Organic Process Research & Development **2006**, *10,* 876–880

Full Papers

Epoxidation of Allyl Chloride to Epichlorohydrin by a Reversible Supported Catalyst with H_2O_2 under Solvent-Free Conditions

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Abstract:

Allyl chloride was epoxidized to epichlorohydrin with H_2O_2 under solvent-free conditions in 94% selectivity using a new reversible supported catalyst, heteropolyphosphatotungstate/silanized silica gel. By the action of H_2O_2 the heteropolyphosphatotungstate dissolves from the carrier surface and forms an active homogeneous reagent. When all H_2O_2 is consumed, the reduced catalyst redeposits on the support carrier. The supported catalyst retains the character of a homogeneous catalyst during reaction but exhibits heterogeneous properties upon work-up. The solid-supported catalyst is easily isolated and can be reused. The reaction system for synthesis of epichlorohydrin therefore avoids the serious pollution issues known from the commercialized chlorohydrin methods. Some other olefins can also be epoxidized by this catalytic system under neat conditions.

Introduction

Epichlorohydrin is an important petrochemical used in the manufacture of epoxy resins, synthetic glycerol, etc. Its worldwide production capacity in 2003 was around 1.24 million tons, and there is continual increase in market demand. The industrial methods for the production of epichlorohydrin are the chlorohydrin method and the allyl alcohol method.[1] Both methods use $Ca(OH)_2$ and produce $CaCl_2$ as a by-product. The chlorohydrin method entails serious environmental pollution issues. The allyl alcohol method imposes fewer threats to the environment, but the process is more complicated, thus leading to higher investment costs. More than 90% of epichlorohydrin in the world is still manufactured today using the chlorohydrin method. Owing to environmental concerns in recent years, there is a strong need for the development of an environmentally friendly process for the production of epichlorohydrin. Direct epoxidation of allyl chloride with hydrogen peroxide is an ideal method.

Hydrogen peroxide is a relatively cheap, environmental friendly oxidant with an atom efficiency of 47%. In recent years, many researchers[2−14] have shown interest in the epoxidation of olefins with hydrogen peroxide. Epoxidation of olefins is an electrophilic reaction; the strong electron-withdrawing effect of chloride atoms in allyl chloride molecules makes it more difficult to epoxidize than non-functional terminal olefins. Only a few examples of epoxidation of allyl chloride have been reported so far.

The epoxidation of allyl chloride by TS-1 zeolite with H_2O_2 was reported by Clerici group and Gao.[15,16] The reaction was carried out at 45 °C for 30 min in the presence of methanol solvent. The selectivity for epichlorohydrin is 92% based on H_2O_2, and the conversion of H_2O_2 is 98%.[15] Presently, this method has not yet been commercialized. Venturello and co-workers had reported a homogeneous catalytic system for allyl chloride epoxidation with $[(C_8H_{17})_3NCH_3]_3[PO_4[W(O)(O_2)_2]_4]$ catalyst and aqueous H_2O_2.[17,18] The reaction mixture was refluxed for 2.5 h in the benzene/water biphasic system to give epichlorohydrin in the yield of 85%. Sun et al. had tried to epoxidize allyl chloride with H_2O_2 generated in situ through an anthraquinone route and $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ catalyst in toluene and tributyl phosphate mixed solvents at 75 °C for 1.5 h to give epichlorohydrin in the yield of 80.5%.[19] Not only do heterogeneous catalytic systems need a large amount of solvents, but also the homogeneous catalytic systems men-

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10.1021/op060108k CCC: $33.50

Table 1. **Decomposition of H_2O_2 by different carriers[a]**

carrier	decomposition of H_2O_2 (%)
macropored microspherical silica gel	53.3
silanized macropored microspherical silica gel	6.2
α-Al_2O_3	12.1
active carborn	100

[a] Reaction conditions: 0.76 g of carrier, 2.51 g of 27.1% H_2O_2, 65 °C, 2.5 h.

tioned above. With the growing concern for the environment and the development of green chemistry, solvent-free and highly selective reactions are the ideal.[20]

Homogeneous catalysts exhibit high activity and good selectivity but are difficult to separate and reuse. The efficient separation and subsequent recycling of homogeneous transition-metal catalysts remain topics that not only constitute a scientific challenge but are also of great commercial relevance. Chemists have developed many methods to solve the separation and reuse problems of the homogeneous catalyst. One of the most important methods is the heterogenized homogeneous catalyst;[21] however, this method usually shows decreased catalytic activity compared with activities of homogeneous analogues.

