

EFFECT OF MORPHOLOGICAL STRUCTURE OF AMINOMETHYL POLYSTYRENE RESIN ON THE CATALYTIC PROPERTIES OF POLYMER- SUPPORTED RUTHENIUM COMPLEXES*

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Abstract Polymer-supported ruthenium complexes $\text{P-Phen-Ru-}\textcircled{1}$, $\text{P-Phen-Ru-}\textcircled{2}$, $\text{P-Phen-Ru-}\textcircled{3}$, $\text{P-Phen-Ru-}\textcircled{4}$, $\text{P-Phen-Ru-}\textcircled{5}$, $\text{P-Phen-Ru-}\textcircled{6}$ and $\text{P-Phen-Ru-}\textcircled{7}$ were prepared using aminomethyl polystyrenes of different morphological structures as supports. A variety of alcohols were oxidized efficiently into the corresponding ketones, carboxylic acids or aldehydes with iodosylbenzene (PhIO) catalyzed by aminomethyl polystyrene-supported ruthenium complexes under mild reaction conditions in acetonitrile. The influences of morphological structure of the polymer supporters on the catalytic properties of these metal complexes were investigated in detail.

Keywords: Alcohol oxidation; Ru-immobilized catalyst; PS-carrier; Morphological structure.

INTRODUCTION

The oxidation of alcohols to form corresponding aldehydes, ketones or carboxylic acids is a significant important reaction in organic chemistry, and these products represent important intermediates for the preparation of various other compounds^[1, 2]. Polymers were widely used as supports for the catalysts in the recent years^[3–7]. The ever-increasing use of polymer supports in combinatorial chemistry, parallel synthesis and various solid phase extraction procedures has focused attention on the molecular and morphological structure of the suspension polymerized styrene-divinylbenzene (styrene-DVB) resins^[8–11]. Ruthenium catalysts are known to possess the ability to catalyze the oxidation of alcohols and other substrates according to the different mechanisms of reaction^[12–15]. In a previous paper, we reported the preparation and the catalytic properties of a polymer-supported ruthenium-containing complex P-Phen-Ru based on the chloromethyl polystyrene resin for the oxidation of alcohols^[16]. A research objective of an ongoing project in our laboratory is to develop clean, simple and recyclable protocols for the oxidation of alcohols and other substrates using environmentally safe reagents. We expect to know the effect of morphological structure of the polymer supports on the catalytic properties of the polymer-supported metal complexes. The aim of this work is to find a way to select and use polymer supports more reasonable and effective. The influences of morphological structure of the supporters on the catalytic properties of the polymer-supported metal complexes were discussed. The polymers which we used were aminomethyl polystyrene with different pore size (microporous and macroporous), nitrogen-substitution and crosslinks. To the best of our knowledge, there is no literature reported on the research dealing with this subject.

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EXPERIMENTAL

Reagents and Instrumentation

Aminomethyl polystyrene resins were obtained from TianJiin NanKai HeCheng Sci&Tech. Co. Ltd., RuCl_3 was purchased from ShanXi KaiDa Chemical Industry Co. Ltd., 1,10-phenanthroline monohydrate was purchased from TianJin FuChen Chemical Reagent Plant. Alcohols used in the reactions were obtained from ABCR GmbH & Co. KG and used as received without further purification. Other used reagents and solvents were analytical pure.

FT-IR spectra were recorded on a Nicolet AVATAR360 IR spectrometer using KBr disks. GC/MS analyses were carried out on a trace HP GC6890/MS5973 equipped with a $25 \text{ m} \times 0.25 \text{ mm}$ SE-54 column and a Shimadzu GC-16A gas chromatograph with a $3 \text{ m} \times 3 \text{ mm}$ OV-17 column. The metal content of the $\text{Phen-Ru-}\textcircled{1}$, $\text{Phen-Ru-}\textcircled{2}$, $\text{Phen-Ru-}\textcircled{3}$, $\text{Phen-Ru-}\textcircled{4}$, $\text{Phen-Ru-}\textcircled{5}$, $\text{Phen-Ru-}\textcircled{6}$ and $\text{Phen-Ru-}\textcircled{7}$ were determined with a Shimadzu ICPV-5600 spectrophotometer under the standard conditions.

