



Phosphonic acid promotion of supported Pd catalysts for low temperature vanillin hydrodeoxygenation in ethanol

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ABSTRACT

Bifunctional catalysts with activity for both hydrogenation and dehydration have been frequently investigated for hydrodeoxygenation (HDO). Here, we report the application of organophosphonic acids (PAs) to Pd/Al₂O₃ catalysts for low-temperature vanillin HDO. Reaction studies indicated that PA-modification significantly improved the liquid-phase HDO activity; the yield to the desirable product, p-cresol (CR), increased from 2.5% to 87% at 50 °C. This improvement was attributed to the creation of metal/acid bifunctional sites upon PA modification. In addition, HDO activity positively correlated with the Brønsted acidity of the PA modifier, which could be tuned by adjusting the PA tail functionality.

1. Introduction

Catalytic reactions typically involve multiple steps and pathways that often require different active-site environments [1]. One approach to achieve high rates for complex reactions is to introduce bifunctional or multifunctional catalysts, by integrating various functions to a single material to synergistically activate different pathways. For example, hydrodeoxygenation (HDO) of biomass-derived oxygenates, an important step in biofuel upgrading, usually involves hydrogenation and hydrogenolysis as two processes that call for different catalytic functions [2,3].

In order to achieve high HDO activity, late-transition-metal/Brønsted acid bifunctional catalysts have frequently been used [2]. During the reaction, the metal component catalyzes the hydrogenation step due to its activity for hydrogen dissociation, while Brønsted acid sites cooperatively facilitate hydrogenolysis by activating the C–O bond [2,4,5]. A convenient approach to introduce this bifunctionality is to employ supported metal catalysts, where the support material carries Brønsted acidity to synergistically catalyze HDO with the metal counterpart. Therefore, support materials that intrinsically contain Brønsted acid sites have often been applied or synthesized, e.g., silica-alumina [6,7] and hybrid metal-organic-framework (MOF)/partially reduced graphene oxide (PRGO) [8]. Recently, Wang et al. reported that amorphous activated carbon (AC) synergistically catalyzed room-temperature HDO of vanillyl alcohol with Pd [9]. Reaction studies suggested that the high HDO activity was due to acid sites on the support. X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption analysis further revealed that carboxyl groups were the

effective acid component on AC; HDO activity linearly increased with the availability of carboxyl groups on the support.

In addition to employing pristine acidic support materials, acid sites can also be introduced by surface modification with acidic functionalities [10–13]. This approach maintains the intrinsic structure of the native support, while also providing the ability to design the near-surface environment in a controllable manner [14–16]. For instance, phosphate/phosphonate modifiers have been applied to metal oxide supports to introduce Brønsted acidity for improving HDO activity for various reaction substrates [10–12]. Nelson et al. reported that by modifying the reducible CeO₂ support with phosphates, the ratio of redox to acidic catalytic sites could be optimized to achieve a high activity for guaiacol HDO [10]. More recently, phosphonate modifiers were applied to Al₂O₃ supports for vapor-phase HDO reactions [11,12]. By changing the tail structure, Brønsted acidity could be tuned to strongly affect HDO activity.

To the best of our knowledge, the use of phosphonic acid monolayers has not been investigated for application in low-temperature liquid-phase reactions, where interactions between the surface and the solvent are expected to play a significant role [17]. Ultimately, we expect that such conditions may allow one to realize the greatest benefits from use of ligand-modified catalysts, since low-temperature operation can help avoid issues with ligand stability, and the ligands can be tuned to influence solvent-catalyst interactions. In this contribution, the organophosphonate-modification approach has therefore been applied to a commercial Pd/Al₂O₃ catalyst for liquid-phase HDO reactions for the first time. We have used vanillin as the probe reactant, a direct product of biomass pyrolysis and a model compound for bio-ol

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upgrading [3,18–20]. The reaction has been reported to strongly depend on reaction temperature [3,18,20]. Below 150 °C, vanillin mainly undergoes hydrogenation to vanillyl alcohol (VA), or deoxygenation of the carbonyl group to the desirable product p-cresol (CR). In order to improve CR selectivity, various Brønsted acid materials such as N-doped carbon [3], zeolites [20], and metal–organic frameworks (MOFs) [13], have been used to support Pd. In addition, other reaction systems, such as water–oil Pickering emulsions, have been reported to improve vanillin HDO due to enhanced product separation [18]. Despite the various approaches used, CR production generally requires a temperature higher than 90 °C; lower temperatures usually lead to complete hydrogenation to VA, while a high selectivity to CR has rarely been reported [19]. In this manuscript, phosphonic acid modifiers (PAs) were applied to Pd/Al₂O₃ catalysts for liquid-phase vanillin HDO. By introducing Brønsted acid sites to the metal oxide support, high yields of CR could be observed below 50 °C. Furthermore, various PA modifiers were utilized to tune the Brønsted acidity, which significantly affected the HDO activity.

2. Experimental

2.1. Materials

The 5 wt % Pd/Al₂O₃, palladium black, vanillin, vanillyl alcohol, 2-methoxy-4-methylphenol (p-cresol), phosphoric acid, styrene, acetic acid, ammonia solution (2.0 M in ethanol), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Methylphosphonic acid (Alfa Aesar), (chloromethyl)phosphonic acid (Acros Organics), methanol (VWR), and ethanol (Decon Laboratories) were purchased from suppliers as specifically indicated. All chemicals were with > = 98% purification grades and used as received without further treatments. Zero-grade air and ultra-high purity H₂ were obtained from Airgas.

