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#### Acceptor-free dehydrogenation of 4-hydroxy-3-methoxybenzyl alcohol to vanillin

#### over palladium complex

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#### Abstract

Pd<sup>0</sup> immobilized on surface-functionalized SBA-15 via in-situ H<sub>2</sub>-reduction were demonstrated as a highly efficient acceptor-free dehydrogenation catalyst for the oxidation of 4-hydroxy-3-methoxybenzyl alcohol to vanillin in excellent yield without additional oxidant in the reaction system. Notably, the reaction medium water could be readily reused without further purification, and the catalyst was highly effective for a variety of alcohols. Moreover, the heterogeneous catalyst could be easily recovered and reused without conspicuous loss of activity indicating excellent potential for industrial application.

#### Introduction

Vanillin is an important aroma molecule because of its widespread applications in food,<sup>1</sup> cosmetic,<sup>2</sup> fine chemical industries,<sup>3</sup> pharmaceutical<sup>4</sup> and nutraceutical.<sup>5</sup> Currently, more than 99% of vanillin is produced by chemical synthesis especially through the glyoxylic acid method (Scheme 1),<sup>6</sup> however, the toxic oxidants<sup>7</sup> and strongly alkaline were used accompanying complicated separation process for harvesting high yields. For example, a cobalt schiff base with ionic substituents on the ligand was used as a catalyst for the oxidation of 4-methyl guaiacol to vanillin (Scheme 2) showing good activity (conversion = 100%, Selectivity = 90%), but the high concentration of NaOH was used, furthermore, the reactions were conducted in organic solvent and the recyclability of the catalyst was disappointing.<sup>8</sup> Over the past few years, extensive efforts have been devoted toward the development of new strategies for the synthesis of vanillin from both economic and green chemistry viewpoints. Water, in contrast to common organic media has gained special attention

because it is much cheaper, nontoxic, abundantly available and environment-friendly.<sup>9</sup> Therefore, there is every reason to believe that water as a solvent in organic reactions is the better options because most of the organic solvents are toxic and volatile.<sup>10</sup> As a matter of fact, in 2012, Augugliaro et al. reported the synthesis of vanillin in water by using the photocatalytic method for the first time, however, the selectivity ranging from 1.4 to 21mol% with respect to the converted substrate.<sup>11</sup>

Nowadays, considerable attention has been paid toward the oxidative dehydrogenation of alcohols to aldehydes and ketones with palladium-based catalysts<sup>12</sup> due mainly to the high activity and selectivity even under atmospheric pressure.<sup>13</sup> As we all known, although a remarkable number of reports on the improvement of the performance of Pd catalysts have been reported, but to our great pity, until now, most of them suffer from the requirement for acid or base additives, the toxic organic solvents and the hydrogen acceptor such as quinone, nitrobenzene, or an olefin. Recently, there have been reports of heterogeneous metal catalysts being applied to acceptor-free alcohol dehydrogenation without additional oxidant in a liquid phase.<sup>14</sup> Undoubtedly, this would represent a much safer, and environmental friendly process, which is in line with the concept of green chemistry.

On this basis, it is of particular interest to know whether it is possible to get high value-added product vanillin by using heterogeneous palladium-containing catalyst in water medium under mild conditions in the absence of any additives. We report here that surface-functionalized SBA-15-supported  $Pd^0$  (Scheme 3) acts as an effective heterogeneous catalyst for acceptor-free dehydrogenation of vanillyl alcohol to vanillin (Scheme 4) using water as the solvent under an atmospheric pressure of N<sub>2</sub>. What is more exhilarating is that the catalyst has good performance in a variety of alcohols, and show excellent chemical and thermal stability as well as good recyclability.



Scheme 1 The synthesis of vanillin through the glyoxylic acid method

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Scheme 2 Catalytic oxidation of 4-methyl guaiacol to vanillin





Scheme 4 Acceptor-free dehydrogenation of vanillyl alcohol to vanillin in water

#### Experimental

#### **Preparation of SBA-15**

The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers.<sup>15</sup> In a typical preparation procedure, 4.0 g of Pluronic P123 was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at

35 °C. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 °C for 20 h. The mixture was aged at 80 °C overnight without stirring. After completion of the reaction, the solid was filtered off and washed with deionized water, and dried overnight. The surfactant molecules were removed thoroughly with hot ethanol/water using a Soxhelet apparatus for 24 h. It was dried in air at 100 °C for 12h.

