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PAPER

Pd(II) immobilized on mesoporous silica by N-heterocyclic carbene ionic liquids and catalysis for hydrogenation^{†‡}

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In this work we synthesized Pd(II) immobilized on mesoporous silica by N-heterocyclic carbene (NHC) ionic liquids (ILs) with different alkyl chain lengths. The catalysts were characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), low-angle X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and nitrogen sorption. The catalysts were used for the hydrogenation of alkenes and allyl alcohol. The results indicated that the catalysts were very active, selective, and stable. The selectivity for the hydrogenation of allyl alcohol to 1-propanol increased with the increase of the alkyl chain length of the ILs. The effect of supercritical CO_2 (sc CO_2) on the hydrogenation of allyl alcohol was also studied, and it was demonstrated that sc CO_2 could enhance the selectivity of the reaction considerably. The XPS study showed that the valence of Pd(II) remained unchanged under hydrogenation conditions.

1. Introduction

Hydrogenation reactions are very important in the petrochemical, pharmaceutical and food industries. Metal complexes consisting of transition metals and ligands are commonly used homogeneous catalysts for hydrogenation.^{1–3} Due to their outstanding activity and chemoselectivity, hydrogenation by Pd-complex catalysts have been studied extensively.^{4,5}

Recently, N-heterocyclic carbenes (NHCs) as ligands in metal-catalyzed reactions have attracted much attention.^{6–8} The strong electron donating ability of NHCs generally is the key factor to prepare transition-metal complexes that are thermally-stable with high activity. The Pd–NHC complexes have been applied in various reactions such as Heck and Suzuki reactions with high catalytic activity.^{9–11} But in the case of hydrogenation, little success has been achieved with the Pd–NHC catalytic system due to the fact that Pd–NHC complexes tend to decompose because of the attack of the hydride on the carbene.¹² Cloke showed that the Pd complex $[\text{Pd}(\text{ItBu})_2]$ (ItBu = *N,N'*-di-*tert*-butylimidazol-2-ylidene) decomposed after exposure to H_2 and formed palladium black and 1,3-bis-*tert*-butylimidazolidine.¹³ In the case of Pd–NHC

catalysts, palladium(0)–NHC catalytic systems have been applied for hydrogenation, but the catalytic activity was relatively low.^{12,14}

Ionic liquids (ILs) can be considered as environmentally more acceptable solvents for organic reactions due to their extremely low vapor pressure. Among them, imidazolium-based ILs have been used as ligands for palladium-mediated organic reactions because they can form an imidazole carbene bond with palladium.^{15,16} Recently, Karimi and Enders described a method for simultaneous immobilization of a NHC–Pd/IL matrix on silica. This system was effectively applied to the Heck reaction with a wide variety of iodo- and bromo-arenes. The catalyst showed high thermal stability and could be reused.¹⁷ Huynh *et al.* presented a solvent-controlled selective synthesis and structural characterization of a *trans*-configured palladium(II) bis(benzimidazoline-2-ylidene) complex, and the results demonstrated that benzannulated N-heterocyclic carbenes derived from benzimidazole were excellent ligands for catalysis.¹⁶

Another attractive feature of ILs is that both the cation and anion moieties can be designed, making it possible to modify ILs for specific applications. A series of task-specific ionic liquids (TSILs) have been designed to bear functional groups that provide particular and predictable properties, such as amine,¹⁸ amide,¹⁹ ether,²⁰ acid,²¹ phosphoryl,²² and thiols.²³ For example, Zhang *et al.* synthesized a TSIL which has a tertiary amino group ($\text{N}(\text{CH}_3)_2$) on the cation, which was used to promote the hydrogenation of CO_2 to produce formic acid, and a satisfactory result was obtained.²⁴ Zhao and co-workers prepared a series of nitrile-functionalized ILs on

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the N-butyronitrile pyridinium based cation, which were used as effective immobilization solvents for palladium-catalyzed Suzuki and Stille reactions.²⁵

Controlling the selectivity of chemical reactions by steric hindrance is an interesting topic, and some results have been reported. For example, Uyemura and Aida succeeded in the control of AIBN-initiated alkylation of cobalt(II) porphyrin with an alkyne in which cobalt(II) porphyrin was encapsulated by a radical-tolerant, large poly(aryl ester) dendritic cage. With the largest, (*m*-[G3]TPP)Co(II), a single organocobalt(III) species was selectively formed with a yield of 91% due to the steric protection by the large dendrimer cage from the access of another molecule of cobalt porphyrin species.²⁶ Jiang and Gao prepared heterogeneous Pd nanoparticle catalysts stabilized by polyamidoamine dendrimers on SBA-15, and the selectivity of the hydrogenation of allyl alcohol could be controlled by using different generation catalysts.²⁷