In the present work, a new reversible supported catalyst (RSC)—quaternary ammonium heteropolyphosphatotungstate compounds supported on silanized silica gel—was designed and prepared for epoxidation of allyl chloride with aqueous H_2O_2 as the oxidant under solvent-free conditions. This catalyst retains the reactivity characteristic of a homogeneous catalyst but at the same time is easy to separate off and reuse. The epoxidation of other olefins by this catalytic system has also been investigated. A possible mechanism of RSC in the epoxidation of olefins is proposed.

Results and Discussion

The nature of carriers plays an important role for the supported catalyst. It is important that the carrier does not promote side reactions and shows good physical characteristics such as high surface area, pore volume, and mechanical strength. In our reaction system the decomposition of H_2O_2 is the main side reaction; thus, the effect of carriers on the decomposition of H_2O_2 was investigated.

Table 1 showed that the decomposition of H_2O_2 by silanized silica gel was less than that for the other carriers. The conversion of H_2O_2 was 6.2% after heating at 65 °C for 2.5 h when silanized silica gel was the carrier. Silanized silica gel also has a large surface area (353.4 m^2/g), high pore volume (0.9395 mL/g), and good mechanical strength, and so it was chosen as a carrier to prepare the supported catalyst. It is well-known that heteropolyphosphatotungstate exhibits good catalytic activity in the epoxidation of olefins with aqueous H_2O_2. The experiments found that heteropolyphosphatotungstate has a certain binding ability to the oxide carrier when it is newly formed. Thus, it was chosen as the active component for the supported catalyst. A quaternary ammonium salt of heteropolyphosphatotungstate was immobilized on this silanized silica gel to form RSC.

Table 2. **Effect of the molar ratio of reactants on the epoxidation of allyl chloride[a]**

allyl chloride/H_2O_2(molar ratio)	Na_2HPO_4 (g)	yield (%)
6:1	0.0040	79.8
8:1	0.0062	85.5

[a] Reaction conditions: H_2O_2 (50.8 wt %): Catalyst=100:1(molar ratio) at 65 °C for 2 h, Na_2HPO_4 was an additive agent. The yield of epichlorohydrin was based on H_2O_2.

Table 3. **Recycling of RSC for the epoxidation of allyl chloride[a]**

catalyst	Na_2HPO_4 (g)	conversion (%)	selectivity (%)
fresh	0.0062	90.6	94.4
cycle 1	0.0053	89.4	94.3
cycle 2	0.0044	88.2	94.8

[a] Reaction conditions: allyl chloride/H_2O_2 (50.8 wt %)/fresh catalyst = 643:78:1 (molar ratio) at 65 °C for 2 h, Na_2HPO_4 was an additive agent. The catalyst was recovered by centrifugation, washed by petroleum ether, and reused in the next reaction without addition of fresh catalyst. The conversion of allyl chloride was based on H_2O_2, and the selectivity to epichlorohydrin was based on allyl chloride.

Allyl chloride was epoxidized selectively by RSC with commercially available 30% or 50% hydrogen peroxide under solvent-free conditions to give similar results. For instance, when allyl chloride was epoxidized by RSC at 65 °C for 2 h with 30.8% H_2O_2 and 50.8% H_2O_2, under solvent-free conditions, the selectivities for epichlorohydrin were 95.3% and 94.4%, respectively, and the yields based on H_2O_2 were 85.4% and 85.5%, respectively, for epichlorohydrin. The additive agent Na_2HPO_4 was used to adjust the pH of the reaction medium to prevent the hydrolysis of epichlorohydrin formed.

The effect of the molar ratio of allyl chloride to hydrogen peroxide on the epoxidation was investigated. The results are collated in Table 2.

When the molar ratio of allyl chloride to hydrogen peroxide decreased from 8 to 6, the yield of epichlorohydrin based on H_2O_2 was reduced from 85.5% to 79.8%. As a result, the molar ratio of allyl chloride to hydrogen peroxide equal to 8 was chosen to carry out the catalyst recycling experiment.

This supported catalyst is reused in the presence of a certain amount of Na_2HPO_4 as shown in Table 3.

The catalyst was recycled two times without addition of the fresh catalyst. For the fresh catalyst, the conversion of allyl chloride based on H_2O_2 was 90.6%, and the selectivity for epichlorohydrin based on allyl chloride was 94.4%. For the two recycled experiments, an almost similar reactivity

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(23) During the filtration at reaction temperature, it is difficult to recover all of the hydrogen peroxide phase, so 1.06 g of 50% H_2O_2 was added. The reaction was performed at 65 °C for 2 h; the H_2O_2 that was consumed was determined by iodometric titration.

