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Epoxidation of styrene by anhydrous hydrogen peroxide over boehmite and alumina catalysts with continuous removal of the reaction water

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Abstract

Boehmite and alumina (obtained from the boehmite by its calcination at different temperatures 300–900 °C) are active and stable catalysts for the selective epoxidation of styrene by anhydrous H_2O_2 to styrene oxide with continuous removal of the reaction water. Influence of the catalyst (boehmite) calcination temperature, H_2O_2/styrene ratio and catalyst loading on the styrene conversion and selectivity for styrene oxide, phenyl acetaldehyde, benzaldehyde and benzoic acid in the epoxidation has been investigated. In the presence of water, the catalyst shows very poor activity and selectivity in the epoxidation. The catalyst also catalyses H_2O_2 decomposition and hence has optimum loading for obtaining high-styrene conversion in the epoxidation.
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1. Introduction

Epoxidation of styrene is commercially important reaction for the production styrene oxide, an important organic intermediate. Earlier studies reported for the epoxidation of styrene were based on the use of TS-1 [1–4], Ti–SiO$_2$ [1,5,6], Ti–MCM-41 [4], and TBS-2 and TS-1 [7] catalysts, using different oxidising agents, such as TBHP [5], aqueous H_2O_2 [1,2,6,7], and urea–H_2O_2 adduct [3]. For all the above catalysts, the use of aqueous H_2O_2 resulted in a very poor selectivity for styrene oxide. High-styrene oxide selectivity (≥80%) could be obtained using urea–H_2O_2 adduct [3] and TBHP [5] as the oxidising agents but only at a low-styrene conversion (18 and 10%, respectively). It is, therefore, of great practical interest to find a much better catalyst for the epoxidation of styrene.

Recently, Mandelli et al. [8] have observed a good activity and selectivity for γ-alumina in the epoxidation of limonene, cyclohexene and 1-octene by anhydrous H_2O_2. However, they observed catalyst deactivation due to accumulation of the reaction water; after a certain reaction period (5 h), the catalyst was deactivated. In the present paper, we report the use of boehmite and alumina (obtained from the boehmite by its calcination at different temperatures), which are not only cheaper but also more active/selective catalysts, for the epoxidation of styrene by an anhydrous H_2O_2 with a continuous removal of the reaction water. Because of the reaction water removal, there was little or no deactivation of the catalyst during the epoxidation.

2. Experimental

Boehmite was a commercial material and, before its use, it was heated in a muffle furnace at 100 or 200 °C for 2 h. Alumina catalysts were obtained by calcining the boehmite in a muffle furnace at different temperatures (300, 400, 500,

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600, or 900 °C) for 2 h. All the catalysts were stored in a desicator.

The boehmite and alumina were characterized by powder X-ray diffraction for their crystalline nature, N_2 adsorption at liquid nitrogen temperature for their surface area and also by ammonia chemisorption at 150 °C for their acidity. The chemisorption of ammonia at 150 °C in the present case is defined as the amount of ammonia retained on the catalyst at that temperature when the catalyst (0.5 g) presaturated with ammonia was swept with a pure inert gas (moisture free N_2 at flow rate of 25 ml min^{-1}) for a period of 0.5 h.

The catalytic epoxidation of styrene over boehmite and alumina catalysts was carried out in a magnetically stirred glass reactor (capacity: 25 cm^3) under reflux (bath temperature: 107 °C), using aqueous H_2O_2 (50% H_2O_2 in water) or non-aqueous (anhydrous) H_2O_2 (24% H_2O_2 in ethyl acetate) as an oxidizing agent and moisture-free ethyl acetate as a solvent, with or without continuous removal of the water formed in the reaction. The continuous removal of the reaction water (when anhydrous H_2O_2 was used as the oxidizing agent) was accomplished by using Dean-Stark trap between the reactor and the reflux condenser. The anhydrous H_2O_2 (24% H_2O_2 in ethyl acetate) was obtained by refluxing an aqueous H_2O_2 (50% H_2O_2 in water) with ethyl acetate, and thereby removing the water from the aqueous H_2O_2, using Dean-Stark trap. The amount of H_2O_2 present in the anhydrous H_2O_2–ethyl acetate or in the reaction mixture after the epoxidation reaction was determined by decomposing the H_2O_2 by MnO_2 and measuring the amount of oxygen produced in the H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5O_2$) quantitatively, using a constant pressure gas collector [9]. The unconverted styrene and reaction products (viz. styrene oxide, phenyl acetaldehyde, benzaldehyde and benzoic acid) were analysed by gas chromatography, using a SE-30 (on chromosorb-W) column and a flame ionization detector. The conversion, product selectivity and product yield were calculated as follows: conversion (%) = (moles of reactant converted × 100) ÷ (moles of reactant in feed); product selectivity (%) = (moles of product formed) × 100) ÷ (moles of reactant converted); and product yield (%) = (percentage of reactant converted to a particular product) or [conversion (%) × product selectivity (%) ÷ 100].

