Epoxidation of propylene by air over modified silver catalyst

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Epoxidation of C_3H_6 to C_3H_6O by air was studied over a silver catalyst modified with alkali or alkaline earth chloride salts. The catalyst preparation factors and the operational conditions could affect obviously the catalytic epoxidation property of the silver catalyst. It was shown that, as a promoter of the silver catalyst, NaCl or $BaCl_2$ is more suitable than LiCl or NH_4Cl. The loading of NaCl should be controlled at about 3.8 wt%. Using a feed gas of 10% C_3H_6/air at a space velocity of 1.75×10^4 h^{-1}, 18.6% C_3H_6 conversion and 33.4% selectivity to C_3H_6O were obtained at 350 °C. Using a feed gas of 5% C_3H_6/air at a space velocity of 2.4×10^4 h^{-1}, 54.0% C_3H_6 conversion and 26.3% selectivity to C_3H_6O were obtained at 390 °C.

Keywords: epoxidation of propylene, modified silver catalyst, preparation of catalyst

1. Introduction

The epoxidation of ethylene over silver catalysts has had significant industrial application for many years and has been studied extensively [1,2]. However, earlier attempts to produce propylene oxide (PO) with the same catalysts have failed, due to a very low activity and selectivity to PO [3–8]. Like in the oxidation of ethylene, there are two competitive reactions in the oxidation of propylene:

(1) Partial oxidation:

$$C_3H_6 + (1/2)O_2 \rightarrow C_3H_6O \quad \Delta G = -88.49\ \text{kJ/mol}$$

(2) Total oxidation:

$$C_3H_6 + (9/2)O_2 \rightarrow 3CO_2 + 3H_2O$$
$$\Delta G = -1957.43\ \text{kJ/mol}$$

It can be seen that the total oxidation is more exothermic than the partial oxidation in the view of thermodynamics. During the study of the epoxidation of ethylene over silver catalysts, years of continuing research and development have led to an increase in the selectivity to ethylene oxide from $<$70% in the late 1960s to about 80% in the late 1980s [9]. Now plants are already operating with a selectivity $>$80% and in the laboratory results close to 90% have been obtained [10]. It was not until recently that a high efficient catalyst for the epoxidation of ethylene has been obtained by two methods. One was a modification of promoters in the silver catalyst and the other, an improvement of the operational conditions. Seeing the situation of the ethylene oxide catalyst mentioned above, it is also possible that a higher efficient catalyst for the epoxidation of propylene will emerge from many fruitful studies. When this paper was completed, the ARCO Chemical scientists reported that, over supported silver containing an inorganic chloride, potassium and other promoters, at 21–25% conversion of propylene 45% selectivity to propylene oxide was obtained at pressures ranging from 30–100 psig [11]. When using a feedstream containing 5 ppm NO, 5 ppm EtCl and 10 mol% CO_2, 60–64% selectivity to propylene oxide was obtained, but the conversion of propylene was only 1.5–2.5%.

In this paper, the preparation of silver catalysts containing alkali or alkaline earth chloride salts for the epoxidation of propylene by air has been studied. New results have been obtained, which is in favor of preparing the fine performance catalyst producing PO in future.

2. Experimental

An unsupported silver pellet was used as the catalyst in order to avoid interaction of silver with the support. The catalyst was prepared as follows: a precipitate was produced by pumping a potassium hydroxide aqueous solution to a mixed aqueous solution of silver nitrate and dextrose stirred by electromagnetics at 20–60 °C. After aging in the matrix solution at 75 °C for 1 h, then filtrating and washing free of alkali with distilled water, the silver precipitate was slurried in the chloride salt solution. While the slurry was stirred up and heated, the water in the slurry was vaporized. Then the catalyst powder was dried at 120 °C for 10 h, and compressed into 2.0 cm discs and broken to 20–40 mesh.

