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A New Quaternary Ammonium Heteropolyoxotungstate Catalyst for Propylene Epoxidation to Propylene Oxide

Ying LÜ, Meng LI, Rong Hua ZHANG, Zu Wei XI, Shuang GAO*

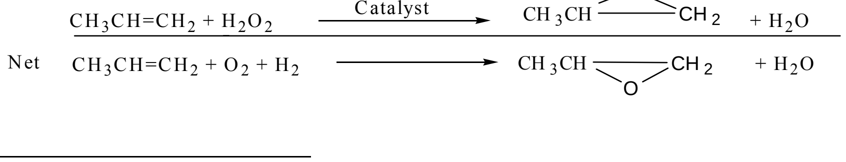
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023

Abstract: A new quaternary ammonium heteropolyoxotungstant (cat.C) is prepared and characterized. And the cat.C also is an reaction-controlled phase-transfer catalyst. The catalytic system of O_2/EAHQ (2-ethylanthrahydroquinone)/cat.c is used for the epoxidation of propylene. Under the optimal conditions, the yield of propylene oxide based on EAHQ is 84.1%, the selectivity for propylene oxide based on propylene is 99.8% and the conversion of propylene based on EAHQ is 84.3%. The cat.c precipitates after the epoxidation reaction for easy separation. The cat. C is stable enough to be recycled three times without any loss in selectivity.

Keywords: Epoxidation, propylene, reaction-controlled phase-transfer catalyst.

Propylene oxide is an important chemical. There are two industrial manufacture methods for propylene oxide production: the chlorohydrin and Halcon methods. In the chlorohydrin method, a large amount of Cl_2 is consumed which rises serious problems of equipment corrosion and environment pollution. In the Halcon method, autooxidation of ethylbenzene or isobutene is used to make alkylhydroperoxide, which acts as oxidant for catalytic epoxidation of propylene to propylene oxide with a large amount of co-products. Production of propylene oxide without co-products in an environment-friendly way has always been an object for many chemists.

Recently, we have reported a reaction-controlled phase transfer catalytic system for propylene epoxidation[1]. The catalyst $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ forms oil soluble active species in the presence of H_2O_2, which can precipitate and easily be recovered. When the propylene epoxidation coupled with the 2-ethylanthraquinone / 2-ethylanthrahydroquinone redox process for H_2O_2 production, O_2 can be used for the epoxidation reaction. The reaction as follows:



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[*] E-mail: sgao@dicp.ac.cn

In this paper, a new quaternary ammonium heteropolyoxotungstant (cat.C) was prepared and characterized. Cat.C also can be used as a reaction-controlled phase-transfer catalyst with good results for propylene epoxidation.

Experimental

Cat.C was prepared as follows: After tungstenic acid was dissolve in aqueous H_2O_2 solution, 85% phosphoric acid was added at about 35°C. Then the solution of cetyltrimethyl ammonium chloride in $C_2H_4Cl_2$ was added under vigorous stirring. The precipitated cat.C was filtrated and dried in air. The yield of the oxidized product was more than 95% on average.

Cat.C was characterized by ICP and ^{31}P NMR. From ^{31}P NMR, it was found that cat.C was a mixture, composing of four species with different W/P ratio. ^{31}P chemical shift of each species was δ 5.26, -0.81, -13.46 and -26.12 ppm, respectively. By ICP, the total W/P ratio of cat.C was determined to be 4.8:1.

2-Ethylanthrahydroquinone solution was obtained by Pd/Al_2O_3 hydrogenation immobile-bed.

70 mL EAHQ solution was oxidized with O_2, then the solution (containing 0.02 mol H_2O_2) was charged into a 250 mL stainless steel autoclave with a glass liner. Cat.C (0.19 g) and benzene (as the internal standard) were added. 3.00 g of propylene was fed into the autoclave. The reaction was stirred at 65°C for 4.5 hours.

