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Sustainable Production of o-Xylene from Biomass-Derived Pinacol and Acrolein

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Abstract: o-Xylene (OX) is a large-volume commodity chemical that is conventionally produced from fossil fuels. Herein, we report an efficient and sustainable two-step route to OX from biomass-derived pinacol and acrolein. In the first step, the phosphotungstic acid (HPW) catalyzed pinacol dehydration in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) selectively afforded 2,3-dimethylbutadiene. The high selectivity of this reaction can be ascribed to the H-bonding interaction between Cl⁻ and the hydroxyl group of pinacol. Besides, the stabilization of the carbocation intermediate by the surrounding anion Cl may be another reason for the high selectivity. Notably, the good reusability of the HPW/[Emim]Cl system can reduce the waste output and production cost. In the second step, OX was selectively produced by the D-A reaction of 2,3-dimethylbutadiene and acrolein, followed by the Pd/C-catalyzed decarbonylation/aromatization cascade in a one-pot fashion. The sustainable two-step process could efficiently produce renewable OX in 79% overall yield. Analogously, biomass-derived crotonaldehyde and pinacol can also serve as the feedstocks for the production of 1,2,4-trimethylbenzene.

The dwindling reserves of fossil resources (such as petroleum, coal and natural gas) and the increasing social concerns about global warming make it imperative to develop sustainable routes

to produce renewable fuels and chemicals. Lignocellulosic biomass is the most abundant and carbon dioxide neutral energy source that can be used as an alternative to the conventional fossil feedstocks for the production of fuels^[1] and commodity chemicals^[2-4]. The past decade has wittnessed substantial achievements in this area. An elegant example is the production of *p*-xylene from biomass, involving a Diels-Alder (D-A) reaction and cascade dehydration of biomass-derived 2,5dimethylfuran (DMF) with ethylene.^[3] Following this process, other valuable chemicals such as aromatic carboxylic acids^[4a–g], toluene^[4h], and styrene^[4i] can also be obtained from biobased furanics and dienophiles. Despite these impressive advances, the exploration of new sustainable routes to other bulk fossil-derived aromatics is still in great demand.

o-Xylene (OX) is a bulk chemical that is industrially produced by the fractional distillation of xylenes from catalytic reforming of petroleum naphtha (Scheme 1). Currently, the world demand for OX was approximately 6 million metric tons per year.^[5] Most of OX (about 90%) is consumed for the preparation of phthalic anhydride, which is an important monomer for the industrial production of plasticizers for PVC products (such as bis(2ethylhexyl) phthalate, DEHP), unsaturated polyesters, and alkyd resins. To fulfill the need of sustainable development, it is highly desirable to exploit a renewable process for the production of OX from biomass.

Pinacol is a renewable *vic*-diol that can be easily prepared by the metal-mediated coupling^[6] or electrolytic reduction^[7] of acetone from the ABE (acetone-butanol-ethanol) fermentation of lignocellulose^[8]. Notably, Zhu *et al.* reported a sustainable photocatalyzed coupling of isopropanol and acetone for the synthesis of pinacol.^[9] This approach is efficient and feasible because the hydrogen generated in the ABE fermentation step



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Supporting information for this article is given via a link at the end of the document. can be used to hydrogenate the acetone to isopropanol. Acrolein the simplest unsaturated aldehyde, can be efficiently formed by the dehydration of glycerol, which is currently oversupplied as a byproduct in the biodiesel production.^[10] Thus, developing new methods for the conversion of acrolein into bulk chemicals will be of great significance in enhancing the biodiesel economy. Herein, a two-step route for the synthesis of renewable OX was first developed using biobased pinacol and acrolein as the feedstocks (Scheme 1). In the first step, the dehydration of pinacol selectively afforded 2,3-dimethylbutadiene. It is wellknown that this reaction is very challenging because of the dominant pinacol rearrangement pathway.^[11] However, the high diene selectivity was achieved in this work by employing [Emim]Cl as the reaction medium and phosphotungstic acid (H₃PW₁₂O₄₀, abbreviated as HPW) as the catalyst. Besides, the good recyclability of the HPW/[Emim]Cl system can reduce the waste output and production cost. In the second step, OX was D-A selectively produced by the reaction of 2.3dimethylbutadiene with acrolein and the following decarbonylation/aromatization cascade in a one-pot fashion.