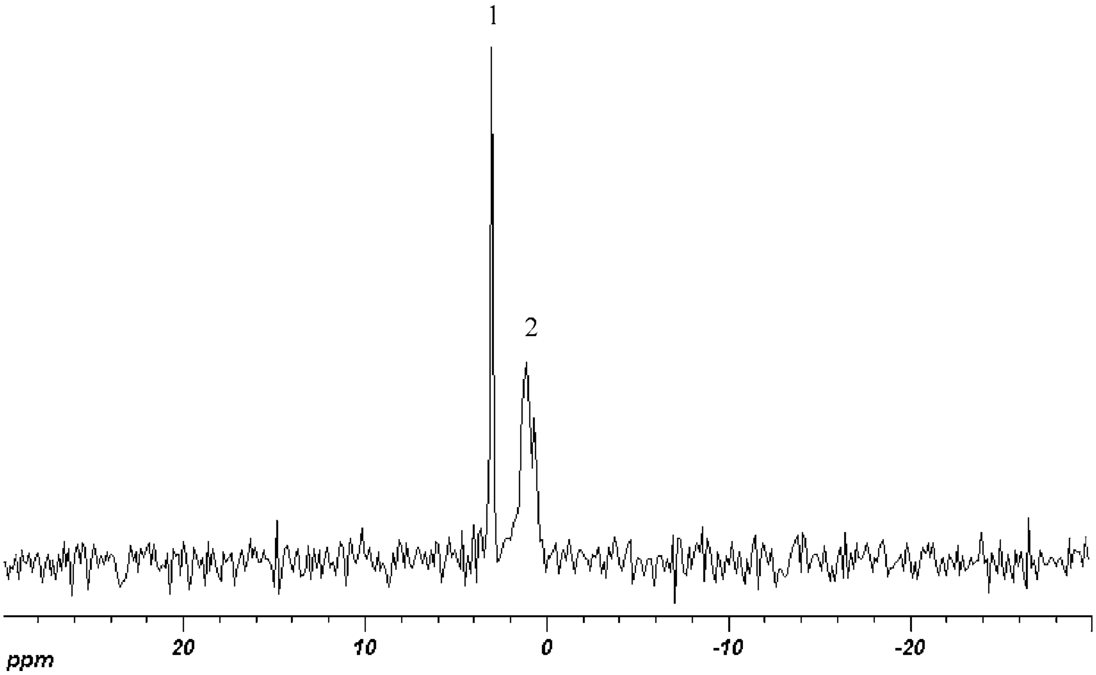

Figure 1. **The ^{13}P NMR spectrum of filtrate.[a] [a]1 is PW4, 2 is PW2 and PW3.**

was observed as compared to that of the fresh catalyst. At the end of the reaction, the recovery efficiency of the catalyst was about 98 wt %.

The changes of RSC during the epoxidation of allyl chloride were investigated. When the reaction of allyl chloride with H_2O_2 was carried out at 65 °C, after 10 min the reaction system was filtered at this temperature, and the filtrate was allowed to continue to react at 65 °C for 2 h. The concentration of epichlorohydrin increased from 1.7% to 13.0%,[23] and hydrogen peroxide was consumed. This indicated the filtrate could perform the catalytic epoxidation continually. At the same time the amount of tungsten in the filtrate was determined by ICP, which revealed that 60.4% of the active component of the RSC was in the filtrate. The ^{13}P NMR analysis of the filtrate (Figure 1) showed it contained the peroxo complex of PW_2-PW_4 species which was proposed to be the active species for the epoxidation of olefins.[24,25] The solid obtained from the above filtration was added again to the fresh allyl chloride, and H_2O_2 was reacted at 65 °C for 2 h. The concentration of epichlorohydrin in the organic phase was 1.6%, much less than 9.5% obtained in the normal epoxidation of allyl chloride using RSC as a catalyst. This indicated that the normal epoxidation of allyl chloride was mostly catalyzed by the active species in the liquid phase. When RSC was only stirred with allyl chloride at 65 °C for 10 min and then filtered at this temperature, the ^{31}P NMR analysis showed that there was no PW active species in the filtrate. All these results obtained above indicated that during the course of the reaction the active component left the carrier support under the action of H_2O_2 and formed a homogeneous active species. This active component afforded the epoxidation of allyl chloride with high selectivity and conversion.

