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Short communication

Non-redox metal ions promoted oxidative dehydrogenation of saturated C—C bond by simple $Pd(OAc)_2$ catalyst

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ABSTRACT

Adding non-redox metal ions to simple $Pd(OAc)_2$ catalyst can remarkably promote oxidative dehydrogenation of saturated C—C bond, and the activity improvement is Lewis acidity strength dependent. Through UV–vis and NMR characterizations of the catalyst, it was proposed that in-situ generated heteronuclear Pd(II)/Zn(II) dimer is the key active species for dehydrogenation.

1. Introduction

Oxidative dehydrogenation of saturated C—C bond around ambient temperature represents one of the promising protocols to obtain the functionalized compounds like olefin, aromatics, and heterocycles [1–3]. Traditionally, those bulky olefinic and aromatic compounds like propylene and styrene are commercially produced by heterogeneous catalysts at high temperature with the release of hydrogen (H_2), which are not suitable for many fine and pharmaceutical products [4,5]. Alternatively, through oxidative dehydrogenation, the energy compensation from water formation can drive the dehydrogenation reaction happens around ambient temperature. In 2011 and later, Stahl and co-workers reported a Pd(II)-catalyzed aerobic dehydrogenation of substituted cyclohexanones to phenols, in which the presence of organic ligands are essential to achieve the good yields [6,7]. Balcells and co-workers alternatively demonstrated another example of dehydrogenation using H_2O_2 as oxidant, in which copper complexes could catalyze oxidative dehydrogenation of alkane including robust *n*-hexane or cycloalkane to *n*-hexene and cycloalkenes, respectively [8]. Liu also reported that reaction-activated palladium catalyst can dehydrogenate substituted cyclohexanones to phenols and H_2 without oxidants and hydrogen acceptors [9].

Recently, non-redox metal ions promoted stoichiometric and catalytic oxidations by redox metal ions have attracted much attention [10–14]. In particular, we further found that the Lewis acid properties of copper(II) play a significant role in Pd(II)-catalyzed Wacker-type oxidations in addition to its redox properties [15], and next explored Al(III) promoted benzene hydroxylation by Pd(II)(bpym) catalyst, non-redox metal ions promoted olefin isomerization and oxidative coupling of indole with olefin by $Pd(OAc)_2$ catalyst [16–18]. The promotion effects were attributed to the formation of heterometallic Pd(II)/Lewis acid complexes which improved C—H bond activation capability of Pd(II) cation. Herein we demonstrate another example of non-redox metal ions promoted C—H activation by Pd(II) catalyst, that is, the presence of non-redox metal ions can remarkably improve the catalytic efficiency of simple $Pd(OAc)_2$ catalyst in aerobic dehydrogenation of the saturated C—C bond to obtain indoles from heterocyclic compounds, and phenols from cycloketone.

2. Experimental

2.1. Materials and methods

All chemical reagents are commercially available and used without further purification. UV–vis spectra were studied on Analytikjena specord 205 UV–vis spectrometer, NMR analysis was performed on Bruker AV400.

2.2. General procedure for indoline dehydrogenation reaction by $Pd(OAc)_2$ with $Zn(OTf)_2$

$Pd(OAc)_2$ (1.12 mg, 0.005 mmol), $Zn(OTf)_2$ (3.63 mg, 0.01 mmol) were dissolved in 5 mL acetonitrile in a glass tube, after stirring for 10 min, indoline (60 mg, 0.5 mmol) were added. The glass tube was equipped with a reflux condenser. Next, the reaction solution was

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magnetically stirred at 353 K in oil bath for 6 h with O_2 balloon. The product analysis was performed by GC using the internal standard method. Control experiments including using $Pd(OAc)_2$, or $Zn(OTf)_2$ alone were carried out in parallel.