The decomposition of H_2O_2 during the epoxidation was studied by measuring quantitatively the amount of oxygen evolved using the gas collector. Before collecting, the reactor effluent gas was bubbled through a concentrated NaOH solution to absorb CO_2, if any, present in the gas.

3. Results and discussion

3.1. Catalyst characterization

The catalysts obtained by the calcination of boehmite at different temperatures are characterized for their crystalline nature, surface area, and ammonia chemisorbed at 150 °C (Table 1). Both the surface area and ammonia chemisorption are passed through a maximum with increase in the calcination temperature. The highest surface area and ammonia chemisorption are observed for the catalyst obtained by the calcination at 400 °C.

3.2. Effect of water on the epoxidation

Results showing a strong influence of the presence of water from the aqueous H_2O_2 or the water formed in the reaction on the styrene conversion and product selectivity in the epoxidation over the boehmite (preheated at 200 °C for 2 h) catalyst are presented in Fig. 1.

When aqueous H_2O_2 was used as the oxidizing agent, the styrene conversion was very low and the selectivity for both the styrene oxide and phenyl acetaldehyde was also very poor (Fig. 1a). Whereas, the use of anhydrous H_2O_2 without the continuous removal of the reaction water has resulted in a significant increase in both the conversion of styrene and selectivity for styrene oxide and phenyl acetaldehyde (Fig. 1b). The conversion and the selectivity, particularly for styrene oxide, are further increased markedly when the anhydrous H_2O_2 with the continuous removal of the reaction water formed in the reaction was employed for the epoxidation (Fig. 1c). All the further runs on the epoxidation were carried out using the anhydrous H_2O_2 as the oxidizing agent with the continuous removal of the reaction water during the epoxidation.

The catalyst could be reused after filtering and washing with ethyl acetate without loosing significantly its original epoxidation activity.

Table 1
Data on characterization of catalysts obtained by calcination of boehmite at different temperatures

Calcination temperature (°C)	Crystalline phases	Surface area (m^2 g^{-1})	Ammonia chemisorbed at 150 °C	
			(mmol g^{-1})	μmol m^2
200	Boehmite	197	0.25	1.27
400[a]	Bohemite (major) γ–Al_2O_3 (minor)	210	0.47	2.24
500	γ–Al_2O_3 (major)	203	0.38	1.87
600	γ–Al_2O_3 (major)	164	0.23	1.40
900	α–Al_2O_3 and γ–Al_2O_3	120	0.11	0.92

