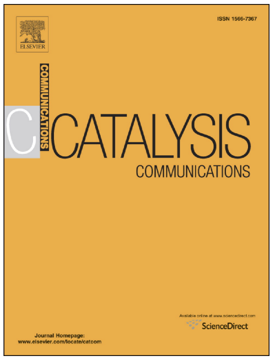

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PII: S1566-7367(19)30385-1

DOI: https://doi.org/10.1016/j.catcom.2019.105924

Reference: CATCOM 105924

To appear in: *Catalysis Communications*

Received date: 26 September 2019

Revised date: 18 December 2019

Accepted date: 31 December 2019

Please cite this article as: R. Wang, L. Qin, X. Wang, et al., Polymer supported N-heterocyclic carbene ruthenium complex catalyzed transfer hydrogenation of ketones, *Catalysis Communications* (2019), https://doi.org/10.1016/j.catcom.2019.105924

Polymer supported N-heterocyclic carbene ruthenium complex catalyzed transfer hydrogenation of ketones

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Abstract

Polymer supported N-heterocyclic carbene ruthenium complex (Poly-Ru-1) was synthesized by free radical polymerization of Ru complex monomer and divinylbenzene. The structure of Poly-Ru-1 was characterized by ^{13}C solid-state NMR spectroscopy, N_2 adsorption-desorption, X-ray photoelectron spectroscopy (XPS). ^{13}C solid-state NMR spectra indicated the complete polymerization of Ru complex monomer. Poly-Ru-1 had the high specific surface area of 286.7 m^2 g^{-1} and ruthenium was in +2 oxidation state. Poly-Ru-1 showed higher catalytic activity than the corresponding homogenous catalyst in transfer hydrogenation of ketones, which was attributed to the high dispersion of the active sites.

Keywords: polymer; support; ruthenium complex; transfer hydrogenation.

1. Introduction

As one of the reactions to produce valuable alcohols, the reaction of transfer hydrogenation of ketones was widely applied in pharmaceuticals, fuels, building blocks and synthetic intermediates in organic synthesis [1-3]. In the transfer hydrogenation reaction, 2-propanol was generally used as hydrogen donor instead of conventional hydrogen gas which usually involved the elaborate experiment setups like high temperature and pressure reactors [4-6]. Transition metal complexes were used to catalyze the transfer hydrogenation of acetophenone. Compared with rhodium and iridium complexes, ruthenium complexes were more suitable for the reaction by virtue of their high activity and low cost [7-9]. The homogeneous ruthenium complex catalysts usually suffered from the difficulty of separation and recycle [10]. To solve these problems, heterogeneous catalysts prepared by immobilizing ruthenium complexes on a variety of solid materials, including organic polymers, silicon and magnetic materials were applied in the transfer hydrogenation reaction [11-14]. Nevertheless, they usually demonstrated poorer activities compared with homogeneous catalysts due to the lower degree of exposure of active sites to reactants [14, 15]. Therefore, it is still a challenge to develop new and efficient activity heterogeneous catalysts.