#### Synthesis of surface-functionalized SBA-15 (B)

In order to synthesis surface-functionalized SBA-15, 0.356g (2mmol) of pyridine-2-carbonyl chloride hydrochloride and [3-(2-aminoethylamino)propyl]trimethoxysilane 0.445 g (2 mmol) were first suspended in 10 mL of dry  $CH_2Cl_2$  in a 50 mL round-bottomed flask. The flask was placed in the ice-water bath under vigorous stirring conditions. After that, the mixture was stirred at room temperature for another 6 h, and the solvent was removed under reduced pressure to obtain A (Scheme 3). The resulting SBA-15 (6 g) was allowed to react with A in refluxing dry toluene (150 mL) under nitrogen for 24 h. The solid was filtered off and washed thoroughly with toluene and ethanol to obtain B (Scheme 3).

## Synthesis of Pd<sup>0</sup> catalyst

The catalyst was then prepared by stirring a mixture of **B** (4 g) and palladium acetate (0.62 mmol, 0.14 g) in dry acetone (100 mL) at room temperature for 24 h. The brown solid was filtered, washed with acetone and ethanol. It was then dried at 140 °C under vacuum overnight. After this process, the resulting solid LnPd(II) was suspended in deionized water and reduced by  $H_2$  for 12 h to obtain catalyst in situ. The powders were filtered, washed with ethanol and deionized water, and dried at 80 °C overnight to obtain the catalyst LnPd, the loading of Pd in the final catalyst was quantified by ICP.

#### General oxidation procedure

Typical procedure given for the oxidation of vanillyl alcohol: A mixture of catalyst (30 mg catalyst LnPd, 4  $\mu$ mol of palladium), vanillyl alcohol (0.2 g, 1.3 mmol), and H<sub>2</sub>O (20 mL) were added into a 50 mL three-necked round-bottomed flask, which was fitted with magnetic stirrer. The reaction was kept at the temperature of 80 °C under

 $N_2$ . Aliquots of the sample were taken from the reaction mixtures at different times, extracted with ethyl acetate and quantified by HPLC. Oxidation of various alcohols was conducted under the same experimental conditions as above.

Recycling tests were carried out by repeatedly using catalyst LnPd in nine consecutive reactions. After each reaction, the catalyst was separated by filtration from the reaction solution, washed with deionized water and ethanol, dried at 353 K under vacuum for 2 h, and reused in the next run under the same reaction conditions.

#### **Results and discussion**

The percentage composition of palladium in the final catalyst is 1.42 wt% quantified by ICP. The small-angle X-ray diffraction patterns of SBA-15 and palladium catalyst are shown in Fig. 1. The fresh SBA-15 displays a strong diffraction peak and two small diffraction for the 100, 110 and 200 planes corresponding to a hexagonal lattice, however, the decrease in peak intensities was observed after immobilization of the Pd complex onto SBA-15, while the  $d_{100}$  peak was almost unchanged. These results indicate that periodicity of SBA-15 was maintained well in the palladium catalysts.

Fig. 2 shows the FT-IR spectra of **B** and catalyst LnPd in the range of 1350-1800 cm<sup>-1</sup>. The infrared spectrum of **B** shows a characteristic band at 1650 cm<sup>-1</sup> assigning to the C=N double bond. After immobilization of Pd on **B**, this band was shifted to 1635 cm<sup>-1</sup>, presumably due to the interaction between metal and ligand. Similar shifting of the band to lower wavenumbers has been also observed in previous studies.<sup>16</sup> Fig. 3 depicts the diffuse reflectance UV-vis spectra of **B** and catalyst LnPd, the UV-vis spectra display strong absorption bands at 275 nm for all the samples. Nevertheless, when palladium catalyst was loaded on **B**, the presence of a very broad band centered at 400 nm is also observed, indicating the coordination chemical bonds between ligand and Pd nanoparticle.

