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Acceptor-free dehydrogenation of 4-hydroxy-3-methoxybenzyl alcohol to vanillin over a palladium complex†

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Pd⁰ immobilized on surface-functionalized SBA-15 *via in situ* H₂-reduction was demonstrated as a highly efficient acceptor-free dehydrogenation catalyst for the oxidation of 4-hydroxy-3-methoxybenzyl alcohol to vanillin in excellent yield without an 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, a heterogeneous catalyst could be easily recovered and reused without conspicuous loss of activity indicating excellent potential for industrial application.

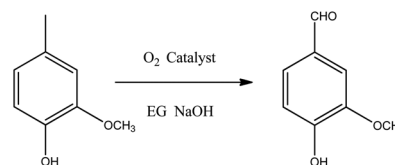
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Introduction

Vanillin is an important aroma molecule because of its wide-spread applications in food,¹ cosmetic,² fine chemical industries,³ pharmaceuticals⁴ and nutraceuticals.⁵ Currently, more than 99% of vanillin is produced by chemical synthesis especially through the glyoxylic acid method (Scheme 1);⁶ however, toxic oxidants⁷ and strongly alkaline conditions were used accompanying a 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 a high concentration of NaOH was used; furthermore, the reactions were conducted in an organic solvent and the recyclability of the catalyst was disappointing.⁸ 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

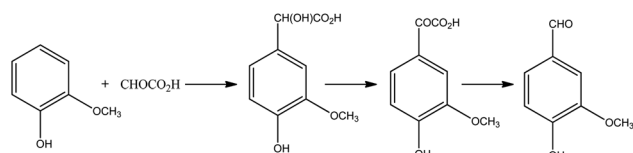


Scheme 2 Catalytic oxidation of 4-methyl guaiacol to vanillin.

much cheaper, nontoxic, abundantly available and environmentally-friendly.⁹ Therefore, there is every reason to believe that water as a solvent in organic reactions is a better option because most of the organic solvents are toxic and volatile.¹⁰ 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 ranged from 1.4 to 21 mol% with respect to the converted substrate.¹¹

Nowadays, considerable attention has been paid toward the oxidative dehydrogenation of alcohols to aldehydes and ketones with palladium-based catalysts¹² mainly due to their high activity and selectivity even under atmospheric pressure.¹³ As we all know, a remarkable number of reports on the improvement of the performance of Pd catalysts have been reported, but to our great pity, most of them require acid or base additives, toxic organic solvents and a hydrogen acceptor such as quinone, nitrobenzene, or an olefin. Recently, there have been reports on heterogeneous metal catalysts being applied to acceptor-free alcohol dehydrogenation without an additional oxidant in the liquid phase.¹⁴ Undoubtedly, this would represent a much safer and environmentally friendly process, which is in line with the concept of green chemistry.

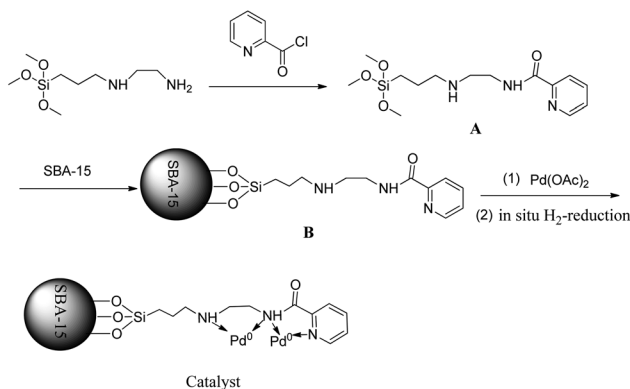
On this basis, it is of particular interest to know whether it is possible to get the high value-added product vanillin by using a heterogeneous palladium-containing catalyst in water



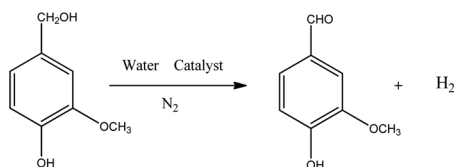
Scheme 1 The synthesis of vanillin through the glyoxylic acid method.

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Scheme 3 Synthesis of heterogeneous palladium catalysts.



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

medium under mild conditions in the absence of any additives. We report here that surface-functionalized SBA-15-supported Pd⁰ (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 N₂. 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.

Experimental

Preparation of SBA-15

The synthesis of SBA-15 has been achieved using a known procedure described by Stucky and his co-workers.¹⁵ 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, washed with deionized water, and dried overnight. The surfactant molecules were removed thoroughly with hot ethanol/water using a Soxhlet apparatus for 24 h. It was dried in air at 100 °C for 12 h.