Herein, we prepared a series of Pd(II)-NHC IL complexes immobilized on mesoporous silica, which were used as catalysts for the hydrogenation of alkenes and allyl alcohol. The results showed that the catalysts were very active, selective and stable. It was also shown that the Pd(II)-NHC IL structure was the main active species for the reactions, and the selectivity for the hydrogenation of allyl alcohol can be controlled by the alkyl chain lengths of the ILs. As far as we know, this is the first work to conduct hydrogenation reactions catalyzed by the immobilized Pd(II)-NHC IL structure.

2. Experimental

2.1 Materials

1-Methylimidazole (99%), 1-butylimidazole (99%), 1-bromodecane, 1-bromohexadecane, imidazole, aqueous ammonia (25 wt%), anhydrous ether, tetrahydrofuran (THF), tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), Pd(OAc)₂, anhydrous methanol, tetrabutyl ammonium iodide (Bu₄NI) were all analytical grade reagents and purchased from Beijing Chemical Company. 3-Triethoxy-silylpropyl chloride (97%) was provided by Aldrich.

2.2 Preparation of N-decylimidazole

In the experiment imidazole (0.68 g, 0.01 mol) was dissolved in THF (5 mL) and then added to a solution of NaH (1.5 equiv.) in THF (15 mL). After stirring for 1 h at room temperature, 1-bromodecane (1 equiv.) was added to the solution followed by Bu₄NI (0.05 equiv.). The mixture was stirred under N₂ for 24 h at room temperature, then filtered, and a yellow liquid was obtained after the filtrate was evaporated. ¹H-NMR (400 MHz, CDCl₃): 7.44 (s, 1H, NCHN), 7.02 (s, 1H, NCHCH), 6.87 (s, 1H, NCHCH), 3.88 (t, 2H, NCH₂CH₂(CH₂)₇CH₃), 1.75 (quint., 2H, NCH₂CH₂(CH₂)₇CH₃), 1.22 (m, 14H, NCH₂CH₂(CH₂)₇CH₃), 0.86 (t, 3H, NCH₂CH₂(CH₂)₇CH₃).

2.3 Preparation of N-hexadecylimidazole

Imidazole (0.68 g, 0.01 mol) was dissolved in THF (5 mL) and then added to a solution of NaH (1.5 equiv.) in THF (15 mL). After stirring for 1 h at room temperature 1-bromohexadecane (1 equiv.) was added into the solution followed by Bu₄NI

(0.05 equiv.). The mixture was stirred under N₂ at room temperature for 24 h and filtered, a yellow solid was obtained after the filtrate was evaporated. ¹H-NMR (400 MHz, CDCl₃): δ 7.45 (s, 1H, NCHN), 7.04 (s, 1H, NCHCH), 6.89 (s, 1H, NCHCH), 3.90 (t, 2H, NCH₂CH₂(CH₂)₁₃CH₃), 1.75 (quint., 2H, NCH₂CH₂(CH₂)₁₃CH₃), 1.24 (m, 14H, NCH₂CH₂(CH₂)₁₃CH₃), 0.87 (t, 3H, NCH₂CH₂(CH₂)₁₃CH₃).

2.4 Preparation of the NHC ILs with different lengths of alkyl chain (IL-1, IL-4, IL-10, IL-16)

NHC ILs with different alkyl chain lengths were prepared. IL-1, IL-4, IL-10, and IL-16 stand for the ILs with alkyl chain lengths of C1, C4, C10, and C16, respectively.

IL-1 was synthesized according to the method reported by other authors.²⁸ In the experiment, 1-methylimidazole (0.82 g, 0.01 mol) and (3-chloropropyl) triethoxysilane (2.41 g, 0.01 mol) were dissolved in toluene (20 mL), and the solution was refluxed at 100 °C for 24 h under N₂ atmosphere. The yellow IL layer was separated from the organic layer by cooling the solution to room temperature. Then the yellow IL layer was thoroughly washed with ether (20 mL × 3) and dried at 60 °C under vacuum for 24 h. ¹H-NMR (400 MHz, CDCl₃): δ 10.80 (s, 1H, NCHN), 7.39 (s, 1H, NCHCH), 7.30 (s, 1H, NCHCH), 4.37 (t, 2H, CH₂N), 4.12 (s, 3H, NCH₃), 3.80 (q, 6H, OCH₂), 2.02 (q, 2H, CH₂CH₂CH₂), 1.21 (t, 9H, CH₃CH₂), 0.60 (t, 2H, SiCH₂).

