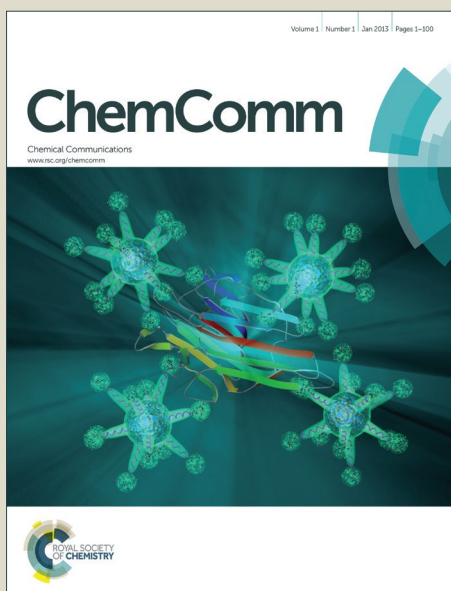


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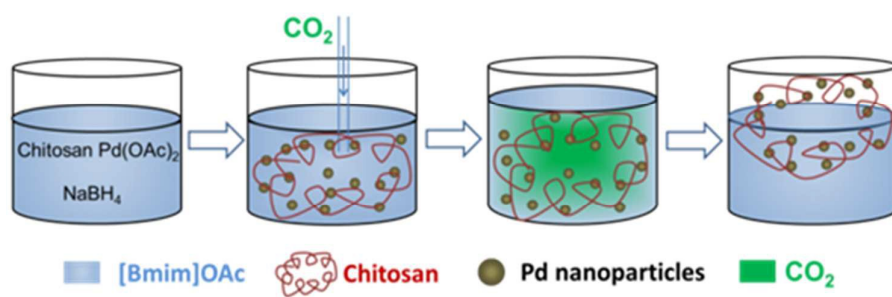
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Graphical abstract

A controllable synthetic route is developed to prepare chitosan supported Pd catalysts in 1-butyl-3-methylimidazolium acetate by using compressed CO₂ as the anti-solvents and regulator.



COMMUNICATION

CO₂ as a regulator for controllable preparation of highly dispersed chitosan-supported Pd catalysts in ionic liquid

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A controllable synthetic route is developed for preparation of chitosan supported Pd catalysts in ionic liquid 1-butyl-3-methylimidazolium acetate ([Bmim]OAc) by using compressed CO₂ as the anti-solvent and regulator. It was found that the dispersion of Pd particles on chitosan and the catalytic activity of the as-prepared catalysts for styrene hydrogenation could be tuned by changing the pressure of CO₂.

Chitosan obtained by the deacetylation of chitin is one of the most widely used biopolymers. It has attracted tremendous attention because of its renewable, biodegradable, and biocompatible properties.^{1,2} Up to now, chitosan has diverse applications in various fields, including pharmaceuticals, ion-exchange resins, industrial separation membranes, cosmeticology, catalyst or catalyst support, etc.³⁻⁵ Particularly, its usage as nano-catalyst support is very attractive because chitosan could stabilize nano-catalyst through the rich hydroxyl and amino groups in its molecular structure. There are some potential advantages of chitosan as the support for nano-metal catalysts, including easy modification or even possibility to use without preliminary modification, high metal dispersion on the surface, rather high thermal stability, and easy recovery, etc. However, the reports on chitosan-supported nano-metal catalysts are relatively limited. The few examples are the Rh, Cu, Ru, Pd, Pt, Au and Ag nanoparticles supported on chitosan by wetness impregnation or coprecipitation methods.⁶⁻⁸ Some drawbacks still exist in these processes, such as using organic solvents, aggregation of the nano-metal particles, acid conditions and degradation of chitosan. Thus, the development of simple and efficient route for the immobilization of noble metal nanoparticles on chitosan to obtain highly efficient and stable catalysts is still an important and interesting topic.