Preparation of the Aminomethyl Polystyrene-Supported Ruthenium Complexes

The aminomethyl polystyrene-supported ruthenium complexes were prepared by a modified method^[8]. Aminomethyl polystyrene was swollen for 24 h in THF before being used. The swollen resin having surface amino groups was added to the solution of NaNO_2 (4%, 2 mL) and HCl (18%, 4 mL). The mixture was stirred at $0\text{--}5^\circ\text{C}$ for 20 min. After diazotization addition of aminomethyl polystyrene, 1,10-phenanthroline monohydrate (0.05 g) was added. The mixture was stirred at 60°C for 1 h, then triethylamine (0.39 mL and 0.30 mL) was added twice to the solution, and the mixture was refluxed for 24 h and 32 h, respectively. Phen was then filtered, washed with THF and dried at 40°C in vacuum.

Phen (0.5 g) was added to a solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.5 g) in THF (10 mL). The mixture was stirred at room temperature for 10 h, then filtered and the product was repeatedly washed with THF until the filtrate became colorless. The ruthenium complexes $\text{Phen-Ru-}\textcircled{1}$ (**1**), $\text{Phen-Ru-}\textcircled{2}$ (**2**), $\text{Phen-Ru-}\textcircled{3}$ (**3**), $\text{Phen-Ru-}\textcircled{4}$ (**4**), $\text{Phen-Ru-}\textcircled{5}$ (**5**), $\text{Phen-Ru-}\textcircled{6}$ (**6**) and $\text{Phen-Ru-}\textcircled{7}$ (**7**) were obtained.

General Procedure for the Oxidation of Alcohols

A typical reaction was carried out as follows: Since the amounts of Ru are different on different catalysts, we choose different amounts of catalysts to keep the same amounts of Ru which participate in the reaction. Phen-Ru (Ru, 8.8×10^{-4} mmol), 1-nonanol (3.0×10^{-2} mmol) and iodosylbenzene (PhIO) (9.0×10^{-2} mmol) were dissolved in 2 mL of acetonitrile. The mixture was stirred for 10 h at room temperature. Formation of products and consumption of substrates were monitored by GC. The identity of products was determined either by comparison with authentic samples using gas chromatography or by GC/MS analysis. The conversion and product selectivity were determined by GC analysis.

RESULTS AND DISCUSSION

Morphological Structure of the Catalysts

In order to investigate the catalytic properties of **1**, **2**, **3**, **4**, **5**, **6** and **7**, we used seven types of the aminomethyl polystyrene-supports with different pore size (microporous and macroporous), nitrogen-substitution and crosslink degree (Table 1, Entries **1–7**). The loading of the ruthenium in the aminomethyl polystyrene-supported complexes **1**, **2**, **3**, **4**, **5**, **6** and **7** are 4.45%, 5.13%, 3.81%, 4.26%, 3.71%, 4.12% and 3.60%, respectively.

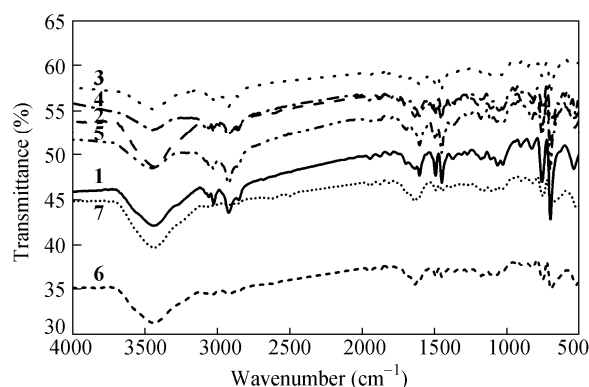
We can see from Table 1 that the nitrogen substitution of aminomethyl polystyrene supports **1–7** are 1.40, 1.50, 1.15, 1.12, 1.13, 1.13 and 1.74 mmol/g, respectively. The ruthenium loading result suggests that higher metal loading will obtain by the utilization of lower crosslinked polystyrene-divinylbenzene or by the utilization of macroporous structure polystyrene-divinylbenzene in the identical reaction conditions.