The SEM image of catalyst is similar to SBA-15 raw material (Fig. 4), showing the characteristic morphology of SBA-15 unchanged, and the TEM image of catalyst is shown in Fig. 5, The specific surface areas 474 m<sup>2</sup>·g<sup>-1</sup> was measured for the catalyst, which significantly decreased compared to the starting SBA-15 ( $706 \text{ m}^2 \cdot \text{g}^{-1}$ ). It can

be noted that all of the samples exhibit type IV isotherms profile (Fig. S1<sup>+</sup>) with a sharp hysteresis loop, which is characteristic of the highly ordered mesoporous materials.<sup>17</sup> The corresponding physical parameters are collected in Table 1, and the BJH pore size distribution is depicted in Fig. S2.<sup>+</sup> It showed that the average pore diameters and specific areas of SBA-15, **B** and catalyst LnPd decrease in sequence, which is in good agreement with the fact that the surface modification indeed happened inside the primary mesopores of the SBA-15. The presence of organic functional groups was further confirmed by NMR spectroscopy.<sup>29</sup>Si NMR spectra for **B** and catalyst LnPd are shown in Fig. 6, distinct resonances can be observed for the siloxane  $[Q^n = Si-(OSi)_n - (OH)_{4-n}, n=2-4; Q^4 \text{ at } -111 \text{ ppm and } Q^3 \text{ at } -101 \text{ ppm}]$ and organosiloxane  $[T^m = RSi(OSi)_m - (OH)_{3-m}, m=1-3; T^3 at -65 ppm and T^2 at -57$ ppm] species.<sup>18</sup> The appearance of  $T^3$  and  $T^2$  peaks confirms a strong covalent linkage between the organic groups and the silica surface. The obtained materials were also characterised by means of solid state <sup>13</sup>C NMR spectroscopy. In the <sup>13</sup>C NMR spectrum (Fig. 7), the strong signal at 47.8 ppm is attributed to the methylene carbons (C<sub>c</sub>, C<sub>d</sub>, C<sub>e</sub>), the peaks for C<sub>c</sub>, C<sub>d</sub> and C<sub>e</sub> cannot be distinguished because of conformational heterogeneity,<sup>19</sup> this phenomenon was also observed in previous studies.<sup>20</sup> The signal at 175 ppm dramatically decreases in height indicates strong chemical bonding between the Pd and amide group, in turn, effects the peak  $C_{\rm f}$  which attached to the amide group. The continued presence of the peak at 175 ppm suggests that the amide groups are not yet saturated with Pd. The thermal stability of B, catalyst LnPd were demonstrated by TGA measurement and it can be observed that the thermal stability almost invariable (Fig. S3<sup>+</sup>, Fig. S4<sup>+</sup>). Three main weight loss peaks can be seen from the DTG curve. The first weight loss peak observed at about 75 °C is due to physically adsorbed water, and the second decomposition peak centered at about 337 °C is attributed from the decomposition of incompletely removed surfactant<sup>21</sup> while the third weight loss peak at about 426 °C can be attributed to the decomposition of the organic Pd complex.

The oxidative dehydrogenation of vanillyl alcohol was studied with 1.42wt % Pd

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catalyst LnPd at 80 °C. As depicted in Table 2, the conversion of vanillyl alcohol is 100 % and the yield of vanillin is >99 % whether it is under the condition of nitrogen or air environment. It is worth mentioning that the reaction in N<sub>2</sub> proceeded at a rate comparable to that in air, indicating that the reaction is hydrogen acceptor-free oxidation reaction. With the aforementioned encouraging results, we further explored the versatility of the catalytic system. As summarized in Table 3, high-yield dehydrogenation was achieved for aromatic alcohols under oxidant-free and anaerobic conditions, which was comparable with the reported reactions under aerobic and acid or base additives conditions. The catalytic activity for the oxidation of various aromatic alcohols is different, especially for diphenylmethanol, which reacted slow because the adsorption of diphenylmethanol onto catalyst is difficult due to steric hindrance. A similar phenomenon has also been observed in previous reports.<sup>22</sup> It should be noted that the previous acceptor-free dehydrogenation of alcohols suffer from high reaction temperature (200-350°C),<sup>14b, 23</sup> low yields, <sup>23, 24</sup> reaction in organic

solvent,<sup>14a</sup> our results represents a novel non-NaOH, non-organic, dehydrogenation oxidation route for the preparation of carbonyl compounds in water, without the addition of hydrogen acceptor.

It is widely held that metallic state (Pd<sup>0</sup>) even in the presence of molecular oxygen could hydrogenolysis of benzyl-type alcohols with the coproduct hydrogen,<sup>25</sup> but according to the table 3, the commonly accepted C-O bond hydrogenolysis phenomenon was not happened in this regime. This fact combined with the presence of amide ligand suggests that catalyst with stronger basicity but no acidity afford

higher selectivity towards benzaldehyde.<sup>19</sup> It strongly indicates that the amide ligands in catalyst not only stabilize the palladium, but also provide alkaline sites for excellent selectivity towards benzaldehyde. Thus, the present catalytic system makes the synthesis of carbonyl compounds a high efficient and environmentally benign chemical process.

