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## PdCl<sub>2</sub> immobilized on metal-organic framework CuBTC with the aid of ionic liquids: enhanced catalytic performance in selective oxidation of cyclohexene†

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Meta-organic framework CuBTC was employed as support to immobilize PdCl<sub>2</sub> with the aid of ionic liquids (ILs). The as-synthesized PdCl<sub>2</sub>-ILs/CuBTC catalyst was studied in selective oxidation of cyclohexene with molecular oxygen as an oxidant and TBHP as an initiator. It is found that the allylic oxidation and radical oxidation processes are main reaction pathways. More importantly, the enhancement of catalytic activity in oxidation of cyclohexene is observed over PdCl<sub>2</sub>-ILs/CuBTC catalyst due to Pd-Cu cooperative catalysis. Furthermore, ionic liquids could play a very favourable role in stabilization of Pd (II) species and improvement of catalyst reusability.

### Introduction

Catalytic oxidation of hydrocarbons is a significant and practical pathway for converting petrochemical by-products into high added-value oxygenated derivatives such as alcohols, diols, epoxides and carbonyl compounds.<sup>1-3</sup> Among them, the allylic selective oxidation of olefins into unsaturated ketones is considered as an important and useful transformation in commercial production of fine chemicals. In particular, the products of cyclohexene oxidation (*e.g.*, cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, *etc*) could act as building blocks for the synthesis of various organic functional intermediates.<sup>4-6</sup> In general, the transition-metal salts or organometallic complexes in solution as homogeneous catalysts,<sup>7-9</sup> in combination with oxidizing reagents (*e.g.* peroxides, inorganic salts, organic oxidants) could demonstrate high catalytic activity, but their utilizations are associated with the work-up of the hazardous

metal residues and the generation of considerable amounts of liquid wastes.

Awareness of the topic in green and sustainable chemistry, a potent driving has been forcing us to develop an environmentally friendly catalytic system for selective oxidation of cyclohexene. In this context, molecular oxygen has been viewed as the most desirable oxidant due to its natural clean, cost-effective, and eco-friendly characteristics. In addition, an efficient and recyclable heterogeneous catalyst is more favourable for the sustainable requirement in catalytic process because of the ease of catalyst separation. Up to now, several alternative solid catalysts have been successfully investigated in oxidation of cyclohexene, such as metal oxide,<sup>10</sup> metal-doped zeolite/mesoporous silica,<sup>11</sup> supported metal nanoparticles<sup>12, 13</sup> as well as immobilization of transition-metal salts/complexes with well-defined active sites.<sup>14</sup>

In recent years, ionic liquids (ILs) as a kind of novel green medium assisting immobilization of transition-metal salts over solid materials have attracted an increasing attention in heterogeneous catalysis. Hagiwara and co-workers<sup>15, 16</sup> reported that palladium acetate was immobilized on amorphous silica with the aid of ionic liquids. Shi *et al.*<sup>17</sup> reported that PdCl<sub>2</sub> and Pd-EDTA held in ionic liquids brushes were immobilized on silica. Karimi and co-workers<sup>18, 19</sup> reported that PdCl<sub>2</sub> salt was immobilized on TEG-imidazolium ionic liquids modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> magnetic material. Khedkar<sup>20, 21</sup> and co-workers demonstrated that metal palladium-containing ionic liquids (ImmPd-IL) was immobilized on SiO<sub>2</sub>. Hajipour *et al.*<sup>22</sup> reported that phosphonium-palladium complex was anchored on the surface of silica nanoparticles. In addition, Bobadilla presented that AuCl<sub>3</sub> was immobilized on ionic liquids functionalized MCM-41 material.<sup>23</sup> All these impressive and instructive works have showed that ionic liquids could be as an effective modifiers or promoters to favour immobilizing transition-metal salts.

In view of support effect, metal-organic frameworks (MOFs) as a novel porous crystalline materials are deemed to the promising catalyst supports due to their extra-surface area, ultrahigh porosity and accessible nanopore. More importantly, the well-defined metal centers within framework are high content and homogeneously distributed, which can be served as a mild catalytically active centres

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† Electronic Supplementary Information (ESI) available: [Experiment sections, ICP-OES analysis, Elemental analysis, Structural model of PdCl<sub>2</sub>-ILs, XRD, Mass Spectra, Uv-vis of solution after reaction, Hot filtration test and reusability of catalyst]. See DOI: 10.1039/x0xx00000x

for oxidation or Lewis acidic reaction.<sup>24, 25</sup> Up to date, a variety of MOFs materials with different metal centres such as Cu,<sup>26</sup> Cr,<sup>27</sup> Fe,<sup>28-30</sup> and Co,<sup>31</sup> have been synthesized. All of them exhibit favourable catalytic activity in oxidation reactions. In addition, MOFs as porous matrix could be employed to introduce a variety of guest species with task-specific catalytic functionality to develop novel MOFs-based heterogeneous catalysts,<sup>32</sup> which might inspire several unprecedented performances in catalysis.

