

Short communication

Aqueous-phase hydrogenation of biomass-derived itaconic acid to methyl- γ -butyrolactone over Pd/C catalysts: Effect of pretreatments of active carbon



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ABSTRACT

The effect of active carbon pretreatment on the catalytic performance of Pd/C catalysts in the hydrogenation of itaconic acid was studied. The catalysts were prepared by deposition–precipitation and characterized by XRD, BET, NH_3 -TPD, TEM and FT-IR. Due to the modification of the surface functional groups, surface structure and surface acidities of active carbon via pretreatment, the Pd/C catalysts showed varied catalytic performances. High dispersion and uniform particles were conducive to the excellent activity of Pd/C catalyst with support copretreated with HNO_3 and NaClO , which exhibited 89.5% selectivity towards methyl- γ -butyrolactone at 180 °C, 4 MPa H_2 for 20 h.

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1. Introduction

Itaconic acid (IA) is an unsaturated dicarboxylic acid, which could be derived from biomass via fermentation process and is selected as one of the 12 major platform molecules by the US Department of Energy [1,2]. The transformation of IA to the primary families of derivatives is well discussed in previous reports [1,3]. Catalytic hydrogenation is an efficient way for the valorization of IA and many high value-added chemicals can be obtained, such as methyl- γ -butyrolactone (MGBL), 2-methyl-1,4-butanediol (2-MBDO) and 3-methyl-tetrahydrofuran (3-MTHF) [2–4].

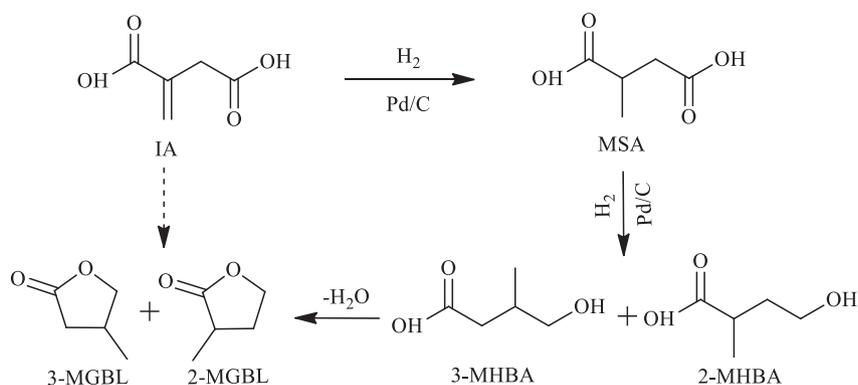
Generally, noble metal catalysts [5–8] were considered to be highly active for the hydrogenation of carboxylic acids, and lots of reports were focused on the hydrogenation of succinic acid, levulinic acid and lactic acid [9–12]. Shao et al., for instance, reported the aqueous-phase hydrogenation of succinic acid to γ -butyrolactone and tetrahydrofuran over Pd/C and Pd-Re/C catalysts [11], and Taipin et al. adopted Pd/TiO₂ catalysts for the hydrogenation of succinic acid [13]. Yan et al. found that the robust Pd nanoparticles were efficient for the hydrogenation of levulinic acid to value-added γ -valerolactone [14,15]. As to the

hydrogenation of lactic acid, mild catalytic reductions have been developed using catalysts bearing Ru for the production of 1,2-propanediol [1,12]. However, only a few studies investigated the hydrogenation of IA to value-added chemicals. Under mild conditions, the double bond in IA undergoes hydrogenation easily [16,17], but further reduction of the carboxylic acid is usually performed under high temperature and high pressure due to the low reactivity of –COOH with molecular hydrogen. Geilen et al. [3,18] reported the hydrogenation of IA to MGBL catalyzed by Ru-complexes and described the mechanism in IA hydrogenation with $[\text{Ru}(\text{TriPhos})\text{H}]^+$. Primo et al. [19] adopted Ru/TiO₂ and Ru/C as catalysts for the hydrogenation of IA. Yu et al. [20] reported the aqueous reduction of IA to 3-MGBL using syngas over Au/ZrO₂ under 4 MPa H_2 for 5 h and the selectivity of 92% 3-MGBL was obtained. However, there appears to be no reports focusing on the hydrogenation of IA to MGBL catalyzed by Pd based catalysts, which are very efficient for the succinic acid hydrogenation for the production of GBL [1,9,11].