IL-4 was synthesized from 1-butyl-imidazole and (3-chloropropyl) triethoxysilane according to the procedure given above for the synthesis of IL-1. ¹H-NMR (400 MHz, CDCl₃): δ 10.90 (s, 1H, NCHN), 7.66 (s, 1H, NCHCH), 7.32 (s, 1H, NCHCH), 4.30 (t, 2H, CH₂N), 4.30 (t, 2H, NCH₂CH₂CH₂CH₃), 3.79 (q, 6H, OCH₂), 1.94 (quint., 2H, CH₂CH₂CH₂), 1.84 (quint., 2H, NCH₂CH₂CH₂CH₃), 1.36 (sext., 2H, NCH₂CH₂CH₂CH₃), 1.14 (t, 9H, CH₃CH₂), 0.88 (t, 3H, NCH₂CH₂CH₂CH₃), 0.53 (t, 2H, SiCH₂).

IL-10 was synthesized from N-decylimidazole and (3-chloropropyl) triethoxysilane. The procedure was also similar to that for preparing IL-1. ¹H-NMR (400 MHz, CDCl₃): δ 10.72 (s, 1H, NCHN), 7.42 (s, 1H, NCHCH), 7.32 (s, 1H, NCHCH), 4.32 (t, 2H, CH₂N), 4.32 (t, 2H, NCH₂CH₂(CH₂)₇CH₃), 3.75 (q, 6H, OCH₂), 1.95 (quint., 2H, CH₂CH₂CH₂), 1.85 (quint., 2H, NCH₂CH₂(CH₂)₇CH₃), 1.14 (m, 14H, NCH₂CH₂(CH₂)₇CH₃), 0.88 (t, 3H, NCH₂CH₂(CH₂)₇CH₃), 0.53 (t, 2H, SiCH₂).

IL-16 was synthesized from N-hexadecylimidazole and (3-chloropropyl) triethoxysilane according to the above procedures. ¹H-NMR (400 MHz, CDCl₃): δ 10.60 (s, 1H, NCHN), 7.46 (s, 1H, NCHCH), 7.34 (s, 1H, NCHCH), 4.28 (t, 2H, CH₂N), 4.28 (t, 2H, NCH₂CH₂(CH₂)₁₃CH₃), 3.72 (q, 6H, OCH₂), 1.95 (quint., 2H, CH₂CH₂CH₂), 1.85 (quint., 2H, NCH₂CH₂(CH₂)₁₃CH₃), 1.12 (m, 14H, NCH₂CH₂(CH₂)₁₃CH₃), 1.11 (t, 9H, CH₃CH₂), 0.79 (t, 3H, NCH₂CH₂(CH₂)₁₃CH₃), 0.58 (t, 2H, SiCH₂).

2.5 Preparation of Pd-NHC IL complexes (Pd-IL-1, Pd-IL-4, Pd-IL-10, Pd-IL-16)

To prepare the Pd-IL-1 complex, IL-1 (3.23 g, 0.01 mol) and Pd(OAc)₂ (0.1 equiv.) were added to a 25 mL round-bottom

flask and the air in the flask was removed by vacuum. The mixture was heated with stirring at 60 °C for 8 h and then heated to 100 °C for 4 h. The by-product in the reaction system was removed using a rotary evaporator under vacuum for 2 h. A pale yellow solution of Pd-IL-1 in IL-1 was obtained. Pd-IL-4, Pd-IL-10 and Pd-IL-16 were synthesized from IL-4, IL-10 and IL-16 with Pd(OAc)₂ using the same procedure. The ¹³C-NMR spectra of these solutions all showed a new peak at about 175 ppm, indicating the formation of Pd-NHC IL complexes.¹⁵

2.6 Preparation of Pd-NHC IL complexes immobilized on silica (IMM-1, IMM-4, IMM-10, IMM-16)

In this paper, IMM-1, IMM-4, IMM-10, IMM-16 denote the Pd-NHC IL complexes immobilized on silica, in which the alkyl chain lengths of the ILs were C1, C4, C10, and C16, respectively.