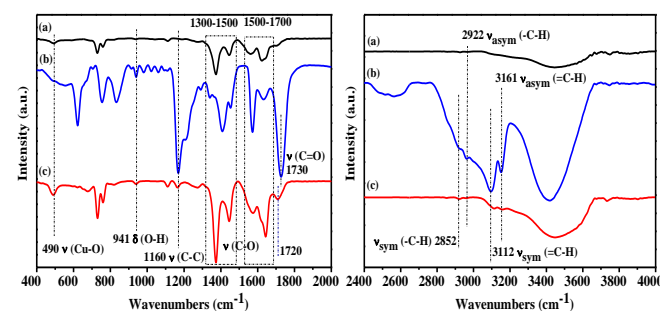
Very recently, a new breakthrough toward the introduction of task-specific ionic liquids into MOFs has attracted the significant interest in catalysis and adsorption after the first example reported from our group.<sup>33-39</sup> In continuation of our previous works, we here employ metal-organic framework CuBTC as support to immobilize PdCl<sub>2</sub> with the aid of 1-carboxyethyl-3-methyl imidazole chloride salt ionic liquids. The as-synthesized PdCl<sub>2</sub>-ILs/CuBTC catalyst was systematically studied in selective oxidation of cyclohexene with molecular oxygen as an oxidant and TBHP as an initiator. It is found that CuBTC support and ionic liquids play a very favourable role in enhancement of catalytic activity and improvement of catalyst reusability.

## Results and discussion

Initially, the structural integrity of CuBTC in as-synthesized catalyst is confirmed by X-ray diffraction (XRD), as shown in Fig. S1. XRD patterns show that the main diffraction peaks are consistent with simulated pattern and pure CuBTC material, apart from a couple of absent peaks and the slight decrease in Bragg intensity. It is therefore confirmed that PdCl<sub>2</sub>-ILs/CuBTC catalyst still could remain original framework structure of CuBTC, although there might be partial damage. The N<sub>2</sub> physical adsorption-desorption isotherm and TG curve of catalyst are shown in Fig. S2 and Fig. S3, respectively. Both of them provide an evidence that PdCl<sub>2</sub>-ILs is introduced inside nanocavities of CuBTC. Furthermore, the chemical composition of catalyst is determined by elemental analysis (EA) and ICP analysis, as shown in Table S1. The loading amount of ionic liquids and Pd (II) are 1.26 mmol/g and 0.40 mmol/g, respectively.

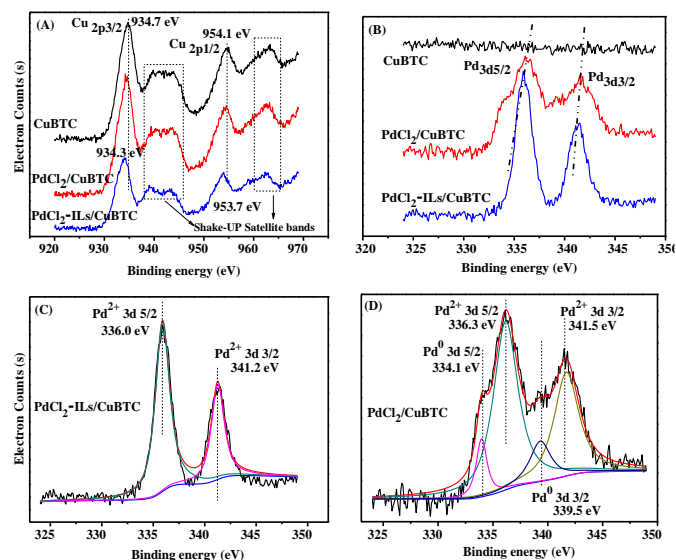
FT-IR spectra of the synthesized PdCl<sub>2</sub>-ILs/CuBTC catalyst are shown in Fig. 1. Compared to pure CuBTC sample and ionic liquids, it is observed that there are several new peaks appearing on PdCl<sub>2</sub>-ILs/CuBTC catalyst. Specifically, the characteristic peaks at 3161 cm<sup>-1</sup> and 3112 cm<sup>-1</sup> are attributed to sp<sup>2</sup> =C-H asymmetrical and symmetrical stretching vibration of imidazole moiety. The band at 2922 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> are assigned to aliphatic C-H asymmetrical and symmetrical stretching vibrations of alkyl chain. The bands at range of 1700-1500 and 1500-1300 cm<sup>-1</sup> are attributed to C-O asymmetrical and symmetrical stretching modes, respectively. The band at 1160 cm<sup>-1</sup> is assigned to the C-C skeleton stretching vibration of alkyl chain. The band at 1720 cm<sup>-1</sup> is attributed to C=O stretching vibrations of carboxyl group. It is worth noting that the wavenumber of C=O stretching vibrations existing in PdCl<sub>2</sub>-ILs/CuBTC catalyst shifts slightly to lower values (red shift) in comparison with the ionic liquids (1730 cm<sup>-1</sup>). One reasonable reason for this phenomenon is the weakening of C=O band when it coordinates with coordinatively unsaturated sites Cu (CUS-Cu). On the other hand, the increased intensity of band at 490 cm<sup>-1</sup> (Cu-O

vibrational mode) could also be observed compared to pure CuBTC sample, which could be due to the new formation of Cu-O bands from -COOH and CUS-Cu.<sup>40, 41</sup> Thus, it is reasonable to conclude that there is an interaction between ionic liquids and CuBTC support.