The acid-catalyzed dehydration of pinacol has two competitive pathways: i) 1,2-elimination of H₂O to diene 2; ii) pinacol rearrangement to pinacolone 3. In most of the cases, this reaction shows a preference on the pinacol rearrangement pathway. In this regard, great efforts were devoted to increasing the diene selectivity. Heteropolyacids (HPAs) have been regarded as green and versatile solid acid catalysts in replacement to the conventional mineral acids.^[12] Therefore, we chose Keggin HPA phosphotungstic acid (HPW) as the catalyst to test the solvent effects on the dehydration of pinacol (Table 1). Just like many previous works,^[11] the dehydration of pinacol in non-polar solvent (e.g. toluene) favored the rearrangement pathway (Entry 1). However, it is surprising to find that the dehydration of pinacol in strong polar solvents (such as dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP)) gave diene 2 as the main product albeit with low yields (Entries 2, 3). These results indicate that the polarity of the solvent seriously affects the dehydration patterns of pinacol.^[13] In view of the fact that ionic liquids (ILs) are endowed with strong electrostatic force and H-bonding interaction,^[14] we surmised that the dehydration in ILs could possibly give a significant increase in the diene selectivity. As we expected, when the reaction was conducted in [Emim]Cl, diene 2 was obtained in 88% yield and only trace amount of pinacolone 3 was detected (Entry 4). From the blank experiments using [Emim]Cl or HPW alone (Entries 5, 6), no diene 2 was observed, indicating that the synergism effect of [Emim]Cl and HPW is essential for the high diene selectivity. The influences of the anion and cation in the imidazolium-based ILs on the reaction were also investigated. When CI was changed to the larger anions such as NTf2 and BF4, the main product switched from diene to pinacolone (Entries 7, 8). Furthermore, the dehydration did not occur in [Emim]OAc (Entry 9). Interestingly, changing the solvent to [Emmim]Cl, which bears a methyl group at the C² position of the ring, afforded diene 2 in a good yield (Entry 10). By varying the alkyl chain length on the cation of ILs, we found that longer alkyl substituent resulted in a decreased diene yield (Entries 11-13). These results reveal that the chemoselectivity of diene 2 is strongly dependent on the chemical structure of ILs.

According to the reported works, there are different H-bonding interactions between the cation and anion in neat ILs.^[14] In particular, the proton at the C²-position is more acidic than other hydrogens, which leads to the formation of a stronger H-bond with the anion (C²-H···X). However, after submitting pinacol to the ILs, the cation and anion of ILs also compete to interact with the hydroxyl group of pinacol through hydrogen bond (C²-H···OH, X···HO), which might account for the increase of diene selectivity. According to the results we obtained, both [Emim]Cl and [Emmim]Cl have good performances for the dehydration of pinacol to diene **2**. These results suggest that the interaction between Cl and the hydroxyl group of pinacol (Cl···HO) plays a dominant role in controlling the diene

selectivity, while the H-bond C²–H···OH is not crucial for the reaction. Besides the H-bonding interaction, the carbocation intermediate could also be stabilized by the surrounding anion CI, which also contributes to the high diene selectivity. In contrast, the low selectivity of diene **2** in [Emim]BF₄, [Emim]NTf₂, and [Emim]OAc can be explained by the weak interactions of the anions with the hydroxyl group. The sterically hindered butyl group probably hampers the interaction between CI and pinacol, thus affording a low yield of diene **2** in [Bmim]CI. Besides the steric hindrance of hexyl group, the aggregation of [Hmim]CI may be another reason for its poor result. It has been reported that with the increment of the alkyl chain length, IL prefers to aggregate, which limits the transfer of electrons and protons.^[15]

Table 1. Effects of solvent on the HPW-catalyzed pinacol dehydration.^[a]