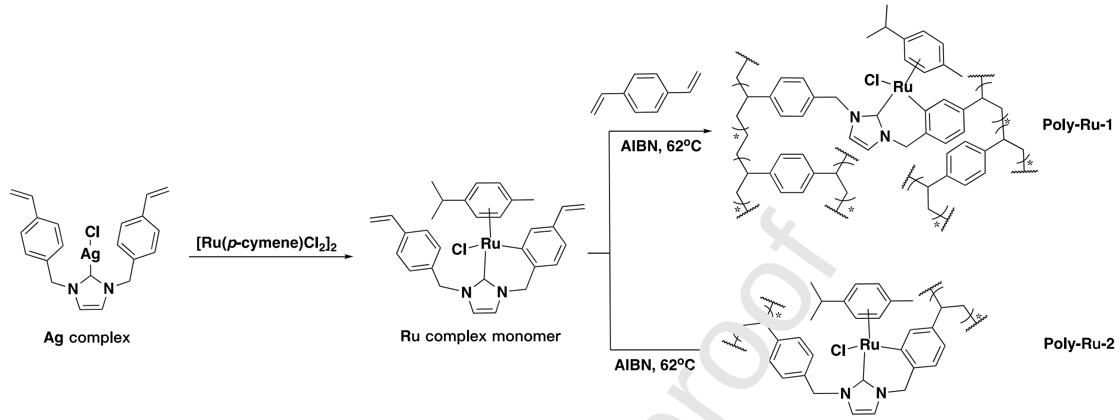
Due to the tunability of ionic liquid structure, functional ionic liquid can be designed according to requirements. The ionic liquids containing vinyl groups have the potential of preparing polymers. Poly(ionic liquid)s (PILs) had been applied as catalysts and showed outstanding catalytic activity in cycloaddition reaction of CO_2, hydrolysis of ethylene carbonates and transesterification reaction [16-20]. Besides, vinyl imidazolium ionic liquids can act as N-heterocyclic carbene (NHC) ligand to coordinate with metal complexes. Through heterogenization of this kind of homogeneous metal complex, the polymer supported metal was prepared and could be utilized in many catalytic reactions [21, 22].

In this paper, the imidazolium ionic liquid containing polymerizable vinyl group was chosen to be the ligand for the metal complex. Polymer supported ruthenium complex, Poly-Ru-1, was prepared through the free radical polymerization of Ru complex monomer and divinylbenzene (DVB). Poly-Ru-1 showed higher activity than the corresponding homogeneous Ru complex monomer in the transfer hydrogenation of acetophenone.

2. Results and discussion

2.1 Synthesis of Poly-Ru-1 and Poly-Ru-2.

The synthetic procedure of catalysts Poly-Ru-1 and Poly-Ru-2 was shown in **Scheme 1**. Ru complex monomer containing polymerizable vinyl group was obtained through the transmetallization of silver complex using [Ru(*p*-cymene)Cl_2]$_2$. Poly-Ru-1 was prepared by the free radical polymerization of Ru complex monomer and DVB using 2,2'-azoisobutyronitrile (AIBN) as an initiator in refluxing chloroform for 24 h. Similarly, Poly-Ru-2 was obtained by the free radical polymerization of Ru complex monomer without any cross-linker. Poly(ionic liquid) (PIL-1) was prepared by free radical polymerization of 1, 3-bis (4-styryl-1-yl) imidazolium chloride and DVB (**Scheme S1**).



Scheme 1. Synthetic procedure of Poly-Ru-1 and Poly-Ru-2.

2.2 Characterizations of Poly-Ru-1 and Poly-Ru-2

The solid-state ^{13}C MAS NMR spectra of Poly-Ru-1, Poly-Ru-2, PIL-1, and the ^{13}C NMR spectrum of corresponding Ru complex monomer were shown in **Fig. 1**. The signals at 108 ppm that belonged to the N-vinyl group disappeared in Poly-Ru-1, Poly-Ru-2 and PIL-1, indicating the full polymerization of the monomers. The signals around 171 ppm in Poly-Ru-1 and Poly-Ru-2 were assigned to C2 atom of imidazolium ring coordinating with Ru atom in comparison with PIL-1. The signals around 82 ppm in Poly-Ru-1 and Poly-Ru-2 were attributed to the benzene ring of p-methyl isopropyl benzene in Ru complex monomer (**Fig. 1b, c**). These results indicated the Ru NHC complex was successfully included in the polymer. The signals around 40 ppm represented the carbon atoms in the polymer chains of PIL-1, Poly-Ru-1 and Poly-Ru-2.