Synthesis of surface-functionalized SBA-15 (B)

In order to synthesize surface-functionalized SBA-15, 0.356 g (2 mmol) of pyridine-2-carbonyl chloride hydrochloride and 0.445 g (2 mmol) [3-(2-aminoethylamino)propyl]trimethoxy-

silane were first suspended in 10 mL of dry CH₂Cl₂ in a 50 mL round-bottomed flask. The flask was placed in an 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 a Pd⁰ 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, and 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 with H₂ for 12 h to obtain the 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

A typical procedure is given for the oxidation of vanillyl alcohol: a mixture of catalyst (30 mg catalyst LnPd, 4 μmol of palladium), vanillyl alcohol (0.2 g, 1.3 mmol), and H₂O (20 mL) was added into a 50 mL three-necked round-bottomed flask, which was fitted with a magnetic stirrer. The reaction was kept at 80 °C under N₂. 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 the 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 peaks 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 d₁₀₀ peak was almost unchanged. These results indicate that the periodicity of SBA-15 was maintained well in the palladium catalysts.

Fig. 2 shows the FT-IR spectra of **B** and the catalyst LnPd in the range of 1350–1800 cm⁻¹. The infrared spectrum of **B** shows a characteristic band at 1650 cm⁻¹ assigned to the

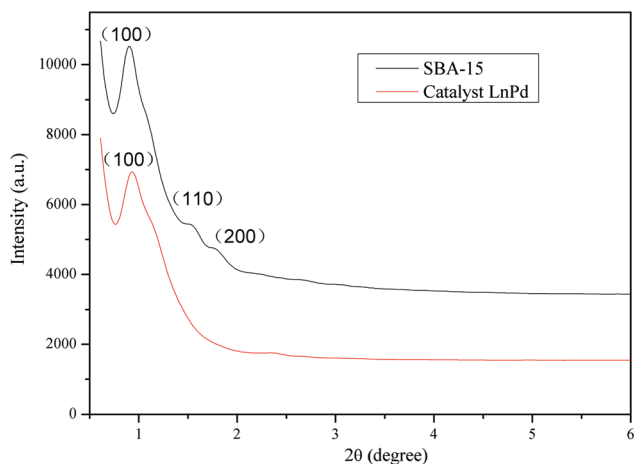


Fig. 1 XRD patterns of SBA-15 and the catalyst LnPd.

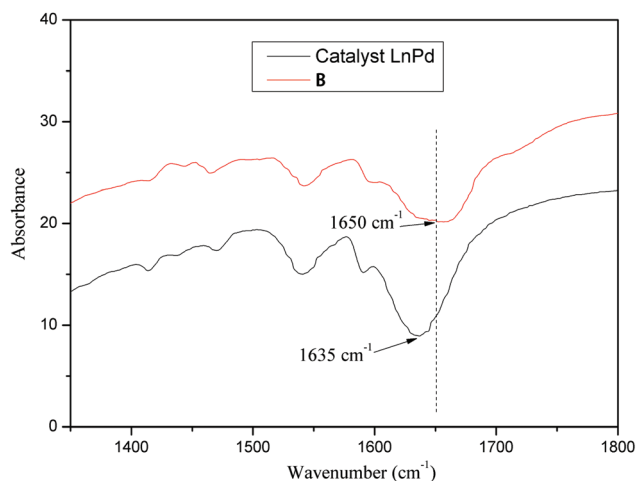


Fig. 2 IR spectra of B and the catalyst LnPd.

C=N double bond. After immobilization of Pd on B, this band was shifted to 1635 cm^{-1} , presumably due to the interaction between the metal and ligand. A similar shifting of the band to lower wavenumbers has also been observed in previous studies.¹⁶ Fig. 3 depicts the diffuse reflectance UV-vis spectra of B and the catalyst LnPd; the UV-vis spectra display strong absorption bands at 275 nm for all the samples. Nevertheless, when a 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 the ligand and Pd nanoparticles.

