

크롬 촉매상에서 HCFC-133a 의 불소화 반응

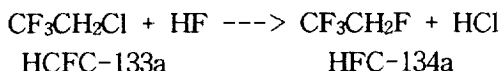
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Fluorination of 1,1,1,2-tetrafluoroethane over chromium oxide

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Introduction

In CFC substitutes, HFC-134a(1,1,1,2-tetrafluoroethane) has zero ozone depletion potential and is a prime candidate for the replacement of CFC-12 in refrigerate systems, medical aerosols, and some foam blowing application. Therefore, many routes of producing HFC-134a have been developed¹⁻³⁾. One of the methods for manufacture of the HFC-134a is reported to be by the way the fluorination of the HCFC-133a(1,1,1-trifluoro-2-chloroethane) using chromium oxide or alumina-supported metal catalysts⁴⁻⁶⁾.



There is little known concerning the active site of these reaction. Previously studies of Cr₂O₃-catalyzed fluorination of chlorofluorocarbons by HF have supposed active form where surface-fluorinated species are the active fluorinating agents⁷⁻⁹⁾ and given the correlation between catalytic activity and redox properties of chromium (III) oxides deduced from TPR-TPO experiments¹⁰⁾.

We have focused our study on the gas-phase catalytic fluorination of HCFC-133a (1,1,1-trifluoro-2-chloroethane) with HF over chromium oxide and this paper present the catalytic activity are related to the surface hydroxide of chromium oxide.

Experiment

The catalyst samples of chromia used in this paper started as hydrogel by precipitation method. The chromium hydroxide was prepared by addition of a solution of ammonia at a uniform rate to a solution of chrome nitrates. The final pH was equal to 7.0 and the hydroxide formed was kept

constantly stirred so as to complete the precipitation. It was then filtered and washed at several times with distilled water and dried in an oven at 135°C for 12h. This material was designated 135.

Fluorination of HCFC-133a was carried out at 360°C under atmospheric pressure in a fixed bed reactor. The reactor was made inconel and heated in a furnace. Hydrogen fluoride and HCFC-133a were fed as a gas from a saturator using carrier gas. The saturator temperature of hydrogen fluoride was maintained at 0°C using ice bath and the saturator of HCFC-133a was held at -44°C using acetronitril bath. The mole ratio of HF/HCFC-133a was controlled at 10/1 in this reaction. The mixed reactants were fed in the reactor at a rate 30cc/min.

Result and discussion

Fluorination of HCFC-133a was performed in non-fluorinated chromium oxides which were prepared by the different methods. These catalysts were activated thermally at 360°C under argon gas. The conversion of HCFC-133a with time-on-stream for these samples is shown in Fig.1. The main reaction product is $\text{CF}_3\text{CH}_2\text{F}$, which result from the halogen-exchange reaction between $\text{CF}_3\text{CH}_2\text{Cl}$ and HF. This reaction also involves $\text{CF}_2=\text{CHCl}$ as a main byproduct. Sample 1 shows higher conversion than the others treated chromium oxide. Conversion of HCFC-133a decrease with increasing treatment temperature in He (sample 2 and 3). Sample 4 that is commercial Cr_2O_3 shows no activity.

The results of X-ray diffraction (XRD) analysis for these samples are shown in Fig.2. Sample 1 catalyst shows amorphous form by broad shape of the diffraction lines. The other samples reveal the presence of the typical diffraction lines of α -cromia in the form of eskolaite with a hexagonal structure. The crystallinity of samples varied as the treatment temperature. Higher treatment temperature of the samples caused more crystallinity than lower treatment temperature(sample 2 and 3). Sample 4 shows the highest crystalliznity in the diffraction line. For this order of the crystallization, IR spectrum given in Fig.3 indicates the splits into two bands at 800-500 cm^{-1} as crystalliniy increase. It is worth noting that the commercial chromium oxide could be obtained through high treatment temperature above 1200°C. Therefore, it is possible to assume that dehydration reaction would be occurred in the increasing treatment process

The infrared spectrum for these samples is shown in Fig.3 Water adsorption on various oxides usually brings about adsorption in spectral region. The 1630-1580 cm^{-1} region is due to bending mode of nondissociated

