

Properties of Chromium (III) Oxides Involved in the Catalytic Gas Phase Fluorination of CF₃CH₂Cl

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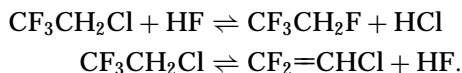
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Received February 13, 1997; revised May 16, 1997; accepted June 17, 1997

The fluorination of chromium oxides reduces the chromium species on the surface. A low fluorination by HF does not modify the total amount of reversibly oxidizable chromium sites, but increases the strength of these sites. Mobile dioxygen (measured by isotopic exchange) was required to obtain a good fluorination activity. These dioxygen species would be exchanged by HF which is probably active in the fluorination of CF₃CH₂Cl and would prevent the irreversibly catalyst fluorination. © 1997 Academic Press

INTRODUCTION

Chromium (III) oxide is a conventional catalyst for chlorine exchange in chloroalkanes. For example, CF₃CH₂F (HFC 134a) is prepared by catalytic gas phase conversion of CF₃CH₂Cl (1–9). At 380°C by using 4 moles of HF per mole of CF₃CH₂Cl, the main reaction is the selective fluorination of CF₃CH₂Cl corresponding to CF₃CH₂F formation. Moreover, competitive elimination of HF gives CF₂=CHCl which accounts for ca 1.2% of the products but can lead to the formation of polymers which cause catalyst deactivation (9, 10):



These two reactions are thermodynamically limited (see the Appendix).

Another typical feature of the fluorination reaction is the role of oxygen. The addition of small amounts of O₂ to the feed has been considered to overcome the deactivation of the catalyst, but there is no explanation for this (1, 2). We noticed that two factors are essential to obtain good activity: one, the presence of reversibly oxidized sites and two, an excess of oxygen in the starting oxide (11, 12). Last the treatment of the oxide with HF at 380°C resulted in its reduction as shown by temperature programmed reductions. All these data prompted us to study the change of the chromium (III) oxide during its fluorination and HF/O₂ exchange.

EXPERIMENTAL

1. Preparation of the Catalyst

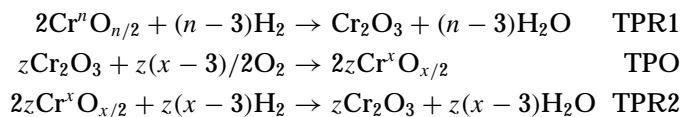
The chromium (III) oxide (9, 13) resulted from the dehydration of chromium hydroxide prepared by the addition of an ammonia solution (5 M) to a solution of chromium nitrate (0.5 M). The final pH was equal to 7.5 and the hydroxide formed was stirred continuously and heated at 80°C for 1 h so as to obtain complete precipitation. The solid obtained was filtered and washed three times with hot distilled water and dried for 16 h in an oven at 90°C. It was then submitted to a dynamic thermal treatment under nitrogen between 300 and 450°C for 8 h. The chromium oxide formed was cooled down under the same vector gas.

X-ray measurements revealed that the chromium oxides were amorphous. After their fluorination, a crystalline phase was observed, exclusively α-Cr₂O₃, alongside amorphous structure (new chromium oxifluorine or chromium fluorine phases were not observed).

2. Chromium Oxide Characterization

The adsorption of nitrogen occurred on a sample (100–200 mg) previously degassed at 300°C with a Flow-Sorb 2300 (Micromeritics) apparatus.

Temperature programmed reduction and oxydation (TPR-TPO) was carried out in a pulse regime by injecting calibrated pulses of hydrogen or oxygen into the catalysts at regular intervals and observing the fraction of the pulse unconsumed by the solid on a recorder coupled to a catharometer detector (14). The reactions involved were



with $n > 3$, $x \leq 6$ (n and x represent respectively the oxidation degree of chromium atom before the first reduction and the oxidation degree of chromium atom after the oxidation) and $0 < z \leq 1$ (z represents the part of chromium reversibly oxidizable after the first reduction).