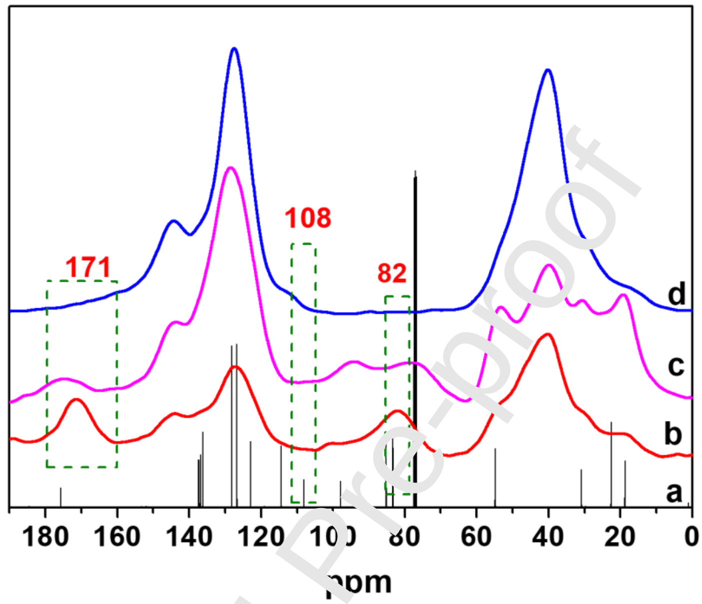


Fig. 1. (a) ^{13}C NMR spectra of Ru complex monomer and solid-state ^{13}C MAS NMR spectra of (b) Poly-Ru-1, (c) Poly-Ru-2, (d) PIL-1.

Specific surface areas of Poly-Ru-1 and Poly-Ru-2 were obtained by the N_2 adsorption-desorption isotherm. Poly-Ru-1 had a specific surface area up to 286.7 m^2 g^{-1} (**Table S1**). The isotherm of Poly-Ru-1 displayed a clear type IV curve with an obvious typical H3 hysteresis loop at the relative pressure P/P_0 ranging from 0.35 to 0.98, which was the feature of mesoporous materials (**Fig. 2**). Similarly, Poly-Ru-2 had a specific surface area of 305.5 m^2 g^{-1}. The high surface area of Poly-Ru-1 and Poly-Ru-2 were attributed to the rigid structure of Ru complex monomer. The slightly difference of surface area between the two samples might be caused by the higher degree of rigid frameworks in Poly-Ru-2. The thermal stability of Poly-Ru-1 and Poly-Ru-2 was measured by Thermo gravimetric analyzer (TGA) (**Fig. S1**). Poly-Ru-1 and Poly-Ru-2 were stable up to 210 ^{o}C. The chemical composition of Poly-Ru-1 and Poly-Ru-2 was determined by element (CHN) analysis and the contents of imidazolium according to nitrogen contents were 0.96 and 1.79 mmol g^{-1} respectively. The ruthenium contents of Poly-Ru-1 and Poly-Ru-2 measured by inductive coupled plasma emission spectrometer (ICP) were 7.6 and 14.3 wt%, respectively, which were close to the theoretical contents of two samples (**Table S1**). The morphology of Poly-Ru-1 and Poly-Ru-2 was characterized by scanning electron microscope (SEM), and SEM images showed that they were composed of irregular solid blocks (**Fig. S2**). The TEM images of the fresh catalysts such as Poly-Ru-1 and Poly-Ru-2 did not observed any ruthenium particles indicating the Ru complex was stable during the polymerization (**Fig. S3a and b**).

