Polymer -Supported Cobalt Catalysts for Hydrogenation of Cyclooctene

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Abstract

Crosslinked beads of poly(styrene-*co*-divinylbenzene-*co*-vinylbenzyl chloride) with Schiff base and non Schiff base chelating ligands, aminopyridine in which N is a donor atom have been prepared. The ligand anchored polymer beads were reacted with cobalt chloride to form polymer-supported cobalt complexes which were characterized by Fourier transform infrared (FT-IR) spectroscopy and atomic absorption spectrometry (AAS). The thermogravimetric analysis (TGA) of the polymer-supported cobalt complexes reveals their thermal stability. Swelling behavior in different solvents was studied. The catalytic activity of the polymer-supported cobalt complexes was evaluated by studying the hydrogenation of cyclooctene to cyclooctane. The influence of various reaction parameters such as temperature, hydrogen pressure, catalyst concentration, reaction time, type of solvent on the hydrogenation of cyclooctene was investigated. The polymer-supported cobalt catalysts containing Schiff base ligand showed higher activity than the non-Schiff base (76-80 and 71% yield, respectively). The catalysts can be reused successfully with slight loss of activity and little leaching of metal from the support.

Keywords: polymer-supported cobalt catalyst, hydrogenation of cyclooctene, Schiff base, non-Schiff base, atomic absorption spectrometry, thermogravimetric analysis

Introduction

Immobilization of catalysts on insoluble supports has gained prominence in recent years. It increases their potential for industrial uses due to the enhancement of thermal and chemical stabilities and ease of separation from the product mixture. Steric crowding around the metal centre in the polymer matrix is mainly responsible for the increase of the product selectivity. Crosslinked polymers with specific properties are widely used as catalyst supports as they are inert, non-toxic, non-volatile and recyclable. Styrene-*co*-divinylbenzene copolymers with reactive end groups have been used by transforming them into ligands with chelating properties [1]. Many cobalt and rhodium complexes have been supported on crosslinked polystyrene through phosphine ligands [2]. Polymer-supported metal catalysts were found to catalyze various reactions: ruthenium catalysts for epoxidation of alkenes [3] or hydrogenation of alkenes [4]; manganese catalysts for epoxidation of alkanes [5], palladium catalysts for reduction of nitroalkanes, nitriles and ketones [6] or hydrogenation of alkenes [7]; rhodium catalysts for hydrogenation of cinnamic acid [8] and cobalt catalysts for oxidation of cyclo- and linear alkanes [9] and copper catalyst for oxidation of alcohols [10]. The problem associated with the long term usage of polymer supported catalysts in a continuous, fixed bed reactor is the loss of metal complex. This occurs because the attached metal is involved in dissociation equilibria under catalytic conditions. The leaching of the metal has been reduced by using chelating ligands [10]. In the present work, we report catalytic activity of polymer-supported cobalt catalysts bearing chelating ligands, aminopyridine, in which N is a donor atom. The chelate effect should result in strong binding to the metal and prevent metal leaching from the catalyst. The anchoring ligands included both Schiff base and non Schiff base. The activity of the obtained polymer-supported cobalt catalysts are tested for the hydrogenation of cyclooctene.

Experimental

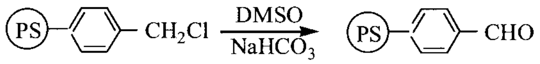
Materials and method

Chloromethylated polystyrene (5.5 mmol of Cl per g of resin and 5% crosslinked with divinylbenzene, 40-60 mesh) or Merrified resin as spherical beads, cobalt chloride and cyclooctene were purchased from Fluka. All other reagents were reagent grade. Solvents were purified by standard methods.

Fourier-transform infrared spectra were recorded using a Nicolet FT-IR Impact 410 Spectrophotometer. A capillary column gas chromatograph GC16A, Shimadzu (DB wax, FID) was used for the determination of products. Thermogravimetric (TGA) measurements were performed using a TA thermogravimetric analyzer (SDT 2960) at a heating rate of 10°C/min under air/nitrogen (30/20) atmosphere. Elemental analysis (EA) was performed by a CHN elemental analyzer (Coleman). Cobalt content was determined using a Varian Spectra-AA300 atomic absorption spectrometer. Hydrogenation reactions were carried out in a stainless steel Parr reactor, Model 4842.