Herein, we investigated the aqueous hydrogenation of IA to MGBL (including 2-MGBL and 3-MGBL) over Pd/C under mild conditions (Scheme 1), and discussed the effects of support treatment on the catalytic performance, for pretreatment could affect the physical and chemical properties of active carbon and further impact the performance of Pd/C catalysts. We also studied the effects of temperature, H_2 pressure and investigated the catalyst durability.

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Scheme 1. Reaction sequence of IA to MGBL.

2. Experimental

2.1. Active carbon pretreatment

A commercially available wooden active carbon (AC, denoted as C₀) with BET surface area of 1600 m²/g was pretreated with 15% HNO₃ at 75 °C for 3 h, and then washed with distilled water until the pH of the filtrate was neutral and dried in vacuum at 100 °C (denoted as C_N). The AC was also treated with 10% NaClO at room temperature for 24 h, washed with distilled water and dried (denoted as C_{Cl}). Then C_N was further treated with NaClO of four different concentrations at room temperature for 24 h. For convenience, they are hereafter called C₁, C₂, C₃ and C₄, where 1, 2, 3 and 4 represented the successively increasing concentrations of NaClO used in the pretreatment. The detailed procedure was provided in the Supporting information (SI).

2.2. Catalyst preparation and characterization

The 3 wt.% Pd/C catalysts were prepared by deposition–precipitation using NaHCO₃ as precipitant and reduced with HCHO and were characterized by XRD, BET, TEM, FT-IR and NH₃-TPD to study their physicochemical properties. The detailed preparation procedures and the characterization techniques were described in the SI.

2.3. Catalytic hydrogenation reaction

Catalytic hydrogenation of IA was performed in a 50 ml autoclave. After 1 wt.% IA aqueous solution and 1.5 mol% Pd catalysts were introduced into the reactor, the reactor was purged with H₂ for five times and then pressurized to the desired pressure at room temperature. After reaction, unconsumed IA was detected by high performance liquid chromatography (HPLC) and products were quantified by gas chromatography (GC). The products were also analyzed by GC or LC coupled with a mass spectrometer (MS). All experiments were performed in duplicate.

3. Results and discussion

3.1. BET analysis

As shown in Table 1, the S_{BET} of Pd/C₀, Pd/C_{Cl}, Pd/C_N were 1591.7 m²/g, 1418.7 m²/g and 1011.1 m²/g respectively, while the S_{BET} of Pd/C₁, Pd/C₂, Pd/C₃ and Pd/C₄ were all below 900 m²/g. As revealed in the TEM images of carbon supports (Fig. S1), the AC structures were altered by the pretreatments, which could be attributed to the oxidability of HNO₃ and NaClO [21–24]. Table 1 showed that pretreatments affected pore size distribution greatly. As the oxidation strength increased, the pore volume and pore size decreased, which could be ascribed to the pore closure

caused by the oxygen-containing functional groups produced by the oxidation treatment with HNO₃ and NaClO [24].

3.2. FT-IR and NH₃-TPD analyses

It could be obviously seen from the FT-IR spectra of the catalysts (Fig. 1) that the characteristic peaks of –COOH at 1708 cm^{−1}, 1520 cm^{−1} and 1328 cm^{−1} existed in the catalysts with support pretreated with HNO₃, which indicated that the acidic functional groups of AC were primarily introduced by HNO₃ pretreatment. The NH₃-TPD results (Table 1 and Fig. S2) showed the Pd/C_N catalyst possessed the highest acid density (2.32 mmol NH₃/g), while Pd/C_{Cl} showed the lowest acid density (0.39 mmol NH₃/g). The acid densities of Pd/C₁, Pd/C₂, Pd/C₃ and Pd/C₄ were all around 1.70 mmol NH₃/g, a notable decrease compared with Pd/C_N. These results indicated that the surface acidity of the catalyst was influenced by HNO₃ and NaClO for their oxidability and acidity–basicity.