Fluorine titration of chromium oxide was carried out at the Elf-Atochem Research Center, Pierre-Bénite. The catalyst mineralization was carried out in a Parr bomb by reaction with sodium peroxide. Fluorine ions were then titrated by a potentiometric method with a specific fluoride electrode.

3. HF/O₂ Exchange

Pulses of HF (or O₂) were injected at 380°C at regular intervals using a calibrated loop. The uptake of HF (or O₂) was measured by gas chromatography which detected the fraction of the pulse unconsumed by the catalyst. In a typical experiment, pulses of HF (5.9 μmol) were injected every 5 min. Helium was used as the flowing gas and the mass of catalyst was 50 mg.

The uptake was considered as finished after 3 h. HF was replaced by O₂ and a similar series of injections was carried out to measure the uptake of dioxygen. To distinguish between the reversible adsorbed and exchangeable HF or O₂, the procedure was modified, so that the reversible adsorbed gas on the catalyst surface was swept over by a current of helium for 3 h. A first adsorption of HF was carried out, then the helium followed by a second adsorption of HF. The difference between the two uptakes gave the amount of reversibly adsorbed HF.

4. Isotopic Exchange of Oxygen

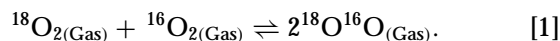
Isotopic exchange experiments were carried out in a recycle microreactor coupled to a mass spectrometer. The masses 32, 34, 36 (for the isotopomers) were monitored every 10 s. The vacuum connection to the mass spectrometer was thermoregulated so as to maintain a constant pressure of 10⁻⁶ mbar in the ionization chamber, while the total pressure in the reactor was 40 bar for the isothermal isotopic exchange and 100 mbar for temperature programmed isotopic exchange. For isothermal isotopic exchange (ISIE) and for temperature programmed isotopic exchange (TPIE), the oxide sample (5 m²) was submitted *in situ* to a pretreatment at 300°C under vacuum pretreatment at 300°C for 30 min, and cooled down to room temperature under vacuum. A 100-mbar dose of pure ¹⁸O₂ was then introduced into the reactor and the temperature increased from 25 to 500°C at 2°C/min for temperature programmed isotopic exchange or at constant temperature (380°C) for 2 h for isothermal isotopic exchange. The temperature programmed isotopic exchange determines the range of exchange temperature.

The pressure variation of oxygen isotopomers P_{36} (¹⁸O₂), P_{34} (¹⁸O¹⁶O), and P_{32} (¹⁶O₂) were then recorded every 10 s. The total pressure ($P_{36} + P_{34} + P_{32}$) remained virtually constant. The number of exchangeable oxygen atoms (N_e) and the initial rate of exchange (R_e^0) were able to be calculated from the partial pressure values (15).

According to the literature (16, 22) three types of exchange, described by the following equations could occur

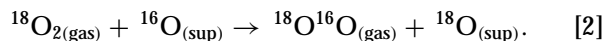
on oxide surfaces:

(a) Homoexchange (or equilibrium) that occurs without appreciable participation of oxygen of the oxide (Eq. [1]),

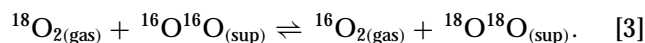


This reaction occurs according to a mechanism of adsorption-desorption. The rate of exchange of oxygen surface species of the oxide is negligible. During this homoexchange, the isotopic oxygen fraction in the gas phase is constant. By using pure isotopic ¹⁸O₂ this type of exchange can not be observed initially.

(b) Simple heteroexchange occurs with the participation of the only one oxygen of the oxide (Eq. [2]),



(c) Multiple heteroexchange occurs with the participation of two oxygen atoms of the oxide at each step of Eq. [3],



For this multiple exchange on oxide surfaces, there are two possible mechanisms: isotopic exchange and "place exchange." These two mechanisms differ by the oxygen surface intermediates involved. The isotopic exchange mechanism occurs through an associative mechanism with a four-atomic (O₄)_{ads}⁻ surface intermediate. By contrast, the "place-exchange" mechanism occurs without requiring a four-atom oxygen intermediate on the surface; this is just a displacement of a preadsorbed molecule by a gas phase molecule. This mechanism does not involve the scission of any O-O bond.