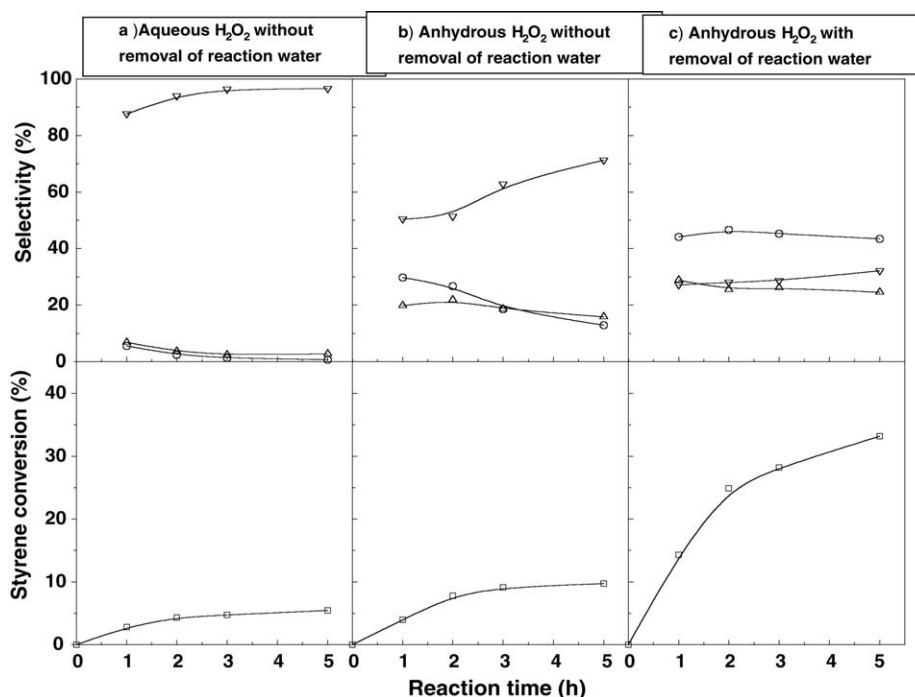[a] The material obtained by calcination of boehmite at 400 °C is less crystalline.

Fig. 1. Epoxidation of styrene over boehmite (dried at 200 °C) by (a) aqueous H_2O_2 (50% H_2O_2 in water), (b) anhydrous H_2O_2 without the continuous removal of the reaction water, (c) anhydrous H_2O_2 with the continuous removal of the reaction water [reaction mixture = 20 mmol styrene + 40 mmol H_2O_2 + 9 ml ethyl acetate or water + 0.4 g catalyst] [selectivity for styrene oxide (○), phenyl acetaldehyde (Δ) and benzaldehyde and benzoic acid (▽)].

3.3. Effect of catalyst calcination temperature on the epoxidation

Results in Fig. 2 show the effect of calcination temperature of boehmite on the conversion and product selectivity in the epoxidation over the catalyst (obtained in the calcination of bohemite) for two different reaction periods (1 and 5 h).

The results (Fig. 2) show that when calcination temperature is increased, both the styrene conversion and the selectivity for styrene oxide are passed through a maximum and that for phenyl acetaldehyde is passed through a minimum. The selectivity for benzaldehyde and benzoic acid also passed through a minimum. The best performance is shown by the catalyst obtained at the calcination temperature of 600 °C (Fig. 2b). This catalyst also could be reused, after filtering and washing with ethyl acetate, for the epoxidation without a significant loss in its original activity.

3.4. Effect of H_2O_2/styrene ratio on the epoxidation

Results showing the influence of H_2O_2/styrene mole ratio on the conversion and product selectivity in the styrene epoxidation over the catalyst (obtained by the calcination of boehmite at 400 °C) are presented in Fig. 3.

When H_2O_2/styrene ratio was increased from 0 to 2.0, the styrene conversion was increased markedly depending upon the ratio but relatively there was only a small effect on the product selectivity.

3.5. Effect of catalyst loading on the epoxidation and H_2O_2 decomposition

Fig. 4 shows the influence of loading of the catalyst (obtained from the calcination of boehmite at 600 °C) on the conversion and product selectivity in the epoxidation.

The increase in the catalyst loading from 16.7 to 66.8 g dm^{-3} resulted an increase in the conversion at the lower catalyst loadings but a decrease in the conversion at the higher catalyst loadings. However, the selectivity for styrene oxide is increased markedly and that for phenyl acetaldehyde or benzaldehyde and benzoic acid is decreased with increasing the catalyst loading.

The dependence on the catalyst loading of the extent of H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5O_2$) is shown in Fig. 5. The H_2O_2 decomposition is increased markedly with increasing the catalyst loading.