To get an insight into the acceptor-free dehydrogenation reaction, special care was taken to conduct two sets of experiments. First, catalyst  $LnPd(\Box)$  was synthesized at the same Pd loading (1.42 wt%) with the as-prepared catalyst LnPd(0), but without the in-situ reduction. The oxidation of vanillyl alcohol was then carried out with catalyst  $LnPd(\Box)$  under the identical conditions. Surprisingly, the conversion of vanilly alcohol was approximately zero. Second, we added additive  $K_2CO_3$  (1.0 equiv) into this reaction, as can be seen in table 4, the conversion of vanilly alcohol dramatically increased and reach the maximum 100% when the reaction time fixed at 17 h. This suggested that  $Pd(\Box)$  species in the catalyst are particularly stable against reducing reagents (alcohols) without a base ( $K_2CO_3$ ) acting as a promoter to cleave the O-H bond to form an alkoxide intermediate, which is in accordance with the previous reports.<sup>26, 27</sup> In comparison with the catalyst LnPd( $\Box$ ), the catalyst LnPd(0) shows higher activity with a significant decrease in reaction time, implying that when  $Pd(\Box)$  species were used for the synthesis of vanillin, there must be an induction period in which a concomitant change of the alcohol to Pd-alcoholate, which in turn triggers the formation of Pd(0) and aldehyde (carbonyl compounds). So, it can be supposed that basic support is not powerful enough to promote  $Pd(\Box)$  species to cleave the O-H bond of the alcohol to form a Pd-alcoholate species, metallic Pd is more effective than  $Pd(\Box)$  species no matter with or without additives. In other words, our results demonstrate that  $Pd(\Box)$  exhibit hardly any catalytic activity for alcohol oxidation in the case of no additives or cocatalysts, whereas reduced Pd catalyst is none the less active in water.

Upon consideration of the above results and previous reports,<sup>28</sup> a plausible reaction

pathway was illustrated in Scheme 5. For catalyst LnPd(II), oxidation reaction can not take place without additives, while with the help of  $K_2CO_3$ , the reaction initiated by formation of a palladium(II)-alkoxide intermediate,<sup>29</sup> which is suffered from  $\beta$ -hydride elimination accompanied by the generation of aldehyde and LnPd<sup>0</sup> (**b**). But the Pd-based catalyst is irreversible due to the oxidant-free system. Then an oxidative addition of O-H band from alcohol (**a**) to the coordinately unsaturated Pd<sup>0</sup> species affords a Pd-alcoholate species, which is transformed into the corresponding carbonyl compounds and a palladium dihydride (**c**) with a  $\beta$ -hydride elimination. Then, hydrogen is liberated from **c** along with the regeneration of Pd<sup>0</sup> species. The above mechanism can also explain why the reaction time is longer with Pd( $\Box$ ) species as catalyst.

Hot-filtration experiments were carried out with the catalyst <u>Ln</u>Pd as follows, dehydrogenation of vanillyl alcohol to vanillin was conducted under the same experimental conditions as the aforementioned, and the catalyst was hot-filtered off after 1 h (conversion 18%). The catalyst-free solution (the filtrate) was allowed to continue reaction for another 6 h, but neither further reaction was observed (HPLC analysis), nor Pd leaching into the solution was detected by ICP. Thus, the present alcohol oxidation undoubtedly proceeds on the Pd species located on the functionalized SBA-15 surface, and that the catalytic reaction was truly heterogeneous under the applied conditions. Furthermore, a leaching experiment of Pd after 5th cycle was conducted under the same experimental procedure as above, the catalyst was removed after 1 h (conversion 17.8%), and there was a slight increase in conversion (18.2% after 6 h). Therefore, the palladium leaching is negligible.