In recent years, ionic liquids (ILs) have been considered as a class of green solvents and received extensive attention because of their unusual properties, such as high thermal and chemical stability, adjustable functions, negligible vapour pressure, non-flammability, and adjustable solvent power for organic and inorganic substances.^{9,10} Due to the good solubility of biopolymers in ILs, applications of ILs in the preparation of bio-based materials have

been studied extensively and various materials based on biopolymers have been prepared in ILs.¹¹⁻¹⁴ Meanwhile, it has been proved that ILs are functional solvents for the synthesis of metal nanoparticles.¹⁵ Therefore, the special properties of ILs provide excellent opportunities for their applications in the preparation of biopolymer supported nano-metal catalysts.¹⁹ However, the separation of ILs and the prepared material is difficult and energy intensive because of the negligible vapour pressure of ILs and the materials.

To date, people usually use anti-solvents such as water, ethanol and acetone to recover materials from ILs.²⁰ However, the regenerated materials generally show high diversity in size, and the distribution of the nano-metal catalysts on the biopolymers is usually not even. The separation of the as-synthesized materials from ILs through green and controlled processes is still a challenging topic for the preparation of biopolymer-based materials in ILs. CO₂ is cheap, non-toxic, non-flammable, and abundant. Compressed or supercritical CO₂ can be obtained with a high-pressure pump. The solvent strength of CO₂ can be finely adjusted by the temperature and pressure of CO₂. Therefore, it is considered as another green solvent and has been widely used as alternative solvent in various fields. Recently, we have successfully precipitated chitosan and cellulose from ILs using compressed CO₂ by disrupting the hydrogen bond between these biopolymers and ILs.^{21,22} These advantages of CO₂ pave a promising way for the synthesis of chitosan-supported nano-metal catalysts in ILs.

Herein, we report the controllable synthesis of Pd/chitosan catalyst with higher Pd dispersion in 1-butyl-3-methylimidazolium acetate ([Bmim]OAc) using compressed CO₂ as a regulator. We found that anti-solvents have significant influence on the size and the distribution of the nano-metal catalysts on the supported biopolymers, hence influencing the activity of the catalysts for the hydrogenation of styrene. The as-synthesized Pd/chitosan catalysts by using CO₂ as the anti-solvent showed a higher activity than those by using ethanol or water. The catalytic performances of Pd/chitosan can be tuned by changing the pressure of the CO₂. Moreover, the catalyst can be easily recovered and reused. We believe that this simple and green route by using CO₂ as the anti-solvent and regulator has great potential in the preparation of nano-metal catalysts supported on biopolymers.

The procedures to prepare chitosan-supported Pd catalysts are illustrated schematically in Fig. 1. NaBH_4 was firstly dissolved in $[\text{Bmim}]\text{OAc}$ to form a solution. Then, the mixture of chitosan and $\text{Pd}(\text{OAc})_2$ was added into the solution gradually. In this process, $\text{Pd}(\text{OAc})_2$ was reduced to Pd nanoparticles by NaBH_4 , and chitosan was dissolved in $[\text{Bmim}]\text{OAc}$ to play the role of stabilizing the as-formed Pd nanoparticles at 373 K. After the mixture of chitosan and $\text{Pd}(\text{OAc})_2$ was dissolved completely, CO_2 was slowly introduced into the solution to reach the desired pressure at 298 K and the system was kept at the pressure for 10 h.²¹ Finally, the chitosan-supported Pd catalysts were regenerated from the ionic liquids by removing CO_2 ,²¹ which could be easily separated. Small amount of ionic liquids absorbed on the chitosan could be removed by ethanol.²¹ For comparison, ethanol and water were also used to generate the chitosan-supported Pd catalysts.

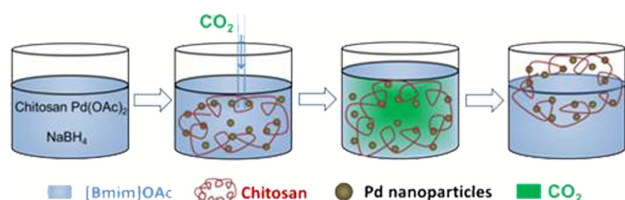


Fig. 1. Schematic diagram of the synthesis of Pd/chitosan in $[\text{Bmim}]\text{OAc}$.