Moreover, the ICP analysis of the reaction medium at the end of the normal epoxidation of allyl chloride showed there was 2.4% of the active component of the RSC in the liquid phase, which is much less than 60.4% obtained after the 10-min reaction. These results showed, after H_2O_2 was consumed, the active component of the catalyst in the reaction medium combined with the carrier again to form the RSC. The proposed mechanism of RSC in the epoxidation is shown in Scheme 1.

In Scheme 1, cycle 1, the active component A on the RSC formed the reversible support process accompanied with the reaction starting and stopping; cycle 2 shows the active species heteropolyphosphatoperoxotungstate, AO_m, from cycle 1 reacts with H_2O_2 in the reaction medium to give the main active species, AO_n, the PW_2-PW_4 peroxo complex of heteropolyphosphatotungstate which catalytically epoxidizes the olefins under homogeneous conditions.

The key of the design and preparation of RSC is that the active component of this catalyst has the ability to bind to the carrier and the reactant. The binding ability between active component and reactant is stronger than that of carrier. Thus, the competing binding occurs when RSC meets with the reactant, the active component combines with the reactant and dissolves from the carrier into the liquid phase to act as a homogeneous catalyst. Therebym it overcomes the lower activity commonly related to supported catalysts. When the reactant is consumed, the active component returns to the carrier surface and forms RSC again.

Under these solvent-free conditions RSC can also catalyze the epoxidation of other olefins (Table 4).

The high selectivities to epoxides (94.7−100%) and conversions based on H_2O_2 (81.8−91.8%) were obtained for all olefins tested apart from cyclohexene. For example, the

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Scheme 1. **Proposed mechanism of the reversible supported catalyst in the epoxidation of olefins**

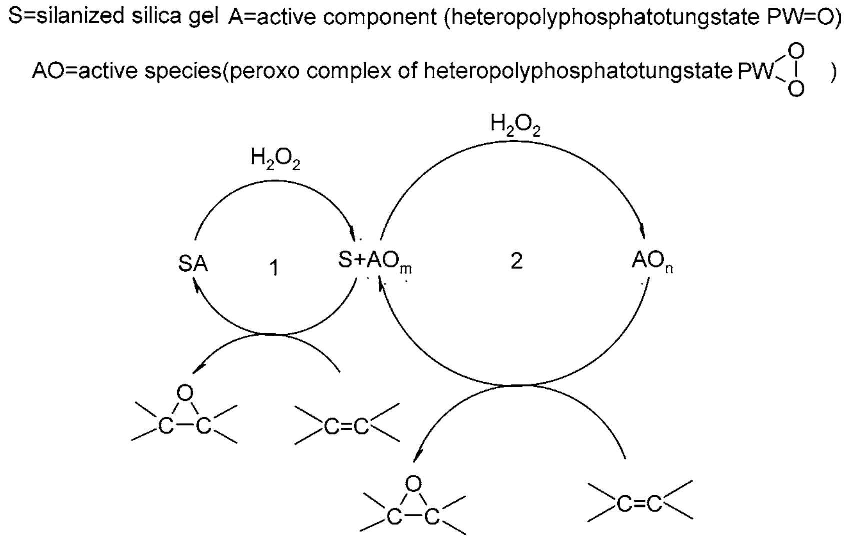

Table 4. **Epoxidation of various olefins by RSC**[a]

olefins	Na_2HPO_4 (g)	temp. (°C)	reaction time (h)	conversion (%)	selectivity (%)
hexene-1	0.030	65	4.0	84.1	94.7
cyclohexene	0.030	55	4.0	87.9	51.8
cyclooctene	–	65	2.5	98.8	98.7
4-vinylcyclohexene	0.024	35	2.5	81.8	98.4[b]
methallyl chloride	0.006	55	6.0	91.0	100

[a] Reaction conditions: The amount of olefins was 10.0 g, olefins/H_2O_2 (50.8 wt %)/fresh catalyst = 1200:200:1 (molar ratio), Na_2HPO_4 was an additive agent. The conversion of olefins was based on H_2O_2, and the selectivity to epoxides was based on olefins. [b] The product is 1,2-epoxy-4-vinylcyclohexane.

selectivity for cyclooctene oxide was 98.7% and conversion based on H_2O_2 of cyclooctene was 98.8% in the catalytic epoxidation of cyclooctene. The epoxidation of hexene-1 gave 94.7% selectivity to hexene oxide and 84.1% conversion based on H_2O_2. In the epoxidation of cyclohexene, only 51.8% of selectivity to cyclohexene oxide was obtained due to the further hydrolysis of cyclohexene oxide formed.