Recycling experiments were carried out with the catalyst LnPd at 80 °C. After each run, the catalyst was separated by filtration, washed with deionized water and absolute ethyl alcohol, and then dried at 80 °C under vacuum for 2 h. The filtrate was extracted with ethyl acetate (4×30 mL), after that, the remaining water and the dried catalyst were reused in the next run. Varying amounts of water was added into the reaction system in order to maintain the content of water (20 mL). The results shown in Table 5 indicate that the catalyst gave the vanillin in >99% yield even after 9 runs,

and the slight increase in reaction time is probably due to the minimal lose of the Pd species during the recovery. TEM image of the catalyst LnPd after multiple uses showed in Fig. 5, compared with the fresh catalyst, the mesoporous structure of the used catalyst almost constant. A comparison of IR spectra of catalyst LnPd before and after several reaction runs did not reveal significant differences (Fig. S5†), no peak at 1650 cm<sup>-1</sup> was observed, indicating that immobilized Pd has always been there. Moreover, as can be observed in Fig. S6†, compared to the catalyst LnPd, the UV-vis absorption spectra of the recycled catalyst LnPd has almost unchanged. Therefore, the catalyst can be promising catalytic materials in dehydrogenation of vanillyl alcohol to vanillin reaction with high activity and stability.

#### Conclusion

In summary, we have developed a highly recoverable and efficient palladium-based catalyst for acceptor-free dehydrogenation of vanillyl alcohol to vanillin in water under mild conditions. Furthermore, the recycled water can be successfully re-used in the next round without any bad effect on product properties. This approach may possess potential for industrial applications in the manufacture of vanillin. Moreover, we have also demonstrated that the catalyst is suitable for various alcohols, therefore meeting the increasing demands for environmentally friendly chemical processes.

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#### List of tables and figures

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Fig. 1 XRD patterns of SBA-15 and the catalyst LnPd.



Fig. 2 IR spectra of B and the catalyst LnPd.

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Fig. 3 UV-vis absorption spectra of B and the catalyst LnPd.



Fig. 4 SEM images of the SBA-15 raw material (left) and catalyst LnPd (right).



Fig. 5 TEM images of catalyst LnPd (a) and recycled catalyst (b).



Fig. 6  $^{29}\mathrm{Si}$  NMR spectrum of the B (left) and Catalyst LnPd (right).



Fig. 7<sup>13</sup>C NMR spectrum of the B (left) and Catalyst LnPd (right).

Sample	$S_{BET}(m^2g^{-1})$	Pore Volume (cm <sup>3</sup> /g)
SBA-15	706	1.08
В	488	0.89
Catalyst	474	0.86

**Table 1** Porosity parameters of SBA-15, **B**, the Catalyst LnPd

Table 2 Influence of reaction atmosphere in the oxidation of vanillyl alcohol<sup>a</sup>

Entry	reaction atmosphere	Time (h)	Yield (%)
1	air	7	>99
2	$N_2$	7	>99

<sup>a</sup> Reaction conditions: vanillyl alcohol (0.2 g), temperature 80 □, catalyst LnPd 30 mg, water (20 mL).

Table 3 (	Catalytic	dehydrogenation of	various	alcohols of	over the ca	talyst LnPd <sup>a</sup>

Entry	Substrate	Product	Time (h)	Yield (%)
1	C) OH	СНО	2	>99
2	OH		5	>99
3	OH		17	>99

 $^a$  Reaction conditions: alcohol (0.2 g), temperature 80  $\square,$  catalyst 30 mg, water (20 mL),  $N_2$  balloon.

Entry	Catalyst	Time (h)	Conv. (%)	Sel. (%)
1	LnPd(□)	20	0	0
2	$LnPd(\Box)^{b}$	17	100	>99
3	LnPd(0)	7	100	>99

Table 4 The oxidation of vanillyl alcohol with different catalysts <sup>a</sup>

<sup>a</sup> Reaction conditions: vanillyl alcohol (0.2 g), temperature 80  $\Box$ , catalyst 30 mg, water (20 mL), <sup>b</sup>

LnPd(II) with K<sub>2</sub>CO<sub>3</sub> (1.0 equiv.) in the reaction system.

Cycle	Time (h)	Conv. (%)	Yield (%)
1	7	100	>99
2	7	100	>99
3	7	100	>99
4	8	100	>99
5	8	100	>99
6	8.5	100	>99
7	9	100	>99
8	9.2	100	>99
9	11	100	>99

Table 5 The recycling study of the catalyst and water in the oxidation of vanillyl alcohol <sup>a</sup>

 $^a$  Reaction conditions: vanillyl alcohol (0.2 g), temperature 80  $^\circ C$ , catalyst LnPd 30 mg, water (20mL),  $N_2$  balloon.



Scheme 5 Indicates the reaction pathways for vanillin.

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## **Graphic Abstract:**

Acceptor-free dehydrogenation of 4-hydroxy-3-methoxybenzyl alcohol to vanillin

over palladium complex without additional oxidant in water