The method was similar to that reported in the literature to prepare porous materials by post-synthesis derivatization of materials from Si-based MCM-41 with bidentate nitrogen ligands.²⁹ Here we describe the procedure to prepare IMM-1 as a representative case. In the experiment, aqueous ammonia was added to a stirring solution of CTAB, then a mixture of TEOS, Pd-IL-1 and neat IL-1 dissolved in methanol was added dropwise, and the final molar ratio of TEOS/Pd-IL-1/IL-1/CTAB/NH₃/methanol/H₂O was 1:0.01:0.08:0.14:8:2:100. The mixture was stirred for 4 h under ambient conditions, then aged at 100 °C for 24 h. The white product was obtained by filtration, washed with water, and dried under vacuum for 24 h. The resulting solid was added to a solution of 250 mL methanol and 6 mL HCl (37%) at 50 °C and the mixture was stirred for 6 h to remove the surfactant. The white solid was then filtered and washed with methanol (20 mL × 3) and dried at 60 °C for 24 h. Similarly, IMM-4, IMM-10 and IMM-16 were synthesized from Pd-IL-4, Pd-IL-10, Pd-IL-16 using the same procedure. The Pd contents of IMM-1, IMM-4, IMM-10 and IMM-16 determined by ICP-AES were 0.19 wt%, 0.15 wt%, 0.17 wt% and 0.087 wt%, respectively.

2.7 Characterization of the catalysts

The FT-IR spectra were collected on a Bruker Tensor 27 spectrometer in KBr pellet form. TEM observation was performed on a transmission electron microscope (JEOL, JEM 1011) at an operating voltage of 100 kV, and the images were electronically captured using a CCD camera. X-ray powder diffraction was performed on an X'PERT SW X-ray

diffractometer operated at 30 kV and 100 mA with Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) data of the as prepared samples were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg-K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Thermogravimetric (TG) measurements were performed on a thermal analyzer (NETZSCH STA 409 PC/PG) with a heating rate of 3 °C min⁻¹. The loading content of Pd in the catalysts was determined by ICP-AES (VISTAMPX).

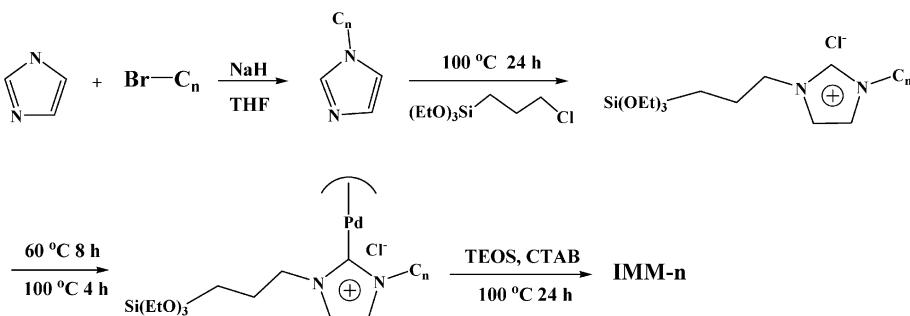
2.8 Hydrogenation reactions

The stainless steel reactor of 6 mL and the experimental procedure were similar to those reported previously.³⁰ We use the hydrogenation of allyl alcohol as an example to describe the experimental procedure. In the experiment, allyl alcohol (0.2 mL) and the catalyst were added into the reactor and then heated to 40 °C. After the introduction of H₂ at the desired pressure, CO₂ was charged into the reactor with a high pressure pump (DB-80) to the desired pressure. The reactor was cooled in an ice bath after a suitable reaction time, and the gases were released slowly passing through a cold trap with DMF absorbent. The solution in the cold trap was mixed with the reaction mixture. The product was analyzed by GC (Agilent 4890 D) equipped with a flame-ionized detector. In the catalyst recycling experiments, the catalyst was separated by centrifugation and was reused after washing with ethanol and drying.

3 Results and discussion

3.1 Synthesis and characterization of the catalysts

The routes to synthesize IMM-1, IMM-4, IMM-10 and IMM-16 are presented in Scheme 1 and the detailed procedures are described in the Experimental section. The ILs were synthesized by the reaction of (3-chloropropyl) triethoxysilane and the corresponding N-alkylimidazole in toluene. After Pd(OAc)₂ was added to the ILs, the mixture was heated at 60 °C for 8 h and then 100 °C for 4 h to form a Pd(II)-NHC complex which was confirmed by ¹³C NMR. The corresponding Pd(II)-NHC immobilized on mesoporous SiO₂ was formed by the reaction of the resulting IL containing Pd(II)-NHC complex and TEOS with CTAB as surfactant.



Scheme 1 Synthesis procedures of IMM-1, IMM-4, IMM-10 and IMM-16.