3.6. General discussion

Results in Fig. 1 clearly show that the boehmite catalyst is deactivated due to the presence of water in the reaction mixture. Sheldon and co-workers [8] have also observed deactivation of alumina by the reaction water in the epoxidation of cyclic and linear olefinic compounds even though anhydrous H_2O_2 was used as the oxidizing agent. Thus to avoid the catalyst deactivation, it is essential to remove the reaction water as soon as it is formed in the epoxidation reaction over boehmite or alumina catalysts.
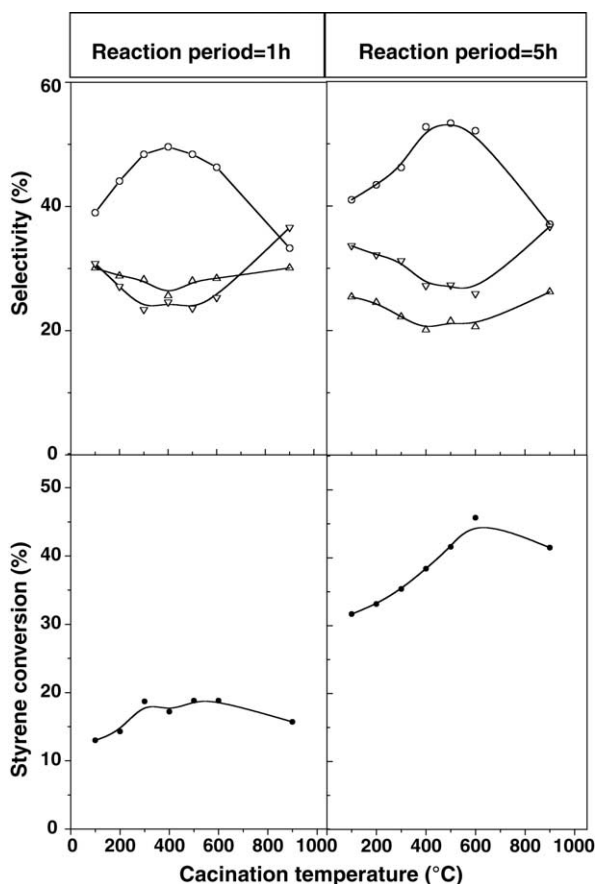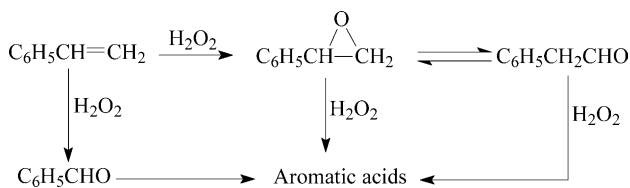
Fig. 2. Effect of catalyst calcination temperature on the epoxidation (with the continuous removal of the reaction water) over boehmite at two different reaction periods [reaction mixture = 20 mmol styrene + 40 mmol H_2O_2 + 9 ml ethyl acetate + 0.4 g catalyst] [selectivity for styrene oxide (○), phenyl acetaldehyde (△) and benzaldehyde and benzoic acid (▽)].

Fig. 3. Effect of H_2O_2/styrene ration on the epoxidation (with the continuous removal of the reaction water) over alumina (obtained by calcining boehmite at 400 °C for 2 h) at to different reaction periods [reaction mixture = 20 mmol styrene + 9 ml ethyl acetate + 0.4 g catalyst + 0–40 mmol H_2O_2] [selectivity for styrene oxide (○), phenyl acetaldehyde (△) and benzaldehyde and benzoic acid (▽)].

Both the boehmite and alumina catalysts show good activity and selectivity in the epoxidation of styrene by anhydrous H_2O_2 with the continuous removal of the reaction water (Figs. 1c, 2 and 3). However, the catalyst (γ-alumina) derived from boehmite by its calcination at 600 °C showed the best performance (both the high activity and selectivity) in the styrene-to-styrene oxide epoxidation. Based on the product formed, a following complex reaction scheme for the styrene epoxidation is proposed.

