DOI: 10.1002/adsc.201000475

An Economical, Green Pathway to Biaryls: Palladium Nanoparticles Catalyzed Ullmann Reaction in Ionic Liquid/Supercritical Carbon Dioxide System

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Received: June 20, 2010; Revised: August 26, 2010; Published online: December 7, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000475.

Abstract: In this paper, an economical, green pathway involving the palladium nanoparticles (Pd NPs) catalyzed reductive Ullmann reaction of an aryl chloride to afford a biaryl with high conversion and selectivity in an ionic liquid (IL)/supercritical carbon dioxide ($ScCO_2$) system was developed. The combination of IL and $ScCO_2$ provides superior advantages in product separation, catalyst recycling and reuse of reaction media over traditional organic solvents. Further investigations showed that the Brønsted-acidic imidazolium IL {e.g., (1-butyl-3-(sulfobutyl)-imidazolium) hydrogen sulfate, $[bmim(HSO_3C_4)][HSO_4]$}, can replace the traditional active hydrogen donor readily with much enhanced product separation efficiency, the use of IL also led to an obvious improved stability of the Pd NPs, which was very helpful for catalyst recycling. Carbon dioxide, a naturally abundant, non-flammable, relatively non-toxic, economical and recyclable "greenhouse" gas, was found to significantly promote the selectivity of the Pd NPs-catalyzed aluminium-induced reductive Ullmann reaction of aryl chlorides. Investigations showed that the Pd NPs catalyst and IL can be recycled for at least five runs, indicating the economic viability of this process.

Keywords: green chemistry; ionic liquids; nanoparticles; palladium; supercritical carbon dioxide; Ullmann reaction

Introduction

There is increasing interest in the development of environmentally benign and economically viable transition metal-catalyzed processes, feasible innovative methodologies including application of "green" reaction media, catalyst immobilization and recycling, reuse of the reaction media and efficient product separation, etc.[1]

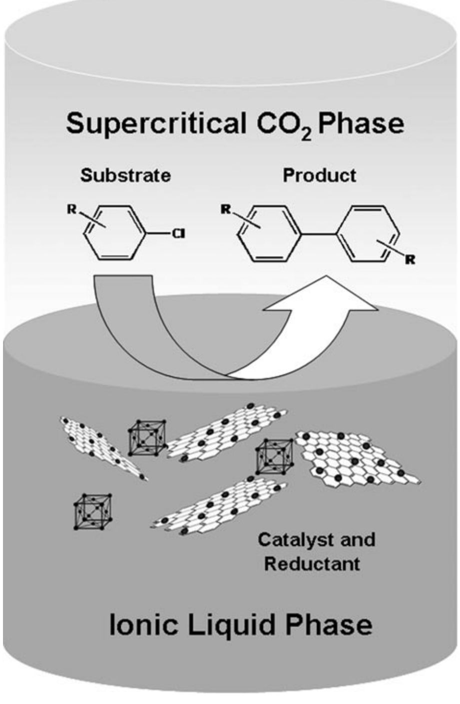
Among various approaches, the combination of IL with supercritical fluids, particularly $ScCO_2$, offers a highly attractive choice. By combination with IL, the dissolved CO_2 significantly increases the mass transport properties of the IL phase. And typically, IL can dissolve large amounts of CO_2, but IL are usually insoluble in $scCO_2$, thus the biphasic IL/$ScCO_2$ system has gained importance in catalysis reactions, in which the catalyst is trapped in the IL phase, the reactant and product can be added and removed from CO_2 phase.[1c,2a] Furthermore, there are multiple options to adjust the solvent properties, besides a vast selection of prospective cations and anions to tailor the properties of the IL, temperature and pressure are also available as variables to adjust the density and solvent power of $ScCO_2$.[2]

Over the past decades, the IL/$ScCO_2$ system has received an increasing amount of attention in the fields of separation, chemical reactions and materials synthesis.[2a,3] For example, Baiker and co-workers[4] performed Pd/[bmim][PF_6]-catalyzed hydrogenations in an IL/CO_2 biphasic system with efficient product separation. The catalytic system exhibited excellent activity and selectivity, showing no obvious deactivation during the reaction cycles. For other typical reactions, Cole-Hamilton and his group have developed a continuous-flow homogeneous catalytic process for the hydroformylation of long-chain alkenes in IL/ScCO_2, the catalyst remained in the reactor at all times, the CO_2 could also be recycled and no other solvents are required.[5] Wai et al. studied the recyclable palladium chloride-catalyzed Heck reaction in an IL/ScCO_2 biphasic system, and found that the coupling efficiency was dependent on the water content of the ionic liquid.[6]

The other important issue for environmentally and economically important organic transformations was a recyclable transition metal, for example, NP-catalyzed transformations with high activities and selectivity. Therefore, designing new catalysts by combining transition metal NPs with an efficient support of choice instead of complicated ligands provides a broad scope for the discovery of novel, highly selective and recyclable catalysts for further applications.[7]

As one of the most important intermediates, biaryls are key building blocks for numerous biochemicals,[8] pharmaceuticals,[9] agrochemicals, dyes,[10] sensors,[11] conductive polymers,[12] and also serve as helpful ligands for asymmetric catalysts,[13] etc. The original and most widely used methodology to access them was *via* the Ullmann reaction, the homocoupling of aryl halides.[14,15] It is usually carried out with copper as the catalyst, however, an excess of copper or harsh reaction conditions[15b,16] are necessary. An effective and milder catalytic alternative was the palladium-catalyzed reductive coupling of aryl halides.[14c–f] In these processes, reducing agents such as aldehyde,[14e] hydrogen gas,[17] formate salts,[18] alcohol,[19] glucose,[20] carbon monoxide,[21] ascorbic acid,[22] amine,[23] zinc[14f] and indium or germanium[10a] etc. were required for closing the reductive coupling cycle. Due to the wide applications of the Ullmann reaction, the development of economical, environmental friendly methods is of crucial importance. Traditional works on the Ullmann reaction were mostly performed in volatile organic solvents. In recent years, some researchers have focused their interest on the Ullmann reaction in clean reaction medias, such as poly(ethylene glycol),[24] ScCO_2[25] (or liquid CO_2[26]) and IL,[14e] etc. However, most of the work encountered various difficulties, such as use of volatile chemicals (co-solvent or reductant), waste of reaction medias, poor catalyst recycling and inefficient product separation, etc. For example, Cotugno and co-workers reported an aldehyde-promoted Ullmann reaction of vinyl and heteroaryl halides in tetraalkylammonium IL under mild conditions.[14e] However, the IL was used for only one run which led to unnecessary waste and environmental pollution, and with the application of the toxic aldehyde that is poorly miscible with the IL, extraction of the reaction products can cause contamination of the IL and diminish the overall simplification of the recycling.