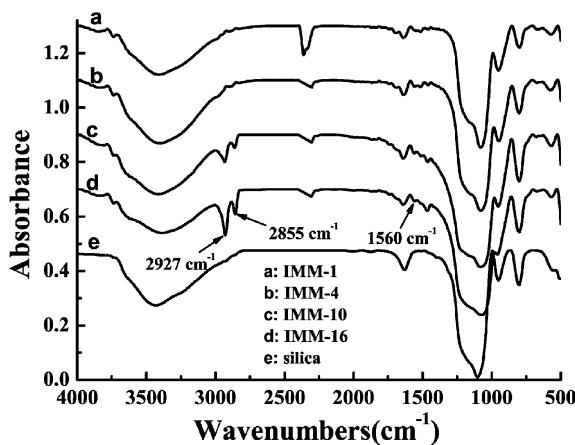


Fig. 1 The FT-IR spectra of IMM-1, IMM-4, IMM-10, IMM-16 and SiO_2 .

IMM-1, IMM-4, IMM-10 and IMM-16 were characterized by TEM, FT-IR, low-angle XRD, TGA and nitrogen sorption, respectively. Fig. 1 gives the FT-IR spectra of IMM-1, IMM-4, IMM-10, IMM-16 and SiO_2 . Compared to the spectrum of SiO_2 , a new weak absorption peak at about 1560 cm^{-1} appeared in the spectra of the four catalysts. It can be attributed to the $\text{C}=\text{C}$ stretching of the imidazole ring, indicating the existence of the ILs in the catalysts.¹⁷ The peaks at about 2927 cm^{-1} and 2855 cm^{-1} are attributed to aliphatic C–H stretching, and as expected the intensity increased as the length of alkyl chains of the ILs increased, suggesting that the ILs were immobilized on the silica.

The four catalysts were examined by TGA. The results in Fig. 2 demonstrated that all four catalysts had weight losses below $180\text{ }^\circ\text{C}$ due to desorbed water and inner water molecules. Further weight loss at higher temperature was attributed to the elimination of the ILs immobilized on the SiO_2 , and the loading of the ILs for the four catalysts were about 9.3 wt%, 9.6 wt%, 11.2 wt%, 10.2 wt%, respectively.

Powder low-angle XRD patterns of the catalysts are shown in Fig. 3. All the samples exhibited peaks at about 2.2° that corresponded to 100 reflections of MCM-41.³¹ This indicates that the periodic channels were formed. Meanwhile, it can be noted that the intensities of diffraction peaks become weaker from IMM-1 to IMM-16 as the length of the alkyl chain is increased.

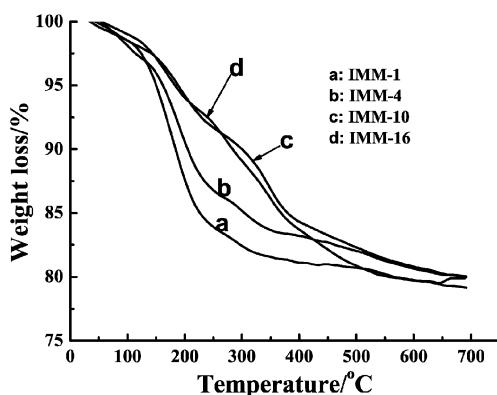


Fig. 2 TGA diagram of IMM-1, IMM-4, IMM-10 and IMM-16.

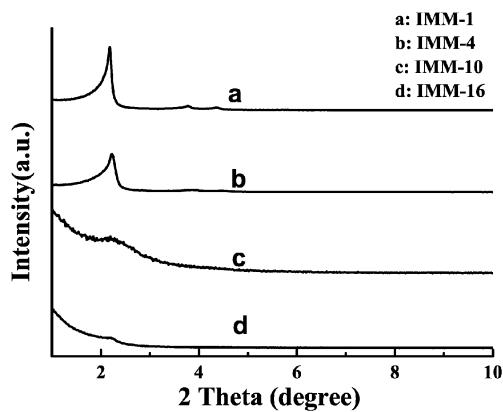


Fig. 3 Low-angle XRD patterns for IMM-1, IMM-4, IMM-10 and IMM-16.

TEM images of IMM-10 are given in Fig. 4, which show two dimensional hexagonal symmetry structures. The other catalysts had similar structures. The TEM images demonstrated that the catalysts had highly ordered pore structures. IMM-10 was characterized by N_2 sorption analysis to determine the surface area and porous characteristics (Fig. 5). The pore size was about 3.27 nm , which agreed with that obtained from the TEM image. The specific surface area of the catalyst was determined to be $187.2\text{ m}^2\text{ g}^{-1}$. On the basis of these characterizations, we can deduce that IMM-n has the structure schematically shown in Fig. 6.