3. Results and discussion

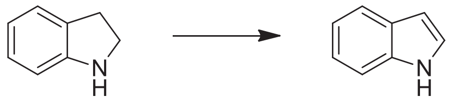
To screen the Lewis acid for the $Pd(OAc)_2$ catalyzed dehydrogenation, an easy substrate, indoline, was first tested for aerobic oxidative dehydrogenation, and the reactions were conducted in acetonitrile with O_2 balloon at 353 K with stirring. The results are listed in Table 1. One may see that, in the control experiment, $Pd(OAc)_2$ alone can offer 38.7% conversion of indoline with 34.3% yield of indole. Without $Pd(OAc)_2$, exposing indoline to the reaction conditions also provided 13.2% conversion with 10.8% yield of indole due to its instability. Adding NaOTf to $Pd(OAc)_2$ did not improve its dehydrogenation efficiency, while adding 2 equiv. of bivalent metal ions like Ca^{2+}, Mg^{2+}, and Ba^{2+} clearly improved the catalytic efficiency of $Pd(OAc)_2$; in particular, adding $Zn(OTf)_2$ to $Pd(OAc)_2$ improved the yield of indole up to 71.0% with 74.2% conversion. However, in the case of trivalent metal ions like Sc^{3+} and Al^{3+}, the catalytic efficiency slightly decreased, giving 61.9% and 55.4% of indoline conversion with 49.0% and 44.2% yield of indole, respectively. This phenomenon is different from those observed in Wacker-type oxidation, olefin isomerization and indole coupling reactions in which a stronger Lewis acid can offer better promotion effect [15,17,18]. Here, the lower efficiency of strong Lewis acid like Sc^{3+} and Al^{3+} can be attributed to its interaction with indoline substrate and indole product which is basic. As shown in entry 9 in Table 1, adding 6 equiv. of NaOTf, which contains identical amounts of OTf^- anion as those in 2 equiv. of $Sc(OTf)_3$, does not improve the catalytic efficiency of $Pd(OAc)_2$, whereas 2 equiv. of $Zn(OTf)_2$ significantly improved the dehydrogenation efficiency. To exclude the role of OTf^- anion in catalysis, we further conducted complimentary experiments for Zn^{2+} with other counter-ions. While $Zn(OAc)_2$, $ZnSO_4$, $ZnCO_3$ and $Zn(OH)_2$ are insoluble in acetonitrile, $Zn(NO_3)_2$ is soluble, and it demonstrated similar promotional effect as well as $Zn(OTf)_2$, providing 62.8% yield of indole with 95.2% of conversion. It clearly demonstrated that it is non-redox metal ion like Zn^{2+}, rather than OTf^-, plays the significant role in accelerating Pd(II)-catalyzed dehydrogenation. In addition, minor palladium black was observed after reaction in the case of using $Pd(OAc)_2$ as catalyst or adding NaOTf to $Pd(OAc)_2$, while adding other bivalent or trivalent Lewis acid to $Pd(OAc)_2$ prevented the palladium black formation, which is similar to those observed in Lewis acid promoted Wacker-type oxidation by $Pd(OAc)_2$ catalyst [15]. It is worth to mention that added Lewis acid alone does not catalyze dehydrogenation as shown in the parentheses of Table 1. In certain cases, the trace metal impurities played significant roles in catalysis [19–22]. In our studies, the control experiments using Lewis acid as catalyst demonstrated ignorable activity for dehydrogenation, thus eliminated the role of impurities in dehydrogenation.

The influence of Zn(II)/Pd(II) ratio on indoline dehydrogenation was displayed in Fig. S2. Increasing the ratio of $Zn(OTf)_2/Pd(OAc)_2$ up to 4 still continuously improved the dehydrogenation efficiency, which is similar to that in Lewis acid promoted Wacker-type oxidation by $Pd(OAc)_2$ catalyst, but different from that in olefin isomerization [15, 17]. In olefin isomerization, increasing the ratio of Al(III)/Pd(II) from 0 to 1 can sharply improve the isomerization efficiency, while further increasing the ratio does not show significant improvement. Catalytic kinetics of 2-methylindoline dehydrogenation also disclosed that adding $Zn(OTf)_2$ displays a clear faster reaction rate than using $Pd(OAc)_2$ alone. As shown in Fig. 1, Lewis acid alone as catalyst shows the identical dehydrogenation rate as that of no catalyst added, supporting that $Zn(OTf)_2$ alone cannot catalyze the reaction. Without Lewis acid, $Pd(OAc)_2$ alone is active but the dehydrogenation rate is pretty slow, however, adding $Zn(OTf)_2$ to $Pd(OAc)_2$ greatly accelerates the dehydrogenation reaction and demonstrates a higher yield of the 2-methylindole product.