Synthesis of polymer with aldehyde functionality

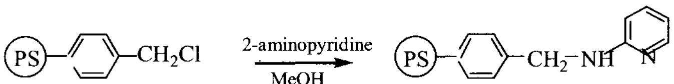
Chloromethylated polystyrene beads (2 g with 5.5 mmol of Cl per g of resin and 5% crosslinked with divinylbenzene) were allowed to swell in 20 ml of dimethylformamide and 0.5 g sodium hydrogen carbonate was added. The reaction was refluxed for 6 h. The polymer with aldehyde functionality was obtained, filtered and dried under vacuum.. [11] The reaction is shown in equation 1.



(1)

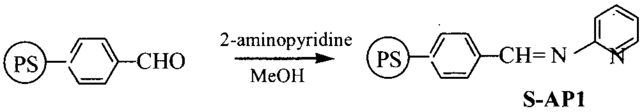
Synthesis of polymer-anchored ligand

Chloromethylated polystyrene beads (1 g) were allowed to swell in 20 ml methanol. Then 2-aminopyridine (2.2 g) in methanol was added, and refluxed for 48 h. The polymer beads (white color) were filtered, washed with methanol and petroleum ether, and dried under vacuum. This polymer-anchored ligand was named as AP1. The reaction is shown in equation 2. For the polymer-anchored Schiff base ligand, the same procedure was conducted, except that chloromethylated polystyrene was replaced with polymer with aldehyde functionality. This synthesized polymer-anchored Schiff base ligand (pale yellow color) was named as S-AP1. The reaction is shown in equation 3.



AP1

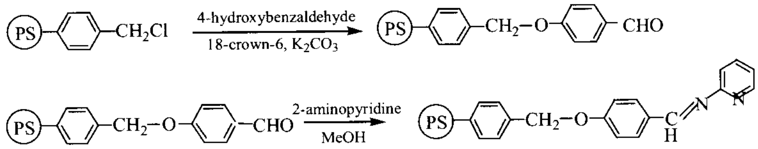
(2)



S-AP1

(3)

For the synthesis of polymer-anchored Schiff ligand with ether linkage, 1 g chloromethylated polystyrene beads were swollen in 20 ml of dry dioxane. This was mixed with 0.6 g 4-hydroxybenzaldehyde, 0.7 g K_2CO_3 and 0.07 g 18-crown-6. The mixture was refluxed under N_2 for 24 h. The polymer beads were filtered, washed with dioxane and warm distilled water, and dried under vacuum. Then the resulting polymer beads were again swollen in 20 ml methanol, and 2.2 g 2-aminopyridine in methanol was added with stirring, and conc. HCl was dropped in. The reaction mixture was refluxed for 48 h. The polymer beads (orange color) were filtered, washed with methanol and dried under vacuum. This synthesized polymer-anchored Schiff base ligand with ether linkage was named as S-AP2. The reaction is shown in equation 4.



S-AP2 (4)

Synthesis of polymer-supported cobalt catalysts

The loading of the cobalt was carried out as follows: 0.5 g of polymer-anchored ligand was swollen in methanol. To this was added 0.3 g hydrated cobalt (II) chloride and the contents were refluxed for 72 h. The polymer beads (light green or blue) were filtered, washed with methanol to remove unreacted cobalt chloride, and dried under vacuum.

Swelling test

The polymer-supported metal catalysts were allowed to swell in different solvents. The %wt swelling of the catalysts was determined by measuring weight difference before and after immersion in solvent.

Hydrogenation of cyclooctene

The polymer-supported metal catalyst was mixed with 50 ml methanol for 30 min before adding into the Parr reactor, followed by the addition of 1.3 ml cyclooctene (10 mmol), flushed with hydrogen twice and then the hydrogen gas pressure was set to the desired pressure and temperature. The stirring speed was set at 600 rpm. After 3 h, an aliquot of the reaction mixture was withdrawn, added with internal standard and analyzed by capillary column gas chromatograph (GC16A, Shimadzu (DB wax, FID)). The experiment without catalyst was also performed.

