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



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A R T I C L E I N F O	A B S T R A C T
Keywords: Bifunctional catalyst Surface modification Brønsted acid site Hydrodeoxygenation Vanillin	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/Al ₂ O ₃ 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-creosol (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 el. 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 nearsurface 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 Al_2O_3 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-oil

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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-creosol (CR). In order to improve CR selectivity, various Brønsted acid materials such as Ndoped 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, 2methoxy-4-methylphenol (p-creosol), 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 phosphonatemodified 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 H_2 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 а lower catalyst loading $(Pd_{total}:styrene = 1:628 \text{ mol/mol})$ 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_3PO_4 @ Pd/Al ₂ O ₃	ClMPA@ Pd/Al ₂ O ₃	Pd black
STY Hydrogenation Initial Rate ^a (s ⁻¹ mol/mol _{TotalPd}) CO Uptake (mol _{CO} /mol _{TotalPd}) BET Surface Area (m ² /g) PA Density ^b (#PA/nm ² (Uncoated-Al ₂ O ₃)) ^c	2.8 ± 0.7 0.19 ± 0.04 81 ± 1 N.A.	$\begin{array}{r} 3.3 \ \pm \ 0.5 \\ 0.04 \ \pm \ 0.02 \\ 40 \ \pm \ 1 \\ 8.5 \ \pm \ 0.7 \end{array}$	$\begin{array}{l} 2.5 \pm 0.3 \\ 0.04 \pm 0.02 \\ 41 \pm 1 \\ 7.48 \pm 0.03 \end{array}$	$\begin{array}{r} 2.4 \ \pm \ 0.2 \\ 0.05 \ \pm \ 0.01 \\ 63 \ \pm \ 2 \\ 4.3 \ \pm \ 0.4 \end{array}$	$\begin{array}{l} 0.8 \ \pm \ 0.3 \\ 0.025 \ \pm \ 0.002 \\ 50^{\rm d} \\ {\rm N.A.} \end{array}$

^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].

the catalyst was rinsed twice with 20 mL methanol in a sonication cleaner and subsequently centrifuged. The methanol supernatant was then poured out and the catalyst was dried in a vacuum desiccator before reuse. The activity of the catalyst was characterized by the rate of creosol production during the first 5 min of the reaction. With vigorous stirring, the solid catalyst was expected to be uniformly dispersed in the reaction mixture; the ratio of the catalyst to the reaction solution was thus held constant within the reactor by simultaneously sampling liquid and catalyst with continuous stirring, and subsequently filtering out the catalyst using a syringe filter ($0.22 \mu m$, nylon). The liquid samples were analyzed by an Agilent 7890 A gas chromatography with a flame ionization detector, using an Agilent HP-5 capillary column.

The concentrations of reactants and products in the reaction solution were determined from peak areas obtained from GC analysis using corresponding response factors, which were measured using a series of standard solutions. The concentrations of the standard solutions were comparable to those in reaction conditions. The product yield (the ratio of product to initial reactant) and rate calculations were both based on concentration. To avoid the ambiguity of turnover frequency (TOF) measurements, the rates here were reported as moles of reactant consumed per mole of total metal catalyst instead of per surface site. Error bars were calculated based on replicate reactions.

3. Results

3.1. Characterization of PA-modified Pd/Al₂O₃ surface

Three PA modifiers – phosphoric acid (H₃PO₄), methylphosphonic acid (MPA), and (chloromethyl)phosphonic acid (ClMPA) – were used to modify Pd/Al₂O₃ catalysts. As shown in Table 1, their coverages varied from 4 to 8 molecules/nm² in the order H₃PO₄ \approx MPA > ClMPA. Compared to previously reported values (2.1 to 5.0 molecules/nm²) [23–25], the density measured in this study was generally higher. The higher coverage could be attributed to PA-multilayer formation by physisorption, as well as organophosphonate adsorption on Pd metal sites as suggested in recent studies [11,12].