**Fig. 1** FT-IR spectra of all samples: (a) Pure CuBTC; (b) ionic liquids; (c) PdCl<sub>2</sub>-ILs/CuBTC.

In order to further verify the interaction between ionic liquid and CUS-Cu centers, as well as ascertain the chemical state of active species present in catalyst, XPS analysis was conducted. The survey spectra are shown in Fig. S4. The presence of new peaks at 399.0 eV, 336.0 eV and 341.2 eV are attributed to N 1s of imidazole ring, Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> of Pd<sup>2+</sup>, respectively. Specifically, the Cu 2p and Pd 3d XPS spectra are shown in Fig. 2. The Cu 2p peaks of pure CuBTC at 934.7 eV and 954.1 eV corresponding to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, as well as the well-known “shake-up satellite bands”, reveal an oxidation state of +2.<sup>42</sup> Interestingly, the bind energy of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> present in PdCl<sub>2</sub>-ILs/CuBTC catalyst shifts from 934.7 eV to 934.3 eV and 954.1 eV to 953.7 eV, respectively. This slight reduction of binding energy is because of CUS-Cu centers receiving the lone pair electrons of carboxyl group. On the other hand, it is observed that the bind energy of Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> present in PdCl<sub>2</sub>-ILs/CuBTC is lower than that in PdCl<sub>2</sub>/CuBTC, which is because of the PdCl<sub>2</sub> coordinating with chloridion.<sup>43, 44</sup>



**Fig. 2** XPS analysis of all samples: (A) Cu 2p spectra; (B) Pd 3d spectra; (C) Pd 3d spectra of PdCl<sub>2</sub>-ILs/CuBTC after peak split and fitting; (D) Pd 3d spectra of PdCl<sub>2</sub>/CuBTC after peak split and fitting.

In the previous study,<sup>17-22</sup> it is assumed that the surface species of immobilized Pd-containing ionic liquids heterogeneous catalyst is PdCl<sub>2</sub>-ILs complex, and anionic component is [PdCl<sub>4</sub>]<sup>2-</sup> (Fig. S5). To further confirm the accurate structure of active species existing in PdCl<sub>2</sub>-ILs/CuBTC catalyst, the homogeneous PdCl<sub>2</sub>-ILs complex was synthesized and characterized by <sup>1</sup>H-NMR and mass spectroscopy (MS). Fig. 3 shows <sup>1</sup>H-NMR spectra of ionic liquids and PdCl<sub>2</sub>-ILs complex. In the case of ionic liquids, a set of proton resonances at 2.97, 3.82, 4.40, 7.31, 7.46 and 8.74 ppm are observed. These <sup>1</sup>H-NMR peaks are assigned to 5-H, 1-H, 6-H, 3-H, 4-H and 2-H nuclei, respectively. For PdCl<sub>2</sub>-ILs complex, it is interesting to note that the chemical shift of all proton resonances with the exception of 1-H and 3-H nuclei shifts to high magnetic field. This indicates that there is a significant change in chemical environment around 5-H, 6-H, 4-H and 2-H nuclei. Electrostatic potential surfaces of cation and anion of PdCl<sub>2</sub>-ILs complex are shown in Fig. 4. It is further confirmed that the positive charge of cation is mainly distributed around b-N atom. When chloridion coordinate with PdCl<sub>2</sub> by complexation to form [PdCl<sub>4</sub>]<sup>(x-2)-</sup>, the apparent charge of complex anion is going to decrease in comparison with single Cl<sup>-</sup>. As a consequence, the shielding effect of H nuclei around b-N atom will be enhanced, in especial 2-H nuclei. This result is consistent with the previous report proposed by Dupont.<sup>45</sup>

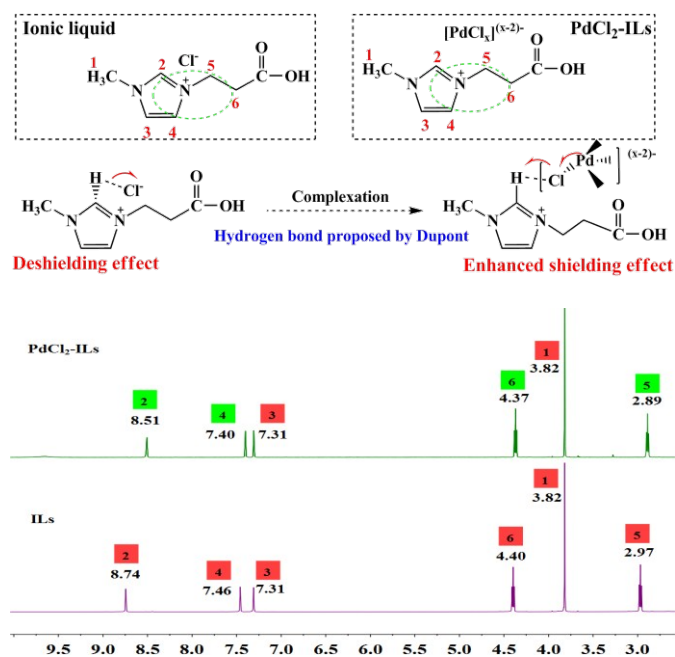


Fig. 3 Structural models and <sup>1</sup>H-NMR spectra of ionic liquids and PdCl<sub>2</sub>-ILs complex.