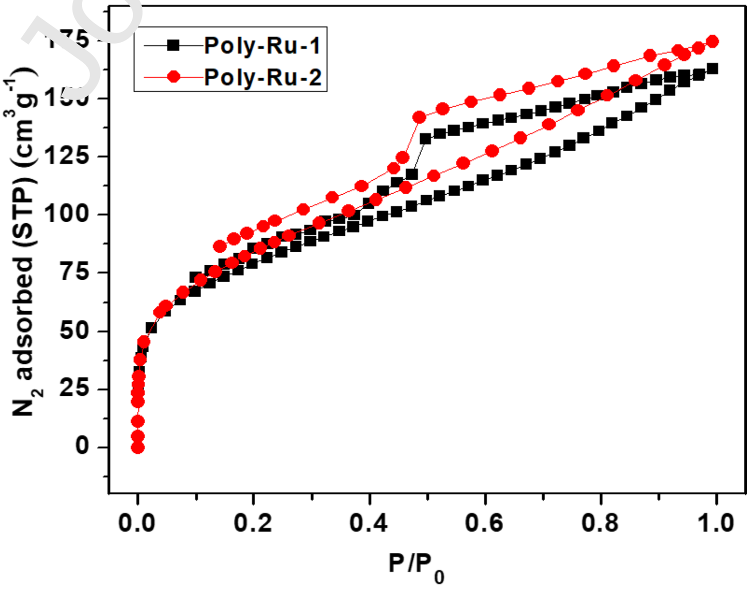
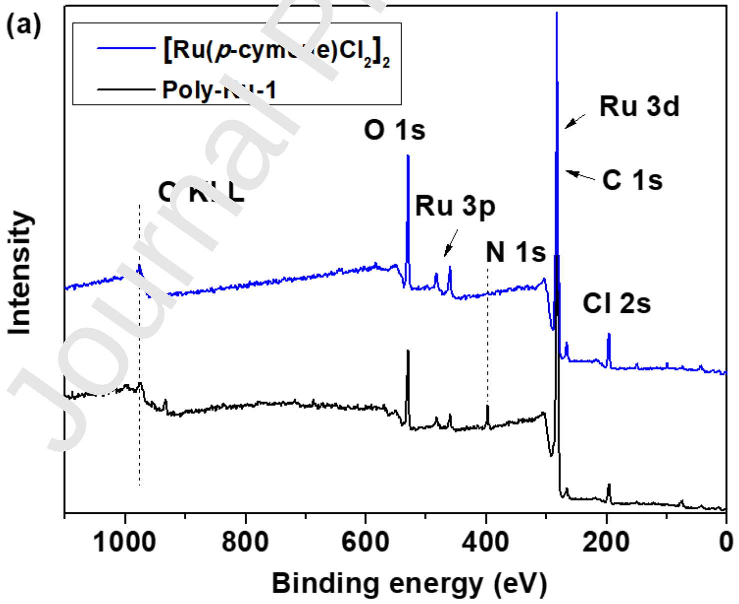


Fig. 2. N_2 adsorption-desorption isotherms of Poly-Ru-1 and Poly-Ru-2.

The X-ray photoelectron spectroscopy (XPS) was employed to further characterize the elemental composition and oxidation state of ruthenium in Poly-Ru-1. XPS of Poly-Ru-1 showed the characteristic peaks of O 1s, N 1s, C 1s, Ru 3p, Ru 3d and Cl 2s (**Fig. 3a**). The Ru $3d_{5/2}$ photoelectron peak in Poly-Ru-1 was observed at 281.6 eV, which was similar to the peak of [Ru(II)(*p*-cymene)Cl_2]$_2$ in **Fig. 3b** and the Ru(II) complex of [RuCl(*R*)-(binap)(*p*-cymene)]Cl reported previously [23]. These results suggested that the ruthenium was +2 oxidation state in Poly-Ru-1.



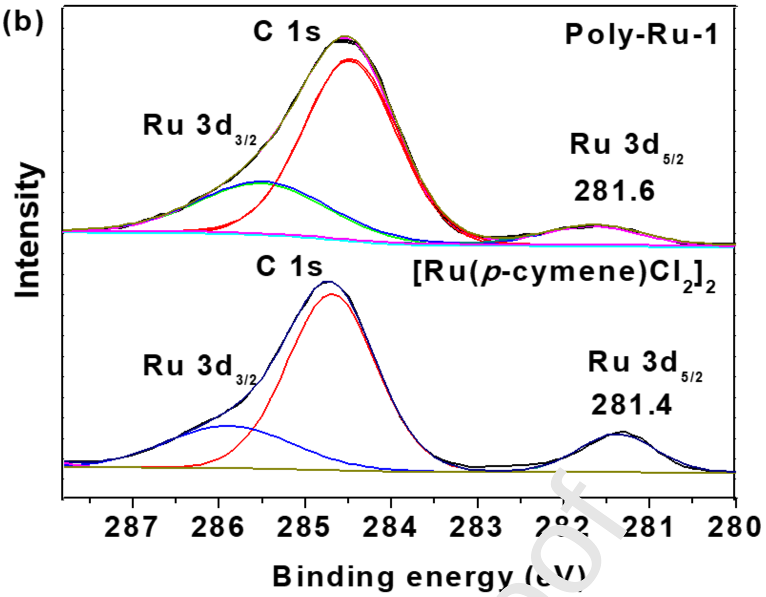
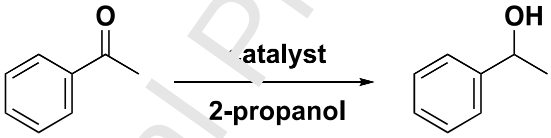