Table 1. The characterization of the aminomethyl polystyrene-supported catalysts

Entry	Aminomethyl polystyrene resins				Ru supported ^c (%)
	Crosslinker (DVB)	Particle size (mesh)	N-substitution (mmol/g)	Pore structure	
1	1%	100–200	1.40	Microporous ^a	4.45
2	1%	100–200	1.50	Macroporous ^b	5.13
3	4%	100–200	1.15	Microporous ^a	3.81
4	4%	100–200	1.12	Macroporous ^b	4.26
5	6%	100–200	1.13	Microporous ^a	3.71
6	6%	100–200	1.13	Macroporous ^b	4.12
7	15%	100–200	1.74	Macroporous ^b	3.60

^a Relative area is 500 m²/g; ^b The average pore diameter is 10 nm;^c Percentage of Ru was determined by ICP analysis.

As show in Fig. 1, the IR spectra of the ruthenium complexes **1**, **2**, **3**, **4**, **5**, **6** and **7** bear similar absorptions. The spectra showed characteristic absorption peaks of aminomethyl polystyrene resins being grafted with phenanthroline and the ruthenium complexes. The absorptions at 1647, 422 and 1450 cm⁻¹ are ascribed to N=N, N—Ru and CH₂—N vibrations, respectively.

**Fig. 1** IR spectra of **1**, **2**, **3**, **4**, **5**, **6** and **7**

Catalytic Properties of the Aminomethyl Polystyrene-Supported Ru Complexes

Most of the oxidations were carried out in 10 mL glass reactors in acetonitrile at room temperature. We used a fixed amount of the 1-nonanol (3.0×10^{-2} mmol) and PhIO (0.86 mmol), and changed the catalysts **1**, **2**, **3**, **4**, **5**, **6** and **7**. We keep the same amount of Ru (Ru, 8.8×10^{-4} mmol). 1-Nonanol is oxidized in this oxidation system to give the corresponding nonanal and nonanoic acid.

The effect of various catalysts was studied in this paper, which is important to the conversion of alcohols. These studies clearly revealed that the catalysts could catalyze the oxidation of primary and secondary alcohols.

In order to evaluate the catalytic activities and product selectivity of these catalysts for the oxidation of the alcohols, the effect of the reaction temperature on the oxidation, the recycling capacity of the complexes **1**, **2**, **3**, **4**, **5**, **6** and **7** (Ru, 8.8×10^{-4} mmol) were investigated according to the oxidation of 1-nonanol.

The effect of morphological structure in different reaction temperatures

In order to investigate the effect of the morphological structure on the conversion of the catalysts in different reaction temperatures, 1-nonanol was selected as substrate. The reactions were carried out in acetonitrile using 1.6 equivalent of PhIO as oxidant catalyzed by **1**, **2**, **3**, **4**, **5**, **6** and **7** at different temperatures such as 15°C, 30°C, 40°C, 50°C and 60°C. The same amount of Ru is 8.8×10^{-4} mmol in different catalysts. The temperature of the oxidation system was controlled by a temperature controller instrument. The reaction temperature clearly influences the oxidation. Temperature near the boiling point of the solvent results in the evaporation so it is

unfavorable for the results of the reactions.

As shown in Fig. 2, the turnover number (TON) of the 1-nonanol was about 21.48 when the reaction was carried out at 30°C by the utilization of **1** (microporous, 100–200 mesh, 1% crosslinked, 500 m²/g). The TON would decrease when the reaction temperature was over 30°C in the case of **1**. TON of about 28.98 could be obtained at 40°C for **2** (macroporous, 100–200 mesh, 1% crosslinked, average pore diameter 10 nm). The TON of about 28.64 would be obtained at 60°C using **3** (microporous, 100–200 mesh, 4% crosslinked, 500 m²/g) as catalyst. There was a clear trend that the TON would increase with the temperature in case of **3**. We can find the same trend when using **7** as catalyst. The TON of about 33.75 would be obtained at 60°C using **7** (macroporous, 100–200 mesh, 15% crosslinked, average pore diameter 10 nm). And when the temperature is 30°C, TON of about 33.75 would be obtained by **4** (macroporous, 100–200 mesh, 4% crosslinked, average pore diameter 10 nm). The optimum temperature for the oxidation of 1-nonanol is 40°C and 50°C by the utilization of **5** (microporous, 100–200 mesh, 6% crosslinked, 500 m²/g) and **6** (macroporous, 100–200 mesh, 6% crosslinked, average pore diameter 10 nm) as catalyst respectively.

