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Complete List of Authors:	Li, Rongrong; Zhejiang University of Technology, Industrial Catalysis Institute of Zhejiang University of Technology; School of Pharmaceutical and Chemical Engineering Zhou, Ze hua; School of Pharmaceutical and Materials Engineering, TaiZhou University, Taizhou, Zhejiang 318000, PR China., Chen, Jingjing; School of Pharmaceutical and Materials Engineering, TaiZhou University, Taizhou, Zhejiang 318000, PR China. Wang, Shiting; School of Pharmaceutical and Materials Engineering, TaiZhou University, Taizhou, Zhejiang 318000, PR China. Zheng, Jianli; School of Pharmaceutical and Materials Engineering, TaiZhou University, Taizhou, Zhejiang 318000, PR China. Chu, Chu; School of Pharmaceutical and Materials Engineering, TaiZhou University, Taizhou, Zhejiang 318000, PR China. Zhao, Jia; Zhejiang University of Technology, college of chemical engineering Fan, Hau-Jun; Prairie View A&M University, Chemistry han, deman; school of pharmaceutical and chemical engineering, taizhou university

The Improved Hydrodechlorination Catalytic Reactions by Concerted Efforts of Ionic Liquid and Activated Carbon Support

*Rongrong Li [1,] *, Zehua Zhou [1], Jingjing Chen [1], Shiting Wang [1], Jianli Zheng [1], Chu Chu [1], Jia Zhao [2], Huajun Fan [3,] *, Deman Han [1,] **

[1] School of Pharmaceutical and Materials Engineering, TaiZhou University, Taizhou, Zhejiang 318000, PR China.

[2] Industrial Catalysis Institute of Zhejiang University of Technology, Hangzhou, 310014, P.R. China.

[3] Department of Chemistry, Prairie View A&M University, Prairie View, Texas 77446, USA.

*Corresponding Authors:

*Tel.: +86 576 88660353. E-mail: lrr@tzc.edu.cn (Rongrong Li)

*Tel.: +86 576 88660177. E-mail: hdm@tzc.edu.cn (Deman Han).

*Tel.: (936) 261-3111. E-mail: hjfan@pvamu.edu (Huajun Fan).

Abstract

The modified and stabilized palladium nanoparticles were prepared successfully by using the ionic liquid, 1-butyl-3-methylimidazolium trifluoroacetate. The activated carbon was used as the support for the palladium catalyst. Instead of using hydrogen

gas, the Pd-catalyzed hydrodechlorination (HDC) reaction in this study used aqueous formic acid-formate buffer solutions as a hydrogen source for its non-flammability. The results showed that both the ionic liquid and active carbon support facilitate Pd active center to effectively carry out the catalytic HDC reaction of 4-chlorophenol (4-CP). The ionic liquid (IL) played a dual role as both solvents and as co-factor to facilitate the reaction. The IL would stabilize, better disperse, and prevent the congregation of palladium nanoparticles. On the other hand, the active carbon provides a stronger binding site for stabilizing the active Pd centers. The catalytic HDC reaction indicated that the turn over frequency (TOF) of ionic liquid with reduced catalyst was about 5~6 times higher than that of the non-ionic liquid mediated catalyst. This excellent catalytic activity suggested that the ionic liquid is dispersing nanoparticles effectively, preventing the creation of Pd nanoparticles cluster through the strong interaction Pd species with ionic liquid (IL). This IL-Pd interaction helped form a protection layer to stabilize the Pd active centers. This study also confirmed that the both Pd^0 and Pd^{n+} states were required for the catalytic HDC reaction. Furthermore, the Pd-catalyst were characterized by different techniques such as Brunauer–Emmett–Telle (BET) surface area analysis, X-ray photoelectron spectroscopy, Transmission electron microscopy (TEM) and Fourier-transform infrared spectroscopy (FT-IR).

Keywords: Ionic liquids; 4-Chlorophenol; Hydrodechlorination; Formic acid

1 Introduction

Chlorinated aromatic hydrocarbons, chlorinated alkanes, olefins, organochlorine pesticides, and other chlorine-containing organic compounds are important chemical raw materials and organic solvents, which are widely used in medicine, leather, electronics and pesticide industries. The waste and by-products in the production and use process pose a threat to the environment and human health. Most of the chlorophenols (CP) are difficult to degrade and bioaccumulate in a long time. Therefore, the degradation of organic chlorides has been a research hotspot in recent years. Catalytic hydrodechlorination (HDC) of organic chlorides is an ideal way to degrade chlorophenols.[1,2,3] The Pd has been commonly used as a hydrodechlorination catalyst because it is more active than Pt and Rh.[4-7] However, the produced chloride by the dechlorination reaction was strongly bound at the active Pd sites that cause the catalyst quickly to lose its catalytic capability.[8] Furthermore, such adsorption also triggered the aggregation and carbon deposition onto the Pd sites, which further aggravate the deactivation of the catalyst.[9] Therefore, it is critical to improving the stability of Pd active center in the HDC reaction.