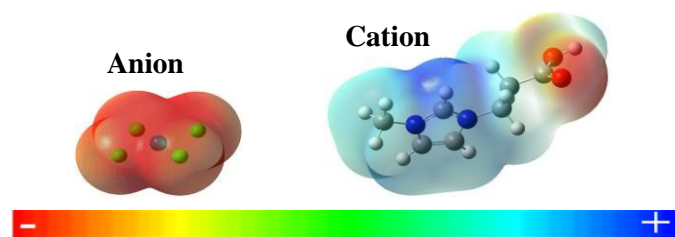


Fig. 4 Electrostatic potential surfaces of cation and anion of PdCl<sub>2</sub>-ILs complex

Mass spectra of PdCl<sub>2</sub>-ILs complex are shown in Fig. S6. It is found that ITMS+cESI full mass spectrum shows a peak at m/z=154.99 corresponding to cationic component of PdCl<sub>2</sub>-ILs complex. ITMS-cESI full mass spectrum shows a peak at m/z=188.98 which is consistent with anionic component [PdCl<sub>x</sub>]<sup>(x-2)-</sup> (X=2.3 by calculation). It appears that there is an apparent error in comparison with theoretical value (X=4), but it is a reasonable expectation because of the instability and sensitive decomposition of anionic component in electronic spray ion source condition. The previous reports in literatures have demonstrated that the metastability of isolated palladium tetrahalide dianions [PdCl<sub>4</sub>]<sup>2-</sup> is thermodynamically unstable fragmentation, and the specific half-life of [PdCl<sub>4</sub>]<sup>2-</sup> is less than 0.1 s in electrospray ion source.<sup>46, 47</sup> Nevertheless, this is the first time to characterize and ascertain the active species (PdCl<sub>2</sub>-ILs) present in heterogeneous catalyst. More importantly, it is indubitable to confirm that there is an interaction between PdCl<sub>2</sub> and ionic liquids. This result is in line with the foregoing XPS characterization.

As-synthesized PdCl<sub>2</sub>-ILs/CuBTC catalyst was tested in oxidation of cyclohexene with molecular oxygen as an oxidant and TBHP as a radical initiator. Initially, a blank experiment, the low conversion could be observed in absence of catalyst, as shown in Fig. 5. The catalyst precursor including ionic liquids, PdCl<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> were also tested, as shown in Table. S1. Ionic liquids and PdCl<sub>2</sub> as catalyst could achieve 5.9% and 7.8% conversion, respectively. The product distribution is only composed of 2-cyclohexene-1-one (=O). For Cu(NO<sub>3</sub>)<sub>2</sub> catalyst, the 2-cyclohexene-1-ol (-OH) and 2-cyclohexene-1-one are detected couple with an increased conversion. Pure CuBTC shows a comparative catalytic activity because its CUS-Cu (II) could be served as oxidizing centers. At this point, the tert-butyl-2-cyclohexenyl-1-peroxide (-OotBu) is detected. It is noteworthy that PdCl<sub>2</sub>-ILs/CuBTC catalyst shows a significant increase in cyclohexene conversion. The maximum conversion reaches 24%. In addition, the product distribution demonstrates that there is almost no generation of cyclohexene oxide (Expo). The 2-cyclohexene-1-ol, 2-cyclohexene-1-one and tert-butyl-2-cyclohexenyl-1-peroxide are major products in catalytic system. The highest selectivity of 2-cyclohexene-1-one is 53.2%. It is therefore supposed that the allylic and radical oxidation are main reaction pathways during the catalytic process.

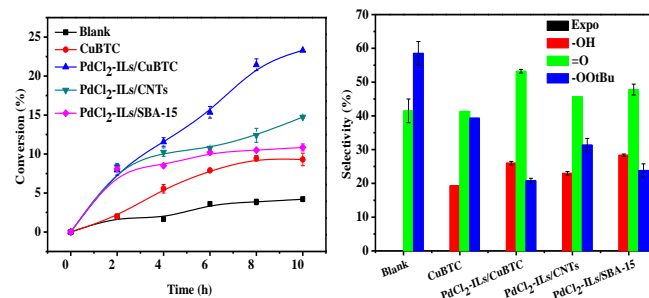
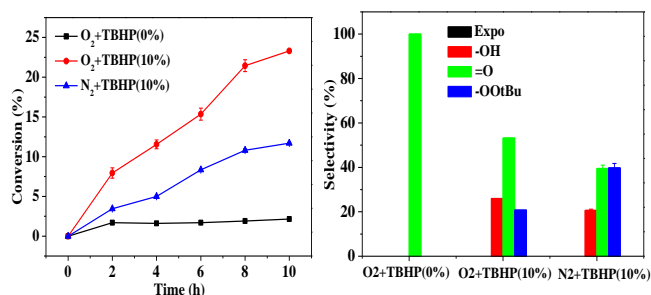


Fig. 5 Catalytic performance of different catalysts in selective oxidation of cyclohexene. Product distribution: trace amount of cyclohexene oxide cannot be quantified by GC. Reaction condition: 10 mL solution of *n*-heptane-TBHP (*n*<sub>TBHP</sub>=10% *n*<sub>cyclohexene</sub>), 6 mmol cyclohexene, 50 mg catalyst, 333 K.



For the sake of comparison, copper-free supports SBA-15 and CNTs were employed to support PdCl<sub>2</sub>-ILs complex. The loading amount of ILs and PdCl<sub>2</sub> were determined by ICP and EA, as shown in Table S1. Furthermore, PdCl<sub>2</sub>-ILs/CNTs and PdCl<sub>2</sub>-ILs/SBA-15 catalysts were tested in selective oxidation of cyclohexene with the same amount of Pd (II) species and identical reaction condition. The corresponding catalytic results are shown in Fig. 5. It is found that both of them achieve the lower conversions of cyclohexene in comparison with PdCl<sub>2</sub>-ILs/CuBTC catalyst. As expected, their catalytic activities are also in the similar level because of the existence of same active species. In addition, it is observed that the selectivity of 2-cyclohexene-1-one obtained from PdCl<sub>2</sub>-ILs/CNTs and PdCl<sub>2</sub>-ILs/SBA-15 is lower than that in PdCl<sub>2</sub>-ILs/CuBTC catalyst. It is therefore supposed that the Pd-Cu cooperative effect could enhance catalytic performance of cyclohexene oxidation.

