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A New Reaction-controlled Phase-transfer Catalyst System

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Abstract: A new reaction-controlled phase-transfer catalyst system was designed and synthesized. In this system, heteropolytungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ was used for catalytic epoxidation of cyclohexene with H_2O_2 as the oxidant. The conversion of H_2O_2 was 100% and the yield of cyclohexene oxide was 87.1% based on cyclohexene. Infrared spectra showed that both fresh catalyst and the recovered catalyst do have completely same absorption peak, indicating the structure of catalyst is very stability and can be recycled.

Keyword: Reaction-controlled phase-transfer catalyst, cyclohexene, epoxidation.

Recently, a new catalyst system, reaction-controlled phase-transfer catalyst system, has been developed[1]. In this catalyst system, the catalyst, which is insoluble in the reaction medium, forms soluble active species by the action of one of the reactants. The active species can subsequently react with other reactants to generate the desired product selectively. When the reactant is used up, the catalyst returns to its original structure and precipitates from the reaction medium. This kind of catalyst not only can be recovered like heterogeneous catalyst[2] but also acts as homogeneous catalyst[3,4]. Since the reaction controlled phase–transfer catalyst system possesses the above advantages, it is significant to design and synthesize. However, up to now, only one catalyst of this system has been reported[1].

In this paper, the heteropolytungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ is used as catalyst in the epoxidation reaction of cyclohexene with H_2O_2 as the oxidant. R.G. Finke *et al*[5] have reported the synthesis of heteropolytungstate anion $[PW_9O_{34}]^{9-}$, and we use this anion and benzyltrimethylammonium as the opposite cation to synthesize the heteropoly-tungstate $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$.

The system exhibits high conversion and selectivity as well as excellent catalyst stability. In this system, the catalyst firstly forms soluble active species and transfers from solid phase to liquid phase under the action of H_2O_2; when H_2O_2 is used up, it returns to its original structure and transfers from liquid phase to solid phase. The catalyst is totally soluble in the reaction system when it is used as homogeneous catalyst in the epoxidation reaction. When the reaction is over, the catalyst precipitates from the reaction system. The reaction is shown in **Scheme 1**.

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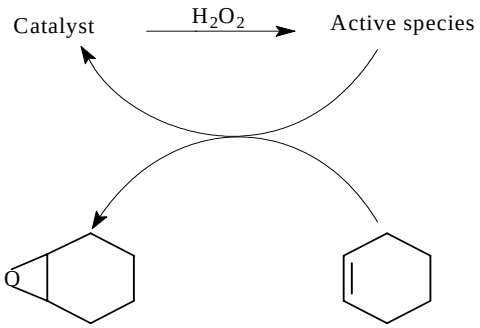
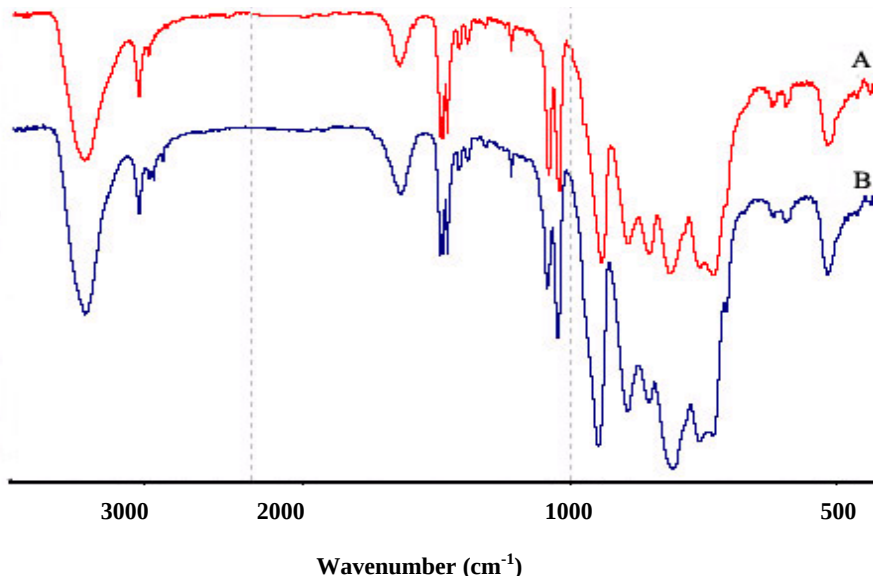
Scheme 1 Cycling process of the reaction



Catalytic reaction conditions were as follows: Forty mmol of cyclohexene was dissolved in a mixed solvent of 30 mL N, N-dimethylformamide and 1, 2-dichloroethane; 10 mmol of 30% H_2O_2 and 0.05 mmol of catalyst $[C_7H_7N(CH_3)_3]_9PW_9O_{34}$ were then added. The reaction was maintained at 70°C until the catalyst precipitated. The cyclohexene and cyclohexene oxide were analyzed by gas chromatography (GC) with the internal standard method. The conversion of H_2O_2 was 100% and the yield of cyclohexene oxide was 87.1% based on cyclohexene. The catalyst was recovered by centrifugation and reused in the next reaction without adding fresh catalyst. The conversion of H_2O_2 and the yield of cyclohexene oxide were almost the same as in the original reaction, indicating the excellent stability of catalyst.

The IR spectra of the fresh and recovered catalyst are shown in **Figure1**. They are the same. It means that the catalyst is very stable and can be reused. Since this catalyst

Figure1 Infrared spectra of the fresh catalyst (**A**) and recovered catalyst (**B**).



can be recycled, the application of this catalyst for the epoxidation of cyclohexene to cyclohexane oxide is very environmentally friendly and economical.

This work offers a new reaction-controlled phase-transfer catalyst system for this purpose: The difficulty of the separation of homogeneous catalysts can be solved successfully by this approach.

References

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