Therefore, the combination of IL and ScCO_2, which can provide superior performances in product separation, catalyst recycling and reuse of IL, would be an excellent alternative "green" choice. Unfortunately, until now, little attention had been paid to the Ullmann reaction in the environmental benign IL/ScCO_2 system. Herein, we report the aluminium-mediated reductive Ullmann reactions of aryl chlorides over graphite-based palladium nanoparticles to afford biaryls with high conversion and selectivity in the environmental friendly IL/ScCO_2 system, which utilized the cheaper aryl chlorides (instead of the much more expensive aryl bromides or aryl iodines) and aluminium (instead of expensive indium or volatile aldehyde, etc.) as the starting reagents. The Brønsted-acidic imidazolium IL, for example, ([bmim (HSO_3C_4)] [HSO_4]), used in this work can replace the traditional active hydrogen donor (H_2O, etc.) readily with much enhanced product separation efficiency. In this unique system, CO_2, a naturally abundant, relatively nontoxic, economical and recyclable "greenhouse" gas, was found to promote the selectivity of the reaction readily. And the IL and Pd NPs involved in IL/ScCO_2 can be used for at least five times, providing a mild, economic, and green route for the synthesis of symmetrical biaryls (Scheme 1).



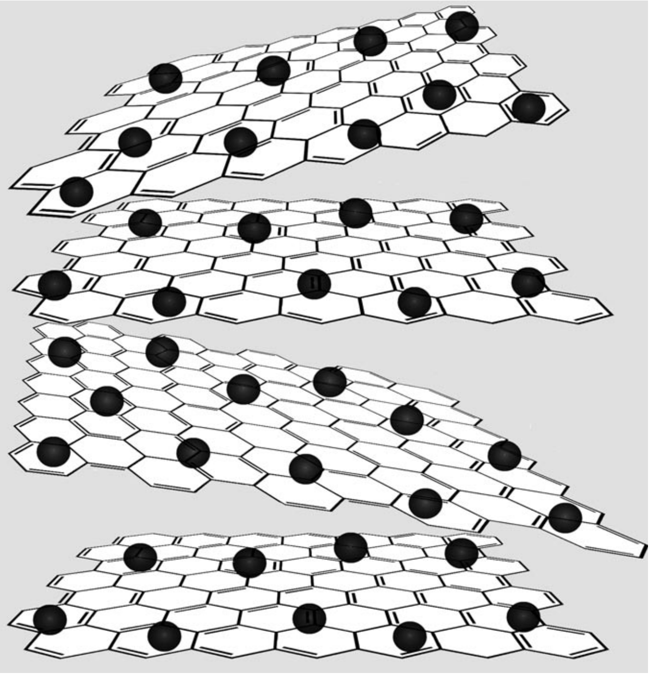
Scheme 1. Illustration of Pd NPs/carbon-catalyzed Ullmann reaction in an IL/ScCO_2 system.

Results and Discussion

Catalyst Preparation

In this work, oxidized graphite (OG, see the Supporting Information) was made by using a modified Brodie method.[27] The distance of the loosely attracted carbon nanosheets of OG became much larger than those in graphite, and some carbon nanosheets were exfoliated to a few-layered ones. To synthesize the supported NPs catalysts, a dispersion of OG was mixed with $PdCl_2$ solution in water. Then the OG and palladium(II) cations were reduced in one step by reduction with $NaBH_4$. Finally, the reduced solid sample with nanoscale Pd loading, designated as Pd NPs/carbon (Scheme 2), was obtained readily, in the structure of which the Pd NPs were scattered randomly on the carbon platelets.

The Pd NPs/carbon was characterized by high-resolution transmission electron microscopy (HR-TEM), scanning electron microscopes (SEM), electron diffraction (Figure 1) and X-ray diffraction (XRD) analyses (see Supporting Information, Figure S1). Figure 1a, b show the HR-TEM images of Pd NPs/carbon. It was easy to see that the carbon platelets were decorated uniformly by the nanosized Pd particles, which were in the size range of 2–10 nm, and a few particles were free from the supports, indicating a strong interaction between the particles and carbon supports. Above results reveal that the present method can produce stable and small-sized Pd NPs. From Figure 1b, we can observe that the Pd NPs have polycrystalline structures, the lattice spacing of which is 0.23 nm, similar to the Pd (111) lattice spacing. The electron diffraction pattern shown in Figure 1c indicates that the NPs supported on the carbon support have a uniform and narrow particle size distribution, which is also confirmed by the SEM image in Figure 1d. The polycrystalline nature of Pd NPs produces four X-ray diffraction rings in sequence from the inner core to the outer perimeter which can be indexed to the (111), (200), (220), and (311) planes of the face-centered cubic Pd, respectively. XRD patterns in Figure S1 (Supporting Information) showed an obvious (002) peak for graphite and (111), (200), (220) peaks for palladium, revealing that the catalyst was a graphite-based nanocomposite.[28] Figure S1 (Supporting Information) also confirmed the maintained presence of crystalline Pd(0) in Pd NPs/carbon. The most representative reflections of Pd(0) are indexed as face-centered cubic (fcc) with unit cell parameter $a = 0.390$ nm. The Bragg reflections at 39.6°, 45.5° and 67.3° correspond to the indexed planes Pd(0) (111), (200), (220) of the crystals.



Scheme 2. Illustration of Pd NPs/carbon.

Investigations of the exfoliation graphite showed that most of carbon sheets were loosely attracted, and some carbon sheets were exfoliated to a few-layered ones, holding a greater surface area than graphite. Therefore it can be used as an optimal catalyst support. Experiments showed that, in the presence of Pd NPs/carbon, the reactions of various aryl chlorides run quite smoothly with good yields (entries 1, 20–26, Table 1).

The Phase Behaviour of the IL/ScCO$_2$ System

ScCO$_2$ has been shown as an environmentally benign solvent with tunable physicochemical properties for increasing reaction rates, and IL can be molecularly engineered for specific physicochemical properties through various substituents and cation/anion selection, for example, viscosity, solubility properties, density, temperature range, acidity/basicity, co-ordination properties, etc. Thus, a biphasic IL/CO_2 system draws on the advantages of each of the respective technologies and helps overcome their challenges.[1c] The IL phase in this unique system is employed to sequester the catalyst and the CO_2 phase becomes the mobile phase for reactants and products. Under high pressure, CO_2 can become miscible with IL, thus eliminating gas-liquid phase boundaries and their inherent mass transfer limitation. Furthermore, CO_2 is very soluble in the IL and reaches approximately 40% mol CO_2 at 50 bar, 65% mol at 100 bar, with only marginal increases in solubility beyond 100 bar.[2a] In contrast, the IL is immeasurably insoluble in the pure CO_2 phase and does not become miscible (critical) even at hyperbaric pressures, for example, 3.1 kbar.