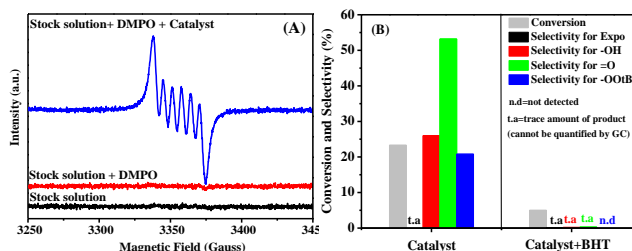
To probe the reaction pathways toward the selective oxidation of cyclohexene, we attempted to change the oxidant and dosage of initiator TBHP. The results are shown in Fig. 6. Firstly, the oxidation of cyclohexene over PdCl<sub>2</sub>-ILs/CuBTC catalyst with O<sub>2</sub> as an oxidant and in absence of radical initiator was studied. This result shows a very low conversion and the sole product (2-cyclohexene-1-one). It is thus assumed that the reaction undergoes a direct allylic oxidation pathway to generate 2-cyclohexene-1-one product. This result indicates that molecular oxygen mainly dominates the allylic oxidation process. Furthermore, another catalytic system, the non-oxidizing N<sub>2</sub> with the same dosage of radical initiator (TBHP), was investigated. It is observed that an increased conversion of ca. 12% is achieved after 10 h. Meanwhile, the tert-butyl-2-cyclohexenyl-1-peroxide and 2-cyclohexene-1-ol are concomitant. The selectivity of 2-cyclohexene-1-one is 40%. This result indicates that the radical initiator TBHP is responsible for the generation of 2-cyclohexene-1-ol and tert-butyl-2-cyclohexenyl-1-peroxide. More importantly, it is indubitable that the combination of O<sub>2</sub> with radical initiator TBHP will result in a significant enhancement of catalytic activity and selectivity of 2-cyclohexene-1-one.



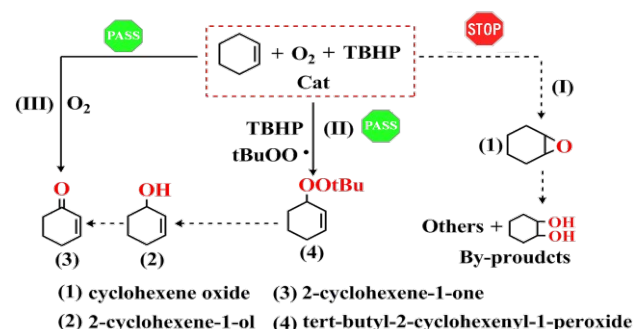
**Fig. 6** Effects of oxidant and radical initiator on oxidation of cyclohexene. Reaction condition: 10 mL solution of *n*-heptane-TBHP ( $n_{\text{TBHP}}=0$  or 10%  $n_{\text{cyclohexene}}$ ), 6 mmol cyclohexene, 50 mg catalyst, 333 K.

In order to further confirm the radical process, the spin-trapping technique combined with electron paramagnetic resonance (EPR) spectroscopy was carried out using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a capture agent, as shown in Fig. 7A. By comparison, a new adduct of DMPO-radical is detected and this should be assigned to oxygen centred radical, most probably the TBHP-derived species according to the similarities with the previous

report.<sup>48</sup> In general, alkoxy and peroxy radical are common species derived from TBHP. To be honest, however, it is difficult to make an exact assignment for the adducts of DMPO-alkoxy or DMPO-peroxy because they are very similar in hyperfine splittings.<sup>49</sup> Considering the product distribution in oxidation of cyclohexene, it is tentatively assumed that the dominating adduct is the latter. Furthermore, a very strong inhibition effect (depressed cyclohexene conversion and product selectivity) is observed (Fig. 7B) when the oxidation of cyclohexene is carried out in the presence of radical scavenger (2,6-di-tert-butyl-methylphenol, BHT).<sup>50, 51</sup> Based on the above results and related literatures,<sup>29, 30</sup> we propose the plausible reaction pathways in selective oxidation of cyclohexene (Scheme 1).



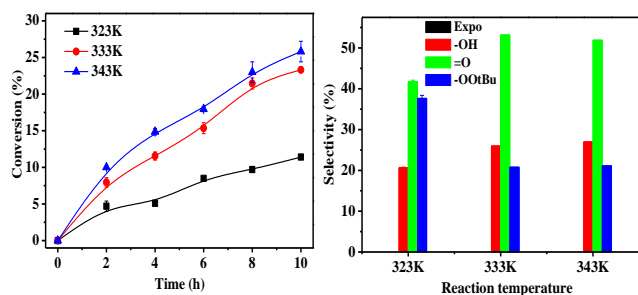
**Fig. 7** Spin-trapping EPR (A) and radical scavenger tests (B). Stock solution is composed of *n*-heptane-TBHP and cyclohexene. Stock solution + DMPO + Catalyst is detected after 2 h at room temperature. Radical scavenger: an equimolar 2,6-di-tert-butyl-methylphenol (BHT) (0.600 mmol, 0.1322 g) with TBHP.



**Scheme 1** The plausible reaction pathways toward selective oxidation of cyclohexene with molecular oxygen as an oxidant and TBHP as a radical initiator. (I) epoxidation pathway (II) radical pathway; (III) allylic pathway.