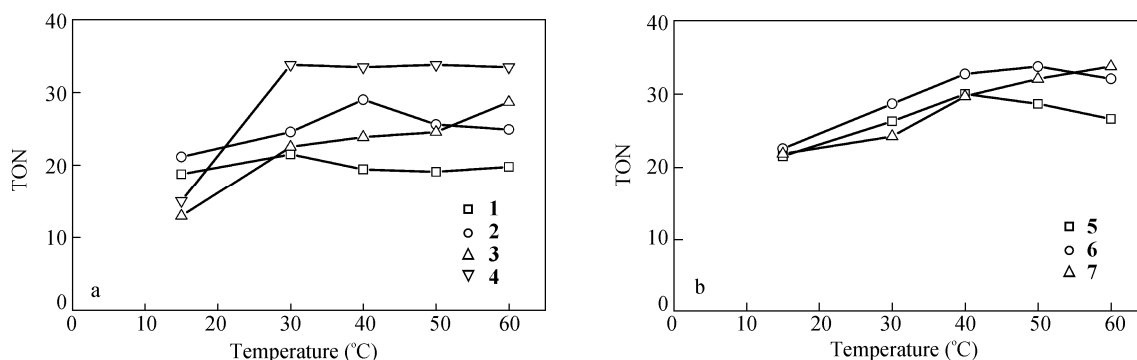


Fig. 2 TON-temperature curves for the oxidation of 1-nonanol with catalysts **1–4** (a) and catalysts **5–7** (b) 1-Nonanol 0.03 mmol; PhIO:1-nonanol = 1.6; Acetonitrile 2 mL; 10 h; Catalysts: **1–7**; Ru, 8.8×10^{-4} mmol

The investigation showed that the optimum temperature for the oxidation of 1-nonanol is 30°C, 40°C, 60°C, 30°C, 40°C, 50°C and 60°C by the utilization of **1**, **2**, **3**, **4**, **5**, **6** and **7** as catalyst, respectively. The result suggests that aminomethyl polystyrene-support with a relatively higher crosslinking can be used at higher temperature compared with those with a lower crosslinking although the discrimination is not great.

The effect of morphological structure in different reaction time

The influence of the reaction time on the conversion, selectivity and TON was investigated by a series of oxidation reactions in which 1-nonanol was also chosen as test substrate for the oxidation. The reaction was done at 30°C in acetonitrile using 3 equivalent of PhIO catalyzed by the complexes in a reaction period of 2–22 h, respectively. The oxidation mixture was taken out with an identical interval at different reaction time, and was determined through the GC record immediately. The results are concluded in Fig. 3. As shown in Fig. 3, the TON almost reaches 100% in 20, 16, 22, 8, 16, 10 and 16 h when **1**, **2**, **3**, **4**, **5**, **6** and **7** were used as catalyst respectively. The same amount of Ru is 8.8×10^{-4} mmol in different catalysts. Compared to those using a catalyst with microporous structure, the TON-time curve with macroporous structure is different. The results suggest that the TON of a catalyst with microporous structure increases slowly than a catalyst with macroporous structure. We do not know for sure the reason why a catalyst with macroporous structure will react more rapidly. The result may be related to the position of the catalytic active center and the diffusibility of the solvents and the reactant through the supports.