Fig. 3. XPS of (a) full scale of Poly-Ru-1 and [Ru(p-cymene)Cl$_2$]$_2$, (b) Ru 3d region of Poly-Ru-1 and [Ru (p-cymene)Cl$_2$]$_2$.

Table 2. Transfer hydrogenation of acetophenone catalyzed by various catalysts[a].



Entry	Cat.	Amount of cat[b]. (mol %)	Base	Amount of base (mol %)	Temp. (°C)	Time (h)	Yield[c] (%)
1	Poly-Ru-1	0.50	KO^{t}Bu	10	82	6	91
2	Poly-Ru-2	0.50	KO^{t}Bu	10	82	6	32
3	Ru complex monomer	0.50	KO^{t}Bu	10	82	6	19
4	Poly-Ru(0)	2.50	KO^{t}Bu	10	82	6	21
5	Poly-Ru-1	0.25	KO^{t}Bu	10	82	6	78
6	Poly-Ru-1	1.25	KO^{t}Bu	10	82	6	96
7	Poly-Ru-1	2.50	KO^{t}Bu	10	82	6	99
8	Poly-Ru-1	2.50	KO^{t}Bu	10	82	0.5	42

9	Poly-Ru-1	2.50	KO^{t}Bu	10	82	1	51
10	Poly-Ru-1	2.50	KO^{t}Bu	10	82	2.5	86
11	Poly-Ru-1	2.50	KO^{t}Bu	10	82	4	95
12	Poly-Ru-1	2.50	KO^{t}Bu	10	40	6	11
13	Poly-Ru-1	2.50	KO^{t}Bu	10	60	6	42
14	Poly-Ru-1	2.50	-	-	82	6	7
15	Poly-Ru-1	2.50	KO^{t}Bu	6	82	6	83
16	Poly-Ru-1	2.50	KO^{t}Bu	8	82	6	90
17	Poly-Ru-1	2.50	KOH	10	82	6	95
18	Poly-Ru-1	2.50	Na$_2$CO$_3$	10	82	6	9

[a] Reaction conditions: acetophenone (0.24 g, 2 mmol), 2-propanol (6 mL).

[b] Base on the amount of Ru in catalyst.

[c] Determined by GC.

2.3 Transfer hydrogenation of ketones

2.3.1 Transfer hydrogenation of acetophenone catalyzed by various catalysts

Transfer hydrogenation of acetophenone and 2-propanol was carried out in the presence of various ruthenium catalysts, including heterogeneous catalysts of Poly-Ru-1, Poly-Ru-2 and corresponding homogeneous Ru complex monomer. The results were summarized in **Table 2**. Poly-Ru-1 gave 1-phenylethyl alcohol in the yield of 91% (**Table 2, entry 1**). However, when the Poly-Ru-2 was applied in transfer hydrogenation, the yield dramatically decreased to 32% (**Table 2, entry 2**). The homogeneous Ru complex monomer also gave a low yield of 19% (**Table 2, entry 3**). Meanwhile, the polymer supported Ru nanoparticles (Poly-Ru(0)) which was prepared by the reduction of Poly-Ru-1 in the presence of NaBH$_4$ afforded

