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Palladium-catalyzed aerobic oxidation of 1-phenylethanol with an ionic liquid additive[†]

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The aerobic oxidation of 1-phenylethanol over a carbon nanotube supported palladium catalyst was improved with an ionic liquid additive [emim][NTf₂], showing an excellent TON of 149 000 which can be maintained for 5 recycle runs.

The selective oxidation of alcohols has been considered as one of the most fundamental organic transformations. The corresponding aldehydes or ketones are employed as high-value intermidiates and components for the pharmaceutical, agrochemical, and perfumery industries.^{1,2} From the viewpoints of atom economy and environmental concern, developing noble metal heterogeneous catalysts and using molecular oxygen or air as the oxidant prevail as an attractive green technology.³ Numerous palladium catalysts with superior catalytic activities have been developed since its first successful application in the aerobic oxidation of secondary alcohols.⁴ Mori et al. reported a hydroxyapatite-supported Pd catalyst highly effective for the aerobic oxidation of benzylic alcohols, particularly giving a TOF of 9800 h⁻¹ for 1-phenylethanol.⁵ Li et al. showed that zeolite-supported Pd nanoparticles of 2.8 nm exhibited an exceptional TOF of 18800 h^{-1.6} More recently, our group has also reported the suface-functionalized TUD-1 supported Pd catalysts with a high TOF of 18 571 h^{-1} for benzyl alcohol oxidation.⁷

Ionic liquids (ILs) have risen as a focus of research interest and made significant progress in the catalytic processes from a green chemistry perspective since the discovery of secondgeneration ILs in 1992.⁸ ILs are generally employed to promote the catalytic reactions in two ways: as a supported phase (supported ionic liquid phase catalysts, SILPCs) and as medium or additive in the reaction.⁹ Making SILPCs, in which active species are immbolized on an IL-functionalized support, is considered as a facible and economic approach.^{10,11} Nonetheless, many studies are also centered at the use of ILs as effective solvents for "green" chemical reactions. ILs can replace the traditional volatile organic and dipolar aprotic solvents in both laboratory and industry-scale production due

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to their unique properties, *i.e.*, non-flammable, non-volatile,
thermally stable, high solvating, and non-coordinating.¹²TON ofMoreover, ILs are regarded as *desingers' solvents* because their
physico-chemical properties can be precisely tuned by a
suitable combination of cations and anions.ed as oneIn addition to a vast number of developments achieved using

ILs as reaction media in transition metal-catalyzed hydrogenation, hydroformylation and coupling reactions,^{13–15} there are several examples of catalytic alcohol oxidation in ILs.¹⁶⁻¹⁸ However, most of them involve homogeneous metal catalysts, which require laborious product isolation and generate large amounts of organic/inorganic waste. Therefore, heterogeneous oxidation in ILs media is preferred as a greener alternative which can also effectively solve the problems involving the decomposition or leaching of active metal centers, poor reactants and catalyst solubility, low activities and selectivities.¹⁹ In this communication, [emim][NTf₂], a non-nucleophilic and hydrophobic IL, was selected as the reaction additive for the selective oxidation of 1-phenylethanol over a carbon nanotubesupported Pd catalyst using molecular oxygen; the reactivity was benchmarked against solvent-free conditions and another representative IL [bmim]Br. The effects of IL nature and content as well as various reaction parameters (reaction time, O₂ partial pressure, O₂ total pressure, reaction temperature, recyclibility) on the catalytic activity were examined.

Several variables have been identified to be important for the success of 1-phenylethanol aerobic oxidation in ILs (Table 1). In the absence of catalyst and ILs (entry 1), only a small amount of 1-phenylethanol converts due to the non-catalytic oxidation.²⁰ Good activity is observed over a Pd/CNT catalyst under solvent-free conditions (entry 2), showing a TON of 111000. Noteworthily, [emim][NTf₂] distinctly affects the catalytic performances. The activity increases sharply upon introducing a small amount of [emim][NTf₂] as an additive, and reaches the maxmium with 1 mL of IL addition, showing an excellent TON of 149000 (entries 3 and 4). The improvement can be attributed to the enhanced solubility of both alcohol substrate and gaseous O2 in [emim][NTf₂], leading to a better substrate-catalyst contact.19 Further adding [emim][NTf2] results in a pronounced decline of catalytic performances (entries 5-7), which may be due to either the low concentration of the substrate or the large mass-transfer resistance in the viscous alcohol-IL mixture. The selectivities toward acetophenone show a similar

