Lacunary Keggin Polyoxotungstate as Reaction-controlled Phase-transfer Catalyst for Catalytic Epoxidation of Olefins

LI, Ming-Qiang(李明强)   JIAN, Xi-Gao*(蹇锡高)   YANG, Yong-Qiang(杨永强)

Department of Polymer Science & Materials, Dalian University of Technology, Dalian, Liaoning 116012, China

A new reaction-controlled phase-transfer catalyst system, lacunary Keggin polyoxotungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ has been synthesized and used for catalytic epoxidation of olefins with H_2O_2 as the oxidant. Infrared spectra were used to analyze the behavior of the phase transfer of catalyst. In this system, the catalyst not only can act as homogeneous catalyst but also as heterogeneous catalyst to be easily filtered and reused. The epoxidation reaction is clean and exhibits high conversion and selectivity as well as excellent catalyst stability.

Keywords   reaction-controlled phase-transfer catalyst, olefins, epoxidation

Introduction

Traditional methods of organic oxidation chemistry on an industrial scale often involve the use of stoichiometric metal reagents or transition metal-bromide/acetic acid systems. These methods lead to the production of large volumes of toxic or corrosive waste.[1] So "environmentally benign" synthetic procedures are of key importance in the development of new chemical processes. This mostly depends on finding a new catalyst to change the reaction conditions. Although homogeneous catalysts are widely applied in catalytic oxidation and some homogeneous catalysts exhibit very high activity and selectivity,[2,3] the difficulty of catalyst separation and reuse in homogeneous catalytic systems restricts their application. The development of reaction-controlled phase-transfer catalyst system resolves the difficulty of catalyst separation and reuse and also keeps the high activity and selectivity of homogeneous catalyst.[4] This kind of catalyst not only can be recovered like heterogeneous catalyst but also acts as homogeneous catalyst. As a very environmentally friendly and economical method for catalytic oxidation, the reaction-controlled phase-transfer catalyst system brings considerable intellectual interest. However, up to now, the reports about this kind of catalyst system are very few.[5]

The structure of lacunary Keggin polyoxotungstate $[PW_9O_{34}]^{9-}$ is less three WO_6 octahedron than Keggin polyoxotungstate $[PW_{12}O_{40}]^{3-}$, so it is named as lacunary Keggin structure. The catalytic function of lacunary Keggin polyoxotungstate has attracted much attention for their moderate catalytic activity.[6] In this paper, we design and synthesize a new reaction-controlled phase-transfer catalyst system composed of lacunary Keggin polyoxotungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$. In this system, lacunary Keggin polyoxotungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ is used for catalytic epoxidation of olefins with H_2O_2 as the oxidant. The system exhibits high conversion and selectivity as well as excellent catalyst stability. Moreover, the co-product of this reaction is only H_2O.

Experimental

Unless specially mentioned, the chemicals used in this work were at least of C.P. grade and were used as purchased.

The preparation of $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$

The $Na_8HPW_9O_{34}\cdot24H_2O$ was prepared and characterized according to literature method.[7] 1.0000 g solid of $Na_8HPW_9O_{34}\cdot19H_2O$ (0.362 mmol), was dissolved in 30 mL of water at 333 K. To this solution was added with stirring 0.6052 g of solid benzyltrimethylammonium chloride (3.258 mmol) and the stirring was continued over about 30 min at 333 K. The precipitate being the product was filtered and washed with water and acetonitrile, then air-dried at room temperature. The yield was 93%. IR (neat, KBr plates): 3436, 3033, 1632, 1474, 1456, 1219, 1078, 1035, 941, 891, 851, 811, 750, 729 cm^{-1}. Anal. calcd for $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$: C 31.12, H 4.13, N 3.56, W 45.84, P 0.91; found C 31.18, H 4.02, N 3.51, W 46.21, P 0.86.

General procedure for the epoxidation

The general procedure for the olefin epoxidation is as follows: 20 mmol of olefin was dissolved in 40 mL of CH_3CN solvent, and 15 mmol of 30% H_2O_2 and 0.2 mmol of catalyst were then added. The reaction was maintained at 343 K with vigorous stirring until the catalyst precipitated. Products were analyzed by GC-MS and gas chromatography (GC) with the internal

Reaction-controlled phase-transfer catalyst

*Chin. J. Chem.*, 2004, Vol. 22, No. 8 **875**

standard method. The catalyst was recovered by centrifugation and used in the next reaction.

Results and discussion

The phase transfer of catalyst in reaction

Scheme 1 shows the cycling progress of the catalytic reaction. In this reaction-controlled phase-transfer catalyst system, under the action of H_2O_2, catalyst $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ named as Q_9PW_9 firstly forms soluble superoxo polyoxometalate $[C_7H_7N(CH_3)_3]_9PW_9O_{42}$ named as $Q_9PW_9(O_2)$ and transfers from solid phase to liquid phase, and the $Q_9PW_9(O_2)$ subsequently reacts with olefins. When H_2O_2 is used up, Q_9PW_9 returns to its insoluble original structure and transfers from liquid phase to solid phase. The phenomenon of reaction control manifests is as follows. When the reaction begins, the catalyst transfers from solid phase to liquid phase and catalyzes reaction as homogeneous catalyst. When the reaction ends, the catalyst settles down to solid phase and can be easily filtered and reused as heterogeneous catalyst. The phase transfer is controlled by the reaction.

