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## Polyurea derived from CO<sub>2</sub> and diamines: highly efficient catalysts for C-H arylation of benzene

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Polyureas derived from CO<sub>2</sub> and diamines were effective for C-H arylation of benzene in the presence of *t*-BuOK, producing biaryl products with various substituents in high yields up to 97%. Dualactivation of  $K^{\dagger}$  and t-BuO, and  $\pi$ ,  $\pi$ -stacking interaction between the substrate and the polymer backbone may account for the superior activity.

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The direct C-H arylation of benzene is a promising reaction to construct C-C bond within biaryl moieties,<sup>1-2</sup> which can be achieved via catalysis over Pd,  $^3$  Rh,  $^4$  Ru,  $^5$  Ir,  $^6$  and Fe  $^{7\text{-}8}$ complexes and organocatalysts.<sup>7-16</sup> Recently, a variety of Ncontaining molecules (e.g., 1,10-phenanthroline<sup>9-11</sup> or its derivatives,<sup>12</sup> N,N-dimethylethane-1,2-diamine,<sup>13</sup> MOF-253 involving bipyridine moieties,<sup>14</sup> amino-linked nitrogen heterocyclic carbenes<sup>15</sup>) and O-containing compounds (e.g., alcohols<sup>16</sup>) have been proved to effectively promote the C-H arylation of benzene in the presence of a strong base (e.g. t-BuOK). Notably, the molecules incorporating with both N- and O-functionalities, such as proline,<sup>17</sup> macrocyclic aromatic pyridone pentamer,<sup>18</sup> vasicine<sup>19</sup> and 2-pyridyl carbinol,<sup>20-21</sup> exhibited synergistic effects from N- and O-functionalities. Although these homogeneous catalysts showed efficient catalytic activity, the heterogeneous catalysts are more desirable for industrial applications owing to the convenience of recovering and recycling of the catalysts.<sup>22</sup> More recently, Ma et al. reported a heterogeneous graphene oxide catalytic system for the C-H bond arylation of benzene, in which both the oxygen functional groups and the graphene  $\boldsymbol{\pi}$  system were found to facilitate the overall reaction.<sup>23</sup> Inspired by the above progress, we envisaged that heterogeneous polymers functionalized by both nitrogen- and oxygen- containing groups may be favourable to catalyze the direct C-H arylation of benzene to biaryl compounds in the presence of strong base.

Polyurea (PU) is a kind of polymer containing urea functional group, which shows high resistance to solvents, acids or bases, and superior thermal stability, thus widely being applied in coatings and corrosion protection areas. Recently, PU has been applied in catalysis due to their strong coordinating ability with metal complex and nanoparticles, showing promising application potentials.<sup>24</sup> For example, PU-encapsulated Pd and Pd-Cu bimetallic catalysts displayed excellent performances in the hydrogenation of styrene oxide and reduction of aryl ketones.<sup>25-26</sup> In our previous work, PU particles were synthesized via the reaction of CO<sub>2</sub> with 1,4-butanediamine, and the PU supported Pd nanoparticles were found to have a mean size <3.0 nm and show high efficiency for selective hydrogenation of o-chloronitrobenzene to o-chloroaniline.<sup>27</sup>

In our continuous work on PU, we discovered that PU derived from CO<sub>2</sub> and diamines could efficiently catalyze the direct C-H arylation of benzene to biaryl compounds in the presence of t-BuOK. Especially PU with aromatic ring in the skeleton displayed high efficiency for benzene arylation with aryl iodides containing both electron-donating and electronwithdrawing groups, producing a series of biaryl products with various substituents in high yields up to 97%. It was indicated that dual-activation of  $K^{\dagger}$  and t-BuO<sup>-</sup> by the urea unit in PU together with  $\pi$ ,  $\pi$ -stacking interaction between the substrate and the polymer backbone accounted for the superior activity of the PU catalysts. In addition, the PU catalysts had high stability and easy recyclability.