Oxidation treatment could introduce oxygen-containing functional groups to the surface of active carbon [23–28], such as –COOH, –OH and –COOR, and such groups generally enhanced the interaction between the support and metal nanoparticles, which could bring about fine dispersion of metal nanoparticles and thus improve the catalytic activity [25]. On the other hand, pretreatment with HNO₃ was an efficient way to increase the surface acidity [24,28]. Herein, oxidation treatment with proper concentration of HNO₃ was mainly to increase the surface oxygen-functional groups in order to improve the dispersion of metal and improve the activity of the catalysts indirectly. However, high concentration HNO₃ was not suitable for its forceful oxidability [21,24,25]. In this study, we selected low concentration HNO₃ and NaClO with low oxidability and basicity to treat active carbon to create oxygen-rich AC surface environment and proper acidity, for the purpose of obtaining suitable catalysts for the IA hydrogenation to MGBL.

3.3. Results of XRD and TEM

As shown in Fig. 2, the catalysts exhibited characteristic diffraction peaks of carbon's crystalline plane (111) around 2θ = 26.6° (JCPDS No. 75-2078), and the peaks at 2θ = 40°, 46.5° and 68.2° were ascribed to the characteristic diffraction peaks of palladium. The weak peaks of Pd indicated that Pd particles were finely dispersed on AC. Small and uniform Pd particles were also confirmed by the TEM results (Figs. 3 and S3), which were favored to improve the activities of catalysts. As shown in Table 1, the Pd particle sizes of the catalysts Pd/C₁, Pd/C₂, Pd/C₃ and Pd/C₄ were smaller than 3 nm, while Pd particle sizes of Pd/C₀, Pd/C_{Cl} and Pd/C_N were 4.97 nm, 3.46 nm and 3.22 nm, respectively. The results suggested that different AC pretreatment influenced Pd particle size. Copretreating with HNO₃ and NaClO led to the decrease of Pd particle size, which was due to the changes of the facial environment of AC.

Table 1
Results of BET analysis, NH₃-TPD and particle size of Pd/C catalysts.

Catalysts	S _{BET} ^a (m ² /g)	PS ^b (nm)	NH ₃ -adsorption (mmol/g)	Pore parameters ^d			
				V _{meso} (cm ³ /g)	r _{meso} (nm)	V _{micro} (cm ³ /g)	r _{micro} (nm)
Pd/C ₀ ^c	1591.7	4.97	0.59	0.627	3.90	0.315	1.62
Pd/C _{Cl}	1418.7	3.46	0.39	0.563	3.89	0.314	1.60
Pd/C _N	1011.1	3.22	2.32	0.296	3.64	0.269	1.54
Pd/C ₁	884.8	2.83	1.71	0.241	3.63	0.232	1.52
Pd/C ₂	825.6	2.92	1.68	0.237	3.61	0.221	1.51
Pd/C ₃	853.2	2.87	1.67	0.231	3.60	0.219	1.49
Pd/C ₄	765.9	2.89	1.79	0.226	3.58	0.212	1.46

^a BET surface area.

^b Particle size calculated by TEM.

^c C₀: carbon as received; C_N: carbon pretreated with HNO₃; C_{Cl}: carbon pretreated with NaClO; C₁, C₂, C₃, and C₄: further pretreatment of C_N with successively increasing concentrations of NaClO.

^d Specific surface areas and pore parameters determined by the N₂ sorption at 77 K.

3.4. Hydrogenation of IA

Initially, we evaluated catalysts with different noble metals and different supports for the hydrogenation of IA. Among the catalysts investigated (Table S1), the Pd/C catalyst was observably more effective and selective in producing MGBL, giving markedly higher yield of MGBL compared with other catalysts in this work. Therefore, we further concentrated on the optimization of the Pd/C catalysts via tuning the support properties aiming to obtain the highest MGBL yield.

