Effects of promoter and moisture on the deactivation of FSO₃H catalyst in the synthesis of HFC-152a by hydrofluorination of acetylene

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Abstract−The effects of promoter type and moisture on the catalytic activity of fluorosulfonic acid (FSO₃H) as a liquid catalyst for the synthesis of HFC-152a by the hydrofluorination of acetylene were investigated. The catalyst containing SnCl₄ as a promoter had a long catalyst lifetime compared to that without any promoter. It was also found that the composition of HFC-152a can be maintained at 100% for a long time by the control of the moisture content.

Key words: HFC-152a, Additives, Liquid FSO₃H Catalyst, Acetylene, Hydrofluorination

INTRODUCTION

Chlorofluorocarbons (CFCs) have been widely used in refrigerant, foam-blowing and aerosol-propellant applications. However, the decomposition of CFCs at the stratosphere induces releasing Cl atoms, which causes the depletion of ozone [1]. To solve this problem, a number of CFCs substitutes have been developed since the Montreal Protocol on Substances that Deplete the Ozone Layer was adopted in 1987.

In recent years, hydrofluorocarbons (HFCs) have been used as CFCs replacement in refrigerant, foam-blowing, aerosol-propellant applications because their structures do not include Cl atom causing ozone depletion. In addition, HFCs can be also used as intermediates in the preparation of other fluorinated hydrocarbons. Especially, HFC-152a (1,1-difluoroethane) shows properties similar to dichlorodifluoromethane (CFC-12), and has a short atmospheric lifetime (1.4 years) and a small global warming potential (122 for a 100 year time horizon) [2,3]. With its small global warming potential, HFC-152a is becoming a more attractive CFC replacement and may find increased use in high-volume applications [4,5].

Processes of preparing HFC-152a by hydrofluorination of vinyl chloride, 1-chloro-1-fluoroethane, 1,1-dichloroethane or acetylene have been widely used [6-8]. Among these methods, hydrofluorination of acetylene in the presence of catalyst can be achieved with the high yield of HFC-152a at mild conditions [7]. HFC-152a is industrially synthesized by the following two steps: (1) vinylfluoride (CH₂=CHF) is prepared by the hydrofluorination of acetylene, and then (2) the addition reaction of hydrofluoride into vinylfluoride yields HFC-152a (CH₃-CHF₂). The reaction chemistry is as follows.

$$CH \equiv CH + HF \rightarrow CH_2 = CHF \qquad \Delta H^o_{(298\,K)} = -23.00 \text{ kcal/mol} \qquad (1)$$

$$CH_2 = CHF + HF \rightarrow CH_3CHF_2 \qquad \Delta H^o_{(298\,K)} = -20.23 \text{ kcal/mol} \qquad (2)$$

These reactions take place effectively in the presence of a cata-lyst. For the gas-phase synthesis, the reaction is performed at 30-400 °C and 1 atm in the presence of the catalysts such as Bi, Mn/Al₂O₃, HgO, HgCl₂, HgF₂/active carbon, Zn-Hg, chromite, CrO₃, Cr₂O₃, AlF₃ and AlF₃/BiF₃, and the yield of HFC-152a is 70-80% [8]. On the contrary, the liquid-phase synthesis achieves high yields (above 90%) of HFC-152a at mild conditions (20-70 °C, 1 atm) [7]. Fluorosulfonic acid, BF₃/liquid HF, KBF₄/FSO₃H, K₂ZrF₆, KAsF₆, K₂TiF₆/FSO₃H and SbCl₄/FSO₃H are used as liquid catalysts for the synthesis of HFC-152a. However, the liquid-phase synthesis has a drawback due to the deactivation of catalyst by the tar formed during the reaction. Thus, the enhancement of the catalyst stability is needed to increase the productivity.

In this study, HFC-152a was synthesized by a liquid-phase reaction in the presence of FSO₃H as a liquid catalyst. Especially, the effects of a promoter and the moisture in acetylene on the lifetime of a catalyst were investigated.

