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Letters to the Editor

Epoxidation of Propylene with Aqueous Hydrogen Peroxide on a Reaction-Controlled Phase-Transfer Catalyst

To the Editor:

Sir: The better result (the selectivity for propylene oxide based on propylene is 92.0%, and the yield based on H_2O_2 is 90.9%) was obtained for homogeneous catalytic epoxidation of propylene with aqueous H_2O_2 on a reaction-controlled phase-transfer catalyst.

Propylene oxide (PO) is one of the most important chemical feedstocks. Current commercial productions usually employ the chlorohydrin process and the Halcon process, which give rise to serious environmental pollution as well as a large amount of coproducts. As a result of increasingly stringent environmental legislation, there is currently much interest in the substitution of enviromentally friendly oxidants in processes involving pollutant oxidants. Selective epoxidation of propylene with molecular oxygen is a great challenge to chemists for both academic and industrial interest. Unfortunately, direct epoxidation of propylene with dioxygen is difficult because of the poor selectivity under the conventional severe conditions. H_2O_2 is also a clean oxidant, and the TS-1 zeolite catalyst for propylene epoxidation with aqueous H_2O_2 in methanol solution has high catalytic activity and selectivity.[1] Moreover, the TS-1 zeolite can be regenerated by calcination or washing with the solvent. However, this method has not yet been commercialized because of economic reasons. Since PO is water soluble, a few homogeneous catalytic systems with aqueous H_2O_2 as oxidant have been reported.[2] Recently, we have reported a reaction-controlled phase-transfer catalytic system for propylene epoxidation with in situ formed H_2O_2.[3]

Herein we disclose a better result on the homogeneous catalytic epoxidation of propylene by 52% H_2O_2 to propylene oxide using the same reaction-controlled phase-transfer catalyst. The catalyst is easily recovered with 94% recovery yield (by weight). The selectivity for propylene oxide is 92.0% based on propylene, and the yield is 90.9% based on H_2O_2.

The catalyst, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$, was prepared according to ref 4.

The catalytic epoxidation reactions were carried out in a stainless steel autoclave with a glass liner of 250 mL capacity. In a typical experiment, toluene (40 mL), tributyl phosphate (30 mL), 52% H_2O_2 (1.74 g), catalyst (0.253 g), and benzene (0.7 g, as internal standard) were added. The weight of gaseous propylene fed into the autoclave was measured by an electronic balance of 6 kg capacity and 0.01 g sensitivity. The reaction was maintained at 65 °C with vigorous stirring for 4.5 h. After the reaction, the autoclave was cooled to 25 °C, and then the gas in the autoclave was discharged. The solution was analyzed by gas chromatography (GC, Agilent 4890D, equipped with a flame ionization detector and a packed column (2.4 m × 2 mm) containing PEG 20M as the stationary phase). The propylene oxide in the gas was ignored. The propylene in the gas was figured by weight.

***Table 1.* Effect of different volume ratios of TBP/toluene**[a]

TBP/toluene (volume ratio)	yield (%)[b]	conversion (%)[c]	selectivity (%)[d]	recovery yield (wt %)
toluene	18.1	66.9	27.0	70.4
1:3	68.6	84.5	80.9	86.8
1:2	82.0	98.4	83.3	86.2
3:4	90.4	98.2	92.0	94.0
1:1	85.8	97.7	87.8	85.8
2:1	56.3	72.2	78.0	27.7
3:1	33.5	46.4	72.2	59.1
TBP	31.5	39.8	79.6	66.0

[a] Reaction conditions: solvent volume was kept at 70 mL, others were the same as the experimental section. [b] Yield of PO was based on H_2O_2 [c] Conversion of propylene was based on H_2O_2. [d] Selectivity for PO was based on propylene.

The tributyl phosphate (TBP)/toluene volume ratio has a great influence on the epoxidation of propylene. The changes of the reaction results with the TBP/toluene volume ratio are listed in Table 1. In this table, the yield of PO, the selectivity for propylene, and the recovered yield of the catalyst all increase with the increase of the TBP/toluene volume ratio and decrease after the volume ratio of TBP/toluene reaches 3:4. It is considered that the water phase is unfavorable to the epoxidation reaction due to the solubility in water and the hydrolysis of PO to propylene glycol. When only toluene was used as the solvent, the yield of PO based on H_2O_2 and the selectivity for PO based on propylene were 18.1% and 27.0%, respectively. With the amount of TBP increasing, the yield and the selectivity became much better. When the volume ratio of TBP/toluene reaches 3:4, the polarity of TBP makes the aqueous/oil biphasic system remain in the same phase, and no aqueous phase dissociates from the oil phase. Thus, the epoxidation reaction cannot be affected by water produced from added 52% $H_2O_{2.}$ Interestingly, higher amounts of TBP had the opposite effect and decreased the propylene oxide yield. As we know, the catalyst, $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$, consists of two parts heteropolyoxotungstate anion and quaternary ammonium cation which have nearly opposite effects on catalyst solubility. When the amount of TBP was in excess, the catalyst could not dissolve completely in the reaction system even under the action of H_2O_2, and the catalytic activity became lower.

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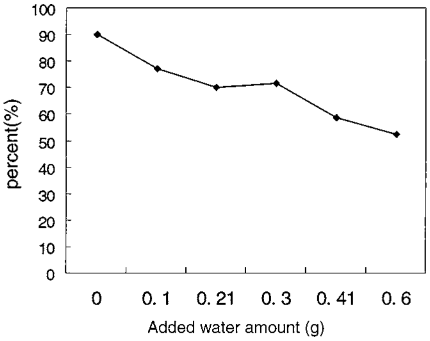

Figure 1. **Influence of water amount on yield of PO. Reaction conditions: toluene (40 mL), tributyl phosphate (30 mL), 52% H_2O_2 (1.74 g), catalyst (0.253 g); temperature (338 K); time (4.5 h).**

The effect of the amount of H_2O for the epoxidation of propylene was also investigated. The results are listed in Figure 1. As shown in Figure 1, the reaction results decrease with increasing the amount of H_2O. The result indicates that it is important to keep the reaction system at the same phase during the epoxidation of propylene.

In summary, this is a better result on the preparation of propylene oxide from propylene by homogeneous catalytic method using aqueous H_2O_2 as oxidant. The route is simple and enviromentally friendly, so that it has potential for industrial application. This research realized the yield of propylene oxide based on hydrogen peroxide is 90.9%, and the selectivity for PO based on propylene is 92.0%. The catalyst can be recovered easily as a precipitate due to reaction-controlled phase transfer.

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