Gomez-Sainero et al.[10] suggested the synergism between the active center of the hydrodechlorination reaction between two valence states of Pd^{n+} and Pd^{0}. It was suggested that Pd^{n+} species would adsorb activated chlorine molecules to form nucleophilic Cl^{-}; while Pd^{0} adsorbs the activated H_2 molecules to form Pd-H bonds. The Pd-H active center then can react with nucleophilic Cl^{-} to complete the

dechlorination reaction. One can see that the stabilization of this Pd species and active center is the key to maintain an effective catalytic activity.

Recent progress demonstrated that the ionic liquid (IL) compounds possess the unique property such as very low vapor pressure, good solubility, high water thermal stability and adjustable acid strength.[11] These properties are beneficial to the catalytic reaction of metal nanomaterials and reactive solvents. Particularly, the IL layer formed by the liquid on the surface of the carrier can make the Pd active nanoparticles dispersed more uniform. For example, the Pd particle size in the IL-palladium-based catalyst decreased from 17 nm to the range of 2.8-4.0 nm.[12] Claus and other[13, 14] found that [BMIM][$N(CN)_2$] or [BMIM][NTf_2] can form a Pd complex with 3d5/2 state. Such Pd complex can modulate the electron binding energy at the Pd center. The increased binding energy subsequently improve the catalytic activity and stability of the catalyst.[15,16] However, IL also has its shortcomings such as low recovery rate due to a loss in the liquid phase of the reaction. To remedy this loss and low recovery, Wasserscheid and others[17, 18] investigated to improve the stability of IL by modifying the carrier and adding the functional groups to form a more stable bond. Alternatively, activated carbon (AC) was widely used in HDC reaction for its large pores volume and specific surface area. These characteristics of AC can provide more active catalytic binding sites on the surface and thus facilitate the catalytic reaction.[10]

In this study, the IL mediated palladium catalyst supported by the activated carbon (Pd-IL/AC-cr) will be synthesized and tested its catalytic property towards the hydrodechlorination (HDC) of 4-chlorophenol (4-CP). “cr” stands for the catalyst

which was treated by calcination and reduction. For comparison, both Pd/AC and Pd-IL/AC-c also be synthesized. We adopted aqueous formic acid-formate solutions as hydrogen source[15] since it is a non-flammable hydrogen source. The catalyst will be characterized by Brunauer–Emmett–Telle (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and fourier-transform infrared spectroscopy (FT-IR), and catalytic properties such as turn over frequency (TOF) values will be monitored and compared.

2 Experimental

The detailed synthesis procedures and chemicals used has been published by the author in the supporting information section of previous published work.[20]

3 Results and discussion

3.1 Catalysts characterization

Table. 1 summarizes the characterization of the prepared catalysts Pd/AC, Pd-IL/AC-c and Pd-IL/AC-cr. For comparison and blank test, active carbon (AC) is also listed in the Table. AC is an essentially microporous solid with a high BET surface of 1209 m^2 g^{-1}, containing micropores and mesopores within a broad distribution between 3.5 and 4.5 nm as shown in Fig 1(a). However, the Pd loading seems to have little effect on the surface area. For example, the Pd deposited complex Pd/AC has slight larger BET surface of 1411 m^2 g^{-1}, while the BET surface decreases slightly with IL mediated complex Pd-IL/AC-cr and Pd-IL/AC-c to 951 and 921 m^2

g^{-1}, respectively. This decrease probably is due to the partial collapse of the pores induced by IL modification through the equivalent-volume impregnation process. Fig 1(b) demonstrates the BJH pore distribution curves of catalysts, which have an obvious condensation step at relative pressures P/ P_0 = 0.4–0.6. It can be seen from the shape of the hysteresis loop of Fig. 1 (b) that the pore structure is a tubular pore structure with both ends open, and the pore diameter is relatively uniform. In general, this open pore structure facilitates the diffusion of molecules, facilitates the adsorption of the reactant molecules on the inner surface and the desorption of the product molecules, thus facilitating the reaction.

