

TEST OF SOME CHLORIDES AND ACTIVATED CARBONS AS CATALYSTS FOR CHLORINATION OF HCFC-133a

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Abstract—Chlorination of HCFC-133a with chlorine was performed over silica-supported NiCl₂, CuCl₂, MnCl₂, and KCl as well as over some activated carbons. The results were compared with those from the thermal chlorination and from other studies. The chlorides tested were found not to practically act as effective catalysts for the chlorination of HCFC-133a to HCFC-123 contrary to the claims in earlier works, and the activated carbons exhibited poorer HCFC-123 yields than the chlorides.

Key words: Carbons, Chlorides, Chlorination, HCFC-133a

INTRODUCTION

HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane) has low ozone depletion potential and is regarded as an alternative of CFC-11 [Nakagawa et al., 1991]. HCFC-123 can be synthesized by thermal chlorination of HCFC-133a (1-chloro-2,2,2-trifluoroethane) with chlorine, but CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane) is subsequently produced as a by-product during the synthesis [McBee et al., 1947; Kotaka et al., 1989; Cremer and Günter, 1989, 1991]. A literature survey has exhibited that some chlorides, fluorides and other materials appear to act as the catalysts for the chlorination of HCFC-133a, and these materials are claimed to increase the selectivity of HCFC-123 [Kotaka et al., 1989; Cremer and Günter, 1989, 1991]. However, owing to a variety of reaction conditions employed and to the lack of kinetic information, evaluation of these results, or comparison of these especially with those from the thermal chlorination, has been difficult to make under the same basis. A recent study has reported the kinetic equations for the thermal chlorination of HCFC-133a from which the selectivity of HCFC-123 can be determined [Yoon et al., 1993], and thus it may now be possible to make a comparison as the kinetic information is available.

In this work chlorination of HCFC-133a with chlorine was performed over silica-supported NiCl₂, CuCl₂, MnCl₂, and KCl as well as over some activated carbons. The results were compared with those from the thermal chlorination and from other studies, and performance of these materials as the catalysts was discussed.

EXPERIMENTAL

Chlorides used were NiCl₂·H₂O (Shinyo Pure Chemical, 97%), CuCl₂·2H₂O (Shinyo Pure Chemical, 97%), MnCl₂·4H₂O (Shinyo Pure Chemical, 98%) and KCl (Osaka Chemical, 98%). Each of silica-supported chloride samples was prepared by impregnating silica gel beads (Oriental Chemical Industries, type B, granules of 2-3 mm diameter) with an aqueous solution of each chloride by using the incipient wetness method and then by drying the

sample at 723 K. Granules of activated carbons having ca. 3 mm of diameter from Kanto, Wako and Scienmeet were used as received.

Details of other chemicals used, experimental apparatus and experimental procedures are described in a previous study [Yoon et al., 1993]. Briefly, HCFC-133a and Cl₂ vapors flowed into a tubular fixed bed reactor, where the reaction occurred under atmospheric pressure. The HCFC's and CFC in the effluent were collected in a dry ice-acetone trap and then analyzed by a GC.

RESULTS AND DISCUSSION

First, let us briefly introduce the results from a previous thermal chlorination study [Yoon et al., 1993]. In the thermal chlorination of HCFC-133a, the chlorination proceeds via a two-step series-parallel reaction, i.e., in the first-step reaction HCFC-133a is chlorinated to HCFC-123, which is further chlorinated to CFC-113a in the second-step reaction. The ratio of the second-step rate constant to the first-step rate constant, α ($=k_2/k_1$), is independent of temperature and has the value of 1.13. Therefore, as is well established for the kinetic analysis of this type of reaction [Levenspiel, 1972], the fractional yield of HCFC-123, i.e. C_R/C_{A0} , and the selectivity S_R which is defined as (moles of HCFC-123 formed)/(moles of HCFC-133a consumed) are given by

$$\frac{C_R}{C_{A0}} = \frac{1}{1-\alpha} [(1-X_A)^\alpha - (1-X_A)] \text{ for } \alpha \neq 1 \quad (1)$$

$$S_R = \frac{1}{X_A(1-\alpha)} [(1-X_A)^\alpha - (1-X_A)] \text{ for } \alpha \neq 1 \quad (2)$$

where C_R =concentration of HCFC-123, C_{A0} =feed concentration of HCFC-133a, and X_A =conversion of HCFC-133a. Thus C_R/C_{A0} or S_R is a sole function of X_A and independent of temperature and feed composition. If any material has good catalytic performance, it should show a higher C_R/C_{A0} ratio (or S_R) at any given conversion or a lower α value.