PUs were synthesized via the copolymerization of CO<sub>2</sub> with 1,4-butanediamine, 1,4-cyclohexanediamine and pxylylenediamine, respectively, catalyzed by  $[n-Bu_4N]_2WO_4$ using N-methyl pyrrolidone (NMP) as the solvent (for experimental details, see ESI), and their chemical structures are shown at the footnote of Table 1. The formation of PUs was revealed by Fourier transform infrared (FTIR) spectroscopy, elemental analysis (Table S1, ESI) and cross-polarization magicangle spinning (CP/MAS) <sup>13</sup>C NMR. In the FTIR spectra of PU (Figure S1, ESI), the urea units was confirmed by the characteristic bands at 1566 cm<sup>-1</sup> (CO-NH), 1625 cm<sup>-1</sup> (C=O), 3324 cm<sup>-1</sup> (N-H), and the respective bands for the methylene

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group around 2950 cm<sup>-1</sup>.<sup>27</sup> The presence of chemical shifts around 159 ppm in CP/MAS <sup>13</sup>C NMR spectra of PU belonged to the carbonyl carbon among the backbone (Figure S2, ESI), and those at 28-48 ppm to methylene carbon, together with 131-138 ppm to the aromatic carbons in **PU-Benz**. Thermogravimetric analysis (TGA) indicated that the resulting PUs were stable up to 300 °C in an air environment (Figure S3, ESI), which met the demands for potential applications in heterogeneous catalysis at high temperatures. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of PU showed morphologies of lamellar structure (Figure S4, ESI), which may be owing to the intramolecular and intermolecular hydrogen bonding formation between urea groups.<sup>28</sup>

The reaction of iodobenzene (1a) with benzene was taken as a model system to identify and optimize the key reaction parameters in the presence of PU and t-BuOK at 130 °C. As shown in Table 1, almost no biphenyl product (2a) was formed when the reaction was conducted in the absence of the PU catalysts (entry 1). Excitingly, all the resultant PUs were effective for the reaction, and especially, 87% yield of biphenyl was obtained in the presence of PU-Benz (entry 2), indicating that PU was indeed a promising catalyst for the arylation of benzene. This result was comparable to the reported heterogeneous graphene oxide (82% yield of **2a** at 120 °C).<sup>23</sup> In contrast, PU derived from aliphatic amines showed lower catalytic activities, with 55% and 46% yields of 2a being obtained in the presence of PU-<sup>c</sup>Hex and PU-<sup>n</sup>Bu, respectively (entries 2 vs. 3, 4), indicating that the chemical structures of PUs influenced the activities of the catalysts considerably. The  $\pi,\,\pi\text{-stacking}$  interaction  $^{29}$  between the aromatic ring of PU-**Benz** and the arene substrate together with the ion- $\pi$ interaction of PU with t-BuOK may be favourable to facilitating the reaction.9, 30 In this coupling system, potassium cation was essential, while other bases with tert-butoxide anion such as t-BuONa, t-BuOLi, as well as weaker potassium bases (KOH and K<sub>2</sub>PO<sub>4</sub>) (entries 5~8) were ineffective. For comparison, U-Benz as the corresponding urea monomer of PU-Benz was examined, and it exhibited inferior catalytic activity (2a yield: 65%) compared with the polymer PU-Benz (entry 9 vs. 2). This implies that the cross-linked hydrogen bonding and  $\pi$ ,  $\pi$ -stacking interaction of aromatic ring within the backbone of **PU-Benz** might facilitate the t-BuO activation and further catalyse the reaction. Both the carbonyl and amino groups within the PU skeleton may show catalytic activity for C-H arylation of benzene in the presence of t-BuOK. To confirm this, several molecules with separate carbonyl and amino groups, respectively, were examined for the reaction. It was demonstrated that 25% yield of 2a was attained catalyzed by equimolar N-methylbenzylamine (Table 1, entry 10), while much higher catalytic activity was observed taking benzylamine as the catalyst (2a yield: 55%) (Table 1, entry 11). 4-Phenylbutan-2-one catalyzed C-H arylation to give 2a in 61% yield, demonstrating the superior catalytic activity for oxygencontaining groups.<sup>23</sup> A physical mixture of homogeneous 4phenylbutan-2-one and *N*-methylbenzylamine showed identical activity (2a yield: 88%) towards PU-Benz (entry 2 vs.