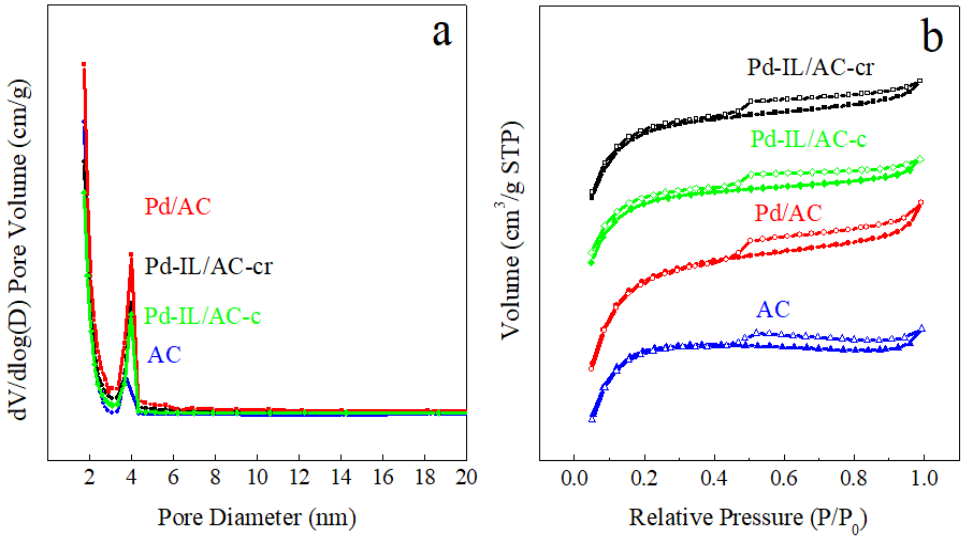

Fig. 1 (a) the pore size distribution plots of catalysts, (b) the BJH pore distribution curve.

Table. 1 Characterization of the catalysts.

Material	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore Size (nm)	Pd(%wt.)[a]	Pd(%wt.)[b]	Pd^0/Pd^{n+}
AC	1209	0.58	1.92	--	--	--
Pd/AC	1411	0.72	2.06	0.23	0.22	1.02
Pd-IL/AC-cr	951	0.49	2.08	0.54	0.52	1.43
Pd-IL/AC-c	921	0.45	2.07	0.52	0.49	0

[a] By the analysis of XPS characterization.

[b] By the analysis of ICP-MS.

Previous studies have demonstrated that the HDC reaction can be influenced by the oxidation state of the Pd centers of the catalyst.[10,21] Therefore, the surface atomic composition of Pd-IL/AC-cr was examined by XPS (Fig. 2a) and the detail XPS of C, N and Pd region are shown in Fig 2b-2d). The content of C, N, Pd and O for Pd-IL/AC-cr are found to be 85.34%, 1.93%, 0.54%, and 12.18%, respectively. In Fig 2b, we can find XPS bands of C=O, C-O and C-C bonds. The C=O and C-O species are probably due to the addition of ionic liquids. The N 1s spectrum of Pd-IL/AC-cr (Fig. 2c) was fitted with two components, which could be attributed to pyridinic-N (398.9 eV), pyrrolic-N (400.8 eV).[25] This doublet in XPS is again due to the introduction of ionic liquids.