In Fig. 1 the results obtained over various chlorides are compared with those from the thermal chlorination. It is clear that all the data points are well fitted to Eq. (1). Table 1 shows compar-

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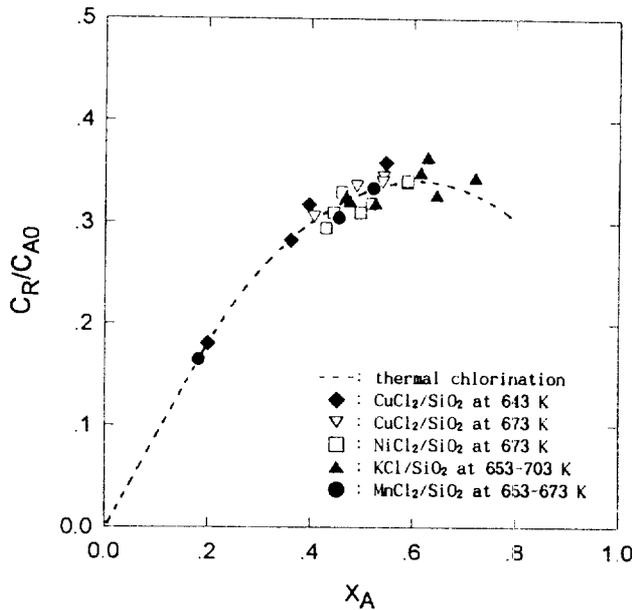


Fig. 1. Fractional yield of HCFC-123 vs. conversion for the chlorination over SiO₂-supported chlorides.

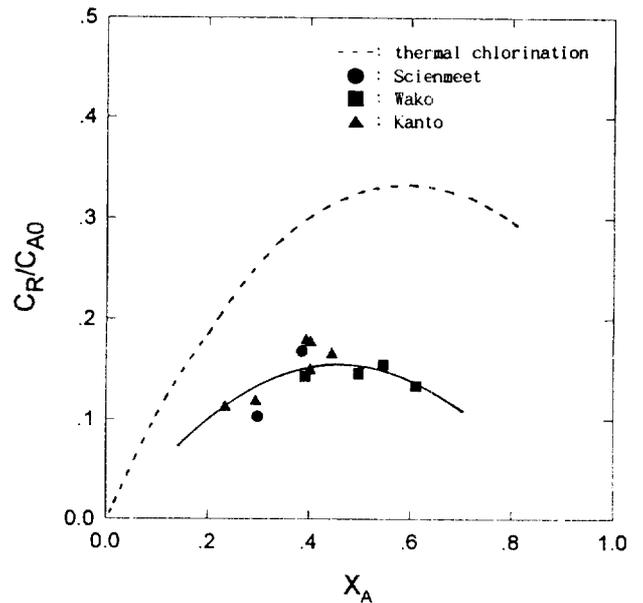


Fig. 2. Fractional yield of HCFC-123 vs. conversion for the chlorination over activated carbons.

Table 1. Comparison of the selectivities in the literature with those from the thermal chlorination

Catalyst	Reaction temp. [K]	Results in [Kotaka et al., 1989]		[Yoon et al., 1993]	
		$C_{B0}^{1)}$	X_A	S_R	$S_R^{2)}$
CuCl ₂ /AlF ₃	643	1/2	0.45	0.75	0.70
FeCl ₃ /AlF ₃	603	1/2	0.32	0.82	0.78
NiCl ₂ /AlF ₃	643	1/2	0.48	0.72	0.68
	603	1/2	0.26	0.83	0.83
AlF ₃	643	1/2	0.51	0.71	0.65
	723	1/2	0.79	0.45	0.4

¹⁾Feed ratio of Cl₂ to HCFC-133a.