The analysis was conducted on a HP-4890 GC equipped with a flame ionization detector and a packed column (2.4 m×2.4 m) containing PEG 20 M as the stationary phase for detecting propylene oxide (PO). The column temperature was programmed from 80°C to 130°C at the rate of 20°C/ min.

As shown in **Table 1**, the cat.C gave good results for the epoxidation of propylene in the period of 3.5-6 hours. In average, the yield of PO was 82.8%, and the selectivity for PO was 96.3%. The catalyst was recovered in 96.0% yield.

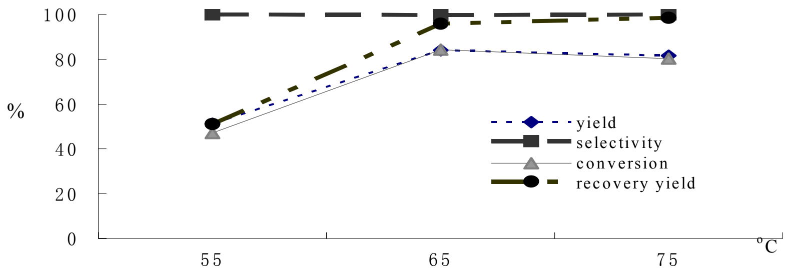
From the **Scheme 1**,the selectivity for propylene oxide was good at 55°C~75°C, but the conversion of propylene was low at 55 °C due to the slow rate of the reaction. When the temperature was 65°C ~75°C, cat.C showed good activity, the yield of PO was over 82% based on EAHQ, the selectivity for PO was 99%, and the recovery yield of the catalyst was more than 96.0%.

Table 1 Epoxidation of propylene under different reaction time with cat-C[a]

Time (h)	Yield [b] (%)	Conversion [b] (%)	Selectivity [c] (%)	Yield with recovered cat.C [d] (%)
6	81.2	86.1	94.4	97.7
5	83.2	87.3	95.3	97.4
4.5	84.1	84.3	99.8	95.9
3.5	82.6	86.3	95.7	93.2

[a] Reaction conditions: 70 mL EAHQ solution(0.02 mol of H_2O_2 *in situ*), cat-C 0.19 g, reaction temperature is 65℃. [b] The yield of PO and conversion of propylene were based on EAHQ.
[c] Selectivity for PO was based on propylene. [d] Recovery yield was by weight.

Scheme 1 Epoxidation of propylene under different temperatures with cat-C[a]



[a] Reaction conditions: 70 mL EAHQ solution (0.02 mol of H_2O_2 *in situ*) , cat-C 0.19 g, the reaction was maintained at the temperature for 4.5 h. [b] The yield of PO and conversion of propylene were based on EAHQ.[c] Selectivity for PO was based on propylene.[d] Recovery yield was by weight.

Table 2 The results of the recycle of the catalyst-C[a]

catalyst	Addition (%)	Time (h)	Selectivity (%)[c]	Yield (%)[b]	Conversion (%)[b]
Fresh	——	8.0	>99	85.9	85.6
Cycle I	6	8.0	>99	81.3	81.0
Cycle II	7	9.5	>99	73.6	73.6
Cycle III	7	9.5	>99	63.4	61.5

[a] Reaction conditions: 70 mL EAHQ solution (0.02 mol of H_2O_2 *in situ*) , fresh catalyst-C 0.19 g, (in cycling reaction a few fresh catalyst has added to amount). reaction temperature was 50℃.

[b] The yield of PO and conversion of propylene were based on EAHQ. [c] Selectivity for PO was based on propylene.

The catalyst was recovered by centrifugation and used in the next reaction With a few fresh catalyst. As shown in **Table 2**, the catalytic selectivity of the recovered catalyst kept stability, but the catalytic activity of the recovered catalyst was reduced during the recycles. The work for improving the stability of cat-C is in progressing.

Acknowledgment

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Reference

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