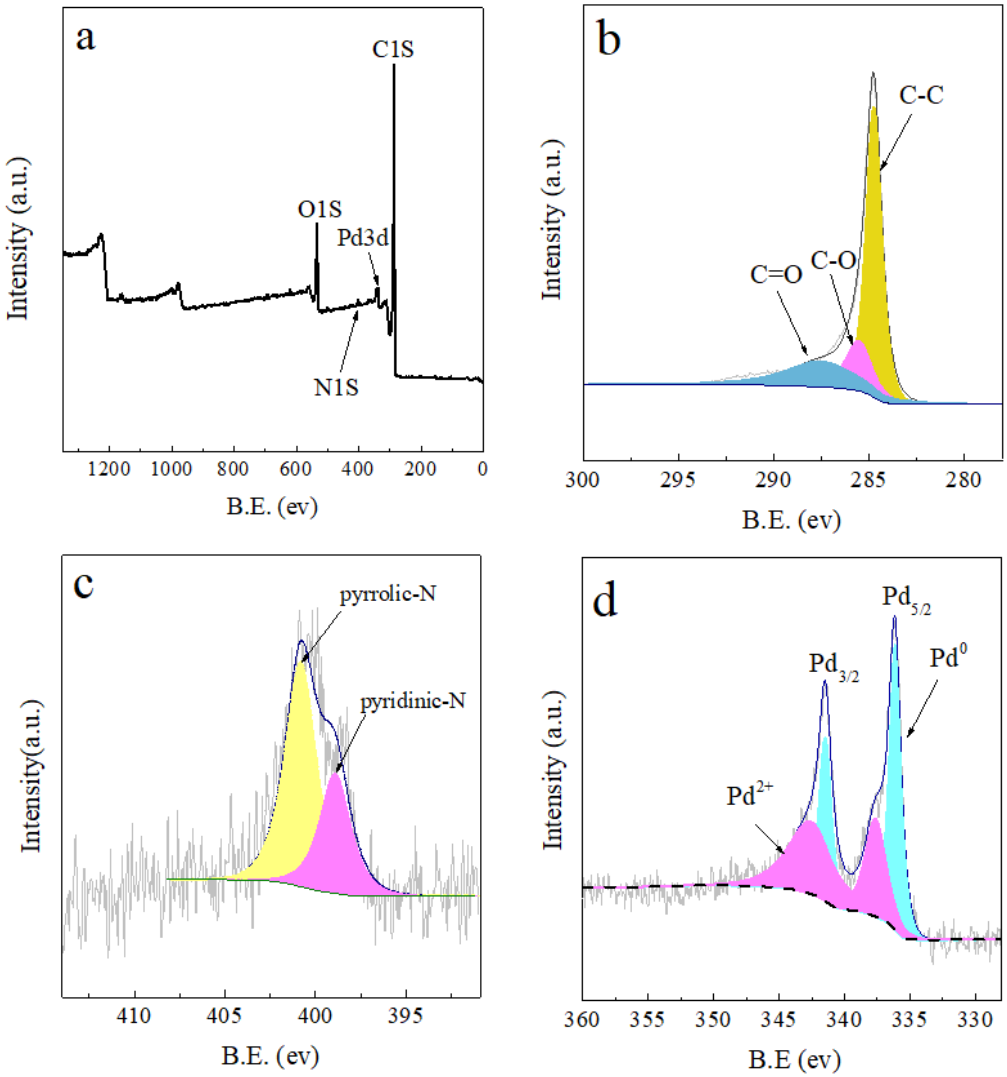

Fig. 2 XPS of Pd-IL/AC-cr. (a) Infrared wide spectrum, (b) C1s, (c) N1s and (d) Pd3d.

Both Pd^0 and Pd^{n+} species were found in Fig. 2(d). The XPS spectra of Pd 3d have a doublet attributed to Pd 3d5/2 and 3d3/2. The Pd 3d5/2 peaks at 336.2 eV and 337.0 eV correspond to Pd^0 and Pd^{2+} species, respectively; while the Pd 3d3/2 peaks at 341.4 eV and 342.8 eV correspond to Pd^0 and Pd^{2+} species, respectively. A previous study[24] showed that the binding energy of the Pd 3d5/2 of the Pd^0 is expected to be at 334.9 eV for bulk Pd. In this work, the binding energy for Pd^0 components of the Pd 3d5/2 of Pd-IL/AC-cr catalyst was found to be 336.2 eV, 1.3 eV higher than that of

bulk Pd. It is interesting to point out that the IL supported catalysts have a higher content of palladium species (0.54%w.t. for Pd-IL/AC-cr and 0.52%w.t. for Pd-IL/AC-c) than non-IL (0.23%w.t. for Pd/AC) as seen in Table. 1. XPS also reveals that the Pd^0/Pd^{n+} ratio increases from 1.02 of Pd/AC to 1.43 of Pd-IL/AC-cr. This might be due to the strong interaction between the anions in IL and the Pd species. All of these factors contribute to the improved catalytic HDC conversion reaction shown in the following "3.2 Activity of the catalysts" section.

The Transmission electron microscopy (TEM) images are utilized to demonstrate the effect of IL on the dispersion of nanoparticle. The TEM results of Pd/AC (a-1, a-2) and Pd-IL/AC-cr (b-1, b-2) are shown in Fig. 3. Comparing with the TEM images of Pd/AC, one can see the smooth nature of the Pd-IL/AC-cr catalyst surface. The smooth surface of Pd-IL/AC-cr catalyst suggests a more homogeneous dispersion of Pd of Pd-IL/AC-cr catalyst onto the active carbon surface. The Pd nanoparticles' average size is estimated at 3 nm, which is comparable to the previous study.[10]