As the PdCl<sub>2</sub>-ILs/CuBTC catalyst showed the best catalytic activity, the effect of reaction temperature was investigated. Fig. 8 shows the results of cyclohexene oxidation at different temperature. It is observed that the reaction temperature has a profound influence on the progress of the cyclohexene oxidation. The cyclohexene conversion increases remarkably when the reaction temperature is increased from 323 K to 333 K. In addition, there is an obvious change in the product distribution. Specifically, the selectivity of 2-cyclohexene-1-one and 2-cyclohexene-1-ol increases, whereas the selectivity of tert-butyl-2-cyclohexenyl-1-peroxide decreases. The reasonable explanation for this phenomenon might be that the tert-butyl-2-cyclohexenyl-1-peroxide is going to decompose into 2-cyclohexene-1-one and 2-cyclohexene-1-ol under high temperature (Scheme 1). However, when the reaction temperature is further increased to 343 K, there is a slight increase in cyclohexene conversion and no significant change in selectivity of 2-

cyclohexene-1-one. This result indicates that an appropriate increase in reaction temperature would be conducive to enhance cyclohexene conversion and selectivity of 2-cyclohexene-1-one.

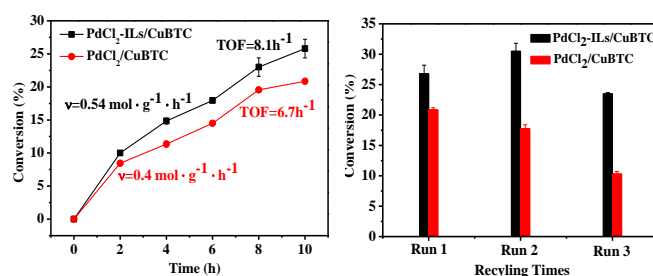


**Fig. 8** Effect of temperature on oxidation of cyclohexene. Reaction condition: 10 mL solution of *n*-heptane-TBHP ( $n_{\text{TBHP}}=10\% n_{\text{cyclohexene}}$ ), 6 mmol cyclohexene, 50 mg catalyst.

To verify heterogeneous nature of PdCl<sub>2</sub>-ILs/CuBTC catalyst, the hot filtration test was carried out by stopping a standard reaction and filtering the catalyst from the reaction mixture after 2 h. The liquid phase was then transferred to another reactor and allowed to react again. The result is shown in Fig. S7. It is found that there is a slight increase in cyclohexene conversion. However, the similar growth trend toward cyclohexene conversion in absence of catalyst could be also observed due to the auto-oxidation process in radical initiator system. Therefore, it is indubitable to rule out the possibility of leaching of the catalytically active species. Furthermore, the solutions after reaction (2 h and 10 h) were monitored by Uv-vis and ICP to determine the leaching of metal Pd (II) and Cu (II) species, as shown in Fig. S8. It is observed that there is no absorption peak in the above solution compared to stock solution containing PdCl<sub>2</sub>-ILs complex. In addition, ICP analysis of solutions after reaction (10 h) shows that copper and palladium concentration are only 127 ppm and 223 ppm, respectively. It is therefore confirmed that the catalytic reaction happened over PdCl<sub>2</sub>-ILs/CuBTC catalyst is truly heterogeneous process. On the other hand, the reusability of PdCl<sub>2</sub>-ILs/CuBTC catalyst is shown in Fig. S9. As can be seen, the catalyst demonstrates an excellent reusability. It can be recycled three times without appreciable change in conversion and selectivity of 2-cyclohexene-1-one. Furthermore, the reused catalyst is characterized by XPS and XRD, as shown in Fig. S10. XPS analysis shows that there is a decrease in bind energy of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> and intensity of the “shake-up satellite bands”. This result reveals that the Cu<sup>2+</sup> species might have been reduced to Cu<sup>+</sup> during the radical oxidation system. The resulting the CuBTC framework might be partial collapse, which is consistent with XRD results. For palladium species of reused catalyst, there is no significant change in Pd 3d spectra, apart from slight decrease in electron counts.

The foregoing characterization results have confirmed that there is an interaction between ionic liquids and PdCl<sub>2</sub>. To better discern the role of ionic liquids in PdCl<sub>2</sub>-ILs/CuBTC catalyst, PdCl<sub>2</sub>/CuBTC catalyst in the absence of ionic liquids was prepared. XRD pattern and PdCl<sub>2</sub> content are shown in Fig. S1 and Table S1, respectively. This catalyst was evaluated in oxidation of cyclohexene with same amount of Pd (II) species and identical reaction condition. The

results are shown in Fig. 9. It is found that PdCl<sub>2</sub>/CuBTC catalyst shows inferior catalytic activity. Specifically, the reaction rate and TOF value are equal to 0.4 mol · g<sup>-1</sup> · h<sup>-1</sup> and 6.7 h<sup>-1</sup>, respectively. However, the reaction rate and TOF value achieved from PdCl<sub>2</sub>-ILs/CuBTC catalyst are equal to 0.54 mol · g<sup>-1</sup> · h<sup>-1</sup> and 8.1 h<sup>-1</sup>, respectively. In combination with the foregoing XPS analysis (Fig. 2 C and D), PdCl<sub>2</sub>/CuBTC catalyst shows two peaks at 334.1 eV and 339.5 eV corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> of Pd<sup>0</sup> species.<sup>52-54</sup> However, the only Pd<sup>2+</sup> species could be observed on PdCl<sub>2</sub>-ILs/CuBTC catalyst. These results indicate that ionic liquids could be in favour of homogeneous dispersion of PdCl<sub>2</sub> species. Furthermore, the difference in their reusability was also compared. It is found that there is a significant decrease of cyclohexene conversion over PdCl<sub>2</sub>/CuBTC catalyst. This result indicates that ionic liquids plays an effective role in stabilization of PdCl<sub>2</sub> active species.