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Entry	Ionic liquid	$V_{\rm IL}/mL$	IL molar fraction (%)	Conv. (%)	Select. ^{b} (%)	$TON \times 10^{4c}$
1	d		0	11.8	100	
2	_	_	0	67.6	90.8	11.1
3	[emim][NTf ₂]	0.5	8.7	77.4	91.8	12.7
4	[emim][NTf ₂]	1	16.0	90.6	96.9	14.9
5	[emim][NTf ₂]	2	23.7	62.8	95.8	10.3
6	[emim][NTf ₂]	3	31.8	59.9	91.6	9.8
7	[emim][NTf ₂]	4	38.3	43.2	93.9	7.1
8	$[\text{emim}][\text{NTf}_2]^d$	1	16.0	42.8	47.9	
9	[emim][NTf ₂] ^e	1	16.0	82.1	91.7	13.5
10	[emim][NTf ₂]	1	16.0	7.1	76.0	1.2
11	[emim][NTf ₂] ^g	1	16.0	58.4	85.0	9.6
12	[bmim]Br ^d	1	19.1	0	0	
13	h		0	60.8	90.2	10.0

Table 1 Variation of reaction conditions for the oxidation of 1-phenylethanol to acetophenone over a Pd/CNT catalyst^a

^{*a*} Reaction conditions: 25 mmol of 1-phenylethanol, 5 mg of Pd/CNT, 20 mL min⁻¹ of O₂, 160 °C, 1 h. Uncertainties: conv. $\pm 0.15\%$, select. $\pm 0.35\%$, TON $\pm 0.08\%$. ^{*b*} Ethylbenzene is the only byproduct. ^{*c*} TON was calculated based on D_{Pd} determined by the CO-stripping method. ^{*d*} No catalyst. ^{*e*} [emim][NTf₂] recovered after reaction. ^{*f*} N₂ used. ^{*g*} Air used. ^{*h*} Pd/CNT recovered after reaction in [bmim]Br.

trend along with conversions in the presence of $[\text{emim}][\text{NTf}_2]$, which is higher than that under the solvent-free conditions, accompanied by a trace amount of ethylbenzene as the only detectable byproduct. In addition, as an environmentally benign reaction additive, $[\text{emim}][\text{NTf}_2]$ can be easily recovered after reaction and re-use in the next run, showing a high TON of 135 000 (entry 9).

The reaction time-conversion correlation was studied for 1-phenylethanol oxidation in [emim][NTf₂] and solvent-free conditions (Fig. 1(a)). Another frequently used IL [bmim]Br was also introduced for comparison. Pd/CNT in [emim][NTf₂] shows superior catalytic activities to solvent-free conditions. [Bmim]Br is detrimental for the reaction, showing an extremely low conversion of 3.1% (TON of 5120) after reacting for 1 h. The plots were fitted with first-order reaction kinetics; the reaction rate constants k are 1.96 ± 0.05 , 0.0346 ± 0.0008 , $1.04 \pm 0.02 \text{ h}^{-1}$ for [emim][NTf₂], [bmim]Br and solvent-free conditions, respectively. Considering the similarity of cations in both ILs, the inferiority of [bmim]Br to [emim][NTf₂] can be addressed by the different nucleophilicities of two anions. [NTf₂]⁻ is considered as a non-nucleophilic and innocent



Fig. 1 Comparison of the effects of reaction parameters for the oxidation of 1-phenylethanol over a Pd/CNT catalyst. (a) Timeconversion plots for reaction; (b) effect of O_2 pressures; (c) effect of reaction temperatures; (d) recyclability of Pd/CNT. Run conditions: see footnote of Table 1.

anion, i.e., more electrophilic compared to Br^{-.21} In Pd-catalyzed alcohol oxidation following a dehydrogenation mechanism, electrons are transferred through a consecutive cycle from alcohol to H-acceptor (i.e., molecular O₂) via Pd active species.²² When Pd nanoparticles are surrounded by an electrophilic environment, the electron transfer is accelarated due to the decreased electron density on Pd, leading to an enhanced catalytic activity. The electrophilicity of [NTf₂]⁻ also accounts for the moderate activity in the absence of a Pd/CNT catalyst (Table 1, entry 8). However, acetophenone and ethylbenzene were produced in approximately equal amounts, suggesting that Pd/CNT can effectively suppress the hydrogenolysis of 1-phenylethanol. Furthermore, in addition to the better solubility of O₂ in IL, the remarkably improved catalytic rate in the [emim][NTf2]-mediated reaction can be attributed to the hydrophobicity of [emim][NTf₂], which enriches the alcohol concentration at the catalyst-liquid interface where the reaction occurs and facilitates the desorption of hydrophobic ketone from catalyst surfaces.²³ On the contrary, the hydrophilic [bmim]Br is prone to adsorb on the catalyst surfaces which are also hydrophilic after acid-pretreatment, thus poisoning the active sites and suppressing the reaction.