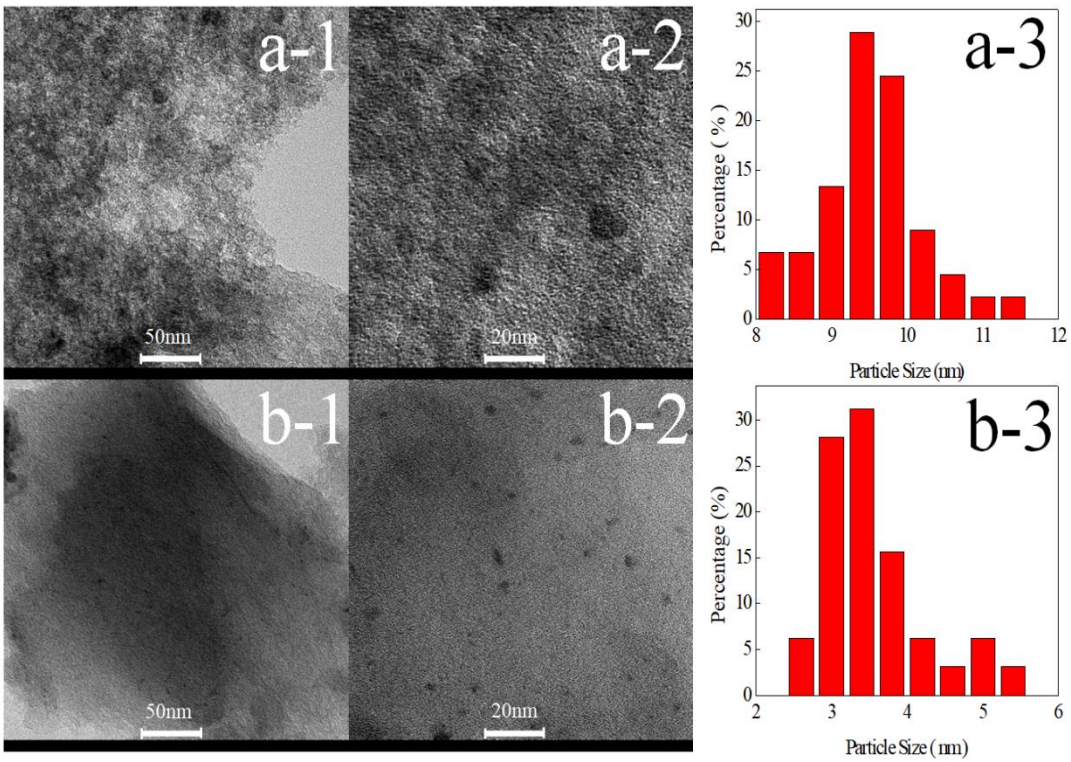

Fig. 3 The TEM image of the Pd/AC (a-1, a-2) and Pd-IL/AC-cr (b-1, b-2) and particle size distribution of the Pd/AC (a-3) and Pd-IL/AC-cr (b-3).

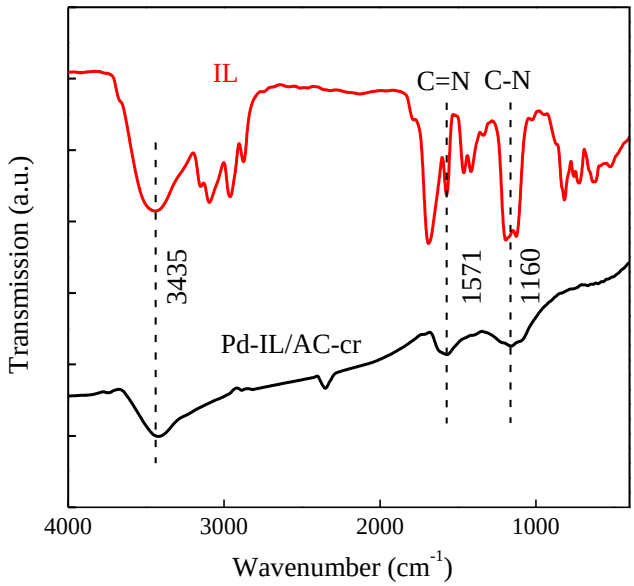

Fig. 4 The FTIR spectra of IL and Pd-IL/AC-cr.