2.2. Catalyst preparation and characterization

The surface area and dispersion of Pd catalysts were characterized by CO pulse adsorption in a custom quartz tube reactor (6.35 mm inner diameter) with a Pfeiffer mass spectrometer. Prior to the measurement, the catalyst was pretreated in situ by a 30-min reduction in a 10 sccm H₂/20 sccm He flow at 120 °C, followed by 30-min purging with He at the same temperature. CO adsorption was performed at 50 °C. The active surface area and dispersion of the catalysts given by the measurement are shown in Table 1.

The Pd/Al₂O₃ catalyst was further modified with phosphonic acids, which are well-known to form organic monolayers on Al₂O₃ and other oxide surfaces [21,22]. The modification was performed by immersing the catalyst into a 10 mM phosphonic acid solution in THF with vigorous stirring for 16 h at room temperature. The total amount of phosphonic acid was controlled at 5–10 times of the amount required to

form a monolayer on the support surface. The mixture was then centrifuged to remove the THF supernatant, followed by annealing at 120 °C in ambient air for 6 h to obtain the chemisorbed phosphonate-modified catalyst. The catalyst was then rinsed with THF for four times to remove any physisorbed phosphonic acid, followed by drying in air overnight.

The PA-modified catalysts were characterized using infrared spectroscopy. The experiments were performed using a Thermo Scientific Nicolet 6700 for diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in an open cell with N₂ flux. For each sample, the background was collected with 400 scans at 1 cm⁻¹ resolution, and 200 scans were used to analyze the samples. In order to further investigate the adsorption geometry of the phosphonic acids, second derivatives of the spectra were obtained to analyze the peak shoulders. The second derivatives were generated using Norris derivative method in the OMNIC software, with a 3-point segment and a gap between segments of 7. BET measurements and inductively coupled plasma mass spectrometry (ICP-MS) were performed to determine the surface area and phosphorus content following modification, respectively. BET measurement was conducted using a Micromeritics Chemisorb 2720 system. The catalyst was pretreated in-situ in 30% N₂ in He at 180 °C for two hours and cooled to room temperature, followed by N₂ saturation in the same atmosphere for measurement.

In order to compare the density of acid sites on different catalysts, ammonia pulse chemisorption was performed in a quartz tube reactor with a mass spectrometer (same as the CO chemisorption system). The catalyst was pretreated at 120 °C in H₂ for 30 min, followed by 270 °C in 20 sccm He flow for 3 h, and cooled down to 100 °C. Ammonia chemisorption was carried out in 100 sccm He flow at 100 °C by manual injection. Error bars were calculated based on replicate measurements.

2.3. Catalytic reactions, yield, and rate calculations

Vanillin hydrogenation/hydrodeoxygenation (HDO) reactions were performed in a 100 mL liquid-phase semi-batch reactor at 50 °C in 200 psi H₂ for one hour, with a stirring rate of 1200 rpm. The reaction solution included 32 mL ethanol (solvent), 267 mg (0.05 M) vanillin (reactant), 20 mg supported Pd catalysts (Pd_{Total}:Vanillin = 1:176 mol/mol), and 1 mL methanol (internal standard for gas chromatography analysis). For Pd black catalyst, 2 mg (Pd_{Total}:Vanillin = 1:88 mol/mol) was used to reach a similar conversion with the Pd/Al₂O₃ catalysts after the reaction course of 1 h. Styrene hydrogenation reactions were performed in the same reactor at room temperature, with a lower H₂ pressure of 30 psi and a lower catalyst loading (Pd_{total}:styrene = 1:628 mol/mol) to obtain a moderate reaction rate. Seven 1 mL liquid samples were taken from the reactor during the 1 h reaction period for vanillin hydrogenation/HDO. For styrene hydrogenation, a total of six samples were taken at 30 s intervals in the first 2.5 min of the reaction to calculate initial rates. For recycling reactions,

Table 1
Characterization of Pd and the Al₂O₃ Support upon PA Modification.

Catalysts	Pd/Al ₂ O ₃	MPA@ Pd/Al ₂ O ₃	H ₃ PO ₄ @ Pd/Al ₂ O ₃	CIMPA@ Pd/Al ₂ O ₃	Pd black
STY Hydrogenation Initial Rate ^a (s ⁻¹ mol/mol _{TotalPd})	2.8 ± 0.7	3.3 ± 0.5	2.5 ± 0.3	2.4 ± 0.2	0.8 ± 0.3
CO Uptake (mol _{CO} /mol _{TotalPd})	0.19 ± 0.04	0.04 ± 0.02	0.04 ± 0.02	0.05 ± 0.01	0.025 ± 0.002
BET Surface Area (m ² /g)	81 ± 1	40 ± 1	41 ± 1	63 ± 2	50 ^d
PA Density ^b (#PA/nm ² (Uncoated-Al ₂ O ₃)) ^c	N.A.	8.5 ± 0.7	7.48 ± 0.03	4.3 ± 0.4	N.A.

^a Reaction conditions: 0.1 M styrene, 15 mg supported Pd catalyst (Pd_{Total}:STY = 1:628 mol/mol), 32 mL ethanol (solvent), 1 mL methanol (internal standard), 298 K, 30 psi H₂, and stirring at 1200 rpm. The initial rate was measured during the reaction course of first 2.5 min.

^b For PA density and acid site density measurements, the error bars were estimated by 2–3 repeated measurements of different batch of catalysts prepared. The same batch of catalysts were used for repeated BET measurements.

^c P content was characterized by ICP-MS analysis. The total surface area was given by BET measurement of the native Pd/Al₂O₃ catalyst, used as the denominator to calculate PA density.

^d Data source: reference [11].

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