To test if the PA modification affected Pd site availability, Pd surface area was measured by CO chemisorption. As an additional measure of site availability, we also evaluated the catalysts for activity in liquidphase styrene (STY) hydrogenation. We employed STY hydrogenation as a probe reaction, hypothesizing that the activity for this reaction would depend chiefly on the number of surface Pd sites due to the structure-insensitivity of this reaction [26,27]. As shown in Table 1, while a decrease of surface sites on modified catalysts was observed by CO adsorption, this apparent blocking effect did not affect the activity for STY hydrogenation within the experimental error. This result was similar to previous findings, in which the blocking effect on a Pd by surface modifiers did not strongly affect active sites for vapor-phase hydrogenation reactions [11,28,29]. For instance, McCue et. al. observed the promotion effect of triphenylphosphine modifiers for acetylene hydrogenation on Pd/TiO2 catalysts [28], despite a notable decrease in the number of active sites as measured by CO pulse chemisorption. The authors partly attributed this specific promoting effect to the inaccessibility of hollow sites and a change of electronic structure by triphenylphosphine adsorption, which weakened CO adsorption to decrease the quantity of measured active sites without substantially decreasing the availability of sites for acetylene hydrogenation. Here in this study, we speculated that there was a similar effect for PA modification that maintained the STY hydrogenation activity while blocking a portion of active sites.

The successful PA modification was further confirmed by observation of P–O stretching modes in DRIFT spectra (Fig. S1). In general, the spectra were similar to those from previous work, which showed that PAs introduced Brønsted acidity to Al_2O_3 supports (Scheme 1) [11,12]. Those previous studies used infrared spectroscopy after pyridine adsorption to show that PA modification was accompanied with a significant increase in the pyridinium band attributed to Brønsted acid sites. This Brønsted acidity was hypothesized to be carried through – OH groups on the PA molecules. Extensive characterization by pyridinium DRIFTS at elevated temperatures indicated that the Brønsted acidity of the modifiers could be tuned by the electron-withdrawing group on the PA molecule [11] or via the use of ligands capable of intramolecular hydrogen-bonding interactions [12]. It should be noted, however, that the adsorption of PA on the support may involve various combinations of configurations for different PAs (see Fig. S1 and associated discussion). Depending on the Brønsted and Lewis acidity of the surface, different PA adsorption geometries could be formed, only some of which contained Brønsted acid sites [30] (Scheme 1). Based on the prior work, we hypothesized that Brønsted acid sites formed from PA modification could promote liquid-phase HDO activity.

3.2. Reaction study of PA-modified $\rm Pd/Al_2O_3$ for vanillin hydrogenation/ HDO

The liquid phase vanillin hydrogenation/HDO (Scheme 2) was performed in a semi-batch liquid phase reactor at 323 K under a constant H₂ pressure of 200 psi. Because vanillin HDO was hypothesized to be enhanced by acid sites [8,31], CIMPA was investigated as a representative modifier among other PA coatings due to its higher acidity (Table S1). Fig. 1 shows the characteristic reaction profile of Pd/Al₂O₃ before and after ClMPA modification. The native Pd catalyst exhibited a high hydrogenation activity to produce vanillyl alcohol (VA), leading to a yield of $\sim 97\%$ after 60 min, while the hydrodeoxygenation (HDO) selectivity remained low at all conversions. After ClMPA modification, the selectivity profile was drastically changed, reaching a creosol (CR) yield of 87% after 60 min. The reaction pathway from vanillin to CR had been previously proposed to be either 1) a one-step direct hydrogenolysis of the C=O bond, or 2) a multi-step hydrogenation-hydrogenolysis process with VA as the intermediate product [2,3]. In this study, the reaction profile indicated that the latter mechanism dominated, as VA was generated in the early stage of the reaction and continued to form CR after the complete consumption of vanillin. Though direct vanillin hydrogenolysis to CR could not be ruled out, either case suggested that the high CR yield was due to an improved HDO activity, instead of suppressing the hydrogenation pathway. In fact, the ClMPA coating increased the initial VA production rate based on total amount of available Pd sites (Table 2), indicating that CIMPA was likely to enhance C=O hydrogenation as well, as discussed in more detail below. Therefore, we hypothesized that the ClMPA modifier improved vanillin HDO activity by introducing Brønsted acid sites, and moderately promoted hydrogenation to VA while strongly promoting hydrogenolysis to CR.