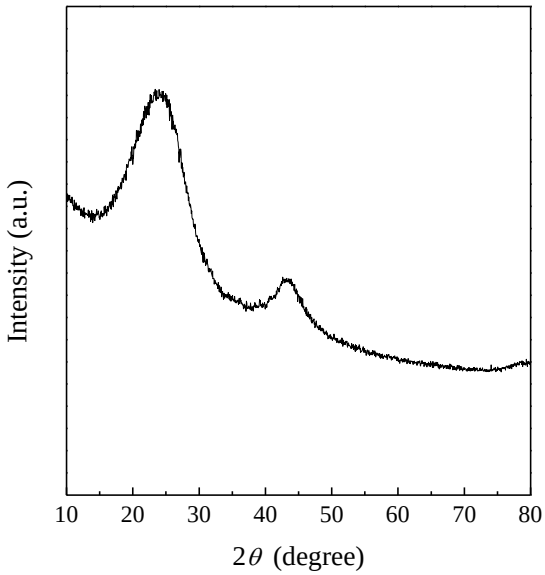

Fig. 5 The X-ray diffraction of Pd-IL/AC-cr.

To examine the binding of the IL on the catalyst, the FTIR spectra of IL and Pd-IL/AC-cr were shown in Fig. 4. The peaks at 1571 cm^{-1} and 1160 cm^{-1} were assigned to C=N and C-N stretching vibrations of IL, respectively, and the broad peak at 3435 cm^{-1} was assigned to N-H stretching. Comparing the FTIR of IL (red in the Fig. 4), the FTIR spectra profile of catalyst indicates that the IL had been successfully loaded on the surface of the catalyst.[26] And the X-ray diffraction of Pd-IL/AC-cr (Fig. 5) also shows that the Pd nanoparticles are so small that no diffraction peaks appear.

3.2 Activity of the catalysts

The catalytic property of the prepared catalysts Pd/AC, Pd-IL/AC-cr, and Pd-IL/AC-c was investigated by the hydrodechlorination (HDC) reaction of 4-chlorophenol (4-CP). We first investigated the effect of initial 4-CP concentration

on the HDC reaction. 0.050 g of Pd-IL/AC-cr catalyst was used in the formic acid-sodium formate buffer solution as the source of hydrogen. The reaction time, the reaction temperature, and stirring rate were set at 2.0 h, 306 K, and 600 rpm, respectively. As shown in Fig. 6, the reaction conversion percentile with 20 mL of 4-CP was drastically different than those of 10 mL or 5 mL of 4-CP. The higher concentration (20 mL) of 4-CP seems to yield HDC reaction in much slower pace over the period and only reached ~20% conversion rate over the 2-hour reaction time. However, the two lower concentration trials (10 mL and 5 mL) would quickly reach the 90% mass conversion of 4-CP in the first 30 min and closer to 100% mass conversion around 1 hour. This suggested that the diffusion effect is effectively eliminated with the lower 4-CP concentration under the current reaction conditions. Therefore, it is safe to rule out the mass transfer limitation under the current experimental conditions.[25]

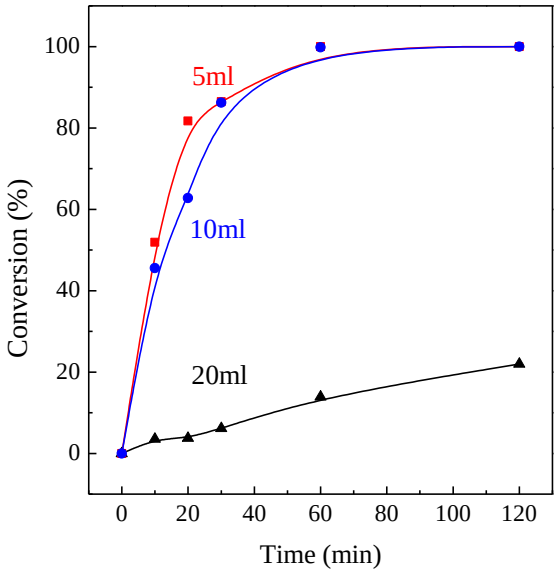

Fig. 6 The catalytic HDC of 4-CP at varied initial 4-CP concentrations using Pd-IL/AC-cr.

Reaction conditions: 0.05 g catalyst, (8 g/L, 4-CP) + 10 mL (1 mol/L HCOOH + 0.8 mol/L HCOONa), Time = 2 h, Temperature = 306 K, Stirring rate = 600 rpm.

To be consistent, the HDC reaction was carried out using 0.05 g of aforementioned catalysts with 10 mL of 4-CP in the formic acid-sodium formate buffer solution as the source of hydrogen. The reaction time, the reaction temperature, and stirring rate were set at 2.0 h, 306 K, and 600 rpm, respectively. For clarification, the active carbon support alone (AC) was also investigated for its role in the catalytic reaction as a baseline. Contrary to the Pd nanoparticles catalyst, no reaction product could be measured when only AC was used in the HDC reaction.