3.2 Hydrogenation reactions

We studied the catalytic activity of the catalysts for the hydrogenation of different alkenes and allyl alcohol. The results of the reactions are shown in Table 1. The catalytic activity of IMM-1, IMM-4, IMM-10 and IMM-16 for allyl alcohol was similar to that of commercial Pd/C. However, the activity of IMM-1 for 1-hexene and cyclohexene was lower than that of Pd/C. This can be explained by the steric effect. Compared to allyl alcohol, 1-hexene and cyclohexene have larger molecular volume, which leads to low TOF.

For the hydrogenation of allyl alcohol catalyzed by IMM-1, IMM-4, IMM-10 and IMM-16, the selectivities for 1-propanol were 80.0%, 80.5%, 84.1% and 84.0%, respectively, which are all higher than that obtained using the commercial Pd/C catalyst, as can be seen from Table 1. This indicates that the ILs can not only immobilize the metal catalyst, but also can enhance the selectivity of the reaction. As reported previously,¹⁷ the key factor in controlling the selectivity of the reaction is the diffusion rate of the substrate to the Pd center, which is controlled by the steric hindrance. The selectivity for the hydrogenation product (1-propanol) increases with increasing length of alkyl chain of the ILs up to C10, but the effect of chain length on the selectivity was not obvious as the size of the chain was increased further. This can be explained by the proposed reaction mechanism shown in Fig. 7.³² There are two catalytic routes in the hydrogenation of allyl alcohol: the hydrogenation reaction to produce 1-propanol catalyzed by hydrogen-saturated Pd and isomerization of allyl alcohol to form the by-product propanal catalyzed by bare Pd. The steric hindrance results in a more significant decrease in

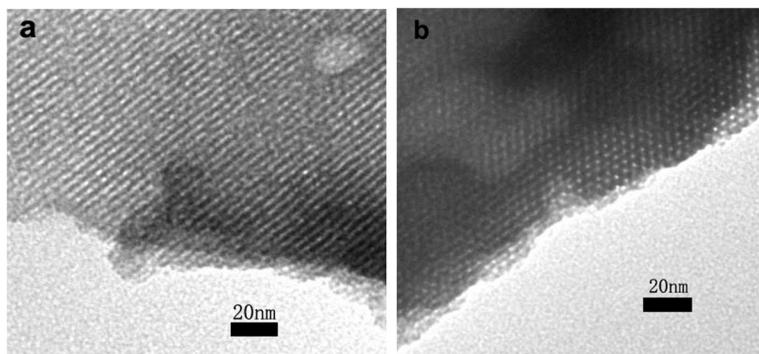


Fig. 4 TEM images of IMM-10.

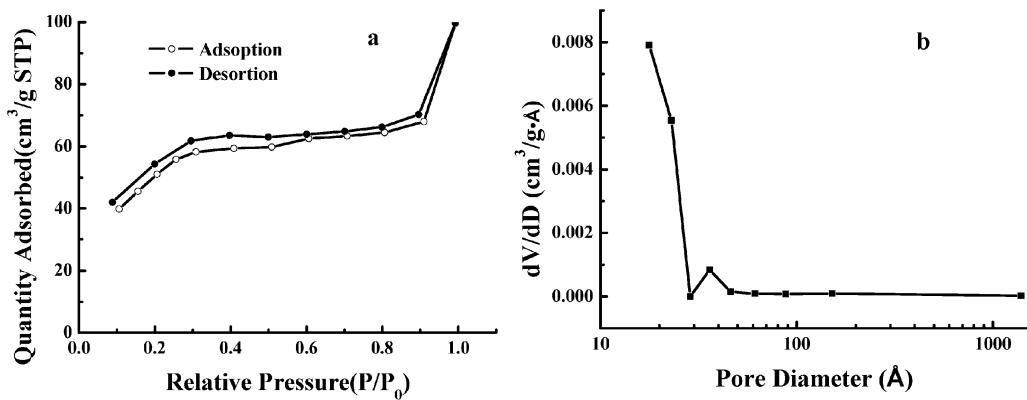


Fig. 5 Nitrogen sorption isotherms (a) and pore size distribution (b) of IMM-10.