Table 2 summarizes the results of IA hydrogenation to MGBL over Pd/C. Complete conversion of IA and 89.5% selectivity of MGBL was obtained over Pd/C₁ at 180 °C under 4 MPa H₂ for 20 h. The Pd/C catalyst with carbon copretreated with both HNO₃ and NaClO displayed the best selectivity to MGBL as revealed in Table 2 and Table S2. These results demonstrated that catalytic activity was influenced by the AC pretreatment, and copretreatment with both low concentration of HNO₃ and NaClO with low oxidability was favorable for the carboxyl acid hydrogenation. From the results of FT-IR and NH₃-TPD, HNO₃ treatment increased the surface oxygen-containing functional groups (especially –COOH) and acidity of catalysts, while NaClO treatment neutralized parts of the surface acidity of catalysts as well as increased the surface oxygen-containing functional groups for its low oxidability and basicity, and thus created suitable environment to disperse Pd particle. Both the XRD patterns and TEM images showed that Pd particles were well dispersed on AC. AC copretreated with HNO₃ and NaClO was conducive to dispersing the Pd particles and improving the hydrogenation activity of Pd/C.

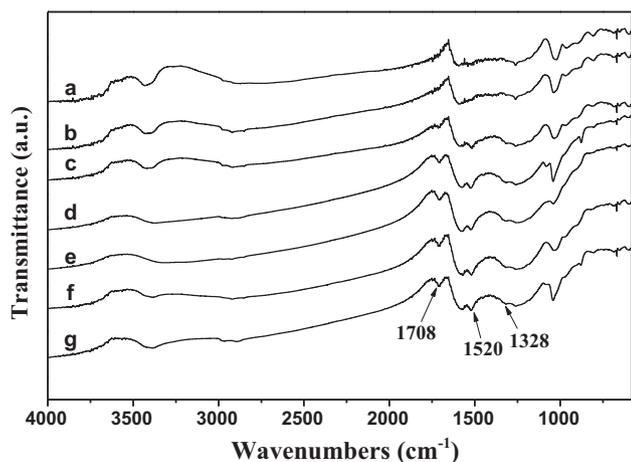


Fig. 1. FT-IR spectra of (a) Pd/C₀, (b) Pd/C_{Cl}, (c) Pd/C_N, (d) Pd/C₁, (e) Pd/C₂, (f) Pd/C₃ and (g) Pd/C₄.

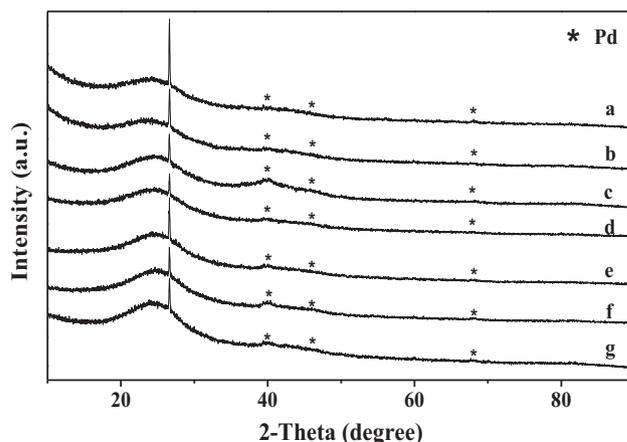


Fig. 2. XRD patterns of (a) Pd/C₀, (b) Pd/C_{Cl}, (c) Pd/C_N, (d) Pd/C₁, (e) Pd/C₂, (f) Pd/C₃ and (g) Pd/C₄.

It should be noted that the IA conversion could reach 100% easily due to the straightforward hydrogenation of the C=C bond. In this study, the yield of MGBL could be up to 89.5%, which was equivalent to or better than other reports [3,19]. Pd/C catalyst was found to be suitable for the hydrogenation of IA to MGBL with negligible formation of gas products (such as CO₂) according to TOC analysis (the carbon balance of the reactions ranged from 89% to 98%) and GC analysis. The intermediate compounds, MSA and HMBA were confirmed by LC–MS (Fig. S4). The catalyst Pd/C₂ was chosen to investigate the influence of temperature, H₂ pressure and reaction time on the hydrogenation of IA for its highest selectivity (Table S2).