To further verify this assumption, ClMPA-modified Pd/Al₂O₃ was treated by NH₃ to poison the acid sites prior to reaction testing. The NH₃ treatment was carried out by immersing the catalyst in a 2 M NH₃/ ethanol solution overnight, followed by pouring out the ethanol supernatant and heating to 60 °C in ambient environment for 4 h to remove excess NH₃ and ethanol [9]. As shown in Table 2, after poisoning the acid sites, the catalyst performed similarly to the uncoated Pd, i.e. the yield to CR dropped by more than 70% after 60 min of reaction (entry 6, 7) with a lowered initial rate similar to that of the native catalyst. The same NH3 treatment was also conducted on the native catalyst, and showed no notable difference from the untreated case (entry 1, 3), indicating that the NH₃ treatment did not affect the Pd surface sites relevant to the reaction. These control experiments suggested that the high HDO activity on the ClMPA-modified Pd/Al₂O₃ could be attributed to the Brønsted acid sites introduced by the modifier. Moreover, when acetic acid was used as a homogeneous acid, a similar improvement of HDO activity was observed for both supported and unsupported Pd catalysts (Table 2, entry 1, 2, 9, 10), again confirming the key role of Brønsted acid sites in vanillin HDO.

We noted that the Brønsted acid sites were hypothesized to

Scheme 1. Possible binding geometries of PA

adsorbed on Pd/Al₂O₃ [30].



Creosol (CR)

Scheme 2. Reaction pathway of vanillin hydrogenation.

Reaction conditions: 0.05 M vanillin, Pd catalyst (Pd_{Total} :Vanillin = 1:176 mol/mol), 32 mL ethanol (solvent), 1 mL methanol (internal standard), 323 K, 200 psi H₂, and stirring at 1200 rpm.



Fig. 1. Reaction profile of vanillin hydrogenation/hydrodeoxygenation on a) native and b) ClMPA-modified Pd/Al_2O_3 catalysts. Reaction conditions: 0.05 M vanillin, 20 mg Pd catalyst (Pd_{Total} :Vanillin = 1:176 mol/mol), 32 mL ethanol (solvent), 1 mL methanol (internal standard), 323 K, 200 psi H₂, and stirring at 1200 rpm.

cooperatively catalyze HDO with the active metal counterpart. To test this hypothesis, the native Pd/Al_2O_3 was physically mixed with ClMPA-modified γ -Al₂O₃ that contained Brønsted acid sites (entry 8); this reaction showed least improvement of HDO activity compared to the native catalyst. Therefore, the enhanced HDO activity required that

acid and metal sites exist on the same support, confirming that the PA modification improved the HDO activity in a bifunctional way.

We hypothesized that the degree of improvement of HDO activity by the bifunctional acid/metal catalyst was related to the Brønsted acidity of the modifier. As shown in Fig. 2, when different PA modifiers were applied to the Pd/Al₂O₃ catalyst, the yield to the HDO product CR exhibited a positive correlation with PA acidity; the highest CR yield was obtained on ClMPA-modified catalyst, which hypothetically had the highest Brønsted acidity. However, it should be noted that comparisons between different coatings are complicated by the significant differences in P densities; for example, the relatively high CR yield with the H₃PO₄-modifier could be related to its higher acid surface coverage compared to ClMPA (Table S2). However, the general observation that more acidic PAs lead to more active catalysts was consistent with previous work for vapor-phase HDO reactions [6,9,11]. This enhancement in HDO activity was found to be insensitive to temperature across the range in the current study (Fig. S3).