The surface area and acidity (ammonia chemisorbed at 150 °C per unit mass of surface) of the catalyst are passed through maximum with increasing the catalyst calcination temperature (Table 1). Both the styrene conversion activity and select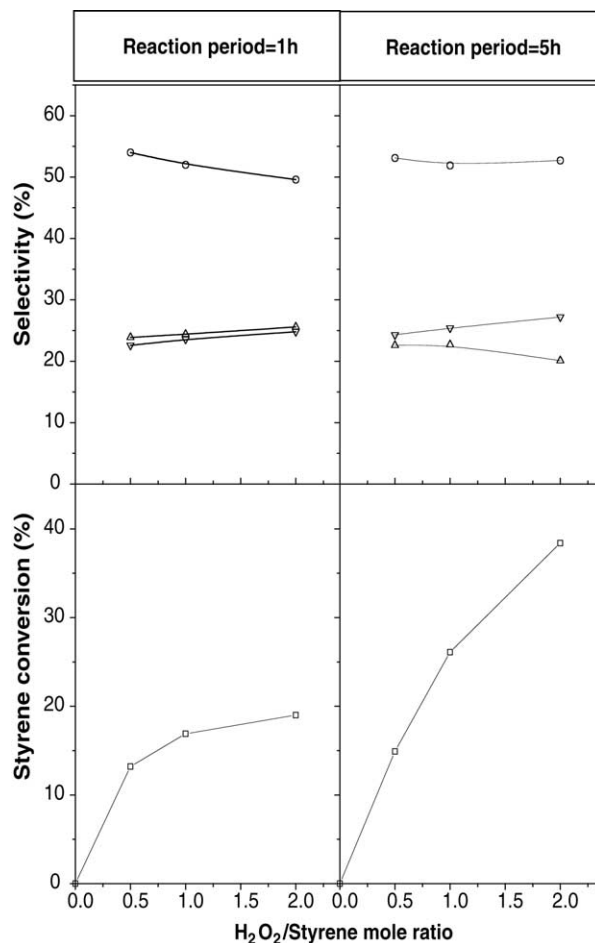ivity for styrene oxide are also passed through a maximum (Fig. 2). The maximum in the two cases, however, does not occur at the same calcination temperature. Nevertheless, there exists some sort of correlation between the surface properties and the catalytic activity/selectivity.

The observed variation of the styrene conversion with the catalyst loading (Fig. 4) is unusual. At the lower catalyst loadings, the increase in the styrene conversion with the catalyst loading is due to the increase of styrene epoxidation rate. However, at the higher catalyst loadings, the H_2O_2 decomposition rate during the epoxidation is much higher than that at lower loadings (Fig. 5) and hence sufficient H_2O_2 is not available for the epoxidation, which ultimately leads to a lower styrene conversion at the higher catalyst loadings. Because of the simultaneously occurring H_2O_2 decomposition and epoxidation reactions, the catalyst loading has an optimum value for obtaining the highest styrene conversion in the epoxidation.

In the epoxidation of styrene by anhydrous H_2O_2 over boehmite or alumina catalyst, >Al–O–OH species, similar to
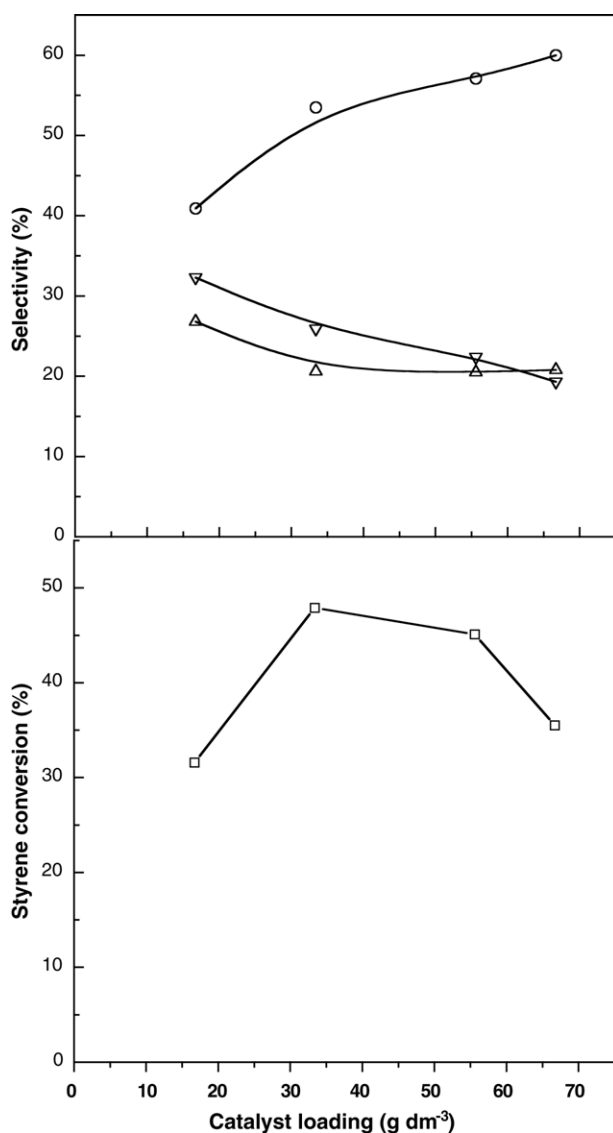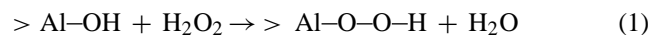
Fig. 4. Effect of catalyst loading on the epoxidation (with the continuous removal of the reaction water) over alumina (obtained by calcination of the boehmite at 600 °C for 2 h) [reaction mixture = 20 mmol styrene + 40 mmol H_2O_2 + 9 ml ethyl acetate + 0.0–0.8 g catalyst and reaction period = 5 h] [selectivity for styrene oxide (○), phenyl acetaldehyde (△) and benzaldehyde and benzoic acid (▽)].