The above results demonstrate that under solvent-free conditions the liquid olefins such as cyclic olefins and terminal olefins, as well as inactive allyl chloride etc., could be epoxized selectively with H_2O_2 in water/oil biphasic system by this RSC.

Conclusions

A new reversible supported catalyst (RSC), quaternary ammonium heteropolyphosphatotungstate supported on silanized silica gel was prepared and used successfully for the epoxidation of allyl chloride with H_2O_2 under solvent-free conditions. In this system the reusable supported catalyst can act as a homogeneous catalyst during the reaction. It is a new immobilizing method for separation and reuse of homogeneous catalysts.

Experimental Section

Macropored microspherical silica gel (40–120 mesh) was obtained from Qingdao Haiyang Chemical Co., Ltd. Other reagents and solvents were obtained from commercial sources and used without purification unless otherwise stated. Infrared spectra were recorded on a NEXUS 470 FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets and prepared by manual grinding using a mortar and pestle. The ^{31}P MAS NMR spectra of solid catalysts with high-power proton decoupling were performed at 161.9 MHz with BBO MAS probe head using 4 mm ZrO_2 rotors and 2.0 s pulse and 2 s repetition time and 2048 scans, with samples spun at 8 kHz and referenced to 85% H_3PO_4. The adsorption–desorption isotherms of N_2 at 77 K were determined with a Quantachrome Instrument. Elemental analysis was performed on a "Carlo Erba" 1140 instrument. The H_2O_2 remaining in the solution was extracted with water and analyzed by iodometric titration. ICP was recorded on an Atom Scan Advantage from Thermo Elemental.

The Preparation of Silanized Silica Gel. A 500-mL Schlenk flask was charged with 10 g of HCl-activated silical gel[22] and sealed by a septum. The flask was heated to 120 °C for 4 h under reduced pressure, and then 50 mL of toluene solution containing 3 g of trimethylchlorosilane was added. The reaction mixture was heated at 120 °C for 2 h, cooled, filtered, and washed with toluene (3 × 30 mL), dried in vacuo to give 9.75 g of product. Surface area is 353.4 m^2/g.

The Preparation of RSC. A suspension of tungstic acid (5.0 g, 20 mmol) in 15 mL of 30% aqueous H_2O_2 was stirred at 60 °C for 30 min and filtered to give a liquid solution. To this solution was added 85% H_3PO_4 (0.58 g, 5 mmol) at room temperature; and then the solution was diluted with 15 mL of water, stirred for 20 min, and to this resulting solution was added with stirring for 5 min 3.23 g (10 mmol) of $[C_{16}H_{33}N(CH_3)_3]Cl$ in 80 mL of dichloromethane. Stirring continued for an additional 30 min. The organic phase was separated, dried over Na_2SO_4, filtered to give a light-yellow solution. To this solution was added 80 mL of dichloroethane, 480 mL of toluene, and 6.24 g of silanized silica gel. The solution was then heated at 65 °C for 2 h, then at 85 °C for 4 h to decompose heteropolyphosphatoperoxotungstate to heteropolyphosphatotungstate for immobilizing on the carrier. The reaction mixture was cooled to room temperature, filtered to give a white solid, and dried in vacuo; surface area is 171 m^2 /g; IR (KBr, cm^{-1}): 3446, 2923, 2853, 1645, 1471, 1096, 943, 846, 811, 758, 742 and 467; ^{31}P MAS NMR (161.9 MHz): −4.4 and −10.4; these data showed the active component on RSC is a mixture of the quaternary ammonium salt of heteropolyphosphatotungstate; the loading amount of active component was 47.6 wt % (to the supported catalyst); the overall composition of the active component is $C_{57}H_{126}N_3$-PW_4O_{16}.

General Procedure for Epoxidation of Allyl Chloride. A 70-mL single-neck flask was charged with 0.8 g (0.2 mmol) of RSC, 0.0062 g of Na_2HPO_4, 1.04 g (15.5 mmol) of 50.8% H_2O_2, 3.0 g of *n*-butyl acetate as the internal standard, and 9.7 g (126.8 mmol) of allyl chloride, The flask was stirred at 65 °C for 2 h, and then the reaction mixture was cooled to room temperature. The allyl chloride and epichlorohydrin were analyzed by GC using the internal standard method.

Acknowledgment

We are grateful to Professor Qingxia Wang for his discussion on the carrier. This work was financially supported by the National Nature Science Foundation of China (No. 20233050) and the Youth Founding of Dalian Government (2005J22JH035).

Received for review May 25, 2006.

OP060108K