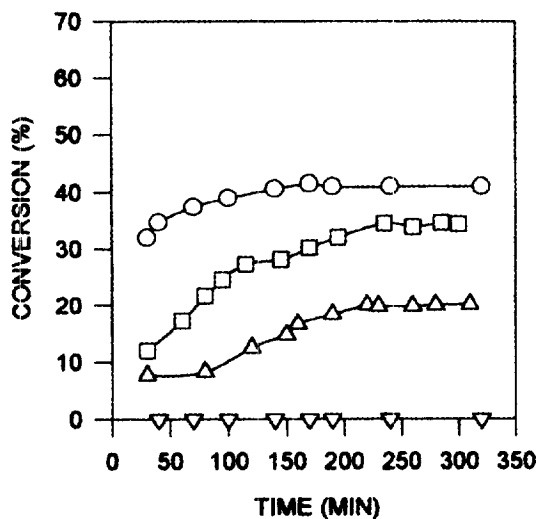


Fig.1 Fluorination of HCFC-133a over chromium oxide with various treatment
 ○: amorphous □: He 400°C ▲: He 800°C
 ▼: commercial chromia

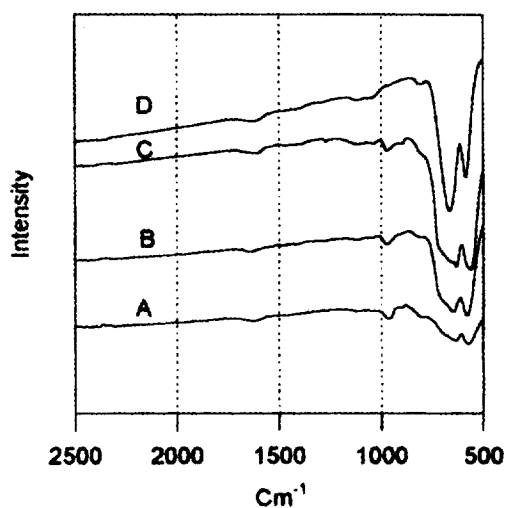


Fig.3 Infrared spectra of chromium oxide

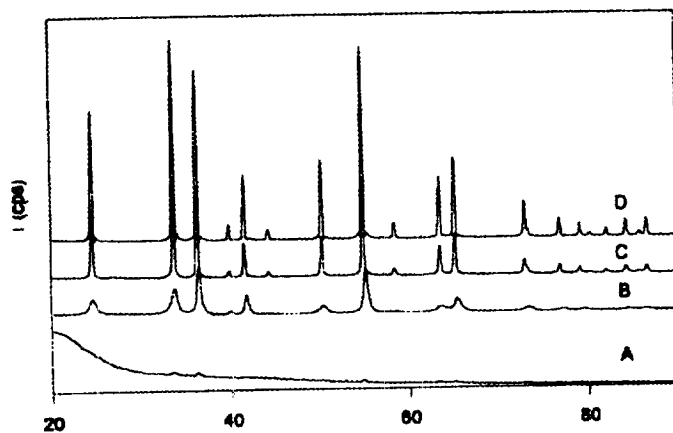


Fig.2 X-ray diffraction analysis for chromium oxide with various treatment
 A : amorphous B : He 400°C C : He 800°C D : commercial chromia

water. The 1000-700 cm^{-1} region is due to bending mode of surface hydroxyls, originated by dissociative water chemisorption¹¹⁾. The spectrum of samples 1,2 and 3 exhibit a few band, but well defined, in the 1000-900 cm^{-1} range (surface hydroxyls bending), that are not presented in the spectrum of sample 4. Chromium oxide (sample 1,2,3) with surface hydroxyls showed the catalytic activity, but sample 4 without Cr-OH surface didn't show the catalytic activity.

We have compared several samples that are quite different in catalytic activity, crystallinity, and IR spectrum. Therefore, We have considered loss of water by condensation process which do not change the CN (coordination number) of Cr⁺³, however the loss of water by condensation involving surface OH- group will generate unsaturated surface species.

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