The catalytic epoxidation of propylene was performed in a microreactor GC system. The size of the quartz glass fixed-bed reactor is $\varnothing 20 \times 600$ mm, in which 2.0 g catalyst was filled. Experiments were carried out at a space velocity of 1.75×10^4 h^{-1} and 0.1 MPa absolute pressure. Air was used as an oxidant. The ratio of propylene to air in the feedstock gas was 1 : 9 with no nitrogen oxide species, alkyl halide or carbon dioxide.

The components in the feedstock gases and exit gases were analyzed using a 102G gas chromatograph, in which a thermal conductance detector (TCD) and $\varnothing 3$ mm $\times$ 2 m

GDX-403 packed columns were used. Hydrogen was used as the carrier gas. The method of carbon balances was used to verify the consumption of propylene in the reaction. Carbon balance was described as $(n_{\mathrm{f}}–n_{\mathrm{e}})/n_{\mathrm{f}}$ (n_{f}, total mole of carbon in the feed gas; n_{e}, total mole of carbon in the exit gas). In this study, the carbon balance was $<\pm4\%$.

3. Results and discussion

3.1. Effect of alkali or alkaline earth chloride salts promoter on catalytic activity

The influence of a chloride salt promoter on the efficiency of the catalyst is shown in table 1. It shows that the cation in chloride salt has a great influence on the efficiency of the catalyst. Using sodium chloride or barium chloride as a promoter, the catalyst exhibits a higher epoxidation activity and selectivity. At 350 °C, the conversion of propylene and selectivity to PO over Ag-NaCl are 18.6 and 33.4%, respectively. Over the Ag-LiCl catalyst, the selectivity to PO is 27.5%, but the conversion of propylene is 8.2% only. Using NH_4Cl as a promoter, the catalyst gives 35% selectivity to PO at 250 °C and its selectivity decreases rapidly with increasing temperature, at >310 °C the selectivity to PO is near to zero. The reason is possibly that NH_4Cl can sublime at a higher temperature (the subliming point of NH_4Cl is about 350 °C), which makes the activity of the catalyst drop. From the results in table 1, we can see, as a promoter of the silver catalyst for the epoxidation of propylene, NaCl is more suitable than other chloride salts.

3.2. NaCl as a promoter of silver catalyst

The effect of the loading of NaCl on the efficiency of the catalyst at 350 °C can be derived from figure 1. It shows that the activity and selectivity of the catalyst is strongly influenced by the loading of NaCl. When the silver catalyst does not contain NaCl, its activity is high, but its selectivity is nearly zero. With increasing NaCl content, the conversion of propylene declines from 18 to 12.1%, then rises to the highest point (25%), while the selectivity rises obviously from zero to the highest point (33.4%). This result indicates that the presence of NaCl can inhibit the deep oxidation of propylene effectively. When the loading of NaCl is 3.8 wt%, the selectivity to PO and conversion of propylene reach 33.4 and 18.6%, respectively. However, an excessive addition of NaCl may result in a drop of the selectivity and conversion. When the catalyst contains 7.4 wt% of NaCl, the selectivity to PO decreases to zero nearly.

Table 1
Effect of the promoter on the efficiency of silver catalyst.

Catalyst[a]		Temperature (°C)				
		250	280	310	350	390
Ag-NaCl	conversion of C_3H_6 (%)	2.2	4.2	7.8	18.6	29.9
	selectivity to PO (%)	51.6	34.5	25.0	33.4	11.9
Ag-$BaCl_2$	conversion of C_3H_6 (%)	2.2	3.4	5.3	24.6	30.6
	selectivity to PO (%)	0	15.5	19.0	26.1	14.7
Ag-LiCl	conversion of C_3H_6 (%)	0	2.3	5.1	8.2	14.1
	selectivity to PO (%)	0	0	12.1	27.5	18.0
Ag-NH_4Cl	conversion of C_3H_6 (%)	0.8	1.2	2.1	3.2	4.6
	selectivity to PO (%)	35.8	17.1	0	0	0

[a] The loading of Cl^- in the catalyst is kept unchangeable and the loading of NaCl in Ag-NaCl is 3.8 wt%.