**Fig. 9** The comparison of catalytic performance between PdCl<sub>2</sub>-ILs/CuBTC and PdCl<sub>2</sub>/CuBTC catalysts. Reaction condition: 10 mL solution of *n*-heptane-TBHP ( $n_{\text{TBHP}}=10\% n_{\text{cyclohexene}}$ ), 6 mmol cyclohexene, 50 mg catalyst.

## Conclusions

In summary, we developed palladium chloride salt immobilized on metal-organic framework CuBTC material with the aid of 1-carboxyethyl-3-methyl imidazole chloride salt ionic liquids. It is found that this catalyst is an effective and reusable heterogeneous catalyst for selective oxidation of cyclohexene with molecular oxygen as an oxidant and TBHP as a radical initiator. The characterization results reveal that the active species of catalyst surface is a complex formed from ionic liquids and PdCl<sub>2</sub>, and there are chemical interactions between ionic liquids and PdCl<sub>2</sub> as well as ionic liquids and CuBTC support. As a result, ionic liquids could play a very favourable role in stabilization of Pd (II) species and improvement of catalyst reusability. In addition, it is observed that Pd-Cu cooperative catalysis between PdCl<sub>2</sub>-ILs complex and CuBTC support could enhance catalytic activity for oxidation of cyclohexene. Interestingly, it is found that the allylic and radical oxidation process are main reaction pathways, while the epoxidation pathway is negligible in this catalytic system. It is further confirmed that molecular oxygen mainly dominates the allylic oxidation process to form 2-cyclohexene-1-one, while the TBHP is responsible for the generation of tert-butyl-2-cyclohexenyl-1-peroxide which is going to decompose into 2-cyclohexene-1-one and 2-cyclohexene-1-ol under high temperature. More importantly, we believe that the knowledge gained from this contribution would provide a new opportunity to develop green and sustainable catalytic system for

selective oxidation of cyclohexene, especially for production of 2-cyclohexene-1-one with high selectivity.

### Acknowledgement

This work was carried out with funding provided by National Natural Science Foundation of China (No. 21076031 and No. 21356001) and Fundamental Research Funds from the Central Universities (No. DUT12ZD219). Prof. Sang-Eon Park expresses his sincere thanks for the "Sea-sky" professorship of Dalian University of Technology.