The catalytic dehydrogenation of other N-heterocyclic compounds which contain secondary amine functional groups also clearly supports that adding $Zn(OTf)_2$ greatly accelerates the dehydrogenation reaction by $Pd(OAc)_2$ catalyst. For examples, in dehydrogenation of 1,2,3,4-tetrahydroquinoline, adding $Zn(OTf)_2$ offered 59.8% conversion with 55.1% yield of quinoline in 12 h at 353 K, whereas using $Pd(OAc)_2$ alone as catalyst only provided 36.2% of conversion with 23.6% yield of quinoline (Table 2). The relatively low conversion of substrate can be attributed to the plausible interaction of indole product with $Pd(OAc)_2$ catalyst which blocks the promotion effect by added Lewis acid. In the case of 2-methylindoline, adding $Zn(OTf)_2$ to $Pd(OAc)_2$ provided 74.0% yield of 2-methylindole with 97.6% conversion of substrate, while $Pd(OAc)_2$ alone gave 43.2% yield with 51.0% conversion. In particular, in a 1 g scale dehydrogenation of 2-methylindoline, a 79.7% yield of 2-methylindole was achieved. In a complementary test, tetrahydrothiopene was employed as substrate, and it provided only 5% of thiopene as product. However, in the absence of Lewis acid, no formation of thiopene was observed, thus also evidenced the promotional effect of Lewis acid in $Pd(OAc)_2$ catalyzed oxidative dehydrogenation.

As reported elsewhere, a stronger Lewis acid may have a better promotional effect on the redox metal ion mediated oxidations [10–14]. Here, due that the strong Lewis acid like Sc^{3+} and Al^{3+} can interact with the tested N-heterocyclic compounds and related products which are basic, the promotional effect of trivalent Lewis acids was not

Table 1
Lewis acid promoted oxidative dehydrogenation of indoline to indole.



Entry	Catalyst	Lewis acid	Conv. %	Yield %
1	–	–	13.2	10.8
2	$Pd(OAc)_2$	–	38.7	34.3
3	$Pd(OAc)_2$	$Sc(OTf)_3$	61.9(12.4)	49.0(9.2)
4	$Pd(OAc)_2$	$Al(OTf)_3$	55.4(17.0)	44.2(12.9)
5	$Pd(OAc)_2$	$Zn(OTf)_2$	74.2(13.8)	71.0(11.2)
6	$Pd(OAc)_2$	$Ca(OTf)_2$	65.8(15.3)	62.4(13.2)
7	$Pd(OAc)_2$	$Mg(OTf)_2$	52.5(12.9)	37.8(7.8)
8	$Pd(OAc)_2$	$Ba(OTf)_2$	70.5(14.1)	67.4(8.4)
9	$Pd(OAc)_2$	6NaOTf	38.8(11.3)	34.7(6.0)

Conditions: $Pd(OAc)_2$ 1 mM, Lewis acid 2 mM, CH_3CN 5 mL, Substrate: 100 mM, O_2 balloon, 353 K, 6 h. The data in parentheses represent the control experiment without $Pd(OAc)_2$.