HO OH HPW Solvent, 130 °C	\succ	+
1	2	3

Entry	Solvent	$E_{T}^{N[b]}$	Yield of 2 / % ^[c]	Yield of 3 / % ^{[c}
1	Toluene	0.099	0	93
2	DMSO	0.444	38	13
3	NMP	0.355	17	8
4	[Emim]Cl	-	88	5
5	[Emim]Cl (without HPW)	-	N.R.	N.R.
6	-	-	0	79
7	[Emim]NTf ₂	0.676	0	71
8	[Emim]BF ₄	0.710	6	93
9	[Emim]OAc	-	N.R.	N.R.
10	[Emmim]Cl	-	83	7
11	[Pmim]Cl	-	63	4
12	[Bmim]Cl	0.614	46	2
13	[Hmim]Cl	0.562	N.R.	N.R.
	R = Et, X = CI, [El R = Et, X = BF ₄ , [R = Et, X = NTf ₂ , R = Et, X = OAc,	mim]CI Emim]BF ₄ [Emim]NTf ₂ [Emim]OAc	R = Propyl, X = Cl, [Pmim]C R = Butyl, X = Cl, [Bmim]Cl R = Hexyl, X = Cl, [Hmim]Cl	I N Et [Emmim]Cl
¹³ C si	HO OH 1 1 Pinac Pinac	col, 75.18 ppr col/[Emim]Cl,	n Pinacol/[Emim]6 74.82 ppm Pinacol/[Bmim]6	3F ₄ , 75.18 ppm Cl, 74.96 ppm

[a] Reaction conditions: pinacol (1.0 g), HPW (100 mg), solvent (4.0 g), 130 °C 16 h. [b] E_1^{\aleph} scale was used to indicate the polarity of organic solvents ar room-temperature ionic liquids. The values were obtained from ref 13. [c] Yield of **2** and **3** were detected by GC using tridecane as the internal standard. DMS = Dimethyl sulfoxide. NMP = *N*-Methyl pyrrolidone. N.R. = No Reaction.

To further demonstrate the H-bonding interaction of pinacol an IL, additional NMR experiments were conducted. From the result shown in Table 1, we can see that the ¹³C shift of C1 atom (pinacol in the mixture of [Emim]Cl and pinacol moves upfield (74.82 ppm, $\Delta \delta = 0.36$ ppm), while [Emim]BF₄ exerts no influence on the chemical shift of pinacol. This phenomenon confirms that there exits H-bond between Cl and the hydroxyl group of pinacol (C_{im}⁺Cl⁻⁻⁻HO). Besides, the mixture of [Bmim]Cl and pinacol also gave a decrease in the shift of C1 atom (74.96 ppm, $\Delta \delta = 0.22$ ppm), but its shift value was lower than that in [Emim]Cl. It is because that the bulky butyl group on the ring weakens the H-bond Cl⁻⁻⁻HO, which led to a low diene yield in [Bmim]Cl.

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Figure 1. Yields of 2 and 3 over different acid catalysts. Reaction conditions: pinacol (1.0 g), catalyst (100 mg), [Emim]Cl (4.0 g), 130 $^{\circ}$ C, 16 h.

Subsequently, the catalytic performances of other HPAs and tungstic acid were examined. As shown in Figure 1, other commonly used Keggin-type HPAs such as phosphomolybdic acid (H₃PMo₁₂O₄₀, abbreviated as HPMo) and tungstosilicic acid (H₃SiW₁₂O₄₀, abbreviated as HSiW) were also found to be active for the reaction. The activity sequence for the investigated HPAs is HPW > HSiW > HPMo, which is consistent with the acid strength sequence of these HPAs.^[16] Tungstic acid can promote the dehydration as well but gave an inferior result.



Figure 2. Yields of 2 and 3 over HPW as a function of the reaction temperature. Reaction conditions: pinacol (1.0 g), HPW (100 mg), [Emim]Cl (4.0 g), 16 h.

We further studied the influence of the temperature on the HPW-catalyzed pinacol dehydration. According to Figure 2, a high yield of diene 2 (88%) was achieved when the reaction was carried out at 130 °C for 16 h. With the increment of the temperature to 140 °C or 150 °C, the yield of diene 2 remained comparable. However, after further increasing the temperature to 160 °C, a slight decrease in the yield of 2 was observed. This can be rationalized because too high temperature resulted in the self D-A reaction of diene 2 (Figures S2, S17, and S18).