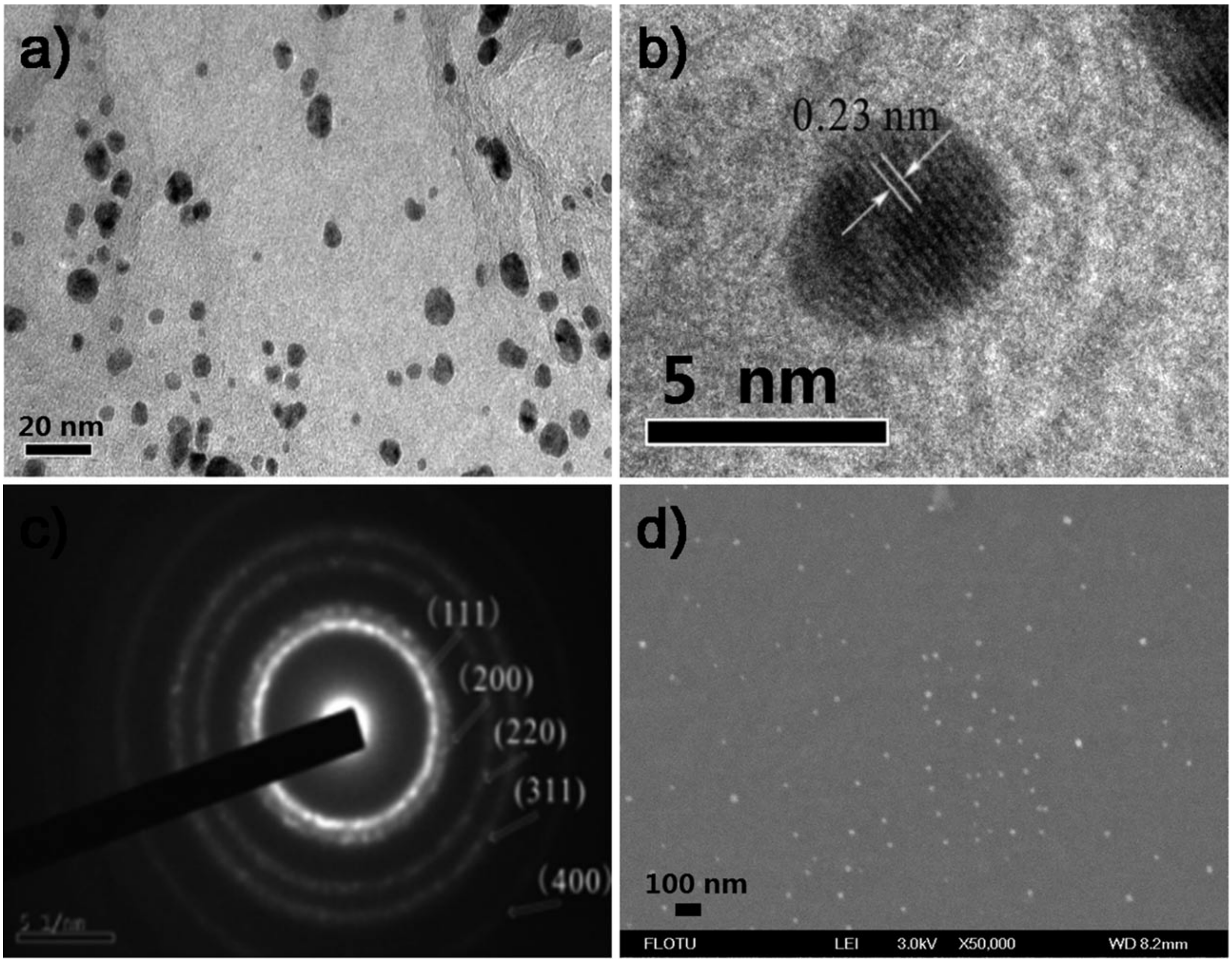


Figure 1. (**a**, **b**) HR-TEM images of Pd NPs/carbon, showing the polycrystalline structure of palladium; (**c**) electron diffraction pattern of Pd NPs/carbon; (**d**) SEM image of Pd NPs/carbon.

More fortunately, the catalyst, for example, graphite-based Pd NPs, is far more dispersable in IL than in $ScCO_2$, thus there is no tendency for the $ScCO_2$ to extract the catalyst. One then obtains essentially pure products from the CO_2 flow without IL or catalyst contamination, and the catalysts solution left behind in the vessel can be reused for several runs, while the conversion remained high through the cycles.

Scheme 3 shows a schematic view of the effect of pressure on the phase behaviour of a reaction system that consists of IL, CO_2 and organic compounds (reactant and product) (Org.). When Pd NPs/carbon and the substrate (ArCl, etc.) solution of IL was exposed to CO_2, large amounts of CO_2 dissolved in the IL, causing the liquid solution to expand forming a vapour-liquid equilibrium (VLE). Further addition of CO_2 causes the liquid phase to split into two liquid phases in equilibrium with a vapour phase [vapour-liquid-liquid equilibrium (VLLE)] at the lower critical end point (LCEP) pressure (3.1 kbar, step II, Scheme 3). As the pressure is further increased, the relative volume of the organic-rich phase increases until it reaches the K-point pressure, where the vapour phase and the organic-rich liquid phase merge into a single supercritical phase (SCF). Above the K-point pressure, the SCF phase (organic-rich phase) and the IL-rich phase become critical and miscible with each other[29] (some authors also believed that under such conditions, the SCF phase and the IL phase can be forced to form one homogeneous liquid phase[30]), thus under such conditions, the reaction can be carried out with much higher activities as compared with a heterogeneous system. As the reaction proceeds (step III, Scheme 3), more and more of the remaining amount of organic compounds in the IL phase are transferred gradually to the upper SCF phase, similar to supercritical fluid extraction from IL. For the case of complete conversion, the CO_2 pressure was released through a decompression valve (controlled at slightly lower than the K-point pressure), the SCF-IL phases equilibrium shifts back to VLLE equilibrium, in this situation, the overwhelming majority of organic (product) has been extracted into the upper liquid and vapour CO_2 phases (step IV,