Test of metal leaching from polymer support

In order to study the metal leaching of polymer-supported cobalt catalyst, it was refluxed in methanol for 24 h. Then, it was filtered, washed with methanol and dried under vacuum at 70°C for 12 h. It was reused for hydrogenation of cyclooctene at the same conditions as the fresh catalyst.

Catalyst recycling

After the hydrogenation reaction, the catalyst was separated by filtration, washed with methanol and dried before use in the subsequent runs.

Results and discussion

Synthesis and characterization of the catalysts

It should be mentioned that in this work, 5% crosslinking was chosen because we have previously studied the effect of % crosslinking on loading of ligand and found that 5% crosslinking is more suitable than 2% or 10% crosslinking [12]. A polymer with high degree of crosslinking has a network consisting of dense and relatively larger number of inaccessible domains leading to less functionalisation.

The polymer-anchored ligands were synthesized by reacting chloromethylated polystyrene beads with 5% crosslinking with ligand (4 equivalents with respect to chlorine content in the polymer). The polymer-anchored ligand containing non-Schiff base, AP1 was synthesized using aminopyridine ligand. The one containing Schiff base, S-AP1 was synthesized by first converting chloro to aldehyde functionality, and then condensed with aminopyridine. The polymer-anchored ligand containing Schiff base ligand with ether linkage, S-AP2 was synthesized from the reaction of the chloromethylated polystyrene beads with 4-hydroxybenzaldehyde, potassium carbonate and 18-crown-6 (mole ratio 20: 10: 1, 4-hydroxybenzaldehyde content is higher than that used in the literature)[13]. After that, the resulting beads with aldehyde moiety were condensed with 2-aminopyridine.

The IR spectra of the chloromethylated polystyrene bead and polystyrene bead with aldehyde functionality are shown in Figure 1

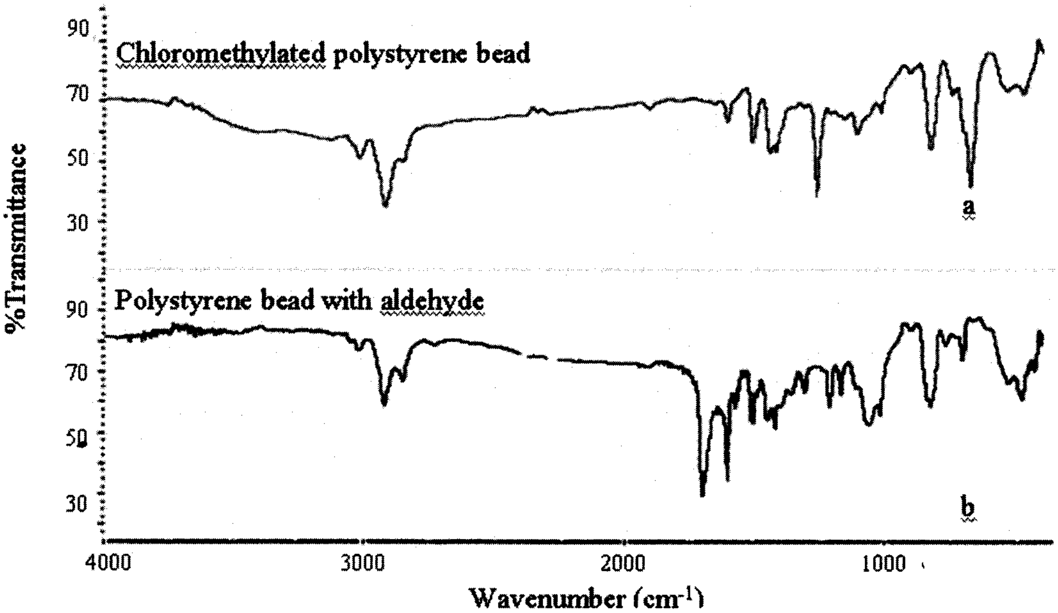


Figure 1. FT-IR spectra of
(a) Chloromethylated polystyrene bead
(b) Polystyrene bead with aldehyde functionality