3.3. Effect of the precipitation temperature of catalyst on catalytic activity

The catalysts Ag-C-1, Ag-C-2 and Ag-C-3 were prepared by precipitation at 20, 40 and 60 °C, respectively, then modified with NaCl (3.8 wt%). Their catalytic activities for the epoxidation of propylene are shown in figure 2. The results show that the precipitation temperature (PT) is an important influence factor to the properties of catalyst. The conversion of propylene over Ag-C-1 precipitated at 20 °C is lower than that over the other catalysts, but the selectivity to PO over Ag-C-1 is the highest (33.4% at 350 °C) among the three catalysts.

In view of a higher yield and productivity of PO, the epoxidation of propylene was operated in the mixture gases of 5% C_3H_6/air at a space velocity 2.4×10^4 h^{-1}. The results at 390 °C are shown in table 2. Over the Ag-C-1 (PT 20 °C) catalyst, 75% conversion of C_3H_6 and 20.2% selectivity to PO have been obtained. Over Ag-C-2 (PT 40 °C), 54% conversion of C_3H_6 and 26.3% selectivity to PO have been obtained. In the two situations mentioned above, the yield of PO is about 15%. This result has not been reported in any literature. In the previous works, when a higher selectivity (e.g., 30–45%) to PO was obtained, the conversion of propylene was very low (<2%); or the conversion of propylene was higher and the selectivity was very low [12,13].

3.4. Study on the operation conditions

3.4.1. The space velocity (SV)

The results in figure 3 show that, with increasing of SV, the conversion of propylene decreases and the selectivity

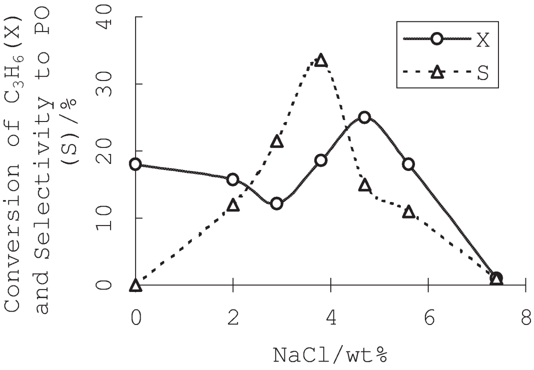

Figure 1. Effect of the loading of NaCl on the efficiency of the catalyst at 350 °C.

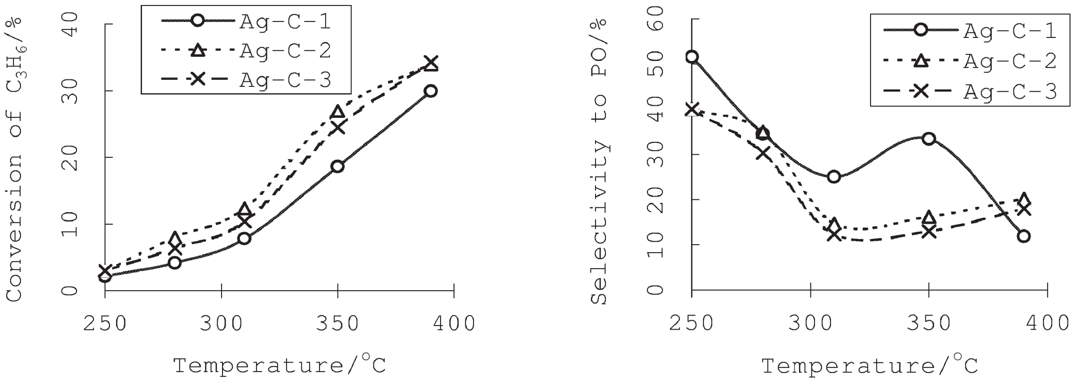

Figure 2. Effect of the precipitation temperature on the performance of catalyst at 350 °C.