EXPERIMENTAL

1. Preparation of FSO₃H Liquid Catalyst

Fluorosulfonic acid (FSO₃H) is one of the strongest Brönsted acids commercially available and used as a laboratory fluorinating agent. FSO₃H as a catalyst was prepared by the reaction between ClSO₃H and HF.

$$ClSO_3H + HF \rightarrow FSO_3H + HCl$$
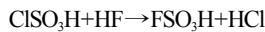
A vessel was charged with a certain amount of ClSO₃H, and an excess HF was injected continuously at room temperature to get the colorless liquid. The FSO₃H obtained by this method had the same catalytic property as the commercial FSO₃H (Aldrich, triple distilled).

2. Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. The apparatus consists of an acetylene storage tank, a reactor with a reflux column, and a condenser. Acetylene is dehydrated by the drying columns (500 cm³) filled with molecular sieve (type 4A, Union Carbide corp.). The flow rate of acetylene is controlled by a
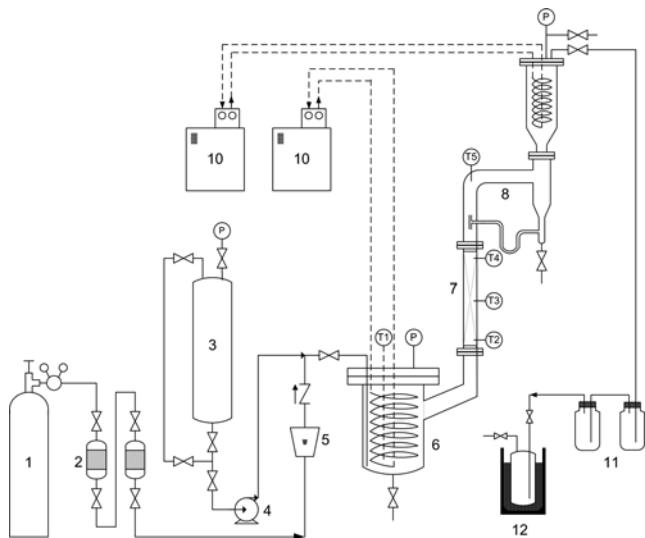
Fig. 1. Schematic diagram of the reaction apparatus.
  1. Acetylene cylinder   7. Reflux column
  2. Drying columns   8. Reflux head
  3. HF storage tank   9. Condenser
  4. Metering pump   10. Circulators
  5. Rotameter   11. NaOH solution
  6. Reactor   12. Product receiver

rotameter in which a needle valve is installed. HF is fed by metering pump (PULSA 680, Pulsafeeder Inc, USA). Gaseous acetylene and liquid HF are mixed at the mixing point, and then the mixture is introduced into the reactor containing liquid catalyst (FSO₃H) and a promoter. The reactor (I.D.=3.5", volume=400 cm³, stainless steel) is equipped with a coil-type heat-exchanger which controls the reaction temperature at 20 °C. The gaseous byproducts and unreacted materials are refluxed in the reflux column (I.D.=3/4", h= 150 cm), which is filled with the structured packing (Sulzer Ltd., Swiss) and equipped with three thermocouples. Finally, HFC-152a passes through a condenser (I.D.=5 cm, h=25 cm) equipped with a coil-type heat-exchanger. The temperature of the condenser ias maintained so that the compounds, which boiling points higher than that of HFC-152a, are refluxed.

RESULTS AND DISCUSSION

Figs. 2 and 3 display the plots of the HFC-152a content in the product as a function of time, showing the lifetime of the catalyst. For all cases, the high yields of HFC-152a (almost 100%) were achieved without the intermediate (vinylfluoride) in an initial state, though the reactions proceeded at a low temperature (20 °C). Based on our previous study, it is suggested that the formation rate of HFC-152a is faster than that of the intermediate (vinylfluoride) from the reaction mechanism [9]. After the elapsed time of several tens hours, the HFC-152a content in the product dramatically decreased. The other compound in the product was unreacted acetylene. These mean that once the deactivation of catalyst occurred, the catalytic activity rapidly reduced.