Fig. 7 showed the catalytic conversion results of 4-CP with the prepared catalysts Pd/AC, Pd-IL/AC-cr, and Pd-IL/AC-c. The results demonstrated that 100% conversion is achieved when the Pd-IL/AC-cr were used, and the only product was a phenol. With the added reduction preparation process, the catalytic activity of Pd-IL/AC-cr increases significantly over that of Pd-IL/AC-c. The turn over frequency (TOF) of Pd-IL/AC-cr catalyst is ~5 times higher than the catalysts of Pd-IL/AC-c. This is consistent with previous studies[10,21] that both Pd^0 and Pd^{n+} states were necessary for the success of the HDC reaction. The Pd active centers with reduction preparation, as demonstrated by the XPS results, would include both Pd states that enhance the catalytic conversion of the HDC reaction. The TOF of Pd/AC is slightly lower than Pd-IL/AC-c. The without the reduction preparation steps, the catalytic activity of both Pd/AC and Pd-IL/AC-c catalysts are less effective in the HDC conversion reaction than Pd-IL/AC-cr. This finding is consistent with the previous

study that the different Pd states (Pd^0 and Pd^{n+}) are important to the HDC reaction.[21] Compared to several other modification methods, our catalysts are more reactive.[22,23] And the catalyst Pd-IL/AC-cr is still stable in multiple cycles of use, which also proves that IL has a great effect on the stability of Pd active centers.(Fig. 8)

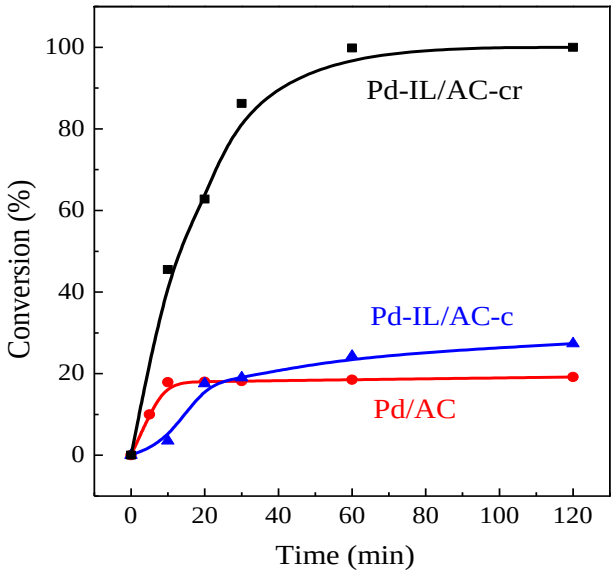

Fig. 7. The conversion of the catalyst Pd-IL/AC-cr and Pd-IL/AC-c and Pd/AC.

Reaction conditions: 0.05 g catalyst, 10 mL (8 g/L, 4-CP) + 10 mL (1 mol/L HCOOH + 0.8 mol/L HCOONa), Time = 2 h, Temperature = 306 K, Stirring rate = 600 rpm.

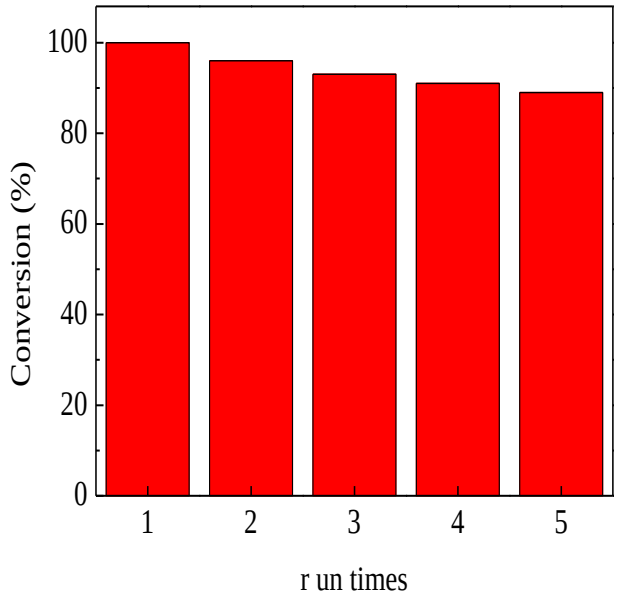

Fig. 8. The conversion of recycled catalyst (Pd-IL/AC-cr)

Reaction conditions: 0.05 g catalyst, 10 mL (8 g/L, 4-CP) + 10 mL (1 mol/L HCOOH + 0.8 mol/L HCOONa), Time = 2 h, Temperature = 306 K, Stirring rate = 600 rpm.