Table 1. Pd NPs-catalyzed Ullmann reaction of aryl halides in IL/ScCO$_2$.[a]

$$\underset{\mathbf{1}}{2\ \text{Ar-Cl}} \xrightarrow[\substack{[\text{bmim}(\text{HSO}_3\text{C}_4)]\,[\text{HSO}_4]/\text{ScCO}_2 \\ 45\ ^\circ\text{C},\ 15.5\ \text{MPa}}]{\text{Pd NPs/carbon, Al(0)}} \underset{\mathbf{2}}{\text{Ar-Ar}} + \underset{\mathbf{3}}{\text{Ar-H}}$$

chlorobenzene: **1a**
1-*tert*-butyl-4-chlorobenzene: **1b**
1-acetyl-4-chlorobenzene: **1c**
2-chlorobenzyl alcohol: **1d**
(2-chlorovinyl)-benzene: **1e**
1,1-diphenyl-2-chloroethylene: **1f**
4-chloroaniline: **1g**
4-chloro-2, 6-dimethylaniline: **1h**
bromobenzene: **1i**
iodobenzene: **1j**

Entry	Aryl halide	CO$_2$[b] [MPa]	Time [h]	**IL-**	Product	Conversion[c] [%])	Yield[d] [%]
1	**1a**	15.5	10	**c**	**2a**	100	99
2[e]	**1a**	15.5	10	**c**	**2a**	23	trace
3[f]	**1a**	0	10	**c**	**2a**	31	n.d.[g]
4[h]	**1a**	15.5	10	–	**2a**	12	0
5[i]	**1a**	15.5	10	–	**2a**	79	53
6	**1a**	1.0	10	**c**	**2a**	12	n.d.
7	**1a**	4.0	10	**c**	**2a**	28	n.d.
8	**1a**	5.0	10	**c**	**2a**	31	n.d.
9	**1a**	6.0	10	**c**	**2a**	36	29
10	**1a**	7.5	10	**c**	**2a**	71	63
11	**1a**	12.5	10	**c**	**2a**	83	74
12	**1a**	13.0	10	**c**	**2a**	97	92
13	**1i**	6.0	10	**c**	**2a**	42	33
14	**1j**	6.0	10	**c**	**2a**	62	55
15[j]	**1a**	15.5	10	**c**	**2a**	78	72
16	**1a**	15.5	10	**a**	**2a**	95	91
17	**1a**	15.5	10	**b**	**2a**	97	94
18	**1a**	15.5	10	**d**	**2a**	19	trace
19	**1a**	15.5	10	**e**	**2a**	91	84
20	**1b**	15.5	8	**c**	**2b**	100	99
21[k]	**1c**	15.5	16	**c**	**2c**	100	96
22[l]	**1d**	15.5	12	**c**	**2d**	99	95
23[m]	**1e**	15.5	12	**c**	**2e**	98	87
24[n]	**1f**	15.5	12	**c**	**2f**	100	98
25[k]	**1g**	15.5	16	**c**	**2g**	98	94
26	**1h**	15.5	10	**c**	**2h**	99	91

[a] *Reaction conditions:* aryl halide (2 mM), Al (0) (108 mg), [bmim(HSO$_3$C$_4$)][HSO$_4$] (3 mL); Pd NPs/carbon (3.0% w/w, 186.2 mg) and ScCO$_2$ (15.5 MPa) at 45 °C for 10 h.

[b] Pressure of CO$_2$.

[c] Determined by GC analysis.

[d] Isolated yield.

[e] In the absence of Al(0).

[f] In the absence of ScCO$_2$.

[g] n.d. = no Ullmann products were detected.

[h] In the absence of IL; some unidentified brown oil was also isolated.

[i] In the presence of H$_2$O instead of IL,

[j] Pd/C was used instead of Pd NPs/carbon, the diameter of the Pd particles in which was 28–34 μm.

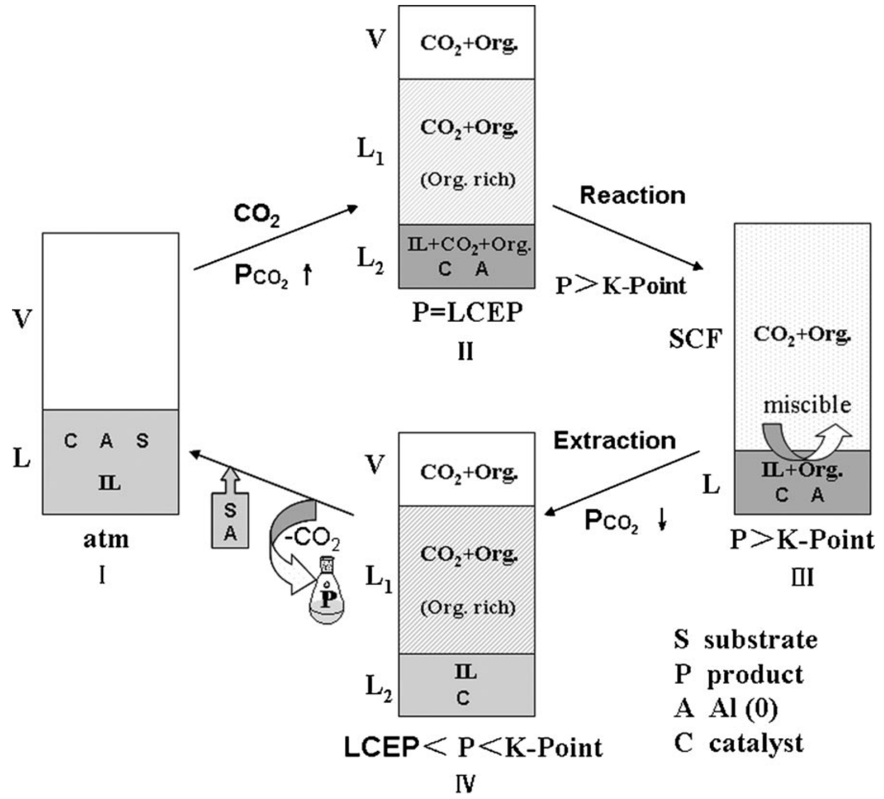
[k] The reaction was conducted at 65 °C.

[l] Pd NPs/carbon (4% w/w, 248.3 mg) was used, some unidentified oil was also obtained.

[m] Pd NPs/carbon (3.5% w/w, 217.3 mg) was needed, some unidentified oil was also observed (2.47%).