3.5. Effects of temperature and H₂ pressure

Fig. 4 shows the influence of temperature on the reaction over Pd/C₂ under 4 MPa H₂ for 20 h. Initially, there was a significant increase in the selectivity of MGBL with temperature increasing from 140 °C to 160 °C, and this increase was not noticeable between 160 °C and 180 °C. As temperature increased to 200 °C, the selectivity of MGBL reduced due to the increasing formation of by-products (e.g., butyric acid, 2-methylpropanoic acid, 2-methyl-1,4-butanediol, 3-methyl-tetrahydrofuran). For the complete conversion of IA could be obtained within very short reaction time, the conversion based on the MSA should be a better standard to clarify the catalyst activity. Both the conversion based on MSA and the selectivity of MGBL at 180 °C were higher than those at 160 °C. Therefore, 180 °C was chosen to investigate the influence of H₂ pressure (Fig. S5). It was under 4 MPa H₂ that the highest selectivity of MGBL could be achieved ranged from 2 MPa to 5 MPa H₂ pressures. The effect of reaction time was discussed in the SI (Fig. S6). To our knowledge, the optimized conditions of 180 °C and 4 MPa H₂ pressure were mild, suggesting that Pd/C catalysts were indeed efficient for the aqueous-phase hydrogenation of IA.

3.6. Recyclability tests

Catalyst recycling tests were performed on the Pd/C₁ catalyst for five runs and the results showed that the Pd/C₁ catalyst exhibited good reusability, as indicated by only slight decreases of the MGBL selectivity over the five repeated runs (Table S3). The spent catalyst was characterized by XRD and TEM and nearly no difference could be observed in the XRD patterns (Fig. S7) and TEM images (Fig. S8) compared with the fresh catalyst, which confirmed that the Pd/C₁ catalyst exhibited high stability in the aqueous hydrogenation of IA to MGBL. The ICP-AES analyses of the resultant liquids showed that no Pd was leached in the liquid, which also indicated that the Pd/C catalyst was robust in the aqueous-phase hydrogenation of IA.