Further investigations on the effects of various reaction parameters will be focused on using [emim][NTf₂] as an additive. N2 and air were employed as alternatives of O2 (Table 1, entries 10 and 11), showing that the catalytic activity increases with a higher O₂ partial pressure. When using N₂, the low alcohol conversion corresponds to the dehydrogenation mechanism where β -H elimination occurs upon dissociative adsorption of the substrate on active sites even in the absence of O₂ but suffers a fast catalyst deactivation due to product deposition on the Pd surface.^{2,22} The considerably low acetophonone selectivity is contributed by the C-O bond hydrogenolysis, affording the formation of ethylbenezne due to the abundant hydride species covered on the Pd surface and consequent catalyst deactivation.²⁴ Therefore, sufficient O₂ is essential to maintain the reaction in the kinetic region where the dehydrogenation but not the mass-transport is the ratelimitting step and to continuously consume surface Pd-H species. Elevating the O₂ total pressure from the atmosphere pressure to 3 atm leads to a drastically increased activity due to the enhanced solubility of O_2 (Fig. 1(b)). Nonetheless, the activity reaches a plateau when further increasing the O_2 pressure, implying that the reaction is of zero order in O_2 .¹ Meantime, it is also speculated that abundant PdO phases may be formed concomitantly in the presence of excess O_2 , resulting in the loss of metallic Pd active sites and consequently surpressed dehydrogenation step.²⁴

The effect of reaction temperature was also examined (Fig. 1(c)). The acetophenone selectivity is well maintained above 95% in the studied temperature range. The activity is hardly detectable at low reaction temperatures, whereas shows a sharp step increase above 100 °C. Despite the increased O_2 solubility, the rate of alcohol dehydrogenation decreases remarkably at low temperatures.²⁴ The high activation energy barrier (71.9 kJ mol⁻¹) to initiate the reaction implies the absence of mass-transfer limitation in this catlaytic system.⁷

Other than recycling the [emim][NTf₂] additive (Table 1, entry 9), the recyclability of a Pd/CNT catalyst was also investigated (Fig. 1(d)). There is only a slight deterioration for both catalytic activity and acetophenone selectivity during the repeated use of catalyst for 5 cycles, which can be contributed by the partial loss of catalysts during the recovery. Therefore, [emim][NTf₂] not only promotes the catalytic performance but also enhances the resistence against deactivation. It has been verified that no observable leaching of the Pd catalyst occurs. Negligible conversion is observed when the liquid filtrate is used as catalyst for further reaction. It is suggested that metal is more resistant against leaching in a less polar solvent,²⁵ which accounts for the catalyst stability in [emim][NTf₂].

The effects of ILs on Pd active sites and CNT supports are further investigated by XPS, TEM and Raman characterizations of fresh Pd/CNT and spent catalysts collected after reaction without any post-treatment. In Fig. 2, fresh Pd/CNT shows two chemical states: metallic Pd and Pd^{δ +} assigned to PdO which is due to incomplete reduction or exposure in air. Nonetheless, Pd^{δ +} disappears after reaction under solvent-free conditions due to the reduction by an

d 3d_{3/2}

340

340

Pd 3d_{5/2}

335

F 1s

685

۶ď

330 355

(f)

75

(a)_{Pď}

350

(c)

350

(e)

700

ntensity,a.u.

Pd/CNT

Pd

345

Pd 3d...

used in [emim][NTf₂]

used in [emim][NTf,]

690

Binding Energy,eV

345

695

used in [bmim]Br

used in [bmim]Br

Binding Energy.eV

335

Br 3d

(d) Pd 3d

Fig. 2 XPS spectra: (a) fresh Pd/CNT; (b) Pd/CNT used under solvent-free conditions; (c) Pd/CNT used in [emim][NTf₂]; (d) Pd/CNT used in [bmim]Br ((a)–(d): Pd 3d region); (e) Pd/CNT used in [emim][NTf₂] (F 1s region); (f) Pd/CNT used in [bmim]Br (Br 3d region).

680

alcohol substrate. Considering the presence of F (Fig. 2(e)), Pd^{δ^+} which is *ca.* 28% of Pd surfaces in Pd/CNT used in [emim][NTf₂] is attributed to Pd-F bonds, indicating the interaction of [NTf₂]⁻ and Pd active sites during the reaction.²⁶ Surprisingly, no Pd signal is detectable in Pd/CNT used in [bmim]Br while the existence of Br has been verified (Fig. 2(f)). TEM observation shows Pd nanoparticles for this particular spent catalyst (Fig. S2(d), ESI⁺) and no Pd leaching occurs during the reaction. We suggest that Pd was covered by a thick layer of [bmim]Br. Two control experiments were carried out to verify this speculation (Table 1, entries 12 and 13). [Bmim]Br alone shows no activity in the oxidation. After the catalyst in [bmim]Br was recovered by washing with acetone and re-used in a new reaction without any additive, comparable activity was observed with the solvent-free condition (entry 2). Therefore, when employed as an additive, hydrophilic [bmim]Br quickly adsorbs and accumulates on catalyst surfaces, resulting in catalyst deactivation. This can be also confirmed by the decreased $I_{\rm D}/I_{\rm G}$ ratio in the Raman spectrum, which implies the diminished CNT defects due to [bmim]Br coverage (Fig. S3, ESI[†]).

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