The SEM image of the catalyst is similar to the SBA-15 raw material (Fig. 4), showing the characteristic morphology of SBA-15 unchanged, and the TEM image of the catalyst is shown in Fig. 5; the specific surface area ($474\text{ m}^2\text{ g}^{-1}$) was measured for the catalyst, which significantly decreased compared to the starting SBA-15 ($706\text{ m}^2\text{ g}^{-1}$). It can be noted that all of the samples exhibit the type IV isotherm profile (Fig. S1†) with a sharp hysteresis loop, which is characteristic

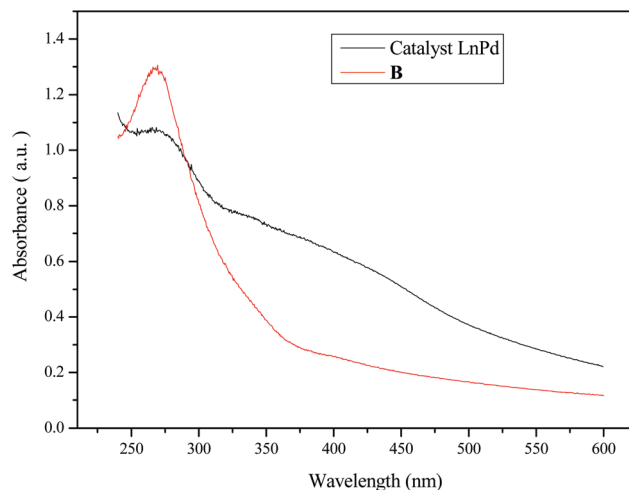


Fig. 3 UV-vis absorption spectra of B and the catalyst LnPd.

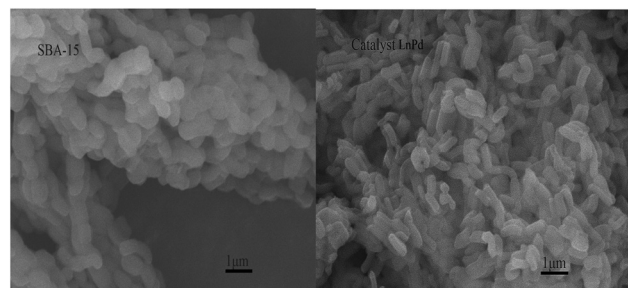


Fig. 4 SEM images of the SBA-15 raw material (left) and catalyst LnPd (right).

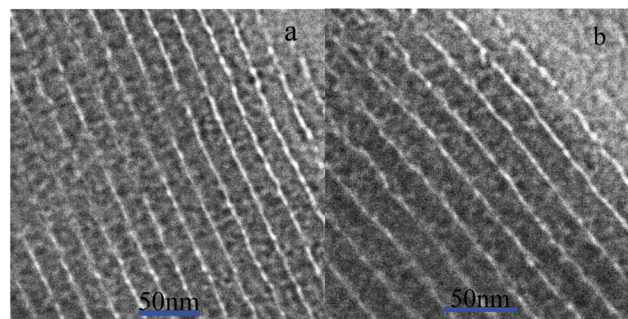


Fig. 5 TEM images of the catalyst LnPd (a) and recycled catalyst (b).

of the highly ordered mesoporous materials.¹⁷ The corresponding physical parameters are collected in Table 1, and the BJH pore size distribution is depicted in Fig. S2.† It showed

Table 1 Porosity parameters of SBA-15, B, and the catalyst LnPd

Sample	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	Pore volume ($\text{cm}^3\text{ g}^{-1}$)
SBA-15	706	1.08
B	488	0.89
Catalyst	474	0.86

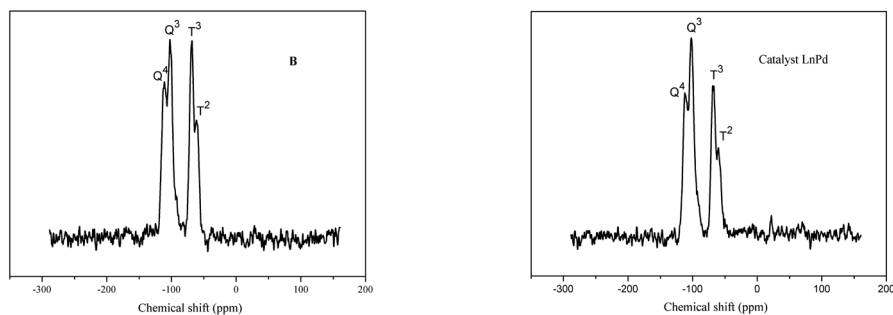


Fig. 6 ^{29}Si NMR spectrum of **B** (left) and the catalyst LnPd (right).