1-phenylethy alcohol in the yield of 21% (**Table 2, entry 4**). This result indicated that the high catalytic activity of Poly-Ru-1 was attributed to the ruthenium complex mainly. The most active catalyst, Poly-Ru-1, was selected to investigated the effects of reaction parameters such as amount of catalyst, time, temperature and type of bases. When the amount of the catalyst increased from 0.25 to 0.50, 1.25 and 2.5 mol %, the yields of 1-phenylethyl alcohol were increased from 78 to 91, 96 and 99%, respectively (**Table 2, entry 1, 5-7**). With extension of reaction time from 0.5 to 6 h, the yield of 1-phenylethyl alcohol increased from 42 to 99 % (**Table 2, entry 7-11**). While the reaction temperature raised from 40 to 82 ^{o}C, the yields of 1-phenylethy alcohol increased dramatically from 11 to 99 % (**Table 2, entry 7, 12, 13**), indicating the high sensitivity of the reaction to temperature. Generally, bases play a vital role in transfer hydrogenation. Without any bases, the reaction hardly proceeded (**Table 2, entry 14**). However, in the presence of KO^{t}Bu, the reaction proceeded very well. With the increase of amount of KO^{t}Bu from 6 to 10 mol %, the yield of 1-phenylethy alcohol increased gradually from 83 to 99% (**Table 2, entry 7, 15, 16**). KOH also gave the high yield of 95% (**Table 2, entry 17**). However, Na_2CO_3 with lower alkalinity afforded the product in relative low yield of 9% (**Table 2, entry 18**). The strong bases facilitated the formation of ruthenium alkoxide by capturing a proton from 2-propanol during transfer hydrogenation, and subsequently alkoxide underwent β-elimination to form ruthenium hydride, an active species in hydrogenation [24-26]. Compared with other reported ruthenium complex catalysts, Poly-Ru-1 had higher activity than other heterogeneous catalysts and comparable activity with homogeneous catalysts (**Table S2**).

During the transfer hydrogenation reaction, Poly-Ru-1, Poly-Ru-2 and Ru complex monomer catalysts turned to black gradually. In order to clarify this phenomenon and further illustrate the reason of the obvious difference of catalytic activity of these catalysts, the TEM was applied to characterize the Ru species distribution of Poly-Ru-1, Poly-Ru-2 and Ru complex monomer after reaction. From the TEM images, there were many ruthenium nanoparticles (Ru NPs) with diameter of 0.8, 1.5 and 2.5 nm in the recycled catalysts such as Poly-Ru-1 (recycled), Poly-Ru-2 (recycled) and Ru complex monomer (recycled) (**Fig. S3c, d, e**). The relatively smaller particles in Poly-Ru-1 (recycled) may be ascribed to the high density of DVB (around 80% by mole), which prevented the aggregation of ruthenium species to form large ruthenium nanoparticles in the polymer matrices. As the Poly-Ru-2 was prepared by self-polymerization of Ru complex monomer (without any cross-linker), the ruthenium species were close to each other and aggregated into Ru NPs easily during the reaction. Furthermore, during the process of reaction catalyzed by Ru complex monomer, the color of reaction mixture changed into black in few minutes (**Fig. S4**), suggesting the reduction of ruthenium complex could produce Ru NPs in a short time (**Fig. S3f**) [27]. Correspondingly, homogeneous Ru complex monomer was easiest to aggregate into larger particles owing to its nature of untrammeled mobility.