3.3. Reusability of ClMPA-modified Pd/Al₂O₃

The reusability of ClMPA-modified Pd/Al_2O_3 was tested by measuring the initial CR production rate during recycling reactions. After each run, the catalyst was rinsed twice with 20 mL methanol in a sonication cleaner to remove the carbonaceous surface species generated during the reaction. The mixture was then centrifuged and the methanol supernatant was poured out, followed by drying in a vacuum desiccator before reuse. As shown in Fig. 3, the native Pd catalyst exhibited a constant low CR production rate during the recycling runs. For ClMPA-modified Pd/Al₂O₃, its high HDO activity was generally retained, exhibiting a 1–2 order of magnitude increase compared to the native Pd/Al₂O₃ catalyst. Furthermore, FT-IR indicated that the ClMPA modifier was stable on the surface after three consecutive runs; the original vibration modes remained after recycling reactions (Fig. S4).

4. Discussion

R = -

 $-OH, -CH_3, -CICH_2$

4.1. Effect of Brønsted acid sites on vanillin hydrogenation/HDO

As discussed above, vanillin HDO appeared to proceed mainly through a two-step hydrogenation-hydrogenolysis process. We hypothesized that: 1) PA introduced Brønsted acid sites to dramatically accelerate the hydrogenolysis step; 2) the acids sites were required to be adjacent to metal sites for synergetic catalysis; 3) HDO activity depended on the pKa of the PA modifier.

However, in addition to activating hydrogenolysis, the Brønsted acid sites were also likely to enhance vanillin hydrogenation, as shown in Table 2. This was most evident on the ClMPA-coated surface where the initial rate doubled after the modification, while upon poisoning the acid sites by NH₃ treatment, the rate decreased to a similar value as the native catalyst (entries 1, 6, and 7). Unlike the frequently reported catalyzing effect of Brønsted acids for the hydrogenolysis or dehydration step in HDO, the role of Brønsted acids in C=O hydrogenation had not been generally recognized. Recently, Hensley et. al. suggested that compared to surface hydrogen atoms, Brønsted acid sites increased the capability of phenol hydrogenation by shuttling protons to and from the reactant [33]. As suggested by density functional theory (DFT) calculations, the proton-mediated mechanism significantly decreased the activation energy of ketone hydrogenation. This promotion of the hydrogenation step further changed the dominant reaction pathway of

Table 2							
Influence of Brønsted	acidity on	vanillin	hydrogenation	/hydrodeoxygenatior	over	different o	catalysts. ^a .

Entry	Catalyst	Time (h)	Conv. (%)	CR Yield ^b (%)	Initial Rate ^c (s ⁻¹ mol _{Vaniillin} /mol _{TotalPd})
1	Pd/Al ₂ O ₃	1	> 99	2.0 ± 0.9	0.29 ± 0.03
2	Pd/Al_2O_3 , acetic acid	1	> 99	75 ± 14	0.35 ± 0.05
3	Pd/Al ₂ O ₃ , NH ₃ treated	1	97 ± 1	2.7 ± 1.8	0.3 ± 0.1
4	Al ₂ O ₃	1	17 ± 7	2.4 ± 1.2	0.004 ± 0.002
5	Al ₂ O ₃ , acetic acid	1	18 ± 10	4.6 ± 0.8	0.002 ± 0.002
6	ClMPA@Pd/Al ₂ O ₃	1	> 99	87 ± 11	0.55 ± 0.08
7	ClMPA@Pd/Al ₂ O ₃ , NH ₃ treated	1	> 99	14 ± 9	0.22 ± 0.03
8	Pd/Al ₂ O ₃ &ClMPA@Al ₂ O ₃	1	> 99	9.8 ± 1.8	0.28 ± 0.07
9	Pd black&Al ₂ O ₃	1	72 ± 15	13 ± 13	0.16 ± 0.09
10	Pd black&Al ₂ O ₃ , acetic acid	1	89 ± 11	76 ± 22	0.18 ± 0.05

^a Reaction conditions: 0.05 M vanillin, 20 mg 5 wt% supported Pd or 2 mg Pd black (Pd_{Total}:Vanillin = 1:176 (1:88 for Pd black) mol/mol), 32 mL ethanol (solvent), 1 mL methanol (internal standard), 323 K, $200 \text{ psi} \text{ H}_2$, and stirring at 1200 rpm.