that the average pore diameters and specific areas of SBA-15, **B** and the catalyst LnPd decrease in a sequence, which is in good agreement with the fact that the surface modification indeed occurred inside the primary mesopores of SBA-15. The presence of organic functional groups was further confirmed by NMR spectroscopy. ^{29}Si NMR spectra of **B** and the catalyst LnPd are shown in Fig. 6, distinct resonances can be observed for the siloxane [$\text{Q}^n = \text{Si}-(\text{OSi})_n-(\text{OH})_{4-n}$, $n = 2-4$; Q^4 at -111 ppm and Q^3 at -101 ppm] and organosiloxane [$\text{T}^m = \text{RSi}(\text{OSi})_m-(\text{OH})_{3-m}$, $m = 1-3$; T^3 at -65 ppm and T^2 at -57 ppm] species.¹⁸ 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 ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum (Fig. 7), the strong signal at 47.8 ppm is attributed to the methylene carbons (C_c , C_d , C_e), the peaks for C_c , C_d and C_e cannot be distinguished because of conformational heterogeneity,¹⁹ this phenomenon was also observed in previous studies.²⁰ The signal at 175 ppm dramatically decreases in height indicating strong chemical bonding between the Pd and amide group, which in turn effects the peak C_f which is 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** and the catalyst LnPd was demonstrated by TGA measurement and it can be observed that the thermal stability is almost invariable (Fig. S3 and S4†). 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 the physically adsorbed water, and the second

decomposition peak centered at about 337 °C is attributed to the decomposition of the incompletely removed surfactant,²¹ 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 1.42 wt% Pd 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 nitrogen or air. It is worth mentioning that the reaction in N_2 proceeded at a rate comparable to that in air, indicating that the reaction is a 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 to the reported reactions under aerobic and acid or base additive conditions. The catalytic activity for the oxidation of various aromatic alcohols is different, especially for diphenylmethanol, which reacted slowly because the adsorption of

Table 2 Influence of the reaction atmosphere on the oxidation of vanillyl alcohol^a

Entry	Reaction atmosphere	Time (h)	Yield (%)
1	Air	7	>99
2	N_2	7	>99

^a Reaction conditions: vanillyl alcohol (0.2 g), temperature (80 °C), catalyst LnPd (30 mg), and water (20 mL).

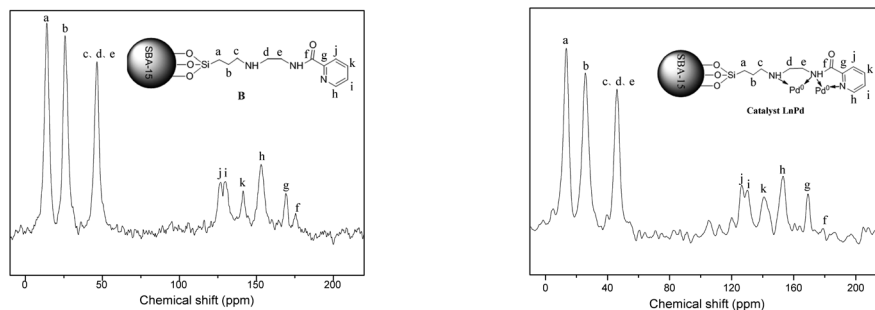








Fig. 7 ^{13}C NMR spectrum of **B** (left) and the catalyst LnPd (right).

Table 3 Catalytic dehydrogenation of various alcohols over the catalyst LnPd^a

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

^a Reaction conditions: alcohol (0.2 g), temperature (80 °C), catalyst (30 mg), water (20 mL), and a N₂ balloon.

diphenylmethanol onto the catalyst is difficult due to steric hindrance. A similar phenomenon has also been observed in previous reports.²² It should be noted that the previous acceptor-free dehydrogenation of alcohols suffers from drawbacks such as high reaction temperatures (200–350 °C),^{14b,23} low yields,^{23,24} and reaction in an organic solvent;^{14a} our results represent a novel non-NaOH, non-organic, dehydrogenation oxidation route for the preparation of carbonyl compounds in water, without the addition of a hydrogen acceptor.

It is widely held that the metallic state Pd⁰ even in the presence of molecular oxygen could perform hydrogenolysis of benzyl-type alcohols with the co-product hydrogen,²⁵ but according to Table 3, the commonly accepted C–O bond hydrogenolysis phenomenon was not observed in this regime. This fact combined with the presence of an amide ligand suggests that a catalyst with stronger basicity but no acidity affords higher selectivity towards benzaldehyde.¹⁹ This strongly indicates that the amide ligands in the catalyst not only stabilize palladium, but also provide alkaline sites for excellent selectivity towards benzaldehyde. Thus, the present catalytic system makes the synthesis of carbonyl compounds a highly efficient and environmentally benign chemical process.