[n] Pd NPs/carbon (3.5% w/w, 217.3 mg) was needed.

Scheme 3), and the resulting V+L1 phases (step IV, Scheme 3), which contained no detectable IL, were vented entirely into a solvent trap vessel with cooling apparatus, simply by further decompression of the CO$_2$, the Ullmann products were conveniently collected through the valve at the bottom of the solvent trap vessel.



Scheme 3. Schematic view of the "green" pathway of the Ullmann reaction. The catalytic cycle consists of cycle preparation (**I**), $ScCO_2$ extraction of the substrate (**II**), SCF phase and IL+Org. phase formation (**III**) and $ScCO_2$ extraction of the product (**IV**), after which new substrate and Al(0) can be added to restart the new catalytic cycle.

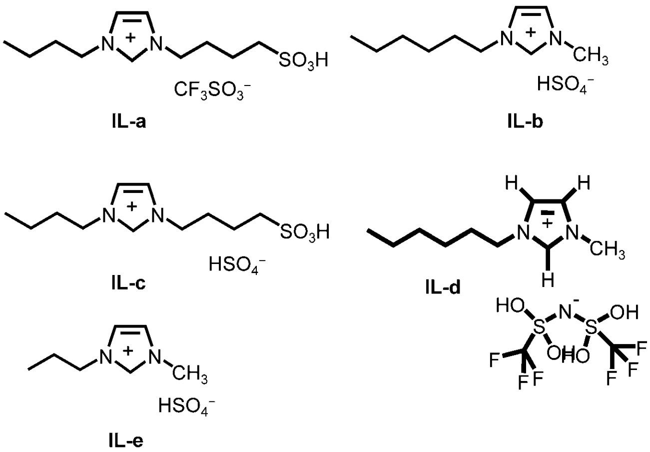
There are multiple strong forces, for example, π-π stacking, hydrogen bonds, etc., between hundreds of IL molecules and carbon nanosheets. Previous reports revealed that the IL environment helps stabilize the NPs catalysts, therefore, the carbon-supported Pd NPs were inclined to remain in the bottom IL phase instead of being extracted by the CO_2 phase. Further reduction of CO_2 pressure led to easy isolation of the product without cross-contamination of IL or catalyst. Once the product is isolated completely, addition of fresh reductant and substrate into the remaining catalyst IL solution led to a new cycle of the Ullmann reaction (step I, Scheme 3).

The Role of the CO_2 in the Ullmann Reaction

A variety of reactions have been performed in IL/$ScCO_2$ system. Most such reports are concerned with the application of CO_2 as reaction media or reactant. The effect of CO_2 on catalyzed reactions in IL is not consistent throughout the literature sources. Some showed that CO_2 can increase the activity, while others indicated a decrease in activity with CO_2 pressure. Regardless, most studies consistently revealed an increase in selectivity (chemo-, regio-, and enantioselectivity). For example, Tumas and co-workers[31] compared the results in a biphasic IL/CO_2 and IL/hexane systems in the olefin hydrogenation and found little difference in the reaction rates with pressurized CO_2 or hexane. Jessop and co-workers[32] performed asymmetric Ru-catalyzed hydrogenations in an IL/CO_2 biphasic system with an enantioselectivity that was tunable with the pressure of CO_2. Leitner and co-workers[33] found that for iridium-catalyzed hydrogenation of aromatic imines, there was an increase in reaction rate with the presence of CO_2 as compared with H_2 pressure alone. For the Ullmann reaction, there are also some recent studies revealed that CO_2 can act as a substrate activating agent to promote the Ullmann reaction.[14f,34]

To identify the real role of the CO_2 in this reaction, a series of experiments on the Ullmann reaction of phenyl chlorides **1a** in the IL/$ScCO_2$ system were conducted. Experiments showed that CO_2 plays a crucial role in the Ullmann reactions of aryl chlorides. In the absence of CO_2, no Ullmann coupling product was detected (entry 3, Table 1). When the CO_2 pressure was increased to 1 MPa, 4 MPa or 5.0 MPa (all lower than the LCEP value, respectively), we still did not observe Ullmann coupling products (entries 6–8, Table 1). Interestingly, experiments revealed that when the pressure was enhanced to 6 MPa, a 29% yield of biphenyl was obtained readily (entry 9, Table 1). Further increases of pressure lead to enhanced yields of the reaction (7.5 MPa, 63.0% yield, entry 10, Table 1). Encouraged by this, a series of experiments conducted at different CO_2 pressures was carried out. We found that an optimal yield of biphenyl was achieved when the pressure was controlled at 15.5 MPa (99.0% yield, entry 1, Table 1). It's noteworthy that previous work had revealed that, for the [hmim][Tf_2N]/$ScCO_2$/*n*-nonanal system at 70 °C, the K-point is 13.61 MPa[29a]. For [bmim(HSO_3C_4)][HSO_4]/$ScCO_2$ at 45 °C, experiments showed that once the pressure was increased over 12.70 MPa, which might be the K-point pressure for this system, a further increase in yield could be obtained. For example, when the CO_2 pressure was controlled at 12.5 MPa (entry 11, Table 1), a 74% yield was obtained. When the pressure was increased to 13.0 MPa, a much enhanced yield was obtained (92%, entry 12, Table 1), indicating that the K-point pressure plays an important role in this reaction, under such conditions, the SCF phase and the IL phase become critical and miscible with each other (near homogeneous manner[30]), therefore, the reaction can be carried out with much higher activities as compared with the heterogeneous system.

In conclusion, besides its role as an economical and environmental friendly reaction medium, the pressure of the CO_2 plays an important role in influencing the activity and conversion of the reaction, the optimal yield can be achieved once the pressure was increased above the K-point pressure.



Scheme 4. Structural formulae of the ionic liquids used in this work.

The Catalyst and Reducing Agent

The aromaticity of the imidazolium cation and graphite layer (Scheme 4) make them possess the possibility of π-π stacking, Meanwhile, [bmim(HSO_3C_4)][HSO_4], which possesses nitrogen and hydrogen atoms in the imidazolium cation, serves as weak H-bond donor.[35] Therefore there are multiple strong forces: π-π stacking, hydrogen bonds and electrosteric forces between [bmim (HSO_3C_4)][HSO_4], molecules and exfoliated graphite nanosheets. As stated above, the bulkiness of IL imidazolium cations, N-imidazolium side chains together with anion of the IL favoured the electrosteric stabilization of NPs, thus in this system, the IL phase was employed to sequester the catalyst and the CO_2 phase becomes the mobile phase for reactants and products. Why does Pd NPs/carbon have such high catalytic performance for the Ullmann reaction? We proposed that, first of all, the exfoliated graphite nanosheets provided a relatively large surface area and high immobilization capacity to deposit highly active catalytic Pd NPs, which is very helpful for the catalytic efficiency. Second, the Pd NPs generated *in situ* by mild reduction can form smaller spherical Pd NPs (a median size distribution of 2–10 nm) dispersed uniformly over the few-layered exfoliated graphite support, which exhibits a superior catalytic performance than the commercial Pd/C catalyst with micron scale palladium particles (in the presence of Pd/C catalyst, 72% yield was obtained, entry 15, Table 1).