^b Yield to creosol was reported after 1 h of the reaction.

^c Initial rates were based on vanillin consumption, obtained during the reaction course of the first minute.



Fig. 2. Yields of vanillin hydrogenation/hydrodeoxygenation on native and modified Pd/Al_2O_3 catalysts, and Brønsted acidity of the modifiers [32]. Reaction conditions: 0.05 M vanillin, 20 mg Pd catalyst (Pd_{Total}:Vanillin = 1:176 mol/mol), 32 mL ethanol (solvent), 1 mL methanol (internal standard), 323 K, 200 psi H₂, and stirring at 1200 rpm.



Fig. 3. Reusability of the phosphonate-coated Pd/Al_2O_3 . Note that these data are also reported on a linear scale in the supporting information (Fig. S5).

phenol deoxygenation compared to the case without available Brønsted acid sites.

In this study, the enhanced vanillin HDO by Brønsted acids was hypothetically due to an activated hydrogenolysis step, or similarly to the acid-promoted phenol deoxygenation, a possible change of reaction pathway. 4.2. Comparison of PA-promoted HDO in liquid-phase vs. vapor-phase conditions

The same PA-modification strategy was previously applied to improve HDO of aromatic oxygenates, such as benzyl alcohol, m-cresol, and phenol, in vapor-phase conditions [11,12]. Similar to liquid-phase reactions, the addition of PA modifiers increased the activity and selectivity for vapor-phase HDO, the activity of which could be tuned by the acid strength or the structure of PA tail. However, some differences were also observed between the two reaction conditions. Zhang et. al. found that the H₃PO₄ modifier outperformed organophosphonic acid modifiers at very short times on stream [11], possibly because H₃PO₄ produced stronger acid sites at the catalyst-vapor interface, as indicated by temperature-dependent pyridine DRIFTS measurements. However, a drastic deactivation was observed for the H₃PO₄ modified catalyst under vapor-phase HDO conditions, due to acid-promoted coke formation. In liquid-phase conditions, however, neither of these two features was observed. In contract to vapor-phase reactions, ClMPA had comparable initial activity with H₃PO₄ for liquid phase HDO. Because acidity was proved to be critical for both liquid- and vapor-phase HDO, we speculated that the relative acidity between ClMPA and H₃PO₄ may be affected by the presence of solvent. As Gould and Xu recently revealed, the choice of solvent could in fact affect the protonation ability of acid sites on zeolites, leading to different liquid- and vapor-phase acidity, and thus in this work, affecting the deoxygenation reaction and possible acid-catalyzed coking [34].

5. Conclusions

PA modification of Pd/Al₂O₃ significantly enhanced the rate and selectivity of low temperature vanillin HDO. Reaction studies indicated that vanillin HDO underwent a hydrogenation-hydrogenolysis pathway, creating VA as the intermediate product. While vanillin hydrogenation to VA dominated on the unmodified catalyst, PA-modification significantly activated the HDO pathway. This activation was due to Brønsted acid/metal synergistic catalysis that required adjacent metal and acid sites. In addition, by changing the electron-withdrawing group on the PA modifier, the Brønsted acidity could be varied to tune HDO activity. While more studies are required to fully understand the reaction mechanism, the current results demonstrated that metal/acid bifunctionality was a key factor to improve HDO activity. Compared to conventional methods that incorporate Brønsted acidity into catalytic systems, PA-modification offered a robust strategy to modify metal oxide-supported catalysts, adding the degree of freedom to precisely control the near-surface environment.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.05.008.

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