To fulfill the need of real application, the reusability of the HPW/[Emim]Cl system for the pinacol dehydration was checked. After each usage, the mixture spontaneously separated into two phases. The upper layer (*i.e.* diene **2**, GC purity > 94%) was isolated by decantation. The lower layer (*i.e.* [Emim]Cl, HPW, and the byproduct water) was recovered by desiccation and reused in subsequent runs. From the result shown in Figure 3, the HPW/[Emim]Cl system can be reused for at least four times without significant loss in the acitivity.



Figure 3. Yields of 2 and 3 over HPW as a function of number of recycling tests. Reaction conditions: pinacol (1.0 g), HPW (100 mg), [Emim]Cl (4.0 g), 130 $^{\circ}$ C, 16 h.

Having established the efficient synthesis of diene **2** from the selective dehydration of pinacol, we then directed our attention toward the solvent-free D-A reaction of diene **2** and acrolein into 3-cyclohexenecarbaldehyde **5**, which was a potential precursor for the production of *o*-xylene (OX) by decarbonylation and aromatization (or dehydrogenation) reactions. According to our observation, the D-A reaction of diene **2** and acrolein can proceed spontaneously in the absence of solvent or catalyst. After being stirred at 100 °C for 2 h, diene **2** and acrolein were almost quantitatively converted to compound **5** (Figures S5, S19 and S20).

As the final aim of this work, we studied the production of renewable OX by the decarbonylation/aromatization cascade of 3-cyclohexenecarbaldehyde 5. As we know, Pd/C is a highly decarbonylation^[4e-g,17] active catalyst for both and dehydrogenation^[2h,18]. Due to this reason, we surmised that Pd/C may promote the production of OX by the decarbonylation/aromatization cascade of compound 5. Just as we anticipated, this reaction can take place at 260 °C under solvent-free conditions, although the OX yield was not very high (Table 2, entry 1). It is interesting that the utilization of toluene (or THF) as solvent significantly improved the OX yield (Table 2, entries 2 and 3). Gratifyingly, 97% yield of OX was achieved when the reaction was conducted in ethyl acetate (Table 2, entry 4), a renewable solvent that can be produced by the esterification of biomass-derived ethanol and acetic acid. In contrast, the attempt of using H₂O as a green reaction medium failed (Table 2, entry 5). The temperature also exerts a great influence on the OX yield over the Pd/C catalyst. With the COMMUNICATION

decrease of the temperature to 240 °C (or 220 °C), a lower OX yield was obtained (Table 2, entries 6, 7).

The catalytic activity of other metals for this cascade process was further assessed. Besides Pd/C, Pt/C and Raney Ni were also found to be active for the process although their activity was lower than that of Pd/C (Table 2, entries 8 and 12). In contrast, the Ru/C, Ir/C, and Ni/C catalysts were totally inactive under the investigated conditions (Table 2, entries 9–11).

Table 2. Screening reaction conditions for the transformation of compound 5 into o-xylene 6 via decarbonylation/aromatization cascade.^[a]

+	CHO <u>100 °C, 2 h</u> 99%		Catalyst
2	4	5	6

Entry	Catalyst ^[b]	Solvent	T∕°C	Yield of 6 / % ^[c]
1	Pd/C	-	260	48
2	Pd/C	Toluene	260	88
3	Pd/C	THF	260	87
4	Pd/C	EA	260	97
5	Pd/C	H ₂ O	260	0
6	Pd/C	EA	240	69
7	Pd/C	EA	220	31
8	Pt/C	EA	260	78
9	Ru/C	EA	260	N.R.
10	Ir/C	EA	260	N.R.
11	Ni/C	EA	260	N.R.
12	Raney Ni	EA	260	39

[a] Reaction conditions: compound **5** (0.28 g, 2.0 mmol), catalyst (28 mg), solvent (0 or 20 mL), argon atmosphere, 600 rpm, 12 h. [b] The catalysts were obtained from commercial sources and the metal content of the supported catalysts was 5% by weight. [c] Yields were detected by GC using tridecane as the internal standard. THF = Tetrahydrofuran. EA = Ethyl acetate. N.R. = No Reaction.