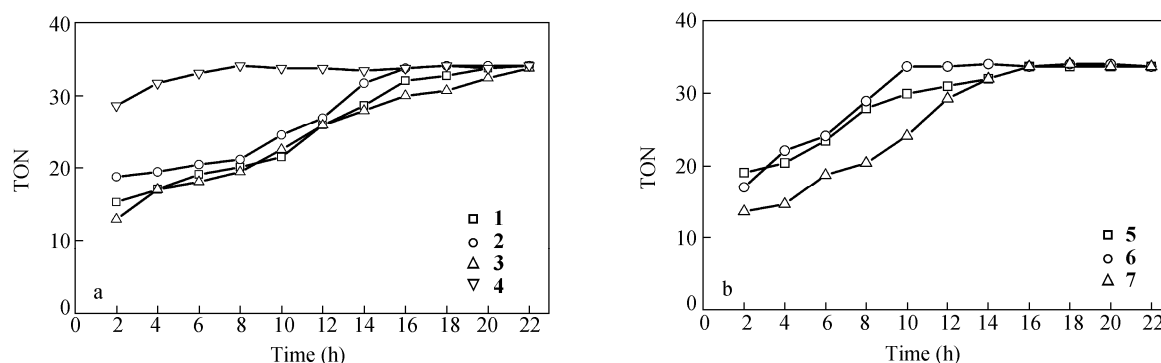


Fig. 3 TON-reaction time profiles for the oxidation of 1-nonanol with catalysts **1–4** (a) and catalysts **5–7** (b)
1-Nonanol 0.03 mmol; PhIO:1-nonanol = 3; Acetonitrile 2 mL; Reaction temperature 30°C; Catalysts: **1–7**; Ru,
 8.8×10^{-4} mmol

Product selectivity

In order to find the effect of these catalysts on the product selectivity for the oxidation of alcohols in higher conversion, the reactions were carried out with PhIO (alcohol = 0.03 mmol, PhIO:alcohol = 3) at 30°C using the complexes as catalysts respectively. A series of alcohols, including aliphatic alcohols, substituted benzyl alcohols, substituted benzhydrol and cyclo-alcohol can be easily oxidized to the corresponding carbonyl compounds under mild conditions. The results were summarized in Table 2. We have not found a different product distributing trend for the oxidation of alcohols due to the utilization of different catalysts **1**, **2**, **3**, **4**, **5**, **6** and **7** respectively.

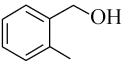
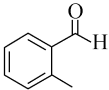
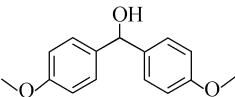
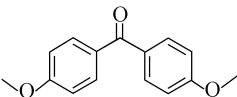
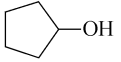
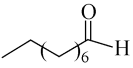
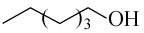
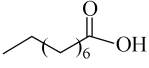
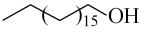
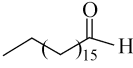
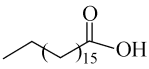
We have found that the product selectivity is influenced by the alcohol structure. For example, the selectivity to aldehyde for the oxidation of 1-hexanol, 1-nonanol and 1-octodecyl alcohol using **1** as catalyst is 0%, 62% and 84% respectively, while that to carboxylic acid is 100%, 38% and 16% in case of **1** (Table 2, entries (4)–(6)). The results show that the selectivity to aldehyde increases but that to carboxylic acid decreases with the aliphatic chain using **1** as catalyst. Table 2 also shows the same trend in case of **1**, **2**, **3**, **4**, **5**, **6** and **7** (Table 2, entries (4)–(6)).

Catalytic oxidation of other alcohols by the different catalysts

A series of other alcohols, including aliphatic alcohols, substituted benzyl alcohol, substituted benzhydrol and cyclo-alcohol were oxidized to the corresponding carbonyl compounds in 10 h in acetonitrile in high conversion with PhIO (alcohol = 0.03 mmol, PhIO:alcohol = 3) at 30°C catalyzed by **1**, **2**, **3**, **4**, **5**, **6** and **7**, respectively. The results are summarized in Table 3. The aliphatic alcohols like 1-hexanol and 1-nonanol which are generally difficult to be oxidized in other catalyst system, are completely transformed to the corresponding carbonyl compounds in 10 h, and cyclopentanol is transformed to corresponding ketones almost quantitatively under the identical reaction conditions.