The chloromethylated polystyrene bead in Figure 1a shows the C-H aliphatic stretching peak around 2900-2950 cm^{-1} and aromatic stretching peaks at 1500-1600 cm^{-1}. The polystyrene bead with aldehyde functionality shows a new peak at 1694 cm^{-1} assigned to C=O stretching vibration of aromatic aldehyde.

In the synthesis of polymer-anchored ligand, each step was monitored using IR spectroscopy. Representative IR spectra of polymer-anchored ligand, S-AP1 and its corresponding cobalt catalyst, cat. S-AP1 are shown in Figure 2. The IR data of all polymer-anchored ligands and their corresponding polymer-supported cobalt catalysts are summarized in Table 1. Possible structures of the catalysts are shown in Figure 3.

Table 1. FT-IR data of polymer-anchored ligands and polymer-supported cobalt catalysts

AP1	Cat. AP1	S-AP1	Cat. S-AP1	S-AP2	Cat. S-AP2	Assignment
3100-3400	3100-3400	3100-3400	3100-3400	-	-	N-H st., CH (pyridine)
-	-	1648	1640	1640	1635	C=N st.
1515	1515	1515	1510	1510	1510	Pyridyl ring breathing
672	672	672	672	645	645	C-Cl st.

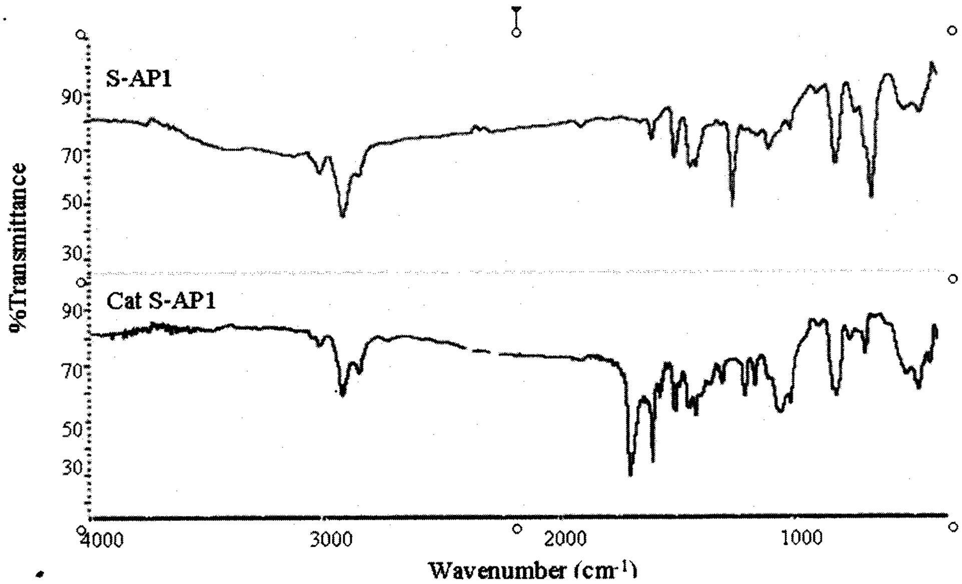
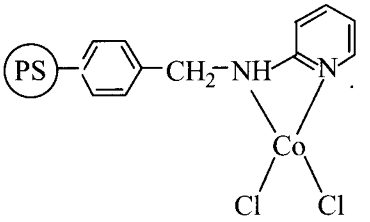
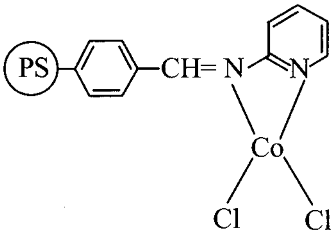


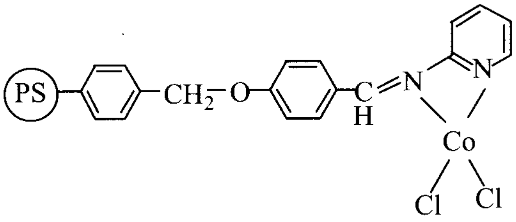
Figure 2. FT-IR spectra of (a) S-AP1 (b) cat. S-AP1



cat. AP1



cat. S-AP1



cat. S-AP2

Figure 3. Possible structures of the catalysts.