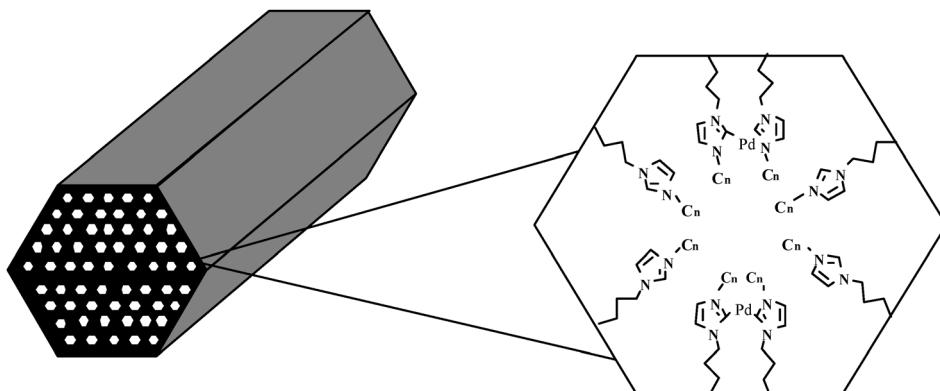


Fig. 6 Schematic structure of the catalyst IMM-n.

the diffusion rate of allyl alcohol than that of hydrogen because of its larger molecular volume. Obviously, the steric hindrance of the catalysts prepared in this work should increase with the length of the alkyl chain of the ILs, leading to an increase of selectivity. But when the chain length was larger than C10, the selectivity of 1-propanol was not changed noticeably because the steric hindrance was large enough.

Fig. 8 shows the XPS spectra of IMM-10 before and after the reaction (entry 7 of Table 1). The binding energies of $Pd^{(II)} 3d_{5/2}$ in the catalyst both before and after the reaction were 337.5 eV, which are very close to 337.9 eV, the typical value of $Pd^{(II)}$.³³ The value is also consistent with that of a $Pd^{(II)}$ -NHC complex reported before.³⁴ According to the XPS spectra the

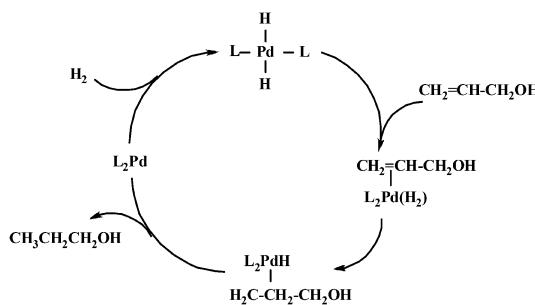
intensity of the peak at about 335.0 eV for $Pd^{(0)}$ is very low, indicating that nearly no $Pd^{(0)}$ nanoparticles formed during the reaction. The HRTEM image in Fig. 9 shows that there were no visible palladium nanoparticles on the wall of the silica after the reaction, and the highly ordered pore structure is unchanged. This also suggests that $Pd^{(II)}$ was the main active species for the hydrogenation reaction. The main reason may be that the $Pd^{(II)}$ in the carbene structure is stable and hydrogen could not reduce it effectively. The detailed reason should be studied further.

The effect of adding CO_2 on the reaction was also studied using IMM-10 as the catalyst, and the results are presented in Table 2. The selectivity increased from 84.1% to 90.2% as the

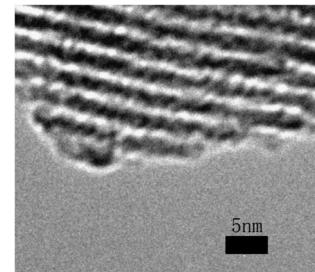
Table 1 Results of catalyst performance for different hydrogenation reactions^a

Entry	Catalyst	Substrate	Time/min	Conversion (%)	Selectivity (%) ^b	TOF/h ⁻¹
1	IMM-1	1-Hexene	100	100	100	6000
2	Pd/C ^c	1-Hexene	50	100	100	12000
3	IMM-1	Cyclohexene	140	100	100	4285
4	Pd/C ^c	Cyclohexene	80	100	100	7500
5	IMM-1	Allyl alcohol	35	100	80.0	17142
6	IMM-4	Allyl alcohol	37	100	80.5	16216
7	IMM-10	Allyl alcohol	40	100	84.1	15000
8	IMM-16	Allyl alcohol	41	100	84.0	14634
9	Pd/C ^c	Allyl alcohol	40	100	74.0	15000

^a Reaction conditions: 40 °C; H₂, 4.00 MPa; the molar ratio of substrate to Pd was 10000. ^b The by-product is propanal. ^c Commercial Pd/C, 5% Pd on carbon powder from Baoji Rock Pharmachem Co., Ltd., China. The detailed characterization was provided previously.³⁰