that proposed earlier by Sheldon and co-workers [8] for the epoxidation of linear or cyclic olefins, seem to be responsible for the styrene epoxidation. These species are expected to be formed by the reaction between the surface hydroxyl groups of the catalyst and the H_2O_2, as follow:

$$> Al–OH + H_2O_2 \rightarrow > Al–O–O–H + H_2O \qquad (1)$$

The presence of water is expected to suppress the formation of Al–O–O–H species, which is consistent with the observations made in the present case. In the presence of water, the Lewis acid sites of the catalyst are expected to be blocked by the strongly adsorbed water molecules, which may also hinder the formation of Al–O–O–H species.
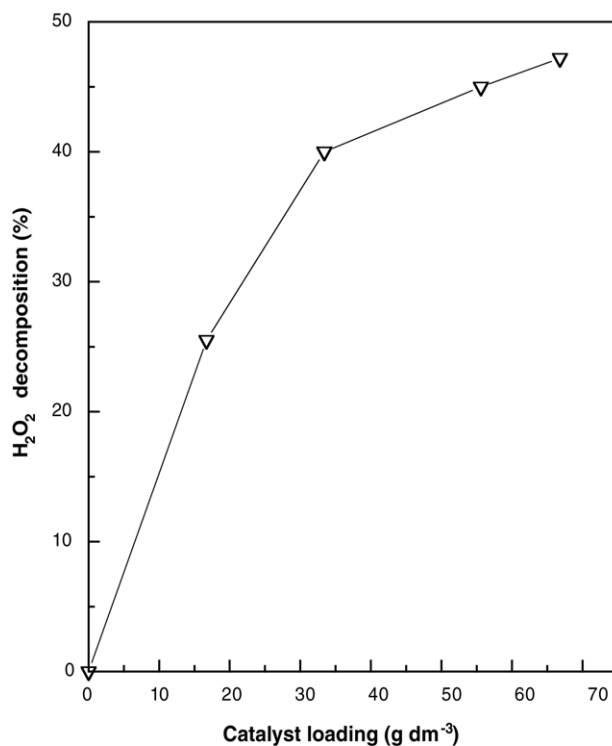

Fig. 5. Effect of catalyst loading on the decomposition of H_2O_2 during the epoxidation (with the continuous removal of the reaction water) over alumina (obtained by calcination of the boehmite at 600 °C for 2 h) [reaction mixture = 20 mmol styrene + 40 mmol H_2O_2 + 9 ml ethyl acetate + 0.0–0.8 g catalyst and reaction period = 5h].

4. Conclusions

Both the boehmite and alumina obtained by calcination of boehmite at different temperatures (200–900 °C) show good activity and selectivity for the epoxidation of styrene by anhydrous H_2O_2 with continuous removal of the reaction water. In the presence of water, the catalyst shows very poor activity in the epoxidation. The alumina (obtained by the calcination of boehmite at 600 °C) catalyst showed the best performance. The catalyst also catalyses the decomposition of H_2O_2 simultaneously with the epoxidation and hence has an optimum loading for obtaining high-styrene conversion activity in the epoxidation process.

Acknowledgement

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