IR spectroscopy was used to confirm the coordination of the ligand and metal to the polymer. As shown in Table 1, the evidence for coordination of ligands onto the polymer support is the appearance and loss of IR bands that corresponds to the introduction of functional groups. For the three catalysts, peaks in the region around 3100-3400 cm^{-1} correspond to N-H stretching vibration or C-H stretching mode of the pyridine [14]. For the polymer-anchored Schiff-base ligands (S-AP1 and S-AP2), a strong peak at 1640-1648 cm^{-1} corresponds to the imine (C=N) stretching vibration which resulted from the subsequent reaction of the aldehyde with an amine group. After loading of cobalt, this peak undergoes a red shift (1635-1640 cm^{-1}), which indicates coordination of the ligand nitrogen to the metal [15]. Pyridyl ring breathing vibrations in all catalysts are observed in the region 1510-1515 cm^{-1}. The C-Cl stretching, in both polymer-anchored ligands and the polymer-supported cobalt catalysts, is exhibited at around 645-672 cm^{-1}.

%C and %H of the catalysts were characterized by elemental analysis, %Co was determined by atomic absorption spectroscopy (AAS) and the data is compiled in Table 2. It can be seen that the Co loading for cat. S-AP1 is higher than cat. AP1, and the Co loading in cat. S-AP2 is the highest.

Table 2. The elemental analysis of polymer-supported cobalt catalysts

Catalyst	%C	%H	%Co
cat. AP1	62.23	6.92	0.16
cat. S-AP1	72.70	6.85	0.64
cat. S-AP2	79.35	5.62	1.23

Thermal stability of the catalysts was determined by thermogravimetric analysis (TGA). The TGA results of the polymer and all catalysts are shown in Table 3. A representative TGA of cat. S-AP2 is shown in Figure 4. It shows a single step degradation peak at 415°C. On the other hand, the polymer-supported cobalt catalyst shows two degradation peaks at lower temperature. This is due to the dissociation of ligand from the catalyst or a partial cleavage of polymeric chains [10a].

Table 3. Thermogravimetric analysis of polymer and cobalt catalysts

Catalyst	Degradation temperatures (°C)	Wt. loss (%)
Polymer bead	415	21
cat. AP1	437, 278	45, 16
cat. S-AP1	440, 246	57, 10
cat. S-AP2	428, 259	36, 14