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Table 1 PU-catalyzed C-H arylation of benzene.<sup>a</sup> PU <sup>t</sup>BuOK Yield/%<sup>b</sup> Entry Catalyst 1 <1 2 PU-Benz 87 3 PU-<sup>c</sup>Hex 55 PU-"Bu 4 46 5° PU-Benz <1 6<sup>c</sup> 0 PU-Benz 7 PU-Benz 0 8<sup>c</sup> PU-Benz 0 9<sup>d</sup> U-Benz 65 10<sup>d</sup> 25 N-methylbenzylamine 11<sup>d</sup> Benzylamine 55 12<sup>d</sup> 4-phenylbutan-2-one 61 13<sup>d</sup> 4-phenylbutan-2-one + N-methylbenzylamine 88 14<sup>e</sup> PU-Benz 0

<sup>a</sup> Reaction conditions: PhI 0.4 mmol, benzene 4 mL, *t*-BuOK 1.2 mmol, **PU-Benz** 12.5mg/**PU-<sup>c</sup>Hex** 10.7 mg/**PU-**<sup>n</sup>**Bu** 9.0 mg (containing 0.07 mmol urea units based on the elemental analysis results in Table S1, ESI), 130 °C, 24 h; <sup>b</sup> Determined by GC using dodecane as an internal standard; <sup>c</sup> 1.2 mmol *t*-BuONa (entry 5), *t*-BuOLi (entry 6), KOH (entry 7) and K<sub>3</sub>PO<sub>4</sub> (entry 8), respectively, was added instead of *t*-BuOK; <sup>d</sup> 4-phenylbutan-2-one 0.07 mmol, amine, 0.14 mmol for entry 10~13. <sup>e</sup> 0.4 mmol TEMPO was added to the reaction mixture.



13). However, 4- phenylbutan-2-one was very unstable in the presence of strong base, e.g. *t*-BuOK, which reacted through nucleophilic attack on the carbonyl carbon and hydrogen transfer of the methylene group, as detected by <sup>1</sup>H and <sup>13</sup> C NMR spectra (Figure S5, ESI), implying impossibility for its recyclability.<sup>21</sup> Nonetheless, carbonyl group of the urea unit in PUs was stable, confirmed by the fact that addition of *t*-BuOK to the suspension of **U-Benz** or **PU-Benz** did not result in any products detectable by NMR and FTIR (Figure S6 and S7, ESI). Subsequently, influences of various factors (*e.g.*, catalyst loading, temperature, volume of benzene, amount of base and reaction time) on the reaction outcome were investigated, and the optimal reaction conditions involved the use of 12.5 mg of **PU-Benz** and 3 equivalents of *t*-BuOK at 130 °C for 24 h (Figure S8, ESI).

The generality of this protocol for other benzene arylation reactions was then examined and the results are summarized in Table 2. Generally, aryl iodides with electron-donating groups were more reactive than electron-neutral ones and those with electron-withdrawing groups. Aryl iodides with para-substituents were more reactive than those with metaor ortho-ones owing to steric hindrance. For example, 97% Published on 22 November 2016. Downloaded by University of Toronto on 22/11/2016 12:50:28

87

97

85

74

28

37

7



<sup>a</sup> Reaction conditions: 1 0.4 mmol, benzene 4 mL, t-BuOK 1.2 mmol, PU-Benz 12.5 mg, 130 °C, 24 h; <sup>b</sup> Determined by GC using dodecane as an internal standard. <sup>c</sup> Yield in the bracket was obtained within 48 h. <sup>d</sup> Yield in the bracket was obtained within 72 h. e 4 mL toluene was added instead of benzene.

yield of 2b was obtained taking 4-iodotulene (1b) as an arylation reagent, while the reactivities of iodobenzene (1a) and 1-fluoro-4-iodobenzene (1f) were much lower, giving 87% yield of 2a and 63% yield of 2f, respectively (entries 1, 2 vs. 6). In addition, the yield of 2f increased to 76% by prolonging the reaction time to 48 h. The coupling of benzene with 1-tertbutyl-4-iodobenzene (1e) was less efficient owing to steric effect of the tert-butyl substituent, affording 58% yield of 2e, which increased to 72% within 48 h. Comparatively, only 28% yield of product (2i) was observed due to a combination of electronic and steric effect of the trifluoromethyl group of 1i (entries 5 vs. 9). The position of the substituents had great effect on the reactivity. For methyl or fluoro-substituted iodobenzenes, the activity was decreased in the order of para-> meta- > ortho-substitution, that is, the yields decreased as 2b (97%) > 2c (85%) > 2d (74%), and 2f (63%) > 2g (15%) > 2h (10%), owing to steric effect (entries 2~4 and 6~8). 83% yield of 2g and 81% yield of 2h were achieved by prolonging the reaction time to 72 h. Notably, less reactive 2-iodothiophene (1j) was also performed to arylate with benzene, producing 2j

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in 37% yield (entry 10). Aryl bromide was tested as well, but only 7% yield of biphenyl was obtained (entry 11).