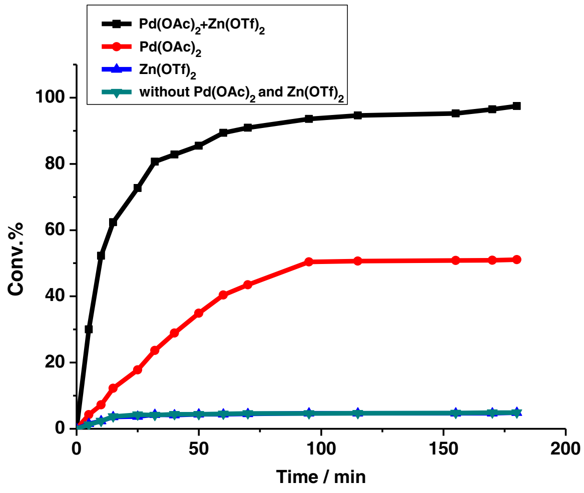
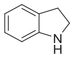
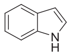
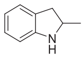
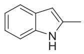
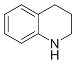
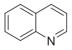
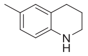
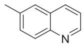
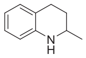
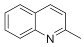


Fig. 1. Time course of dehydrogenation from 2-methylindoline. Conditions: $Pd(OAc)_2$ 1 mM, Lewis acid 2 mM, CH_3CN 5 mL, substrate 100 mM, O_2 balloon, 353 K.

Table 2
Dehydrogenation of different N-heterocyclic compounds by $Pd(OAc)_2$ in the presence of $Zn(OTf)_2$.[a]

Entry	Substrate	T/h	Conv. %	Products	Yield %
1		6	77.4(34.4)		71.0(32.6)
2		3	97.6(51.0)		74.0(43.2)
3[b]		12	59.8(26.2)		55.1(23.6)
4[c]		24	47.0(23.3)		34.0(18.7)
5[d]		24	62.1(46.9)		50.9(37.6)

The data in parentheses come from control experiments using $Pd(OAc)_2$ alone.

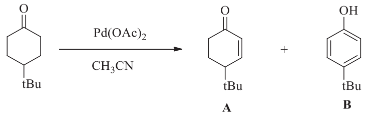
[a] Conditions: $Pd(OAc)_2$ (1 mol%, 1 mM), $Zn(OTf)_2$ (2 mol%, 2 mM), CH_3CN (5 mL), substrate (100 mM), O_2 balloon, 353 K.

[b] Substrate (50 mM).

[c] Substrate (100 mM), 363 K.

[d] Substrate (20 mM), 363 K.

Table 3
Lewis acid promoted oxidative dehydrogenation of cyclic ketone by $Pd(OAc)_2$ catalyst.



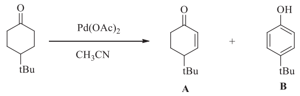
Entry	Lewis acid	Conv. [%]	Yield A [%]	Yield B [%]
1	–	8.9	4.6	–
2	$Zn(OTf)_2$	14.1	7.6	–
3	$Al(OTf)_3$	68.2	28.7	10.3
4	$Sc(OTf)_3$	64.3	37.7	15.7

Reaction conditions: CH_3CN 3 mL, $Pd(OAc)_2$ 8 mM, Lewis acid 16 mM, 4-*tert*-butyl-cyclohexanone 80 mM, 20 atm O_2, 353 K, 24 h.

impressively observed in dehydrogenation. Compared with amines, cyclic ketones are mostly neutral, and have much more robust C—H bond. Here, 4-*t*-butyl-cyclohexanone was selected as substrate for oxidative dehydrogenation, and the results are summarized in Table 3. Clearly, due to the robust C—H bond in ketone, the promotional effect of Zn^{2+} is minor, providing only 14.1% conversion of ketone with only 7.6% yield of 4-*t*-butyl-cyclohexenone and no *t*-butylphenol formation was detected, however, it is still slightly better than using $Pd(OAc)_2$ alone. Adding $Al(OTf)_3$ to $Pd(OAc)_2$ giving 68.2% conversion of ketone with 28.7% yield of 4-*t*-butyl-cyclohexenone and 10.3% yield of *t*-butylphenol formation. Remarkably, adding 2 equiv. of $Sc(OTf)_3$ to $Pd(OAc)_2$ offered 37.7% yield of 4-*t*-butyl-cyclohexenone with 15.7% yield of 4-*t*-butylphenol product, while the conversion is 64.3%. Clearly, stronger Lewis acid can provide much better promotional effect in oxidative dehydrogenation by $Pd(OAc)_2$ catalyst as well those in previous studies [15,17,18]. Although it is not clear the dehydrogenation of indoline proceeds by C—C or C—N (followed by tautomerization) bond oxidation (vide supra), the oxidative dehydrogenation of cycloketone to the phenols has clearly indicated that adding Lewis acid to simple $Pd(OAc)_2$ can substantially improve its hydrogen atom abstraction ability.