For reducing agent, in the past decades, reagents such as aldehyde, hydrogen gas, formate salts, glucose, carbon monoxide, ascorbic acid, amine, zinc, indium or germanium, etc. were used in the Ullmann reaction. Most of them are volatile or toxic, and some are very expensive. In this work, we choose aluminium, which is much cheaper and more available, as the reducing agent. In the presence of aluminium, the reductive Ullmann reactions of different aryl halides proceeded smoothly with desired yields (entries 1, 20–26, Table 1). In contrast, when the reactions were carried out without addition of aluminium, only trace amounts of biaryl product were detected (entry 2, Table 1), indicating the crucial importance of aluminium as reducing agent.

Reactions of Different Aryl Halides

Although aryl bromides and aryl iodides are much more active (the results in entries 9, 13 and 14 indicate their activity differences, Table 1), they are much more expensive than aryl chlorides. For economical considerations, we choose aryl chlorides, although less active they are much cheaper, as the substrate. After a series of attempts, we found that in the presence of Al(0), the Pd NPs/carbon-catalyzed reaction can proceed with 29% yield in the [bmim(HSO_3C_4)] [HSO_4]/ $ScCO_2$ system at 6 MPa of CO_2 pressure (entry 9,

Table 1). Although the yield was still very low, it fostered our hope for further research.

Excitingly, we found that when the pressure was increased to 15.5 MPa, an optimal yield for the Ullmann reaction of phenyl chloride was obtained (99%, entry 1, Table 1). Detailed investigations showed that the optimal conditions were: biphenyl chloride (2 mM), Al(0) (108 mg), [bmim(HSO_3C_4)] [HSO_4] (3 mL), Pd NPs/carbon (3.0% w/w, 186.2 mg) and $ScCO_2$ (15.5 MPa) at 45 °C for 10 h.

To study the efficiency and scope of the palladium nanoparticles-catalyzed Ullmann reactions of aryl chlorides, the optimal reaction conditions were applied to a variety of aryl chlorides. And the results are summarized in Table 1 (entries 1 and 20–26, Table 1). As shown in Table 1, Ullmann reactions of various aryl chlorides (**1a–1h)** bearing different substituents ran smoothly in the IL/$ScCO_2$ system in the presence of Al(0) and Pd NPs/carbon. The results in Table 1 also indicate that the reaction rates depend on the structures of the aromatic chlorides. For instance, aryl chloride **1b**, which bears an electron-donating substituent, needed a shorter reaction period (8 h, entry 20, Table 1) as compared with aryl chloride **1a** (10 h, entry 1, Table 1). When aryl chlorides bearing electron-withdrawing substituents were studied (e.g., **1c**), longer reaction times and higher reaction temperatures were needed, for example, for the reaction of **1c**, the substrate was converted into **2c** readily in 96% yield after 16 h (entry 21, Table 1). Meanwhile, we also noticed that aryl chlorides **1e** and **1f** with ene structures required prolonged reaction periods in comparison with **1a** and **1b**, homocoupling products **2e** and **2f** were afforded in good yields (87% and 98%, respectively, entries 23, 24, Table 1). For aryl chloride **1g**, although containing an electron-rich substituent ($-NH_2$) in its structure, due to the strong acidic conditions of the IL, this group was converted to $-NH_3^+$ readily, which is a typical electron-withdrawing substituent. Therefore, the Pd NPs-catalyzed Ullmann reaction of **1g** can proceed smoothly with desirable yields (94%, entry 25, Table 1) by employing a reaction time of 16 h. For aryl chloride **1h**, the $-NH_2$ group was also converted to $-NH_3^+$ in the strong acidic condition, thus the structure of aryl chloride **1h** contains both electron-donating and electron-withdrawing substituents, and experiments showed that the reaction runs smoothly with 91% yield of **2h** (entry 26, Table 1) without an obviously prolonged reaction time, indicating the overlapping effects of this two types of substituents.

Catalyst Support and Active Hydrogen Donor

In conventional work[14f], H_2O or alcohol was selected as a precursor of hydrogen, providing abundant active hydrogen. However, use of H_2O led to difficult product separation and complicated phase behaviour in the reaction system. For example, when IL was replaced by H_2O, the PdNPs/carbon-catalyzed Ullmann reaction proceeded with 79% conversion, while the isolated yield was only 53% (entry 5, Table 1), indicating the much decreased isolation efficiency of the Ullmann product. This can be explained by inferior intermiscible behaviour of H_2O and $ScCO_2$ in the H_2O/$ScCO_2$ system. In fact, we anticipated that we can use an active hydrogen donor without loss of the product isolation efficiency. Therefore, attempts to find an alternative active hydrogen donor matching such requirements are necessary.

The Brønsted-acidic imidazolium IL can release active hydrogen readily.[36] Significantly, after a series of efforts, we found that Brønsted-acidic imidazolium IL, for example, [bmim(HSO_3C_4)] [HSO_4], can replace the traditional active hydrogen donor readily, thus we can make full use of the superior advantages of IL/$ScCO_2$, so that the much declined product isolation efficiency induced by the traditional hydrogen donor can be avoided. Experiments showed that when [bmim (HSO_3C_4)] [CF_3SO_3] (**IL-a**) was used, the reaction runs smoothly with a much enhanced isolated yield (91%, entry 16, Table 1) compared with the results using H_2O, showing the superior advantages of IL in product separation. Similarly, when [hmim][HSO_4] (**IL-b**) was used, the reaction runs smoothly with 94% yield (entry 17, Table 1). To further indentify the role of acidic IL, [emim][HSO_4] (**IL-e**) was also chosen, an 84% yield was obtained (entry 19, Table 1). Such results indicated that acidic imidazolium ILs can replace the traditional active hydrogen donor readily with much enhanced product isolation efficiency. Further investigations can also prove the important role of IL as the hydrogen donor: When the reaction was carried out in the absence of any IL, no Ullmann product was detected (entry 4, Table 1). And when [hmim][Tf_2N] (**IL-d**), which does not contain any active hydrogen in its structure, was used, only a trace amount of Ullmann product can be detected (entry 18, Table 1), revealing that acidic IL with active hydrogen can act as active hydrogen donor.