Furthermore, the improved catalytic activity of Pd-IL/AC-cr over Pd-IL/AC-c and Pd/AC is further facilitated by better dispersed Pd^0 species, which is the result of IL effects and active carbon support. First of all, the Pd-IL/AC-cr had higher Pd^0 loading over Pd^{n+} species evidenced by XPS as shown in Table 1. This directly increased the amount of active center to carry out the HDC reaction. This probably is associated with the electron-deficient nature of the active Pd sites at the Pd nanoparticles.

Secondly, the stronger metal-AC support interactions are evidenced by the binding energy for Pd^0 components at 336.2 eV, a value 1.3 eV higher than that associated with bulk Pd as shown in Fig. 2(d). This is consistent with the previous study that Pd^{n+} sites could activate the C-Cl bond via abstraction of nucleophilic chloride anion and Pd^0 sites adsorb the activated H_2 molecules to form Pd-H bonds, which in turn

would react with nucleophilic Cl^{-}[8]. Thus, it completes the dechlorination reaction. Therefore, the increased binding energy not only improves the stability of the catalytic centers but also increases the catalytic active Pd^0 centers.[15]

Thirdly, the dispersion is facilitated by the IL and reduced the congregation of Pd nanoparticles. It is well-known that the Pd 3d electronic level binding energy is dependent on the size of the Pd nanoparticles.[27] As the diameter of the Pd nanoparticles decreases, the binding energy of a given component shifts to higher values. The estimated Pd nanoparticle size is estimated at ~ 3nm. The interaction of the Pd centers with the N atoms of IL would form an IL (mono) layer to partially protect the Pd^0 against oxidation. Such interaction would further be enhanced through the ionic-polar interaction between the Pd centers and IL. Therefore, such interaction with the IL provides the protection and stabilization of Pd nanoparticles.[28]

4 Conclusions

In summary, the modified and stabilized palladium nanoparticles Pd-IL/AC-cr are prepared successfully through calcination and reduction process on active carbon support by using the ionic liquid 1-Butyl-3-methylimidazolium trifluoroacetate. The IL provides a favorable environment for the formation of metal nanoparticles with a small diameter (~3nm) and even-size distribution under mild reaction conditions. The IL plays an important role in stabilizing, dispersing, as well as maintaining the Pd nanoparticles for the HDC reaction of 4-CP. The reduced Pd-IL/AC-cr catalyst is 5~6 times more effective for HDC reaction than Pd-IL/AC-c and Pd/AC catalysts. This

excellent catalytic activity could be attributed to well disperse nanoparticles, the reduced Pd species, and the strong interaction between Pd nanoparticles and IL.

Acknowledgments

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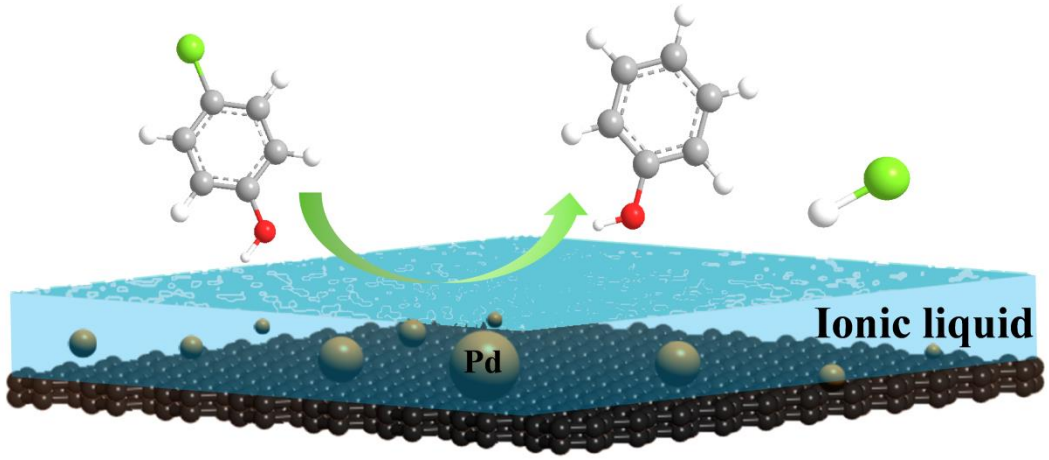

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