Fig. 2 shows the representative transmission electron microscopy (TEM) images of the as-synthesized catalyst obtained by using compressed CO_2 at 9.2 MPa as the anti-solvent. From the figure, we confirmed that Pd nanoparticles could be highly dispersed on chitosan and the size of the particles is about 3–5 nm. From the high-resolution TEM (HRTEM) image shown in Fig. 2c, the interplanar distance of the nanoparticles can be clearly observed and measured to be 0.23 nm, corresponding to Pd (111). Meanwhile, the synthesized catalysts by using CO_2 as the anti-solvent (Figs. S1c–S1f) had better dispersion than the ones by using water (Fig. S1a) and ethanol (Fig. S1b) as the anti-solvents. It is obvious that the Pd particles aggregated into large cluster when using water and ethanol as the anti-solvents. This control experiment confirmed that CO_2 exceeded the conventional liquid solvents for preparation Pd/chitosan in ILs. Furthermore, it is indicated that the particles had better dispersion with the increase of the pressure as shown in Fig. S1c–1f.

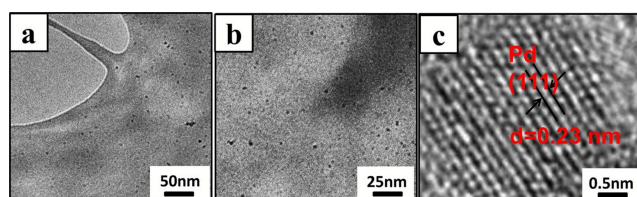


Fig. 2. TEM and HRTEM images of the catalyst prepared with compressed CO_2 at 9.2 MPa as the anti-solvent.

X-ray diffraction (XRD) patterns (Fig. 3) further revealed the crucial role of CO_2 in the preparation of chitosan-supported Pd catalysts. No obvious Pd peaks exist in case of CO_2 . This could be caused by the better dispersion of Pd with ultrafine particles²³ by CO_2 , which was consistent with the TEM results shown in Fig. 2 and Fig. S1. When using ethanol or water as the anti-solvent, we could see in the figure that there was one characteristic peak of Pd(0) at about $2\theta=40^\circ$ ascribing to Pd(111),²⁴ which indicated the aggregation of Pd nanoparticles.

In addition, the XRD patterns of the as-prepared Pd/chitosan all showed one broad peak at about $2\theta=20^\circ$, which were identical to that of the raw chitosan, indicating the structure of chitosan was not changed after immobilizing Pd on it.

The loading content of the Pd on chitosan obtained by using different anti-solvents was determined by ICP-AES method (Table S1). From Table S1, we could see that higher Pd loading content could be obtained by using ethanol (Chit-Pd-

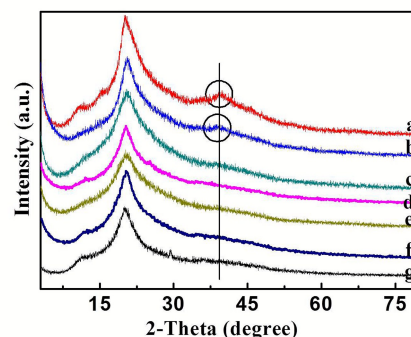


Fig. 3. Powder X-ray diffraction pattern for chitosan and Pd/chitosan obtained by using different anti-solvents. (a) Water; (b) Ethanol; (c) 7.2 MPa CO_2 ; (d) 9.2 MPa CO_2 ; (e) 12.2 MPa CO_2 ; (f) 14.2 MPa CO_2 ; (g) raw chitosan.

Ethanol) or water (Chit-Pd- H_2O) than that by CO_2 at different pressure (Chit-Pd-7.2 MPa, Chit-Pd-9.2 MPa, Chit-Pd-12.2 MPa and Chit-Pd-14.2 MPa). This is probably resulted from the stronger solvent power of ethanol and water than CO_2 .²⁵ Meanwhile, the Pd loading content increased with the increasing pressure of CO_2 because the solvent power also increased with the increase of CO_2 pressure from 7.2 MPa to 14.2 MPa.²² The low Pd loadings did not detract the activity of the catalyst,²⁵ which was proved by the high activity for the hydrogenation of styrene presented as follows.

