

Propylene production by co-reaction of ethylene and chloromethane over SAPO-34

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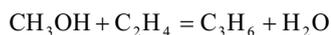
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ABSTRACT

The co-reaction of chloromethane and ethylene was studied over H-SAPO-34 catalyst. Higher propylene selectivity and higher chloromethane conversion than those in the case of sole chloromethane or ethylene feed were observed. The effect of co-feeding ethylene with chloromethane on the shortening of induction period was also investigated. It is suggested that the methylation of ethylene plays an important role in the co-reaction system. The investigation of reaction conditions on reactant conversion and product distribution showed that the conversions of the reactants increased with increasing contact time and reaction temperature, and that the selectivity to propylene increased with decreasing contact time.

1. INTRODUCTION

Propylene is a versatile building block for the production of a variety of important monomers, polymers and intermediates. The well-known propylene derivatives include polypropylene, acrylonitrile, propylene oxide, cumene/phenol, oxo alcohols, acrylic acid, isopropyl alcohol and oligomers, etc. The global propylene demand is recently growing faster than that for ethylene and expected to reach more than 91 million tons by 2010 at a growth rate of 4.7%/year [1, 2]. As well known, the primary sources of propylene have been as a by-product of ethylene production in steam crackers and from refinery FCC streams. The rapid increase of the propylene demand has aroused the interests of developing new processes of propylene production. Besides the improvement of the conventional technology for higher propylene yield, new technologies, such as propane dehydrogenation, olefins metathesis [3, 4], catalytic cracking of higher alkenes [5], MTO and MTP - a methanol-to-olefins process optimized for propylene yield [6], have been developed. Among the novel technologies, those to produce more propylene at the expense of ethylene may be more practical or economically advantageous, depending on the demand and alternative value for ethylene versus propylene. Recently, Svelle and co-workers observed the formation of propylene from the methylation of ethylene by methanol over H-ZSM-5 with isotopic labeling technology [7].



This type of reaction may provide a practical route to the selective production of propylene from the co-feeding of ethylene and methanol, the advantage of which lies in that the added atom of carbon chain comes from methanol that is a relatively cheap feedstock.

In the present study, chloromethane was used as the co-feed with ethylene. As well known, methanol is produced from methane/coal in an indirect pathway via syngas as intermediate. Another methylation agent, chloromethane could be directly produced from methane through oxyhydrochlorination over a supported CuCl catalyst [8, 9]. In addition, the co-reaction of chloromethane and ethylene might be different from that of methanol and ethylene, in regard to the different chemical properties between chloromethane and methanol. H-SAPO-34 was used as catalyst, the small pores of which were expected to decline the formation of higher olefins, such as butene and pentene, caused by the further methylation of propylene.

2. EXPERIMENTAL

SAPO-34 was synthesized by a hydrothermal method according to the literature [10] from a gel composition of 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.1 SiO₂ : 3 R : 50 H₂O, where R is triethylamine as the template. Pseudoboehmite, orthophosphoric acid (85 wt. %) and colloidal silica were used as the sources of aluminum, phosphorus and silicon, respectively. The resulting gel was crystallized under autogenous pressure at 200 °C for 24 h. The product was filtrated, washed, dried at 120 °C for 12 h, and calcined at 550 °C for 3 h. The catalysts were prepared by binding the calcined H-SAPO-34 with silica.

The catalytic reactions were performed in a fixed-bed stainless steel tubular reactor (9mm i.d.) at atmospheric pressure. The feeds contained chloromethane and ethylene with helium as dilute gas. The flow rate of chloromethane was fixed. To keep the contact time constant, the flow rate of helium was varied at different ethylene proportions. For comparison, sole chloromethane or ethylene was fed in some reaction runs. The products were analyzed using on-line gas chromatography (Varian GC3800) equipped with a FID detector and a PorapLOT Q-HT capillary column. In all the reaction runs with chloromethane, HCl was observed in the products as a balance of Cl from chloromethane (not listed in the product distribution).