To figure out the reaction pathway, we performed the decarbonylation/aromatization cascade of compound **5** over Pd/C catalyst at 220 °C. From Figure S7, the decrease of reaction temperature led to a low OX yield and the appearance of 1,2-dimethylcyclohex-1-ene **7** in the products. On the contrary, 3,4-dimethylbenzaldehyde **8** was not identified in the mixture. This phenomenon indicates that the reaction first undergoes decarbonylation, followed by aromatization to generate OX (Scheme 2). To further confirm this pathway, we conducted the reaction at 260 °C for 4 h and detected 1,2-dimethylcyclohex-1-ene **7** in the mixture as well (Figure S8). From the results, we can also see that the aromatization of **7** is the rate determining step in the process.



Scheme 2. Possible reaction pathway for the conversion of compound 5 to OX

We also tried to combine the D-A reaction and the following decarbonylation/aromatization cascade into a one-pot fashion (Scheme 3). To do this, a mixture of 2,3-dimethylbutadiene and acrolein was first stirred at 100 °C for 2 h. After that, ethyl acetate and Pd/C were added in sequence and the system was stirred at 260 °C for 12 h. As we expected, a high yield (90%) of OX was achieved by this method. In real application, this is advantageous because the isolation of compound **5** can be avoided, which will further improve the efficiency and economy of the process. Taking into account of the optimum diene yield in the first step, the renewable OX was produced in 79% overall yield from pinacol and acrolein via such a two-step route.

Crotonaldehyde is another commonly used unsaturated aldehyde that can be prepared by the self-aldol condensation of biomass-derived acetaldehyde. 1,2,4-Trimethylbenzene (TMB) is a bulk chemical that is widely used as a gasoline additive and a precursor to trimellitic anhydride for the production of plasticizers for PVC products (such as tri(2-ethylhexyl) trimellitate, TOTM) and polyester resins. Analogously, a twostep route for the production of renewable 1,2,4trimethylbenzene from pinacol and crotonaldehyde was also proposed (Scheme 3). The detailed information was given in the supporting information (Figures S11 and S12). A high overall yield of 1,2,4-trimethylbenzene (83%) was achieved through this sustainable process.



Scheme 3. A sustainable two-step route for the production of renewable oxylene and 1,2,4-trimethylbenzene.

In summary, we have developed an efficient and sustainable two-step route for the production of OX from biomass-derived pinacol and acrolein. In the first step, the HPW-catalyzed pinacol dehydration in [Emim]Cl selectively afforded 2,3-

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dimethylbutadiene. The utilization of [Emim]Cl as solvent significantly improved the 2,3-dimethylbutadiene selectivity which can be ascribed to the H-bonding interaction between Cl and the hydroxyl group of pinacol. Besides, the stabilization of the carbocation intermediate by the surrounding anion Cl⁻ may be another reason for the high selectivity. Notably, the good reusability of the HPW/[Emim]Cl system can reduce the waste output and production cost. In the second step, D-A reaction of 2,3-dimethylbutadiene with acrolein and the following Pd/Ccatalyzed decarbonylation/aromatization cascade were successfully combined into a one-pot fashion. The intensified two-step process could efficiently produce renewable OX in 79% overall yield. Analogously, biomass-derived crotonaldehyde and pinacol can also serve as the feedstocks for the production of 1,2,4-trimethylbenzene.

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Keywords: Biomass • *o*-Xylene • Pinacol dehydration • acrolein • decarbonylation and aromatization

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Layout 1:

COMMUNICATION

Herein we develop an efficient and sustainable two-step route for the production of o-xylene from biomassderived pinacol and acrolein. Noteworthy features of this route include a recyclable HPW/[Emim]Cl system for the selective pinacol dehydration to 2,3-dimethylbutadiene, and a one-pot process for the production of OX by the D-A reaction of 2,3-dimethylbutadiene with acrolein and the following decarbonylation/aromatization cascade.



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Sustainable Production of o-Xylene from Biomass-Derived Pinacol and Acrolein