Table 2
Effect of the precipitation temperature on the performance of catalyst.

Catalyst	Precipitation temperature (°C)	Conversion of C_3H_6 (%)	Selectivity to PO (%)
Ag-C-l	20	75.0	20.2
Ag-C-2	40	54.0	26.3
Ag-C-3	60	44.1	16.8

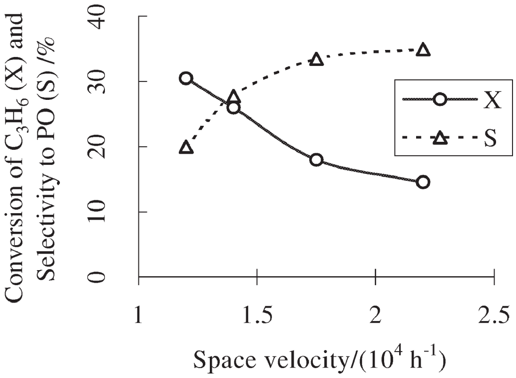

Figure 3. Effect of the space velocity on the catalytic oxidation of propylene.

to PO increases. As PO is an intermediate compound during the oxidation of propylene, a shorter contact time (a higher SV) can lead to the reactant gases leaving through the catalyst bed fast, thereby inhibiting the deep oxidation of propylene and thus yielding product PO. Simultaneously, a higher SV can lead to declination of the conversion of propylene. The suitable SV is about 1.8×10^4 h^{-1}.

3.4.2. The composition in feedstock gas

From the results in figure 4, it can be seen that at <70% air in the feed gas, the activity and selectivity of the catalyst do not vary much with the change of air content. As air content in the feed gas is >70%, the activity and selectivity increase rapidly with increasing air content. When air content in the feed gas is 90%, the conversion of propylene and selectivity to PO reach 18.6 and 33.4%, respectively. When the air content reaches 95%, the selectivity drops suddenly to 10%. This shows that, in order to maintain a high activity and selectivity of the catalyst, the air content in the reactant gas should be controlled at ~90%. That is to say, the volume ratio of propylene to oxygen should be selected at about 1 : 2, which complies with Portela's results [14].

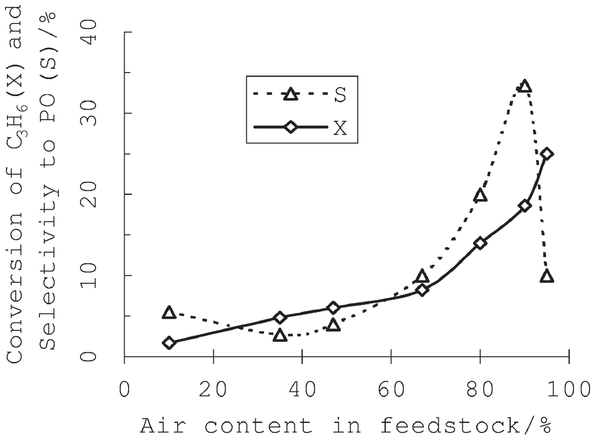

Figure 4. Effect of the air content in feedstock on the catalytic epoxidation of propylene.

4. Conclusions

For the silver catalyst used in the epoxidation of C_3H_6 to C_3H_6O by air, the catalyst preparation factors and the operational conditions could affect obviously the catalytic epoxidation property. In the silver catalyst, NaCl or $BaCl_2$ is more suitable as a promoter than LiCl or NH_4Cl. The loading of NaCl should be controlled at about 3.8 wt%. Using the unsupported silver catalyst modified with NaCl and a feedstream of 5–10% C_3H_6/air at a higher space velocity of $1.75–2.4 \times 10^4$ h^{-1}, a high conversion of propylene and selectivity to C_3H_6O were obtained.

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