3. RESULTS AND DISCUSSION

3.1. The effect of ethylene proportion

Table 1 presents the reaction results of the chloromethane/ethylene mixture of different proportions. Over SAPO-34, chloromethane can be converted to HCl and hydrocarbons, and the hydrocarbon products include ethylene, propylene, C1-C3 alkanes and C4+ hydrocarbons [11, 12]. Under the present reaction conditions, when sole chloromethane was fed, the conversion was 11.3 %, and a propylene selectivity of 48.1 % was obtained. Co-feeding ethylene and chloromethane resulted in sharp increase in chloromethane conversion. Meanwhile, obvious ethylene consumption was observed in the case of co-feeding, especially when the ethylene proportion was higher in the feed (91.3% in the feed mixture), though ethylene was one of the products when only chloromethane was fed, as reported by other researchers [13, 14]. In comparison, the conversion of sole ethylene over SAPO-34 was rather low (1.48%), as the reaction temperature was not very high (723K). Besides, the propylene selectivity, ranging from 61.3% to 67.1% in the case of co-feeding, was obtained, which was higher than that of either chloromethane or ethylene conversion on the same catalyst.

Table 1
Effect of C₂H₄ proportion in the feed

Inlet / C-mol %					
C ₂ H ₄	100	91.3	85.6	74.8	0
CH ₃ Cl	0	8.7	14.4	25.2	100
Outlet / C-mol %					
C ₂ H ₄	98.5	87.0	84.3	75.0	1.33
C ₃ H ₆	0.89	5.39	4.94	6.09	5.43
C ₄ ⁺	0.49	3.01	2.32	2.72	3.86
CH ₃ Cl	-	3.01	8.14	15.9	88.7
C ₁ ⁰ -C ₃ ⁰	0.07	0.26	0.20	0.17	0.35
Coke	0.04	0.13	0.11	0.11	0.32
C ₂ H ₄ conv. %	1.48	4.65	1.52	-0.27	-
CH ₃ Cl conv. %	-	52.1	43.4	36.9	11.3
C ₃ H ₆ Sel. C-mol%	60.3	61.3	65.3	67.1	48.1

*T=723K, CT = 0.78s (for chloromethane), TOS = 6min

3.2. The effect of the shortening of induction period

An induction period was observed in the conversion of chloromethane over SAPO-34 [12], and it was also found that the induction period might be shortened by adding a small amount of propylene to the reactor before admission of the chloromethane feed. To make it clear whether the increase of chloromethane conversion observed in the present study was caused by the shortening of the induction period owing to the addition of ethylene, three reaction runs successively with chloromethane/ethylene mixture, chloromethane and ethylene, were carried out, respectively, on the same catalyst sample. The results are displayed in Table 2.

Table 2
Results of the successive reactions on the same catalyst sample

Run No.	1	2	3
Reaction Time	6min.	2min.	2min.
Inlet / C-mol %			
C ₂ H ₄	91.3	0	100
CH ₃ Cl	8.7	100	0
Outlet / C-mol %			
C ₂ H ₄	87.0	6.39	97.4
C ₃ H ₆	5.39	8.67	1.60
C ₄ ⁺	3.01	5.16	0.79
CH ₃ Cl	3.01	78.8	-
C ₁ ⁰ -C ₃ ⁰	0.26	0.49	0.11
Coke	0.13	0.44	0.06
C ₂ H ₄ conv. %	4.65	-	2.56
CH ₃ Cl conv. %	52.1	21.1	-
C ₃ H ₆ Sel. C-mol%	61.3	41.0	62.5

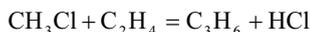
*T=723K, CT = 0.78s

After the reaction of co-feeding chloromethane and ethylene for 6 minutes (Run 1), the catalyst bed was blown with helium, and then the chloromethane was fed (Run 2). The effluent was analyzed by on-line gas chromatography after 2 minutes of reaction. Though the conversion of chloromethane was higher (21.1% in table 2) than that over fresh catalyst (11.3%), it was much lower than that obtained in the co-reaction of ethylene and chloromethane as shown in table 1.