Scheme 1 Cycling process of the catalytic reaction
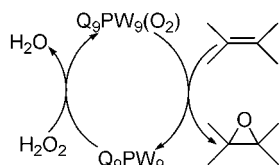
IR spectra

Figure 1 shows the infrared spectra of Q_9PW_9 (a), $Q_9PW_9(O_2)$ (b) and recovered Q_9PW_9 (c). Comparing

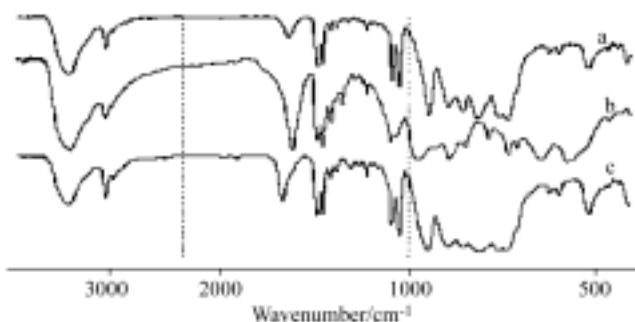**Figure 1** Infrared spectra of Q_9PW_9 (a), $Q_9PW_9(O_2)$ (b) and recovered Q_9PW_9 (c).

the infrared spectra of recovered Q_9PW_9 with those of fresh Q_9PW_9, we can see that they have completely the same absorption peak: the feature peaks for P—O stretching bands (1077.1, 1035.3 cm^{-1}), W=O band (941.4 cm^{-1}), W—O_b—W vibration bands (891.4, 851.4 cm^{-1}), W—O_c—W vibration bands (811.6, 750.4 cm^{-1}).[8,9] These same infrared spectra indicate that of catalyst is very stable and can be recycled.

The infrared spectrum of $Q_9PW_9(O_2)$ (b) shows W—O_b—W vibration bands (893.4, 853.4 cm^{-1}) and the W—O—O vibration bands (637.1, 569.9 cm^{-1}),[10] but not the W—O_c—W vibration bands (811.6, 750.4 cm^{-1}). However, the infrared spectra of Q_9PW_9 (a) and recovered Q_9PW_9 (c) show W—O_b—W vibration bands (891.4, 851.4 cm^{-1}) and the W—O_c—W vibration bands (811.6, 750.4 cm^{-1}), but not the W—O—O vibration bands (637.1, 569.9 cm^{-1}). These results offer that the ratio of intramolecular O atoms to W atom in Q_9PW_9 is not enough for its coordination number, so this W atom will interact with O atoms of another molecule (forming a W—O_c—W bond), thus forming complicated polymeric structures, which gives rise to its insolubility in organic solvents. When Q_9PW_9 reacts with H_2O_2 to form the W—O—O, the coordination number of the W atom with intramolecular O atoms increases, and the intermolecular interaction (W—O_c—W) decreases, which leads to a dramatic reduction of intermolecular bonds. As a result, $Q_9PW_9(O_2)$ becomes soluble in organic solvents.

Epoxidation of olefins

Epoxidation of olefins catalyzed by Q_9PW_9 with 30% H_2O_2 at 343 K is shown in Table 1. Under the reaction conditions employed, no epoxidation reaction occurred even after 10 h when allyl chloride was used as the substrate (Entry 3). Since the molar ratio of the substrate to H_2O_2 was 4 : 3, the theoretical maximum conversion of the olefins was 75%. So the resulting conversions of the olefins based on the olefins (67%—69%) were high. At the same time good epoxide selectivities (92%—98%) based on olefins and high olefin conversions based on H_2O_2 (98%) were obtained. Thus, high yields of the epoxides based on H_2O_2 (91%—94%) were achieved in the epoxidation system of Q_9PW_9. This is another characteristic of this new epoxidation system, with which high utilization efficiency of the reductant, that is much higher than 50%, could generally be obtained.[11]

Table 1 Epoxidation of olefins catalyzed by Q_9PW_9 with 30% H_2O_2 at 343 K

Entry	Substrate	Time/h	Based on olefin		Based on H_2O_2	
			Conversion/%	Selectivity/%	Conversion/%	Yield/%
1	Cyclohexene	4	69	92	98	91
2	1-Octene	10	67	98	98	94
3	Allyl chloride	10	0	0	0	0