To find more optimal results, we tried to combine the [bmim (HSO_3C_4)][HSO_4] (**IL-c**) with $ScCO_2$, and found that a further enhancement in yield can be achieved (99%, entry 1, Table 1), this obviously improved yield might be due to the fact that when both IL cation and anion contained active hydrogen, the IL molecule can provide more hydrogen more efficiently, leading to an improved conversion and yield.

Products Separation

In the IL/ScCO$_2$ system, CO$_2$ extraction provides an efficient method for product isolation. In our experiments, by simple depressurization of CO$_2$, the biaryl products, which finally exhibited a solvent-free and analytically pure form as a colourless crystalline material, can be isolated easily from the catalyst solution of IL by CO$_2$ extraction without cross contamination of IL or catalyst. In the experiments summarized in Table 1, no signals associated with the IL were detected during NMR and GC-MS analyses of the products. Samples from each run were analyzed by ICP measurement, demonstrating that the palladium content was below the detection limit of the instrument (<1 ppm) in all cases, and that no significant leaching of metal compounds into the products had occurred. All the above results showed that the environmentally friendly IL/ScCO$_2$ system can provided a highly efficient products separation route for Ullmann products.

IL and Catalyst Recycling

The IL/ScCO$_2$ system showed advantages in reaction activity and selectivity, product separation and catalyst/IL recycling, however, the selection of the IL that will hold a Pd NPs catalyst was crucially important, different IL choices would influence the CO$_2$ solubitity in IL and phase behaviour of the combined system. Previous work showed that both the IL anion and alkyl substituent on the cation can influence the solubility of CO$_2$ in IL.[32,37]

Most ILs have no measurable vapour pressure, and, thus, they have been considered as "green" media, however, their toxicity in soil and water eco-systems must be understood carefully. And for economic considerations, most IL are quite expensive, the optimal method would be recycling of the IL in these reactions. Meanwhile, the Pd NPs show a relatively strong trend towards agglomeration. In most of the catalytic reactions, it is necessary to use an additional stabilizer or a solid support material. Here, the Pd NPs support on exfoliated graphite was one of the ways to prevent Pd NPs from undergoing agglomeration. In addition, research has revealed that catalyst solutions in IL are significantly less air sensitive than catalyst solutions in conventional organic solvents. This may be due to the fact that the IL environment helps stabilize the NPs catalysts. It is assumed that the bulkiness of IL imidazolium cations favour the electrosteric stabilization of NPs, and the N-imidazolium side chains can also stabilize the metal (0) NPs. The anion of the IL is also helpful due to electronic interactions with the metal surface.[35]

In our experiments, we found that excellent catalytic activities can be achieved for at least 5 runs. The conversions for the first, second and third runs were 100%, 99% and 100%, respectively (entries 1–3, Table 2), and slight declines in conversion were seen for the fouth and fifth runs (98% and 97%, respectively, entries 4, 5, Table 2). Investigations showed that the recycling performance of the catalyst in IL/ScCO$_2$ had superior advantages over other systems combined with ScCO$_2$. For example, when the H$_2$O/ScCO$_2$ system was chosen instead of IL/ScCO$_2$, the conversions for the first and second runs were 74% and 41%, respectively, and sharply declined conversion for the third run (29%, Table 1), all were obviously decreased on comparison with the conversions obtained in the IL/ScCO$_2$ system, indicating an inferior efficiency of the H$_2$O/ScCO$_2$ system. In fact, in this system, IL plays an important role in the recycling of the Pd NPs/carbon catalyst. As stated above, the IL environment helps stabilize the NPs catalysts. This can be observed by TEM and SEM images shown in Figure S2 (Supporting Information). As shown in Figure S2a and b (Supporting Information), when the IL was used in the recycling cycles, no obvious Pd NPs catalyst agglomeration was found after 3 cycles. The diameters of the Pd NPs were still in the small and narrow range similar to the diameters for the first run (Figure 1a, b). When the IL was replaced by H$_2$O, serious Pd NPs agglomeration occurred after three runs of reaction (Figure S2c, d, Supporting Information). Such results can explain the sharp declination of conversion in the recycling experiments of the H$_2$O/ScCO$_2$ system.

Table 2. The Ullmann reaction of phenyl chloride in IL/ScCO$_2$ (conversion as a function of the number of the cycles).[a]

Entry	Catalyst solution in [bmim(HSO$_3$C$_4$)] [HSO$_4$]	Conversion [%][b]
1	fresh	100[c]
2	Recycled from run 1	99[d]
3	Recycled from run 2	100[e]
4	Recycled from run 3	98
5	Recycled from run 4	97

[a] [bmim(HSO$_3$C$_4$)][HSO$_4$] (**IL-c**) was used, formation of biphenyl, before each run, fresh phenyl chloride (2 mM), and Al(0) (108 mg) were added to the catalyst solution of IL in the stainless vessel.

[b] Determined by GC analysis.

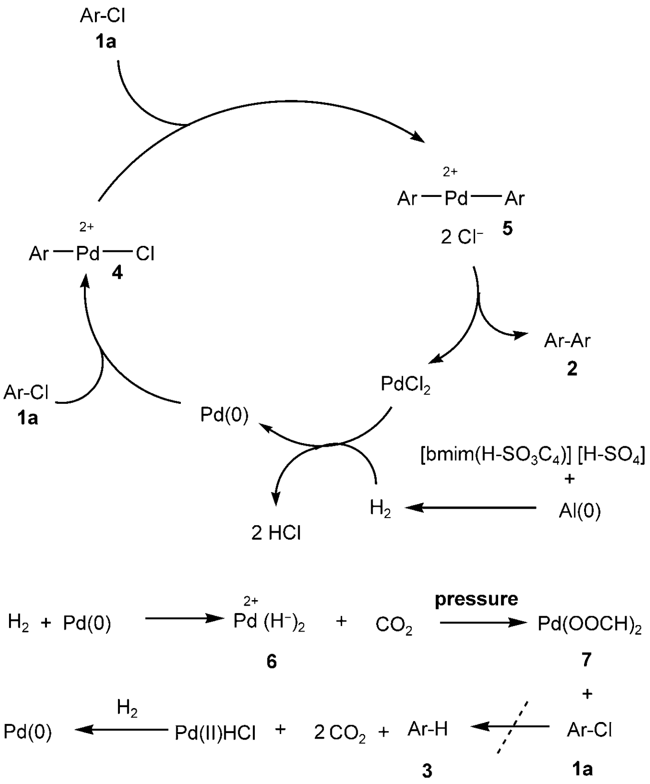
[c] When H$_2$O (3 mL) was used instead of **IL-c**, 74% conversion was obtained.