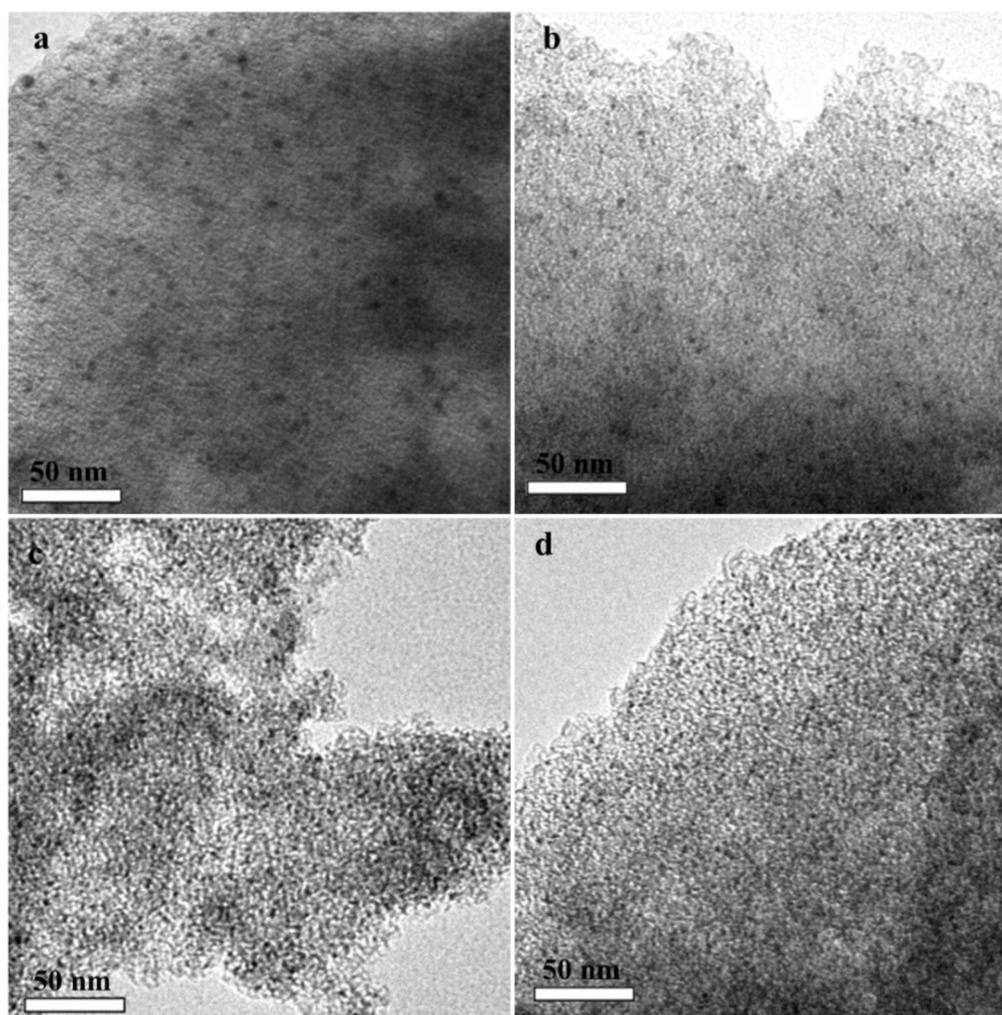


Fig. 3. TEM images of (a) Pd/C₀, (b) Pd/C_{Cl}, (c) Pd/C_N and (d) Pd/C₁.

4. Conclusions

Pd/C catalysts were efficient for the IA hydrogenation to MGBL. Pretreatments of the active carbon exerted significant influence on the activities of Pd/C catalysts, which mainly altered the surface functional groups, structure and acidities of active carbon. Catalysts pretreated by low concentration HNO₃ and NaClO with low oxidability solution exhibited superior selectivity to MGBL among the catalysts. At 180 °C, 4 MPa H₂ for 20 h, the best catalyst showed complete conversion with 89.5% total selectivity to MGBL.

Table 2
Hydrogenation of IA to MGBL over Pd/C catalysts^a.

Catalysts	IA (MSA) ^b conv. (%)	Selectivity (%)			
		2-MGBL	3-MGBL	MGBL	Others ^c
Pd/C ₀	100 (58.1)	19.4	31.1	50.5	49.5
Pd/C _{Cl}	100 (83.4)	28.2	44.4	72.6	27.4
Pd/C _N	100 (87.6)	30.3	48.4	78.7	21.3
Pd/C ₁	100 (94.6)	33.9	55.6	89.5	10.5
Pd/C ₂	100 (93.2)	32.4	53.5	85.9	14.1
Pd/C ₃	100 (92.4)	32.2	53.4	85.6	14.4
Pd/C ₄	100 (90.1)	31.9	52.2	84.1	15.9

^a Conditions: 1% IA aqueous solution, 180 °C, 4 MPa H₂, 20 h, 800 rpm.

^b Data in parenthesis showed the conversions based on MSA.

^c Others: mainly MSA, MHBA and 3-MTHF.

Acknowledgments

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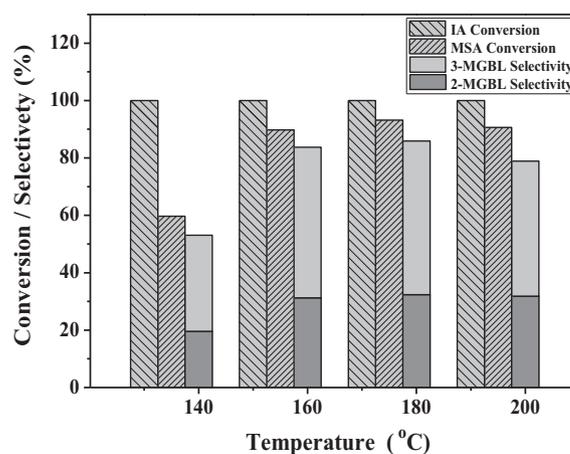


Fig. 4. Effect of reaction temperature on the IA hydrogenation over Pd/C₂ catalyst under 4 MPa H₂ for 20 h.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.12.017>. This data include MOL files and InChiKeys of the most important compounds described in this article.

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