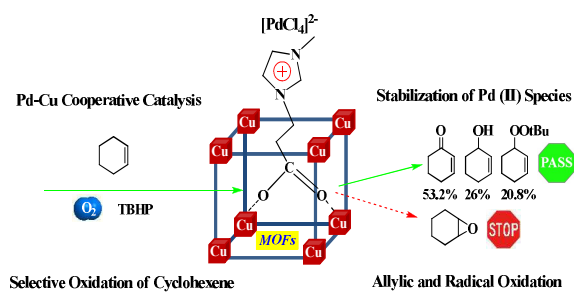
### References

- R. Burch, D. Crittle and M. Hayes, *Catal. Today*, 1999, **47**, 229-234.
- M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings and F. King, *Nature*, 2005, **437**, 1132-1135.
- R. Burch and M. Hayes, *J. Mol. Catal. A: Chem.*, 1995, **100**, 13-33.
- S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Macromolecules*, 2000, **33**, 303-308.
- J. E. Audia, L. Boisvert, A. D. Patten, A. Villalobos and S. J. Danishefsky, *The J. Org. Chem.*, 1989, **54**, 3738-3740.
- M. Polla and T. Frejd, *Tetrahedron*, 1991, **47**, 5883-5894.
- A. Noels, A. Hubert and P. Teyssie, *J. Org. Chem.*, 1979, **166**, 79-86.
- Z. Lei, *Reactive and Functional Polymers*, 2000, **43**, 139-143.
- D. M. Boghaei and S. Mohebi, *J. Mol. Catal. A: Chem.*, 2002, **179**, 41-51.
- C. Zhang, Y. Ozawa, Y. Hayashi and K. Isobe, *J. Org. Chem.*, 1989, **373**, C21-C25.
- L. Chen, G. Chuah and S. Jaenicke, *Catal. Lett.*, 1998, **50**, 107-114.
- C. Della Pina, E. Falletta, L. Prati and M. Rossi, *Chem. Soc. Rev.*, 2008, **37**, 2077-2095.
- N. Dimitratos, J. A. Lopez-Sanchez and G. J. Hutchings, *Chem. Sci.*, 2012, **3**, 20-44.
- Y. Deng, Z. Ma, K. Wang and J. Chen, *Green Chem.*, 1999, **1**, 275-276.
- H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi and T. Suzuki, *Org. Lett.*, 2004, **6**, 2325-2328.
- H. Hagiwara, *Synlett*, 2012, 837-850.
- X. Shi, X. Han, W. Ma, J. Fan and J. Wei, *ChemInform*, 2012, **43**, no.
- B. Karimi, F. Mansouri and H. Vali, *Green Chem.*, 2014.
- B. Karimi, F. Mansouri and H. Vali, *ChemPlusChem*, 2015, **80**, 1750-1759.
- M. V. Khedkar, T. Sasaki and B. M. Bhanage, *ACS Catal.*, 2013, **3**, 287-293.
- M. V. Khedkar, A. R. Shinde, T. Sasaki and B. M. Bhanage, *J. Mol. Catal. A: Chem.*, 2014, **385**, 91-97.
- A. R. Hajipour and G. Azizi, *RSC Adv.*, 2014, **4**, 20704-20708.
- L. F. Bobadilla, T. Blasco and J. A. Odriozola, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16927-16934.
- A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Catal. Sci. Technol.*, 2011, **1**, 856.
- A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, 4192-4194.
- S. S.-Y. Chui, S. M.-F. Lo, J. P. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.
- G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.
- L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. Férey and G. D. Weireld, *J. Am. Chem. Soc.*, 2009, **131**, 8775-8777.
- K. Leus, M. Vandichel, Y.-Y. Liu, I. Muylaert, J. Musschoot, S. Pyl, H. Vrieliink, F. Callens, G. B. Marin and C. Detavernier, *J. Catal.*, 2012, **285**, 196-207.
- K. Leus, I. Muylaert, M. Vandichel, G. B. Marin, M. Waroquier, V. Van Speybroeck and P. Van Der Voort, *Chem. Commun.*, 2010, **46**, 5085-5087.
- S. Wang, W. Yao, J. Lin, Z. Ding and X. Wang, *Angew. Chem.*, 2014, **126**, 1052-1056.
- J. Juan-Alcañiz, J. Gascon and F. Kapteijn, *J. Mater. Chem.*, 2012, **22**, 10102.
- Q.-x. Luo, M. Ji, M.-h. Lu, C. Hao, J.-s. Qiu and Y.-q. Li, *J. Mater. Chem. A*, 2013, **1**, 6530-6534.
- Q.-x. Luo, X.-d. Song, M. Ji, S.-E. Park, C. Hao and Y.-q. Li, *Appl. Catal. A: Gen.*, 2014, **478**, 81-90.
- Q.-x. Luo, B.-w. An, M. Ji, S.-E. Park, C. Hao and Y.-q. Li, *J. Porous Mater.*, 2015, **22**, 247-259.
- K. Fujie and H. Kitagawa, *Coord. Chem. Rev.*, 2016, **307**, 382-390.
- N. Khan, Z. Hasan and S. H. Jhung, *Chem. Commun.*, 2015.
- N. A. Khan, Z. Hasan and S. H. Jhung, *Chem. Eur. J.*, 2014, **20**, 376-380.
- K. Fujie, T. Yamada, R. Ikeda and H. Kitagawa, *Angew. Chem. Int. Ed.*, 2014, **53**, 11302-11305.
- Y. Feng, H. Jiang, S. Li, J. Wang, X. Jing, Y. Wang and M. Chen, *Colloids. Surf. A: Physicochem. Eng. Asp.*, 2013, **431**, 87-92.
- J. Ethiraj, F. Bonino, C. Lamberti and S. Bordiga, *Micropor. Mesopor. Mater.*, 2015, **207**, 90-94.
- C. W. Li and M. W. Kanan, *J. Am. Chem. Soc.*, 2012, **134**, 7231-7234.
- Z. Zhang, M. Xu, W. Ho, X. Zhang, Z. Yang and X. Wang, *Appl. Catal. B: Environ.*, 2016, **184**, 174-181.
- Z. Sheykhifard, M. Ranjbar, H. Farrokhpour and H. Salamati, *J. Phys. Chem. C*, 2015, **119**, 9534-9542.
- J. E. Dullius, P. A. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer and A. De Cian, *Organometallics*, 1998, **17**, 815-819.
- P. Weis, O. Hampe, S. Gilb and M. M. Kappes, *Chem. Phys. Lett.*, 2000, **321**, 426-432.
- X.-B. Wang and L.-S. Wang, *Phys. Rev. Lett.*, 1999, **83**, 3402.
- T. K. Shing, Y.-Y. Yeung and P. L. Su, *Org. Lett.*, 2006, **8**, 3149-3151.

49. M. Sankar, E. Nowicka, E. Carter, D. M. Murphy, D. W. Knight, D. Bethell and G. J. Hutchings, *Nat. Commun.*, 2014, **5**.
50. D. H. Barton, H. Patin and F. Launay, *New J. Chem.*, 1998, **22**, 559-563.
51. D. H. Barton and H. Patin, *New J. Chem.*, 1998, **22**, 565-568.
52. A. S. Roy, J. Mondal, B. Banerjee, P. Mondal, A. Bhaumik and S. M. Islam, *Appl. Catal. A: Gen.*, 2014, **469**, 320-327.
53. Z. Mandegani, M. Asadi, Z. Asadi, A. Mohajeri, N. Iranpoor and A. Omidvar, *Green Chem.*, 2015, **17**, 3326-3337.
54. M. B. Boucher, B. Zugic, G. Cladaras, J. Kammert, M. D. Marcinkowski, T. J. Lawton, E. C. H. Sykes and M. Flytzani-Stephanopoulos, *Phys. Chem. Chem. Phys.*, 2013, **15**, 12187-12196.



# Graphical Abstract



PdCl<sub>2</sub> immobilized on CuBTC with the aid of ILs shows an enhanced catalytic performance in cyclohexene oxidation due to Pd-Cu cooperative catalysis and stabilization of Pd (II).