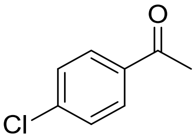
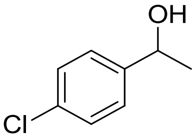
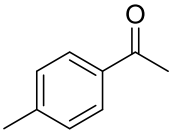
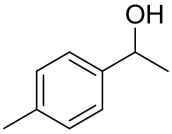
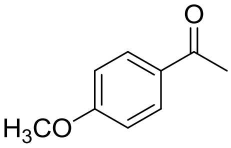
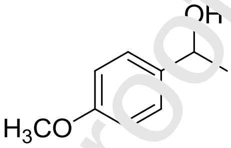
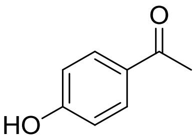
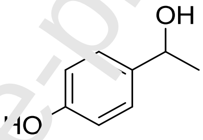
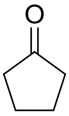
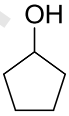
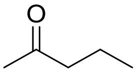
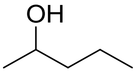
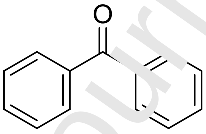
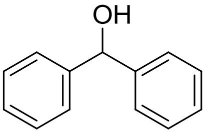
2.3.2 Transfer hydrogenation of various ketones catalyzed by Poly-Ru-1

To investigate the generalities of heterogeneous Poly-Ru-1 catalyst, various ketones were applied for transfer hydrogenation under the optimized reaction conditions (**Table 3**). The aromatic ketones with electron withdrawing or electron donating groups had excellent yields of 94-99% (**Table 3, entry 1-4**). The aliphatic ketones such as cyclopentanone and 2-pentanone afforded the corresponding alcohols in the yields of 89% and 92%, respectively (**Table 3, entry 5, 6**). The benzophenone achieved a slightly less activity with yield of 83%, presumably ascribed to the steric hindrance of bulky substrates [28].

3. Conclusion

In conclusion, polymer supported N-heterocyclic carbene ruthenium complex, Poly-Ru-1, a kind of heterogeneous catalyst, was successfully developed *via* free radical polymerization of Ru complex monomer and divinylbenzene (DVB) as the cross-linker. Poly-Ru-1 had a high specific surface area and good thermal stability. Poly-Ru-1 had much higher catalytic activity (99% yield) than that of homogenous catalyst Ru complex monomer (19% yield) in transfer hydrogenation of acetophenone with 2-propanol. The higher activity of Poly-Ru-1 was attributed to well dispersed ruthenium species in the polymer which prevented their aggregation. The heterogeneous catalyst Poly-Ru-1 also showed good generalities for various ketones.

Table 3. Poly-Ru-1 catalyzed the transfer hydrogenation of various ketones [a]

Entry	Substrate	Product	Yield [b] (%)
1			99
2			96
3			94
4			95
5			89
6			92
7			83

[a]Reaction conditions: Ketones (0.24 g, 2 mmol), Poly-Ru-1 (2.5 mol %), 2-propanol (6 mL), potassium tert-butoxide (10 mol %), 6 h, 82 °C. [b] Determined by GC.

4. Experimental

Synthesis of Ru complex monomer

The Ru complex monomer was synthesized by transmetallization method with silver carbene complex. The silver carbene complex (2.23 g, 5 mmol) was dissolved in 30 mL anhydrous dichloromethane in a 50 mL round bottom flask equipped with a magnetic stirrer under the protection of N_2. Then the [Ru(*p*-cymene)Cl_2]$_2$ (1.53 g，2.5 mmol) was added into the flask and the reaction mixture was stirred at room temperature for 12 h in the dark. After reaction, the solvent was removed under reduced pressure distillation. The orange product was recrystallization in dichloromethane/pentane (1:5). The desired product was obtained in a yield of 88% (1.40 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8 Hz, 4H), 7.28 (m, 3H), 6.82 (s, 2H), 6.71 (dd, *J* = 20, 12 Hz, 2H), 5.86 (s, 2H), 5.77 (d, *J* = 20 Hz, 2H), 5.62 (s, 2H), 5.37 (d, *J* = 8 Hz, 2H), 5.27 (d, *J* = 8 Hz, 2H), 5.06 (d, *J* = 8 Hz, 2H), 2.85 - 2.92 (m, 1H), 2.04 (s, 3H), 1.24 (d, *J* = 8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.60, 137.34, 136.85, 136.20, 128.13, 126.66, 122.88, 114.40, 108.01, 97.92, 85.13, 83.31, 54.84, 30.79, 22.61, 18.77. LCMS (ESI, positive ions) calcd for $C_{31}H_{33}N_2RuCl$ [M+H$^+$] 571.1454, found 571.4749.