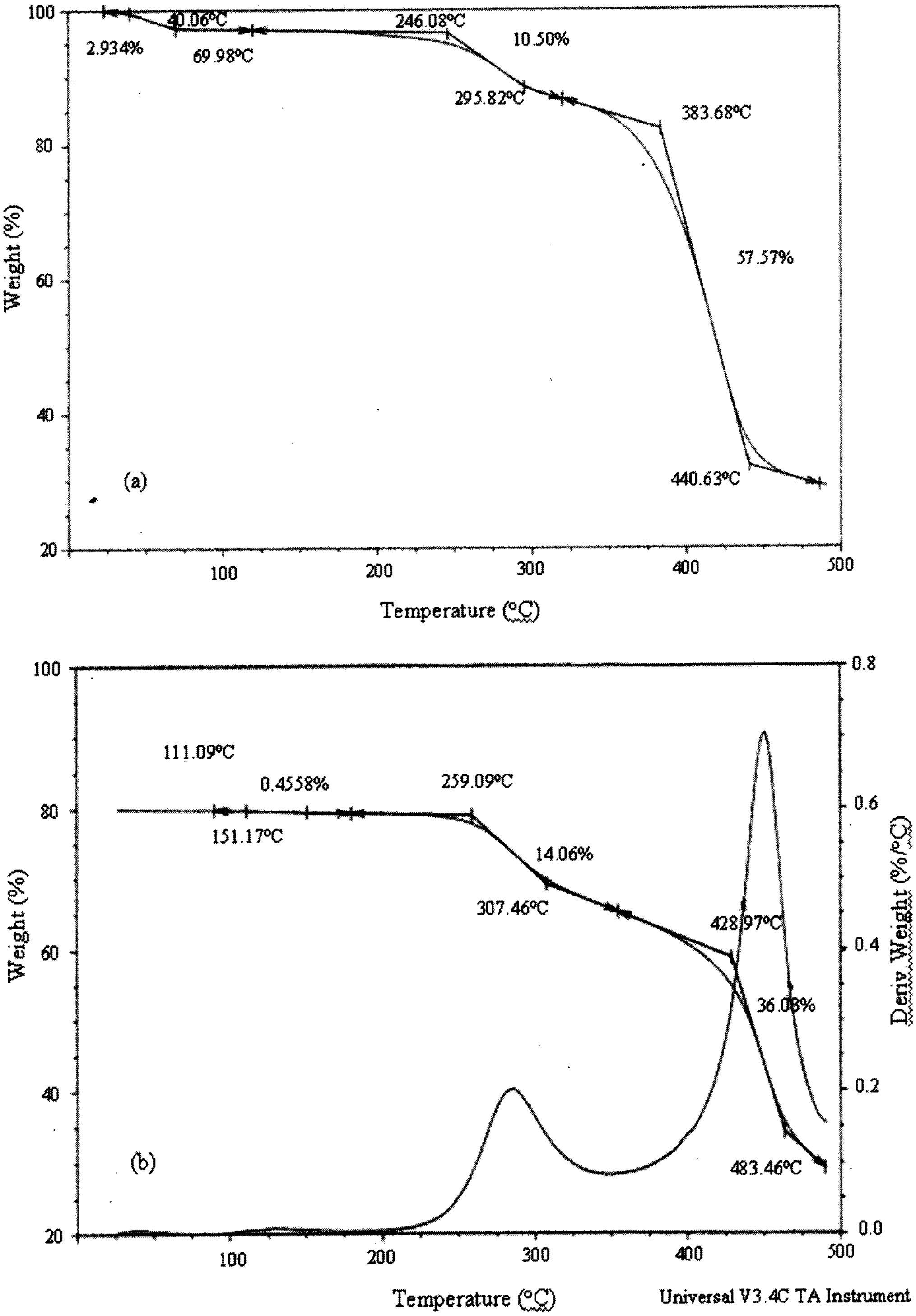


Figure 4. The thermogravimetric curve of cat. (a) cat S-AP1 (b) cat S-AP2

Swelling test

The choice of the suitable solvent is an important factor for studying the catalytic behavior of polymer supported catalysts. Polar solvents were generally found to be better swelling agents than non-polar solvents. In this work, a swelling test was performed on the catalysts using several solvents and the results are shown in Table 4. The swelling is high in polar solvents. This result agreed well with that reported by Antony and our previous result [3, 12]. Maximum swelling was observed in methanol. Therefore, it was chosen as a suitable solvent. Another reason is that it has good miscibility with the cyclooctene.

Table 4. Swelling test of the catalysts

Solvent	% wt. swelling
Methanol	41-46
Ethanol	30-34
Dimethylformamide	38-40
Acetonitrile	35-39
Hexane	5-7

Table 5. Hydrogenation of cyclooctene under different reaction conditionsusing cat. S-AP1

Entry	Co (x10^{-3} mmol)	temp °C	pressure atm.	%yield	TON
1	2	60	3	55	2750
2	2	60	6	61	3050
3	2	60	9	76	3800
4	2	50	9	57	2850
5	2	70	9	47	2350
6	1	60	9	55	5500
7	4	60	9	58	1450

Condition: Cyclooctene 10 mmol., methanol 50 ml; time 3 h
TON, turnover number = mmol cyclooctane/mmol Co

Catalytic activity

The hydrogenation of cyclooctene was performed by varying reaction parameters: catalyst concentration, temperature and pressure using cat. S-AP1. The results are shown in Table 5.