The properties of the as-synthesized catalysts were also characterized by Fourier transform-infrared (FT-IR) technique and the results were given in Fig. S2. The FT-IR spectra of the different as-prepared Pd/chitosan materials demonstrated all characteristic bands of raw chitosan. The broad band at 3500 cm^{-1} corresponded to the absorption of OH in the structure of chitosan, which masked the signal of N-H stretching vibration.²⁶ The narrow bands at 2900 cm^{-1} was assigned to the stretching vibrations of CH and CH_2 groups. The bands for the vibrations of NH_2 group were found in the $1660\text{--}1530\text{ cm}^{-1}$ range, indicating the presence of the NH_2 group.^{7,27} Importantly, there is a change in relative intensities in the region of deformational NH group vibrations ($1500\text{--}1680\text{ cm}^{-1}$),²⁴ which are consistent with the changes in the intra and intermolecular hydrogen bonding of chitosan chains in the catalyst. This may be caused by the interactions between Pd nanoparticles and N-H groups of chitosan.²⁸

Based on the above results, it is obvious that CO_2 was unique for preparing the highly dispersed chitosan-supported Pd catalysts. In the process, CO_2 played two key roles to prepare the highly dispersed Pd catalyst. Firstly, CO_2 could change the solvent strength of $[\text{Bmim}]\text{OAc}$ for chitosan by the volume expansion of the solution, the carboxylation reaction between $[\text{Bmim}]\text{OAc}$ and CO_2 , and reduction of the polarity and net donating ability of hydrogen bonds,²⁹ which could destroy the interaction between chitosan and $[\text{Bmim}]\text{OAc}$ and thus decrease the solubility of chitosan.

[Bmim]OAc. Therefore, chitosan was regenerated from [Bmim]OAc by using CO₂ as the anti-solvent. Secondly, when CO₂ was charged into [Bmim]OAc, the decreasing of the density, viscosity, surface tension and solvent power of the ionic liquid phase was favourable to Pd nanoparticles to be adsorbed on chitosan from the CO₂-expanded ionic liquid solution.^{29,30} Owing to the unique properties of CO₂, such as low viscosity, rapid diffusivity and absence of surface tension, the Pd nanoparticles preferably were loaded on the chitosan with high dispersion when chitosan was regenerated from [Bmim]OAc. Previous reports have shown that carbene may be formed in the ionic liquid BmimOAc, and carbene could react with CO₂ by the carboxylation reaction.²² However, in this study, the results showed that this reaction did not influence the catalysts preparation.

The as-synthesized Pd/chitosan catalysts by using different anti-solvents were used to catalyze the hydrogenation of styrene at different conditions, and the results were listed in Table 1. The six catalysts showed different catalytic activity for the reaction. Among them, the catalyst obtained with a CO₂ pressure of 14.2 MPa (Chit-Pd-14.2 MPa) was the best (Table 1, entries 1 and 2) with TOFs of 12538 and 4876 obtained at 50 °C and 25 °C, respectively. In contrast, the TOFs obtained from the catalysts with ethanol as the anti-solvent (Chit-Pd-Ethanol) are 10716 and 3322 (Entries 11 and 12). At the same time, the catalysts with water as the anti-solvent (Chit-Pd-H₂O) give the lowest TOFs (9148 and 3124, respectively in entries 9 and 10). It is obvious that the catalysts using CO₂ as the anti-solvents showed better performance than the ones using ethanol and water as the anti-solvents. There were two reasons for this phenomenon. Firstly, the Pd nanoparticles by using CO₂ as the anti-solvent had better dispersion than the ones by using ethanol or water as the anti-solvent, which had been proven by the tests of TEM and XRD. This could result in the better activity of the catalysts obtained by using CO₂ as the anti-solvent. Secondly, the Pd/chitosan composite obtained from CO₂ had more loose structure than the ones from ethanol and water, which was intuitive and had been proved by the previous work.²² The loose structure was beneficial for mass transfer and then increased the reaction rate. The two reasons above resulted in the better activity when using CO₂ as the anti-solvent. Importantly, Chit-Pd-14.2MPa still maintained good activity when the H₂ pressure decreased to 1 atm (Table 1, entry 13). The TOF value was also higher than Pd/ZIF or Pd/C in DMF under the similar reaction conditions (Table 1, entries 14 and 15).^{31,32} It should be noted that for Entries 1 and 3, different time was used for calculation of TOF since the yield have already exceed 99% at the studied reaction time. Fig. S3 also gave consistent tendency on the performance of catalysts prepared by different anti-solvents. Furthermore, we also found from the data in Table 1 and Fig. S3 that the activity of the as-prepared catalysts using CO₂ as the anti-solvents increased with the increasing pressure of CO₂ because higher CO₂ was beneficial for the dispersion of the Pd nanoparticles and the formation of the loose structure of chitosan.

