



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%).

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1. Introduction

The 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 nanoparticle 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

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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 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 hydrogenation.

2. Experimental

2.1. Catalysts preparation and characterization

Pd_{LV-1}/Boehmite (0.78 wt.% Pd) was prepared according to a one-pot fully US-assisted protocol: Pd(OAc)₂ (Alfa Aesar, 99%) and Boehmite (Wako Pure Chemicals Ind., Ltd., (Al₂O₃) 60%) were sonicated in water in the presence of Luviquat™ (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_{US-MW}/Boehmite (0.88 wt.% Pd) was prepared according to a two-step protocol: the dispersion of Pd(OAc)₂ 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 H₂ 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 (Fig. 1). The over-hydrogenated product is 1,4-butanediol (BaD). The hydrogenation was performed in various polar solvents, at varying H₂ pressures (0.5–3.0 MPa) and temperature (50–90 °C) values. The versatility of the SynthWave reactor was used to provide precise control of key reaction parameters. For reactions at room temperature (RT) 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-5 ms capillary column with the following characteristics: 30 m length, 0.25 mm ID and 0.25 μm film thickness.

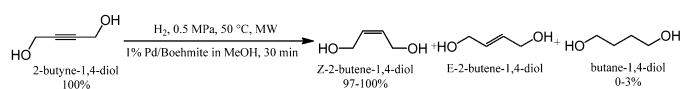


Fig. 1. MW-assisted hydrogenation of 2-butyne-1,4-diol with Pd/Boehmite.

3. Results and discussion

In our previous study, the activities of Pd_{LV-1}/Boehmite or Pd_{US-MW}/Boehmite in DPA hydrogenation were higher than those with the Lindlar catalyst at 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_{LV-1}/Boehmite and Pd_{US-MW}/Boehmite under MW irradiation

The hydrogenations of ByD with Pd_{LV-1}/Boehmite and Pd_{US-MW}/Boehmite were performed under MW irradiation in water [28]. The results are listed in Table 1.

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 H₂ pressure were below 20%. When the reaction was performed with the Lindlar catalyst under the same conditions, 10% conversion was similarly obtained. As a 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_{LV-1}/Boehmite and 65% with Pd_{US-MW}/Boehmite under 0.5 MPa of H₂ pressure. Meanwhile, the selectivity to Z-BeD was maintained at 98–100%. The higher activity of Pd_{LV-1}/Boehmite compared to Pd_{US-MW}/Boehmite was also observed under MW irradiation.

3.2. Role of solvents

Alcohols such as methanol (MeOH), ethanol (EtOH), isopropanol (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.

In order to understand the solvent effect on the activity and selectivity of ByD hydrogenation, reactions were carried out at the 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 RT 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_{US-MW}/Boehmite (entry 5, Table 2). Similar results were observed with water-MeOH mixtures (entries 7–8, Table 2), but the results were

Table 1
Hydrogenations of ByD for 30 min in water.

Entry	P _{H₂} (MPa)	T (°C)	Pd _{LV-1} /Boehmite		Pd _{US-MW} /Boehmite	
			C _{ByD}	S _{Z-BeD}	C _{ByD}	S _{Z-BeD}
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_{ByD}: ByD conversion (%); S_{Z-BeD}: 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%).

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