The experimental results show that %yield increased with the increase of pressure (entries 1-3). It was found that the reaction performed at 60°C gave higher yield than at 50°C and 70°C (entries 3-5). %Yield was increased with the increased concentration of catalyst. However, the turnover number was decreased when the concentration of the catalyst was increased.

Next, the activities of the other catalysts synthesized in this work were compared under the same optimized condition. The results are collected in Table 6. In order to ascertain the effects of the ligand on the catalyst, control experiments using $CoCl_2$ in methanol were performed under the same reaction conditions (entry 2). At 60°C, H_2 pressure 9 atm, the result shows that no hydrogenation occurred.

Table 6. Hydrogenation of cyclooctene using various cobalt catalysts

Entry	Catalyst	% Yield	TON
1	none	0	0
2	$CoCl_2$	0	0
3	cat. S-AP1	76	3800
4	cat. S-AP2	80	4000
5	cat. AP1	71	3550

Conditions: Cyclooctene 10 mmol, catalyst $2x10^{-3}$ mmol of Co, temperature 60°C, H_2 pressure 9 atm, and methanol 50 ml

The results show that for the reaction performed without catalyst, no product yield was obtained. The polymer-supported cobalt catalysts bearing Schiff base 2-aminopyridyl ligand showed higher %yield than the catalyst bearing non-Schiff base 2-aminopyridyl ligand (entry 3 vs 5). This is in good agreement with our previous result [12], of which polymer-supported ruthenium catalysts containing the 2-aminopyridyl ligand, non-Schiff and Schiff base, were compared. For cat. S-AP2 which contains Schiff base with ether linkage, the activity is a little higher than cat. S-AP1 (entry 4 vs 3).

Test of catalyst leaching from polymer support

The polymer-supported catalyst was filtered after the reaction, and the filtrate was analyzed for Co content. No metal leaching was found.

Catalyst recycle

One of the main objectives of using supported catalyst or supporting a homogeneous metal complex onto a polymer support is to be able to recycle the catalyst. In this work, the catalysts were separated from the reaction mixture after each experiment by filtration, washed with methanol, and dried before using in subsequent runs. The results show that the catalysts show a slight decrease of activity (4-9%) in the first three cycles. Thereafter, a higher decrease (24%) was observed due to leaching of the metal ions from the catalyst, which was confirmed by determining cobalt content after completion of the experiment.

Conclusion

Polystyrene beads with 5% crosslinking can be used as the support for the synthesis of the polymer-supported cobalt catalysts. The catalysts show leaching stability due to the chelating effect of the polydentate ligands. The catalysts containing chelating Schiff base ligands are more effective towards hydrogenation of cyclooctene than the non-Schiff ligand.

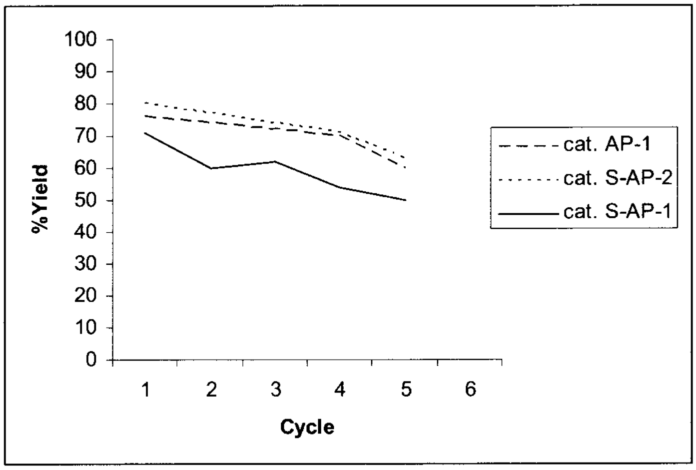


Figure 5. %Yield of the catalyst recycling.

Acknowledgements

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