 0.88% Pd/Boehmite ( $\text{Pd}_{\text{US-MW}}$ /Boehmite) prepared by MW-assisted reduction, the conversion of 2-butyne-1,4-diol achieved only 65% in 30 under the same conditions. The herein described favourable MW effects have led to high ByD conversion and selectivity to BeD being achieved at even higher ByD concentrations (5-20 wt%) and reaction volumes (20 mL) at 70 or 90 °C.

In pure alcohols such as MeOH, EtOH and iso-propanol, the complete hydrogenation of 2-butyne-1,4-diol was achieved without formation of 2-butene-1,4-diol in 30 min at 0.5 MPa. The addition of water to alcohols clearly reduced the hydrogenation activity, leading to 100% conversion of 2-butyne-1,4-diol with 92-95% selectivity to 2-butene-1,4-diol with  $\text{Pd}_{\text{US-MW}}$ /Boehmite. Reduction of the amount of Pd/Boehmite also reduced the activity, resulting in 99-100% conversion of 2-butyne-1,4-diol with 100-97% selectivity to 2-butene-1,4-diol after 30 min at 0.5 MPa in MeOH with 5% of catalyst amount to substrate.

Due to the higher activity with  $\text{Pd}_{\text{LV-1}}$ /Boehmite, the conversion of diphenylacetylene or phenylacetylene reached 100 or 96% with 95 or 91% selectivity to (Z)-alkene, respectively, after 30 min without heating in hexane. With  $\text{Pd}_{\text{US-MW}}$ /Boehmite, the conversion of diphenylacetylene reached 100 % with 99% selectivity to Z-stilbene after 30 min at 0.5 MPa and 50 °C with MW heating in hexane, while with  $\text{Pd}_{\text{US-MW}}$ /Boehmite and 1% quinoline, the full conversion of phenylacetylene 100 % with 93% selectivity to styrene was obtained in 30 at 0.1 MPa and 50 °C with MW heating.

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## References and Notes

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