Synthesis of polymer supported ruthenium complex (Poly-Ru-1)

The Poly-Ru-1 was prepared by radical polymerization of Ru complex monomer and DVB using AIBN as initiator. Ru complex monomer (1.25 g, 2 mmol), DVB (1.04 g, 8 mmol) and AIBN (0.12 g, 5 wt%) were stirred at 10 mL refluxing chloroform for 24 h. The solvent was removed by decantation and the residue was washed with chloroform. The product was dried under vacuum at 50 °C for 6 h. Orange solid was obtained in the yield of 96 % (2.20 g).

Synthesis of polymer supported ruthenium nanoparticles (Poly-Ru(0))

The polymer supported ruthenium nanoparticles (Poly-Ru(0)) was prepared by reducing the polymer supported ruthenium complex (Poly-Ru-1) with $NaBH_4$ aqueous solution. Poly-Ru-1 (0.1 g) and $NaBH_4$ (aq) (10 mL, 1g/L) were stirred at refluxing for 1 h. The reaction mixture was filtered and the residue was washed with deionization water. The product was dried under vacuum at 50 °C for 6 h. Black solid was obtained in the yield of 99 %.

General experimental procedures for the transfer hydrogenation of ketones

Catalyst Poly-Ru-1 (0.5 mol % based on Ru), base (10 mol %), substrate (2 mmol) and degassed 2-propanol (6 mL) were added to a 50 mL round-bottom flask with a magnetic stirrer. The reaction mixture was stirred under N_2 atmosphere at 82 °C for 6 h. After the reaction mixture was cooled to room temperature, the solid catalyst was removed by centrifugation and washed with acetone (5×3 mL). The combined liquid phase was analyzed by GC using mesitylene as an internal standard.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21573072, 21773068, 21811530273), the National Key Research and Development

Program of China (2017YFA0403102) and Shanghai Leading Academic Discipline Project (B409).

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Author contributions

Use this form to specify the contribution of each author of your manuscript. A distinction is made between five types of contributions: Conceived and designed the analysis; Collected the data; Contributed data or analysis tools; Performed the analysis; Wrote the paper.

For each author of your manuscript, please indicate the types of contributions the author has made. An author may have made more than one type of contribution. Optionally, for each contribution type, you may specify the contribution of an author in more detail by providing a one sentence statement in which the contribution is summarized. In the case of an author who contributed to performing the analysis, the author's contribution for instance could be specified in more detail as 'Performed the computer simulations', Performed the statistical analysis', or 'Performed the text mining analysis'.

If an author has made a contribution that is not covered by the five predefined contribution types, then please choose 'Other contribution' and provide a one sentence statement summarizing the author's contribution.

Manuscript title: Polymer supported N-heterocyclic carbene ruthenium complex catalyzed transfer hydrogenation of ketones

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☑ Conceived and designed the analysis

Determined the aim of research and made a plan about this research work.

☑ Collected the data

Completed all the experiments about the research including preparation of catalyst and application.

☑ Contributed data or analysis tools

Analyzed the data from experiments using professional chemical software.

☑ Performed the analysis.

According to the data and results obtained, analyzed and made reasonable explanation.

☑ Wrote the paper

Wrote the paper and took full participation in revise of manuscript.

☑ Other contribution

Made the other supplementary experiments to explanation the results of the experiment. In addition, made a graphical abstract.

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☑ Performed the analysis

Provided guidance for key problems.

☑ Wrote the paper

Provided guidance during the process of revise about the manuscript.

☐ Other contribution

Declaration of interests

☑The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights:

- Polymer supported N-heterocyclic carbene ruthenium complex was prepared.
- The Poly-Ru-1 efficiently catalyzed the transfer hydrogenation of ketones.
- The Poly-Ru-1 showed superior catalytic activity than the Ru complex monomer.