[d] When H$_2$O (3 mL) was used instead of **IL-c** in the reaction cycles, 41% conversion was obtained.

[e] When H$_2$O (3 mL) was used instead of **IL-c** in the reaction cycles, 29% conversion was obtained.

Possible Mechanism for the Ullmann Reaction

Based on previous work,[14,15,38] a plausible mechanism for the Pd NPs/carbon-catalyzed reductive Ullmann reaction of aryl chloride is shown in Scheme 5. In this process, aluminium can react with acidic imidazolium IL, for example, [bmim(HSO_3C_4)] [HSO_4] or [bmim(HSO_3C_4)][CF_3SO_3], etc. at high pressure generating H_2 readily. To begin with, Pd(0) could react with Ar–Cl (**1a**) to give intermediate **4** (ArPdCl). Then the intermediate **4** reacts with another **1a** molecule giving intermediate **5**, successively, a reductive elimination process of intermediate **5** then occurs, releasing biaryl product **2** and $PdCl_2$. The obtained $PdCl_2$ can be reduced by H_2 regenerating the active Pd (0) species readily to finish the cycle. It is noteworthy that a primary side-reaction would occur at the same time. Firstly, Pd(0) could also react with H_2 giving intermediate **6** [$Pd^{2+}(H^-)_2$], which could then react with **1a** affording the main side product Ar–H (**3**). Thus the greatest challenge might be how to minimize the possibility of the side reaction forming side-product **3**. Fortunately, in this reaction, in the presence of $ScCO_2$ at high pressure, no obvious side products had been detected. It is assumed that CO_2 chooses to insert into the Pd–H bond of **6** to form $Pd(OOCH)_2$ (**7**). With CO_2 insertion, a much enhanced steric hindrance was achieved in intermediate **7** than in intermediate **6**, the barricaded intermediate **7** inclined to react with HCl readily affording the active Pd(0) spcies instead of reaction with **1a** giving side-product **3**. Therefore, in the presence of $ScCO_2$, the reaction proceeded with high selectivity towards the Ullmann coupling product **2**.



Scheme 5. Possible mechanism for the Pd NPs/carbon-catalyzed Ullmann reaction of an aryl chloride.

Conclusions

In conclusion, we have demonstrated an environmentally benign process: the highly active and recyclable exfoliated graphite-supported palladium nanoparticles-catalyzed reductive Ullmann reaction of aryl chloride in an ionic liquid/supercritical carbon dioxide system. The application of cheaper chemicals, such as aryl chlorides (instead of expensive aryl bromides or iodides), aluminium (instead of expensive indium, etc.) and the naturally abundant, non-flammable, relatively non-toxic, economical and recyclable "greenhouse" gas CO_2 make this kind of process quite attractive. The Pd NPs catalyst and ionic liquid can be recycled for at least five runs, indicating the economic viability of this process. The employment of the ionic liquid/supercritical carbon dioxide system leads to immobilization, activation, and stabilization of the Pd NPs catalyst that would be impossible in classical organic media separately. And the Brønsted-acidic imidazolium ionic liquid can replace the traditional active hydrogen donor readily with much enhanced product separation efficiency. Experiments also show that carbon dioxide can significantly promote the selectivity of the Pd NPs-catalyzed aluminium-induced reductive Ullmann reaction of aryl chloride. Alhough high pressure is used in this work currently, the cheapness of CO_2 and superior performance of the reaction system in catalyst/IL recycling and product separation would make up for this deficiency. Further studies on the phase behaviour of different ionic liquids in supercritical carbon dioxide for Ullmann reactions under much lower CO_2 pressures are underway in our laboratory.

Experimental Section

Typical Procedure for Pd NPs/Carbon Preparation

Oxidized graphite (OG, see Supporting Information) was made by using a modified Brodie method.[25] To synthesize the supported Pd NP catalysts, the obtained OG (20 mg) was suspended in water (20 mL), the mixture was then sonicated for 15 min. After adjusting the pH value of the system to 10, $NaBH_4$ (200 mg) was added slowly to the mixture under stirring, the mixture was then sonicated for another 5 min and stirred for 24 h under room temperature. Finally, the solid sample with Pd loading was collected after thorough washing with ethanol and deionized water so that the unsupported Pd(II) cation can be removed completely. The sample was vacuum-dried at 60 °C for 24 h, affording the supported catalyst Pd NPs/carbon.

Typical Procedure for Ullmann Reactions in IL/ScCO$_2$

Aryl halide (2 mM), Al(0) (108 mg), [bmim(HSO_3C_4)][HSO_4] (3 mL) and Pd NPs (3.0% w/w, 186.2 mg) were added into a 10.0-mL high-pressure stainless vessel, which was sealed and connected to a CO_2 supply. The vessel was charged with CO_2 gradually until a pressure of 5.0 MPa was obtained and heated at 45 °C to a stabilized pressure of 7.0 MPa, then more CO_2 was added to obtain a pressure of 15.5 MPa. The system were stirred under above conditions for 10 h, successively, the stirrer and temperature controls were then switched off, CO_2 was gradually released into the solvent trap (20.0 mL). The IL and Pd NPs/carbon remaining in reactor vessel can be washed with 1,2-dimethyl-3-hydroxy-4-pyridone (DHPO, 3 mL, recycled by ion exchange) for 3 times, and then distilled under reduced pressure to remove DHPO residues, affording the active catalyst IL solution for further reaction. The solvent trap vessel was then disconnected and allowed to cool. By simple further decompression of the CO_2, the obtained product was collected through the valve on the bottom of the solvent trap conveniently. The resulting organic solid was washed with ethanol and purified with TLC to give the biaryl products.

Supporting Information

Materials and characterization, synthesis procedure for the oxidized graphite, supplementary characterization of the recycled catalyst together with details of the spectroscopic data of the biaryls **2a–h** are given in the Supporting Information.

Acknowledgements

We are grateful to the Shanghai Science Foundation (10ZR1432000) and Foundation of Guangxi Zhuang Autonomous Region of China (NOs. 200626152, 200508193, 200925066) for financial support.

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