To gain an insight into the acceptor-free dehydrogenation reaction, special care was taken to conduct two sets of experiments. First, the catalyst LnPd(II) 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 the catalyst LnPd(II) under identical conditions. Surprisingly, the conversion of vanillyl alcohol was approximately zero. Second, we added additive K₂CO₃ (1.0 equiv.) into this reaction, as can be seen in Table 4,

Table 4 The oxidation of vanillyl alcohol with different catalysts^a

Entry	Catalyst	Time (h)	Conv. (%)	Sel. (%)
1	LnPd(II)	20	0	0
2	LnPd(II) ^b	17	100	>99
3	LnPd(0)	7	100	>99

^a Reaction conditions: vanillyl alcohol (0.2 g), temperature (80 °C), catalyst (30 mg), and water (20 mL). ^b LnPd(II) with K₂CO₃ (1.0 equiv.) in the reaction system.

the conversion of vanillyl alcohol dramatically increased and reached the maximum 100% when the reaction time was fixed at 17 h. This suggested that Pd(II) species in the catalyst are particularly stable against reducing reagents (alcohols) without a base (K₂CO₃) acting as a promoter to cleave the O–H bond to form an alkoxide intermediate, which is in accordance with the previous reports.^{26,27} In comparison with the catalyst LnPd(II), the catalyst LnPd(0) shows higher activity with a significant decrease in reaction time, implying that when Pd(II) species were used for the synthesis of vanillin, there must be an induction period in which a concomitant change of the alcohol to Pd-alkoholate occurs, 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(II) species to cleave the O–H bond of the alcohol to form a Pd-alkoholate species, metallic Pd is more effective than Pd(II) species no matter with or without additives. In other words, our results demonstrate that Pd(II) exhibits hardly any catalytic activity for alcohol oxidation in the case of no additives or cocatalysts, whereas the reduced Pd catalyst is none the less active in water.

Upon consideration of the above results and previous reports,²⁸ a plausible reaction pathway is illustrated in Scheme 5. For the catalyst LnPd(II), oxidation reaction cannot take place without additives, while with the help of K₂CO₃, the reaction initiated by the formation of a palladium(II)-alkoxide intermediate,²⁹ which suffered from β-hydride elimination accompanied by the generation of aldehyde and LnPd⁰ (b). But the Pd-based catalyst is irreversible due to the oxidant-free system. Then an oxidative addition of the O–H bond from alcohol (a) to the coordinately unsaturated Pd⁰ species affords a Pd-alkoholate species, which is transformed into the corresponding carbonyl compounds and a palladium dihydride (c) with a β-hydride elimination. Then, hydrogen is liberated from c along with the regeneration of Pd⁰ species. The above mechanism can also explain why the reaction time is longer with Pd(II) species as the catalyst.

Hot-filtration experiments were carried out with the catalyst LnPd 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

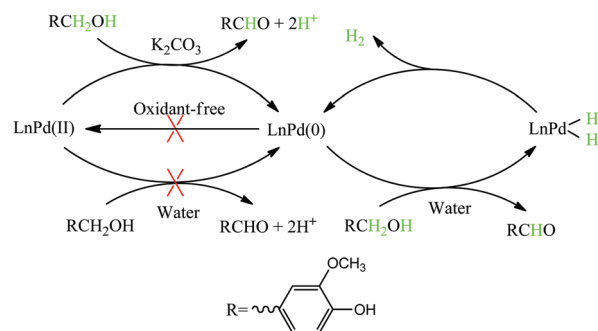
**Scheme 5** The reaction pathways to vanillin.

Table 5 The recycling study of the catalyst and water in the oxidation of vanillyl alcohol^a

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

^a Reaction conditions: vanillyl alcohol (0.2 g), temperature (80 °C), catalyst LnPd (30 mg), water (20 mL), and a N₂ balloon.

allowed to continue the 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 the catalytic reaction was truly heterogeneous under the applied conditions. Furthermore, a leaching experiment of Pd after the 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, 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 were added into the reaction system in order to maintain the water content (20 mL). The results shown in Table 5 indicate that the catalyst gave vanillin in >99% yield even after 9 runs, and the slight increase in reaction time is probably due to the minimal loss of the Pd species during the recovery. A TEM image of the catalyst LnPd after multiple uses is shown in Fig. 5, compared with the fresh catalyst, the mesoporous structure of the used catalyst remained almost constant. A comparison of the IR spectra of the catalyst LnPd before and after several reaction runs did not reveal significant differences (Fig. S5†), no peak at 1650 cm⁻¹ 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 have remained almost unchanged. Therefore, the catalyst can be a promising catalytic material in the dehydrogenation of vanillyl alcohol to vanillin with high activity and stability.

Conclusion

In summary, we have developed a highly recoverable and efficient palladium-based catalyst for the acceptor-free de-

hydrogenation 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 the 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 of environmentally friendly chemical processes.

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