The reusability of the catalyst PU-Benz was examined, and it was indicated that 86% yield of bipenyl 2a was still obtained after the catalyst was reused for five times (Figure 1) (for experimental details, see ESI), suggesting good reusability and stability. The structure of the recycled PU-Benz was kept well as detected by FTIR and CP/MAS <sup>13</sup>C NMR (Figure S9, ESI).



Figure 1 Recyclability test of PU-Benz. Reaction conditions: PhI 0.4 mmol, t-BuOK 1.2 mmol, PU-Benz 12.5 mg, benzene 4 mL, 130 °C, 24 h. Yield of 2a was determined by GC using dodecane as an internal standard.

Further investigation was performed to gain a deep insight into the reaction mechanism. Firstly, consistent with the involvement of aryl radicals in the arylation reactions reported before,<sup>10, 21</sup> addition of one equivalent of free radical scavengers of TEMPO ceased the reaction and no product was obtained (Table 1, entry 14) in the presence of PU-Benz. The ESI-MS characterization of the CH<sub>3</sub>OH solution of U-Benz and t-BuOK with 1:1 molar ratio showed a peak at 279, ascribing to  $[\mathbf{U}-\mathbf{Benz} + K]^+$  species from the coordination of  $K^+$  with the urea group. This implies that  $K^{\dagger}$  may coordinate with the urea unit within the backbone of PU-Benz during the reaction process. Moreover, the interaction of the anion t-BuO with the urea unit was also witnessed by <sup>1</sup>H NMR spectra of **U-Benz** with *t*-BuOK (Figure S6). The signal of methylene group in U-Benz was located and split as dual peaks at 4.35 and 4.37 ppm by the adjacent N-H, which was merged as a single peak at 4.36 ppm after addition of equimolar t-BuOK, indicating the hydrogen bonding formation between N-H and t-BuO<sup>-</sup>. This interaction was further evidenced by the signal of N-H in U-Benz located at 5.69 ppm, which became a broad one in the presence of t-BuOK. In the FTIR spectrum of PU-Benz, the sharp peak centred around 3324 cm<sup>-1</sup> for N-H vibration was obviously receded in the spectrum of the physical mixture of PU-Benz and t-BuOK (Figure S7).

Based on the above findings and related results reported by others,<sup>10-11, 21, 23</sup> we speculated that interactions of the potassium cation and tert-butoxide anion with the urea unites and aromtic ring in the backbone of PU-Benz acted synergistically to catalyze the C-C bond formation reaction. A radical-mediated catalytic mechanism was proposed (Scheme 1). The potassium cation and tert-butoxide anion was activated by the urea unit among the skeleton of PU-Benz, which

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subsequently transferred a single electron to aryl iodide 1, affording the intermediate aryl radical anion I. And then, aryl radical II was formed by departure of iodide anion, and then reacted with benzene to generate a biary radical III. Oxidation of III by the previously formed radical cation of *t*-BuOK produced the biaryl cation IV. Finally, deprotonation of IV by a *tert*-butoxide anion furnished the biary product 2. Notably,  $\pi$ ,  $\pi$ -stacking interaction between aryl ring within the polymer chains with the arene substrate played an important role in attracting the substrate to the vicinity of the catalytic center, and stabilizing the resultant intermediates.



In conclusion, PUs derived from  $CO_2$  and diamines, especially **PU-Benz** with aromatic ring among the skeleton, was proved to be an efficient heterogeneous catalytic material for C-H arylation of benzene in the presence of *t*-BuOK, together with broad substrate scope, high stability and easy recyclability. Both urea and benzene functionalities among the polymer backbone were important for the catalytic process, realizing dual-activation of K<sup>+</sup> and *t*-BuO<sup>-</sup>, together with  $\pi$ ,  $\pi$ -stacking interaction between the substrate and the polymer backbone, and thus resulting in good catalytic activity. Based on the efficient coordination of urea units with alkali metal cations, applications of polyurea materials in hydrogentransfer reactions were under investigation.

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