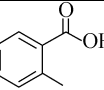
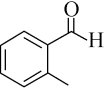
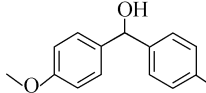
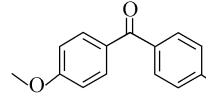
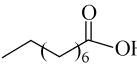
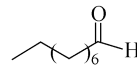
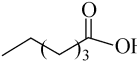
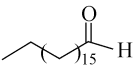
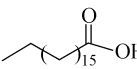
As shown in Table 3, when 2-methylbenzyl alcohol, 4,4-dimethoxydibenzhydrol and cyclopentanol are oxidized by these catalysts, we find that the TON for catalyst with microporous structure of 1% crosslinked, 4% crosslinked and 6% crosslinked (**1**, **3** and **5**) is higher than for catalysts with macroporous structure of them (**2**, **4** and **6**) (Table 2, entries (1)–(2)). The results for the oxidation of 1-nonanol, 1-hexanol and 1-octodecyl show that the TON of the catalysts with microporous structure of 1% crosslinked, 4% crosslinked and 6% crosslinked (**1**, **3** and **5**) is lower than the catalysts with macroporous structure of them (**2**, **4** and **6**) (Table 2, entries (4)–(6)). We find that cyclopentanol is oxidized by catalyst with microporous structure of 1% crosslinked (**1**) and 6% crosslinked (**5**). The TON is higher than for catalysts with macroporous structure of them (**2** and **6**). However, the result of the TON of catalyst of 4% crosslinked (**3** and **4**) is on the contrary (Table 2, entries (3)).

Table 2. Selectivity to the main product for the oxidation of alcohols catalyzed by aminomethyl polystyrene-supported Ru complexes

Entry	Substrate	Product	Product selectivity (%)	
(1)			1	100
			2	95
			3	100
			4	98
			5	100
			6	100
			7	56
(2)			1	44
			2	72
			3	100
			4	100
			5	100
			6	100
			7	79
(3)			1	100
			2	100
			3	100
			4	100
			5	100
			6	100
			7	100
(4)			1	62
			2	38
			3	35
			4	65
			5	95
			6	84
			7	16
(5)			1	95
			2	80
			3	20
			4	60
			5	40
			6	100
			7	100
(6)			1	84
			2	16
			3	66
			4	34
			5	69
			6	41
			7	88
			1	12
			2	74
			3	26
			4	55
			5	45
			6	95
			7	95

Reaction condition: alcohol 0.03 mmol, PhIO:alcohol = 3, acetonitrile 2 mL, 10 h at 30°C; Catalysts: **1** 2 mg (Ru, 8.8×10^{-4} mmol), **2** 1.7 mg (Ru, 8.8×10^{-4} mmol), **3** 2.3 mg (Ru, 8.8×10^{-4} mmol), **4** 2.1 mg (Ru, 8.8×10^{-4} mmol), **5** 2.4 mg (Ru, 8.8×10^{-4} mmol), **6** 2.2 mg (Ru, 8.8×10^{-4} mmol) and **7** 2.5 mg (Ru, 8.8×10^{-4} mmol); Reaction selectivity was determined by GC analysis.

Table 3. Oxidation of alcohols catalyzed by aminomethyl polystyrene-supported Ru complexes

Entry	Substrate	Product	Conv (%)		TON
(1)			1	79	26.98
			2	35	11.93
			3	94	36.27
			4	86	29.31
			5	91	31.02
			6	84	28.64
			7	54	18.41
(2)			1	> 99	33.75
			2	91	31.02
			3	99	33.75
			4	90	30.68
			5	90	30.68
			6	82	27.95
			7	95	32.39
(3)			1	100	37.28
			2	60	34.09
			3	70	23.86
			4	71	24.20
			5	83	28.29
			6	65	22.16
			7	75	46.60
(4)			1	63	21.48
			2	72	24.54
			3	66	22.50
			4	99	33.75
			5	88	30.00
			6	99	33.75
			7	71	17.39
(5)			1	100	34.09
			2	100	34.09
			3	81	27.61
			4	90	30.68
			5	79	26.93
			6	90	30.68
			7	100	34.09
(6)			1	66	22.50
			2	84	28.64
			3	89	30.34
			4	96	32.73
			5	99	33.75
			6	99	33.75
			7	95	32.39