As well as in indoline dehydrogenation, increasing the ratio of Pd(II)/Sc(III) from 1:0.5 to 1:1 sharply improves the dehydrogenation efficiency of 4-*t*-butyl-cyclohexenone, while further increasing ratio still improves the dehydrogenation efficiency as shown in Table 4. In particular, increasing the $Sc(OTf)_3$ loading sharply drives the transformation of 4-*t*-butyl-cyclohexenone to 4-*t*-butylphenol. In the 1:1 ratio

Table 4
The influence of Pd(OAc)/$Sc(OTf)_3$ on 4-*t*-butyl-cyclohexenone.



Entry	$Pd(OAc)_2$:$Sc(OTf)_3$	Conv. [%]	Yield A [%]	Yield B [%]
1	1:0.5	15.2	7.4	–
2	1:1	52.3	41.2	2.6
3	1:2	64.3	37.7	15.7
4	1:4	75.3	26.1	23.2

Reaction conditions: CH_3CN 3 mL, $Pd(OAc)_2$ 8 mM, 4-*tert*-butyl-cyclohexanone 80 mM, 20 atm O_2, 353 K, 24 h.

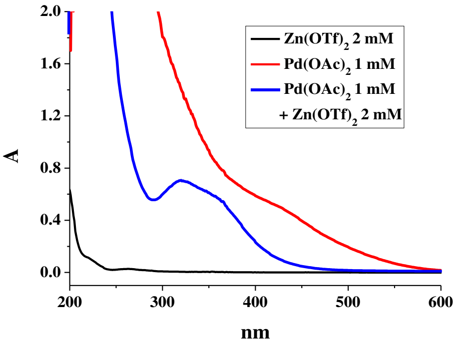


Fig. 2. The UV–visible spectra of the $Pd(OAc)_2$ plus $Zn(OTf)_2$ in acetonitrile.

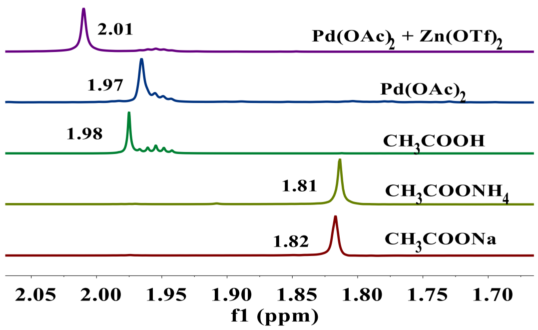
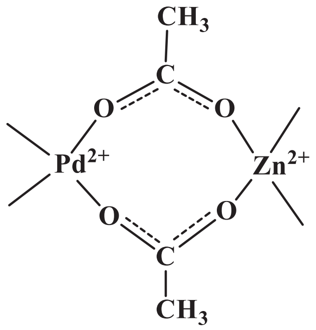


Fig. 3. ^{1}H NMR spectra of Pd(OAc)$_2$/Zn(OTf)$_2$ with related compounds in acetonitrile-d$_3$.



Scheme 1. Proposed heteronuclear Pd(II)/Zn(II) dimer for dehydrogenation.

of Pd(II)/Sc(III), it provided 41.2% yield of 4-*t*-butyl-cyclohexenone with only 2.6% yield of 4-*t*-butylphenol, while in the case of 1:4 ratio, it offered 26.1% yield of 4-*t*-butyl-cyclohexenone with 23.2% yield of 4-*t*-butylphenol, and the conversion of 4-*t*-butyl-cyclohexanone is 75.3%.