Two series of experiments were carried out to examine the recyclability of Chit-Pd-14.2MPa at 50 °C with the reaction time of 30 and 55 min, respectively. The yields of ethylbenzene for the five repeated runs are shown in Fig. 4. There was no detectable decrease of the yield of ethylbenzene in the two series of experiments, indicating that the catalyst was very stable. The excellent stability was also supported by the results of thermogravimetric analysis (TGA) and TEM. Fig. S4 gives

the thermogram of raw chitosan and the as-prepared Pd/chitosan catalysts. It is obvious that the decomposition of the polysaccharide framework in the samples occurred at about 260 °C,^{27,33} which was much higher than the reaction temperature (50 °C) in our catalytic experiments. The TEM image of the used Chit-Pd-14.2MPa was embedded in Fig. 4. The figure showed that the dispersion of Pd nanoparticles on chitosan did not change noticeably after it had been used five times compared with the result shown in Fig. S1f.

Table 1. Catalytic activity of various catalysts for the hydrogenation of styrene.^a

Entry	Catalyst	Temperature (°C)	Time	Yield (%) ^b	TOF ^c
1	Chit-Pd-14.2MPa	50	55min	>99	12538
2	Chit-Pd-14.2MPa	25	2h	84	4876
3	Chit-Pd-12.2MPa	50	1h	>99	12460
4	Chit-Pd-12.2MPa	25	2h	76	4734
5	Chit-Pd-9.2MPa	50	1h	97	12006
6	Chit-Pd-9.2MPa	25	2h	67	4276
7	Chit-Pd-7.2MPa	50	1h	93	11006
8	Chit-Pd-7.2MPa	25	2h	53	3470
9	Chit-Pd-H ₂ O	50	50min	99	9148
10	Chit-Pd-H ₂ O	25	2h	82	3124
11	Chit-Pd-Ethanol	50	40min	99	10716
12	Chit-Pd-Ethanol	25	2h	93	3322
13 ^d	Chit-Pd-14.2MPa	25	3h	17	651
14 ^{d,e}	Pd/ZIF	25	---	---	307
15 ^{d,f}	Pd/C in DMF	25	---	---	377

^aReaction conditions: styrene 2 g, H₂ pressure 2 MPa, catalyst 20 mg. ^bYield of ethylbenzene and determined by GC. ^cTurnover number (TON)=mol of product (ethylbenzene) per mole of Pd; TOF=TONh⁻¹. ^dThe H₂ pressure was 1 atm. ^eThe data was obtained from reference 34. ^fThe data was obtained from reference 35.

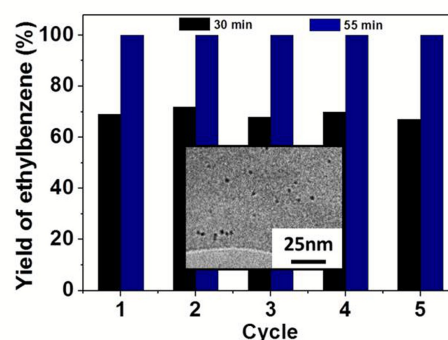


Fig. 4. Yields of ethylbenzene in the five repeated cycles for the two series of experiments. Reaction conditions: temperature: 50 °C; styrene 2 g; Chit-Pd-14.2 MPa 20 mg; H₂ pressure 2 MPa.

In summary, Pd/chitosan catalysts were synthesized in ionic liquid [Bmim]OAc by using CO₂ as the anti-solvent and regulator. The Pd/chitosan catalysts obtained using CO₂ as the anti-solvent had better catalytic activity than the ones obtained using ethanol or water as the anti-solvents for the catalytic hydrogenation of styrene. There was almost no activity loss after the catalyst was reused for five times. The high dispersion of Pd and the more loose structure were responsible

for the better catalytic activity of the Pd/chitosan obtained by using CO₂ as the anti-solvent. The finding in this work paves a new way towards the development of green and controllable routes that can be used in the preparation of biopolymer-supported (cellulose and chitosan) nano-catalysts.

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Notes and references

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