Reaction condition: alcohol 0.03 mmol, PhIO:alcohol = 3, acetonitrile 2 mL, 10 h at 30°C, catalysts: **1** 2 mg (Ru, 8.8×10^{-4} mmol), **2** 1.7 mg (Ru, 8.8×10^{-4} mmol), **3** 2.3 mg (Ru, 8.8×10^{-4} mmol), **4** 2.1 mg (Ru, 8.8×10^{-4} mmol), **5** 2.4 mg (Ru, 8.8×10^{-4} mmol), **6** 2.2 mg (Ru, 8.8×10^{-4} mmol) and **7** 2.5 mg (Ru, 8.8×10^{-4} mmol); Percentage conversion was determined by GC analysis.

The recycling of the catalysts

In order to investigate catalyst recycling, a series of experiments were carried out using 1-nonanol as substrate with PhIO in acetonitrile at 45°C for 10 h using 8.8×10^{-4} mmol of **1**, **2**, **3**, **4**, **5**, **6** and **7** as catalysts. The amount of Ru is 8.8×10^{-4} mmol in different catalysts, and the results of experiment could be discussed with conversion. The same as the results are discussed with TON. When the catalyst is repeatedly filtered out and submitted to a new reaction batch without any further treatment, the conversion for the **1** is lowered to 57%, 49% and 27% from the original 59%, the conversion for the **2** is lowered to 83%, 77% and 31% from the original 90%, the conversion for the **3** is lowered to 54%, 48% and 26% from the original 78%, the conversion

for the **4** is lowered to 79%, 65% and 54% from the original 99%, the conversion for the **5** is lowered to 53%, 45% and 40% from the original 86%, the conversion for the **6** is lowered to 79%, 69% and 54% from the original 95% and the conversion for the **7** is lowered to 78%, 69% and 60% from the original 86% after 2, 3, and 4 cycles respectively. As is shown in Table 4. **1**, **2** and **3** can be recycled although the catalytic activity is lowered compared to those of the starting activity. The complex **1**, **3** and **5** possesses a relative lower activity for recycling compared with the complexes **2**, **4**, **6** and **7**. The results showed that the catalysts with a higher crosslinker support possess better recycling properties compared to those with a lower crosslinker support.

Table 4. The recycling of the aminomethyl polystyrene-supported Ru complex catalysts

Catalysts	Recycling times and conversions			
1	59 (1)	57 (2)	49 (3)	27 (4)
2	90 (1)	83 (2)	77 (3)	31 (4)
3	78 (1)	54 (2)	48 (3)	26 (4)
4	99 (1)	79 (2)	65 (3)	54 (4)
5	86 (1)	53 (2)	45 (3)	40 (4)
6	95 (1)	79 (2)	69 (3)	54 (4)
7	86 (1)	78 (2)	69 (3)	60 (4)

Recycling times are shown in the parentheses; Reaction condition: alcohol 0.03 mmol, PhIO:alcohol = 3, acetonitrile 2 mL, 10 h at 45°C, respectively, catalysts: Ru, 8.8×10^{-4} mmol; Percentage conversion was determined by GC analysis.

CONCLUSIONS

In summary, polymer-supported complexes **1**, **2**, **3**, **4**, **5**, **6** and **7** were prepared using aminomethyl polystyrenes of different morphological structures as supports. The complexes showed that they act as highly active catalysts for the oxidation of alcohols with high TON using PhIO as oxidant. The ruthenium loading result suggests that higher metal loading will be obtained by the utilization of lower crosslinked or macroporous structure polystyrene-divinylbenzene in the identical reaction conditions. The effect of morphological structures of the aminomethyl polystyrene supports on the catalytic properties of these metal complexes was investigated in detail through the reactions at different temperatures and reaction time. The results showed that the complexes with a higher-crosslinking could be used at a relatively higher temperature, and the complexes with a macroporous structure were more active. The recycling experiments showed that all the complexes reported in this study can be recycled, and the catalysts with a higher crosslinking support possessed better recycling properties.

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