Utilizing the promoter can enhance the catalytic activity of FSO₃H. Fig. 2 shows the effect of the promoter on the lifetime of catalyst.
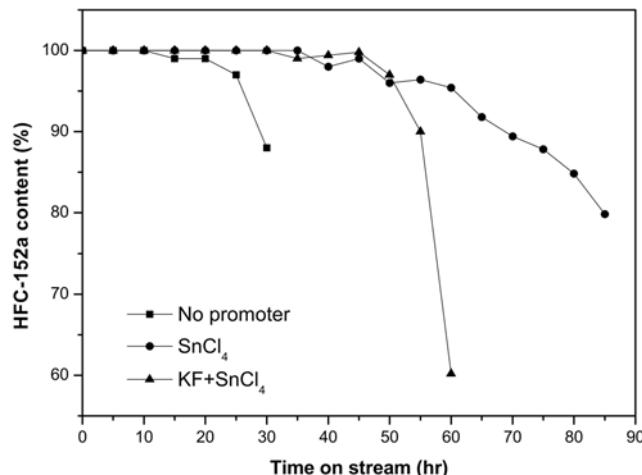

Fig. 2. The effect of a promoter on the liquid catalyst for HFC-152a synthesis obtained from fluorination of acetylene: feed rate of HF=100 g/hr, feed rate of C₂H₂=60 g/hr.
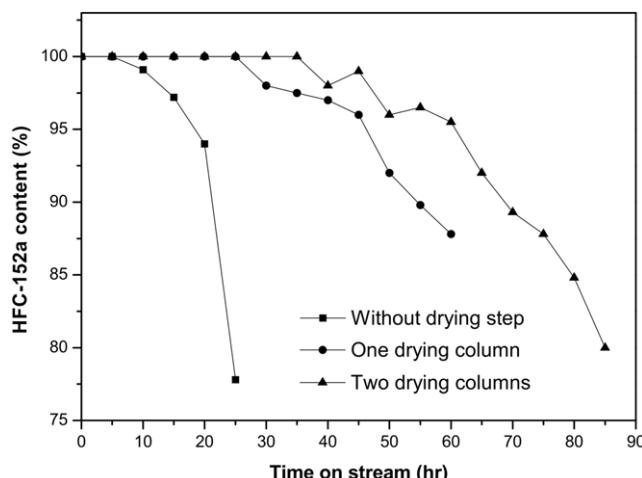

Fig. 3. The effect of moisture in acetylene on liquid catalyst for HFC-152a synthesis obtained from fluorination of acetylene: feed rate of HF=100 g/hr, feed rate of C₂H₂=60 g/hr.

When the reaction was performed without any promoter, a decrease in the HFC-152a content in the product occurred after 10 hrs, and the HFC-152a content decreased to 88% after 30 hrs. When KF (14 g) and SnCl₄ (35 g) were used, the catalytic activity was maintained for 50 hrs, which was two times longer than that performed without any promoter. For the use of only SnCl₄ (24 g) as a promoter, the HFC-152a content in the product was maintained at 100% as long as that for the use of both KF and SnCl₄, and the deactivation of the catalyst proceeded more slowly. These results show that the use of the promoter enhances the lifetime of catalyst. Especially, SnCl₄ not only improves the catalyst stability but also reduces the deactivation rate of the catalyst.

FSO₃H violently reacts with water, leading to the generation of heat. In order to investigate the effect of the moisture in acetylene on the synthesis of HFC-152a, three types of acetylene were used: (1) without drying, (2) after passing through one drying column, and (3) after passing through two drying columns. Fig. 3 shows the

effect of the number of times acetylene passed through the drying column on the catalytic activity. When acetylene was used without drying process, the yield of HFC-152a was maintained at 100% for 10 hrs, and then the catalytic activity drastically dropped. However, the use of acetylene which was dehydrated by the drying column led to extending the lifetime of catalyst to 30 hrs. In addition, the deactivation of catalyst proceeded more slowly. When acetylene passed through the two drying columns, the catalyst stability was maintained for a longer time than that with the acetylene which passed through one column. From these results, it is suggested that the moisture in the precursor accelerates the deactivation of the catalyst, and then induces a decrease in the total yield of HFC-152a through the entire process. Thus, the precursors have to be dehydrated to avoid the deactivation of catalyst by the moisture.

In conclusion, the lifetime of FSO_3H including a promoter ($SnCl_4$) was two times longer than that without promoter, and the moisture easily reduced the catalytic activity of FSO_3H. Thus, the total yield of HFC-152a through the entire process can be improved by the selection of the suitable promoter and the removal of the moisture in chemical reagents.

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