Compared with the epoxidation results of cyclohexene and 1-octene, the yield of the epoxide based on H_2O_2 went up from 91% to 94%. While at same time the reaction time required to reach maximum yield of the epoxide based on H_2O_2, was lengthened from 4 to 10 h, as shown in Figure 2, indicating that epoxidation of cyclohexene is faster than that of 1-octene. These results reveal the fact that the epoxidation activity of the olefins is enhanced with the decrease of C=C stability from 1-octene to cyclohexene in this epoxidation system.
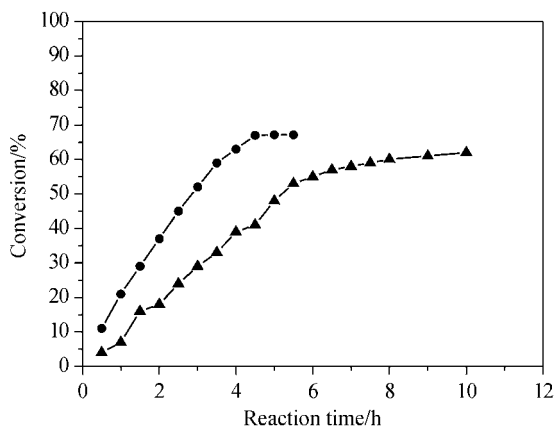

Figure 2 Influence of reaction time on the epoxidation of olefins catalyzed by Q_9PW_9 at 343 K. Circle: cyclohexene, triangle: 1-octene.

Table 2 shows the epoxidation of cyclohexene in different solvent. The selectivity and conversion are based on cyclohexene. In DMF (*N,N*-dimethylformamide), the selectivity of cyclohexene is low, the rate of catalyst recovery and the conversion of cyclohexene are

less. So the solvent of CH_3CN is more appropriate for the reaction, and in this condition, the conversion is the largest. On the other hand, since $[C_7H_7N(CH_3)_3]_9P-W_9O_{34}$ and active species are insoluble in $C_2H_4Cl_2$, we can use the mixed solution of $C_2H_4Cl_2$ and CH_3CN to make the rate of catalyst recovery maximize. We find that the best ratio of CH_3CN to $C_2H_4Cl_2$ is 2 : 1, but the reaction time is longer than in the single solvent of CH_3CN, as shown in Table 2.

The catalyst is recovered by centrifugation and is used in the next run with 85% recovery yield (This is because particle of recovered catalyst is too small to be completely concentrated. The recovery yield is obtained by weight). By 3 times recycle reaction, catalytic activity and selectivity of the recovered catalyst are practically the same as those of the fresh catalyst, indicating the excellent stability of the catalyst.

Conclusions

In this work, lacunary Keggin polyoxotungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ has been synthesized as a reaction-controlled phase-transfer catalyst. This catalyst can act as homogeneous catalyst and can be easily filtered and reused like heterogeneous catalyst. Infrared spectral analysis of the phase transfer catalyst indicates that the intermolecular interaction is the main reason of the catalyst transfer between the solid phase and liquid phase. The products are epoxide of olefins and H_2O with no co-product being formed. All these show that the catalyst system is very environmentally friendly. This work offers a new approach for the separation of homogeneous catalysts.

Table 2 The epoxidation of cyclohexene in different solvent

Solvent/mL : mL	Rate of catalyst recovery/%	Reaction time/h	Selectivity/%	Conversion/%
DMF	70	6	89.4	57
CH_3CN	85	4	92	69
DMF, $C_2H_4Cl_2$ /2 : 1	73	5	88	56
DMF, $C_2H_4Cl_2$ /3 : 1	71	5.5	87	58
CH_3CN, $C_2H_4Cl_2$ /2 : 1	87	4.5	91	68
CH_3CN, $C_2H_4Cl_2$ /3 : 1	83	4.2	91.5	69

References

1   Khenkin, A. M.; Neumann, R. *Adv. Synth. Catal.* **2002**, *344*, 1017.

2   Sato, K.; Aoki, M.; Takagi, J. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2287.

3   Venturello, C.; Ricci, M. *J. Org. Chem.* **1986**, *51*, 1599.

4   Xi, Z W.; Zhou, N.; Sun, Y.; Li, K. L. *Science* **2001**, *292*, 1139.

5   Li, M.-Q.; Jian, X.-G. Han, T.-M.; An, Y. *Acta Chim. Sinica* **2004**, *62*, 540 (in chinese).

6   Kamata, K.; Yonehara, K.; Sumida, Y.; Yamaguchi, K.;

Hikichi, S; Mizuno1, N. *Science* **2003**, *300*, 964.

7   Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.

8   Gao, F.; Yamase, T.; Suzuki, H. *J. Mol. Catal. A: Chem.* **2002**, *180*, 97.

9   Kuznetsova, L. I.; Detusheva, L. G.; Fedotov, M. A. *J. Mol. Catal. A: Chem.* **1996**, *111*, 81.

10   Venturello, C.; D'Aloisio, R. *J. Org. Chem.* **1988**, *53*, 1553.

11   Sun, Y.; Xi, Z .W.; Cao, G. Y. *J. Mol. Catal. A: Chem.* **2001**, *166*, 219.

(E0311032   ZHAO, X. J.)