To address the origins of the promotional effect in dehydrogenation by Pd(OAc)$_2$/Zn(OTf)$_2$, the catalytic system was characterized by UV–vis and NMR technologies. As shown in Fig. 2, in acetonitrile Pd(OAc)$_2$ alone demonstrates a yellowish colour, having a shoulder absorbance band above 400 nm involving the ligand-to-metal charge transfer as expected. Adding 2 equiv. of Zn(OTf)$_2$ to Pd(OAc)$_2$ yields a new absorbance band with a maximum near 320 nm, indicating the formation of a new Pd(II) species, which is similar to that adding Sc(OTf)$_3$ to Pd(OAc)$_2$ in acetonitrile [15]. In ^{1}H NMR spectra (Fig. 3), the chemical shift of 1.97 ppm of Pd(OAc)$_2$ alone can be assigned to the methyl group of acetate in the Pd$_3$(OAc)$_6$ trimer as those in literature [23,24]. Adding Zn(OTf)$_2$ to Pd(OAc)$_2$ downshifts this methyl group to 2.01 ppm. In ^{13}C NMR spectra (Fig. 4), Pd(OAc)$_2$ displays one chemical shift at 21.15 ppm and another at 173.73 ppm, corresponding to the methyl and carbonyl groups of acetate bridges in Pd$_3$(OAc)$_6$, respectively. Adding Zn(OTf)$_2$ downshifts the carbonyl group to 178.56 ppm and the methyl group to 22.03 ppm, also indicating the new coordination environment of acetate. All of these UV–vis and NMR characterization clearly evidenced the formation of new Pd(II) species after adding Zn(OTf)$_2$ to the acetonitrile solution of Pd(OAc)$_2$. According to previous studies in similar Pd(OAc)$_2$/Lewis acid system [15,17,18], and the reported formation of heterobimetallic Pd(II) dimers with Ba^{2+}, Ca^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Ce^{4+} through acetate bridge [25,26], here, similar Pd(II)/Zn(II) dimer with acetate bridge can be reasonably proposed in this Pd(OAc)$_2$/Zn(OTf)$_2$ system (Scheme 1), and it serves as the key active species for oxidative dehydrogenation.

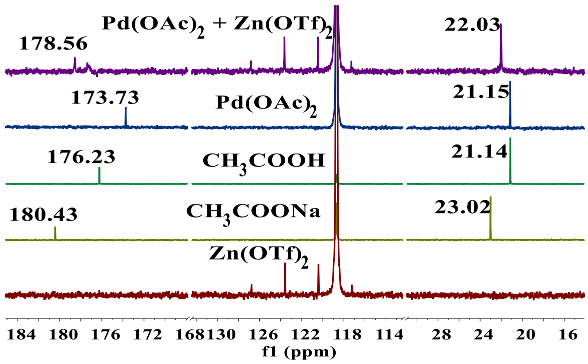


Fig. 4. ^{13}C NMR spectra of Pd(OAc)$_2$/Zn(OTf)$_2$ with related compounds in acetonitrile-d$_3$.

4. Conclusions

This work demonstrated that adding non-redox metal ions to simple Pd(OAc)$_2$ catalyst can remarkably improve its dehydrogenation activity for feasible C—H bond in indolines to indole and derivatives, and for the robust C—H bond in cyclic ketone to enone and phenols; in particular, the activity improvement is Lewis acidity strength dependent on added non-redox metal ions. Through UV–vis and NMR characterizations of the catalyst, it was proposed that in-situ generated heteronuclear Pd(II)/Zn(II) dimer is the key active species for dehydrogenation.

Acknowledgments

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Supplementary materials include detailed experimental procedures, UV–vis characterization of catalyst, graph of Zn(II)/Pd(II) ratio on catalytic efficiency, and GC–MS graphs of 4-*t*-butyl cyclohexanone.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.11.007.

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