Especially, the propylene selectivity was very close to that of the chloromethane conversion without the pre-reaction, and much lower than that for the co-feeding. This implies that, although the induction period was shortened by co-feeding ethylene, it was not the dominant cause for the increase of chloromethane conversion.

After the reaction Run 2 (lasted for 2 minutes) and the following helium blowing, the conversion of ethylene was examined on the same catalyst sample (Run 3). The products including propylene, C1-C3 alkanes and C4+ hydrocarbons was analyzed by on-line gas chromatography at 2 minutes on stream. The selectivity for propylene was 62.5 %, slightly higher than the result obtained on the fresh catalyst. The ethylene conversion increased to some extent when compared with the result on fresh catalyst, but it was still low with respect to that obtained in the co-reaction of ethylene and chloromethane.

Based on the fact of our experiments and the information from the literature, it is suggested that the methylation of ethylene with chloromethane plays a great role in the enhanced conversion and propylene selectivity.



3.3. The effects of reaction conditions

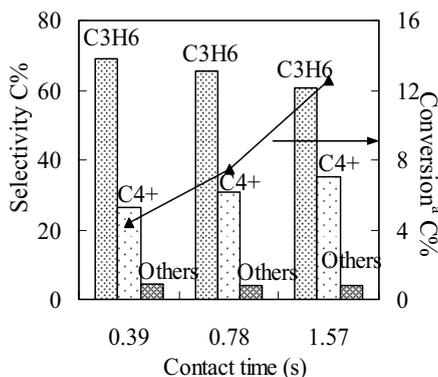


Fig. 1. Product selectivity versus contact time
*C₂H₄ (C %) = 87.5%, T = 723K, TOS = 6min
^a calculated by dividing all C atoms in the products by the total number of C atoms in the feed

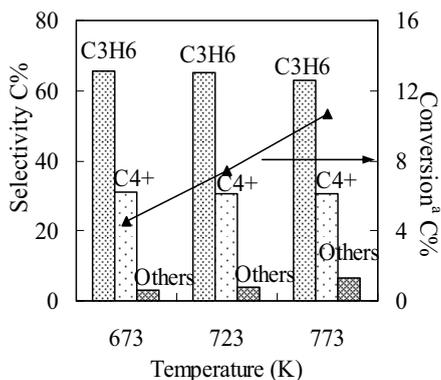


Fig. 2. Product selectivity versus temperature
*C₂H₄ (C %) = 87.5%, CT = 0.78s, TOS = 6min
^a calculated by dividing all C atoms in the products by the total number of C atoms in the feed

The effects of reaction conditions, such as temperature and contact time (CT) were investigated. As shown in Fig. 1, the propylene selectivity decreased with increasing CT, while C₄⁺ hydrocarbon products increased. This increase of higher hydrocarbons might be

caused by the enhancement of further methylation of propylene. The overall conversion (obtained by dividing all C atoms in the products by the total number of C atoms in the feed) increased with prolonging contact time.

The influence of reaction temperature is illustrated in Fig. 2. The overall conversion increased with increasing reaction temperature. But the selectivity of propylene varied very little with the temperature. In fact, in the range from 673K to 723K, the propylene selectivity was nearly constant.

In addition, the selectivity of paraffins and coke (defined as 'others') at 773K increased nearly one fold compared with which at 723K, as depicted in Fig. 2, which implies that the hydrogen transfer and coke formation on the catalyst became faster as reaction temperature increased.

4. CONCLUSION

The co-feeding of chloromethane and ethylene increases the conversion of both component and the propylene selectivity, when compared with that in the case of either sole chloromethane or ethylene feed. From the control experiments, it is concluded that the methylation of ethylene plays an important role in the co-reaction system, even though adding ethylene does shorten the induction period.

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