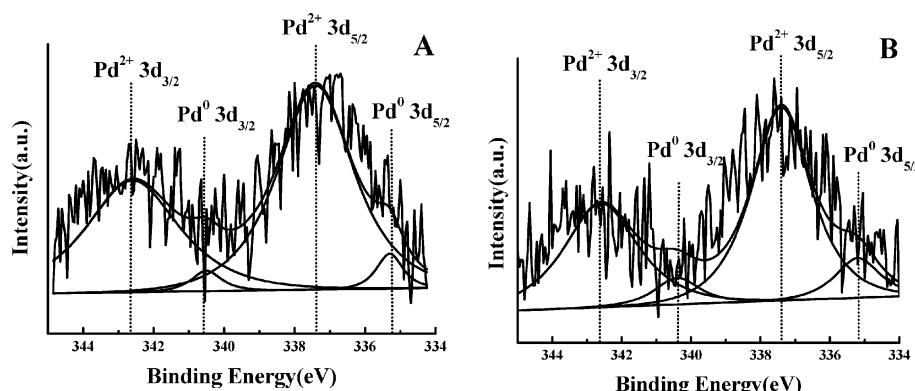
**Fig. 7** The possible mechanism of the hydrogenation of allyl alcohol.

pressure of CO₂ changed from 0.0 to 7.0 MPa at a fixed H₂ pressure of 4.0 MPa. When the pressure of CO₂ exceeded 7.0 MPa, the selectivity was nearly independent of CO₂ pressure. It is very difficult to give the exact reasons for CO₂ enhancing the selectivity of the reaction. One of the main reasons may be that H₂ is miscible with gaseous or supercritical CO₂, and CO₂ can enhance the miscibility of gases and imidazolium based ionic liquids.³⁵ Therefore, it can be deduced that the concentration of H₂ near the Pd(II) in the ionic liquid layer of the catalyst can be higher than that in the absence of CO₂, and thus more H₂ can be adsorbed by the catalyst. As discussed above, the hydrogenation reaction to produce the product 1-propanol is catalyzed by hydrogen-saturated Pd and isomerization of allyl alcohol to form the by-product propanal is catalyzed by bare Pd. Therefore, CO₂ can enhance the selectivity for the desired product.

**Fig. 9** HRTEM image of recovered IMM-10 after the reaction.**Table 2** The conversion and selectivity of hydrogenation of allyl alcohol catalyzed by IMM-10^a

Catalyst	Time/min	P _{CO₂} (MPa)	Conversion (%)	Selectivity (%) ^b
IMM-10	40	0.0	100	84.1
IMM-10	40	3.0	100	85.6
IMM-10	40	7.0	100	90.2
IMM-10	40	10.0	100	89.3
IMM-10 ^c	40	7.0	100	89.0
IMM-10 ^d	40	7.0	100	90.1
IMM-10 ^e	40	7.0	100	88.8
Pd/C ^f	40	7.0	100	74.0

^a Reaction conditions: 40 °C; the molar ratio of allyl alcohol to Pd was 10000. ^b The by-product is propanal. ^c The catalyst IMM-10 was reused for the first time. ^d The catalyst IMM-10 was reused for the second time. ^e The catalyst IMM-10 was reused for the third time. ^f Commercial Pd/C, 5% Pd on carbon powder from Baoji Rock Co. Ltd, China.

**Fig. 8** XPS spectra of IMM-10 before (A) and after (B) the reaction (entry 7 of Table 1).

The reusability of the catalyst IMM-10 was tested. The results are also given in Table 2. The catalytic activity and selectivity did not change after the catalyst was reused three times. The Pd content of fresh catalyst and recycled catalyst were determined by ICP-AES. The Pd content of the catalyst remained almost unchanged after being reused three times.

4. Conclusions

Pd(II) supported on mesoporous silica by NHC ILs with different alkyl chain lengths has been prepared. The catalysts have high activity and selectivity for the hydrogenation of alkenes and allyl alcohol. The XPS study indicates that the valence of Pd(II) remained unchanged after the hydrogenation reaction. For the hydrogenation of allyl alcohol to 1-propanol, the selectivity is considerably higher than that of the commonly used Pd/C catalyst, and the selectivity increased with an increase in the length of the alkyl chain of the ILs. This can be explained by the fact that the steric effect of an IL with a longer hydrocarbon chain is more pronounced, which is favorable to increasing the selectivity for the desired product. In addition, scCO₂ can also improve the selectivity of the reaction considerably.

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