²⁾Calculated from Eq. (1) at the same conversion with $\alpha=1.13$.

ison of the selectivities from the thermal chlorination with those in the literature [Kotaka et al., 1989] which were obtained over AlF₃ and AlF₃-supported chlorides. The S_R values in the above literature appear slightly higher than those from the thermal chlorination, but if the deviations normally occurring in any experiment, such as shown in Fig. 1, are taken into account, the difference is not considered to be meaningful. Therefore, it is concluded that such chlorides as tested in this study do not actually act as effective catalysts for the chlorination of HCFC-133a.

Fig. 2 shows the results obtained over activated carbons, and the yields of the desired product (HCFC-123) are substantially lower than those from the thermal chlorination; the α value was about 4. This is due to the fact that activated carbons are good adsorbents for HCFC's and CFC's [Kang et al., 1989; Lim et al., 1994] and have relatively large pore volumes, which results in longer residence time of HCFC-123 and thus higher conversion of HCFC-123 to CFC-113a. No other by-products than HCFC-123 and CFC-113a were observed over the activated carbons, while trace amounts of by-products (considered as CFC-112, CFC-112a,

HCFC-1120 and unidentified other products) were detected over the CuCl₂/SiO₂ and NiCl₂/SiO₂ catalysts.

SUMMARY

Chlorides such as CuCl₂, NiCl₂, MnCl₂ and KCl do not practically act as effective catalysts for the chlorination of HCFC-133a to HCFC-123, contrary to the claims in previous studies. Activated carbons exhibit poorer HCFC-123 yields than the chlorides. To obtain HCFC-123 in high selectivity it may be suggested that good catalysts should be able to protect one of the hydrogen in HCFC-133a during the course of chlorination, hopefully by forming a H-catalyst adsorption bond rather than a Cl-catalyst adsorption bond, and such catalysts are being searched for.

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NOMENCLATURE

- C_{A0} : feed concentration of HCFC-133a [mol/m³]
- C_{B0} : feed concentration of chlorine [mol/m³]
- C_R : concentration of HCFC-123 [mol/m³]
- k_1 : rate constant for the chlorination of HCFC-133a to HCFC-123 [m³/mol·s]
- k_2 : rate constant for the chlorination of HCFC-123 to CFC-113a [m³/mol·s]
- S_R : selectivity of HCFC-123 (moles of HCFC-123 formed)/(moles of HCFC-133a consumed) [-]
- X_A : conversion of HCFC-133a [-]
- α : ratio of the rate constants, k_2/k_1 [-]

REFERENCES

Cremer, H. R. and Günter, S., Jap. Pat. (Kokai) 91-52832, 1991;

- Deutsch. Pat. 3923248, 1989.
- Kang, S. H., Lee, T. J., Bae, K. S., Ahn, H. W. and Kim, Y. K., "Adsorption of Methylene Chloride and Freon-12 on the Some Adsorbents", *HWAHAK KONGHAK*, **27**(4), 404 (1989).
- Kotaka, Y., Homoto, Y. and Honda, T., Jap. Pat. (Kokai) 89-290638, 1989.
- Levenspiel, O., "Chemical Reaction Engineering", 2nd ed., pp. 185-195, Wiley, New York, 1972.
- Lim, J. G., Chang, W. C., Lee, T. J., Shim, J. J., Choi, D. K. and Lee, Y. Y., "Adsorption Equilibria of Freon-113 on Activated Carbons", *HWAHAK KONGHAK*, **32**(3), 341 (1994).
- McBee, E. T., Hass, H. B., Bittenbender, W. A., Weesner, W. E., Toland, Jr., W. G., Hausch, W. R. and Frost, L. W., "Fluorinated Derivatives of Ethane", *Ind. Eng. Chem.*, **39**(3), 409 (1947).
- Nakagawa, S., Sato, H. and Watanabe, K., "Isobaric Heat Capacity Data for Liquid HCFC-123", *J. Chem. Eng. Data*, **36**(2), 156 (1991).
- Yoon, K. J., Shim, G. I., Park, K. Y. and Kim, H. S., "A Kinetic Study on Thermal Chlorination of 1-Chloro-2,2,2-trifluoroethane", *Korean J. Chem. Eng.*, **10**(4), 220 (1993).