Initial rate of exchange. The initial rate of exchange R_e^0 being equal to the rate of the disappearance of ¹⁸O from the gas phase, it was possible therefore to determine R_e^0 by Eq. [4],

$$R_e^0 = -\frac{N_A}{S \cdot R} \left(\frac{V_r}{T_r} + \frac{V_c}{T_c} \right) \left(2 \frac{dP_{36}^0}{dt} + \frac{dP_{34}^0}{dt} \right), \quad [4]$$

where dP_{36}^0/dt and dP_{34}^0/dt are the initial slopes of the partial pressures of ¹⁸O₂ and ¹⁶O¹⁸O and N_A is the Avogadro number, P_T is the total pressure, S is the oxide BET area (m⁻²), R is the gas constant, V_r and V_c respectively are the volumes of the heated and unheated zones of the reactor, and T_r and T_c respectively are the temperatures of the heated and unheated zones of the reactor.

Number of exchanged oxygen. The number of oxygen atoms exchanged at each time N_e^t is given by Eq. [5] at each temperature and calculated after the

$$N_e^t = (\alpha_g^0 - \alpha_g^t) N_g, \quad [5]$$

where (α_g^0) is the initial atomic fraction of isotopic oxygen

in the gas phase. We can first define the oxygen 18 atomic fraction in gas phase at each time α_g^t as

$$\alpha_g^t = \frac{\frac{1}{2}p_{34}^t + p_{36}^t}{p_{36}^t + p_{34}^t + p_{32}^t},$$

where N_e^t is calculated after the adsorption phase of the $^{18}\text{O}_2$ which is very fast and does not modify the initial amount of $^{18}\text{O}_2$.

5. Catalytic Activity

The fluorination of $\text{CF}_3\text{CH}_2\text{Cl}$ was carried out at 380°C under atmospheric pressure in a fixed bed dynamic reactor. In a first operation, the catalyst was fluorinated *in situ* for 2 or 70 h by HF mixed with nitrogen (ratio $\text{N}_2 : \text{HF} = 5 : 4$) at 380°C . $\text{CF}_3\text{CH}_2\text{Cl}$ was then injected into the reactor in the presence of HF. The operating conditions of this fluorination of $\text{CF}_3\text{CH}_2\text{Cl}$ were: temperature = 380°C , catalyst weight = 50 mg, contact time = 0.01 s.

HF : $\text{CF}_3\text{CH}_2\text{Cl}$: $\text{N}_2 = 4 : 1 : 5$. The same operation was repeated with a nonfluorinated catalyst. The catalytic activity for the $\text{CF}_3\text{CH}_2\text{F}$ formation was measured both over the prefluorinated and the nonfluorinated catalyst after a 2 h reaction with $\text{CF}_3\text{CH}_2\text{Cl}$.

The products resulting from the reaction were injected with an automatic sampling valve into a GIRA GC 181 gas phase chromatograph and analyzed with a flame ionization detector. The separation was carried out in a capillary column DB5 (J and W Scientific).

RESULTS

During the fluorination of $\text{CF}_3\text{CH}_2\text{Cl}$, a fluorination of the catalyst could be observed which could modify the catalyst performances. In this paper we study the modifications of the catalyst during its fluorination (at different degrees of fluorination). We attempt to establish the role played by an oxygen catalyst in the fluorination activity. Table 1

TABLE 1

Catalytic Activity and Oxydo-Reducibility of Chromium (III) Oxide (Prepared by Activation of the Chromium Hydroxide at 380°C under Nitrogen) at Different Degrees of Fluorination

Degree of fluorination (F/Cr)	0	0.59	1.6
S (BET) ($\text{m}^2 \cdot \text{g}^{-1}$)	178	114	111
Activity ($\text{mmol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$)	51	51	25
Activity ($\text{mmol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$)	0.29	0.45	0.23
TPR1 (H/Cr)	0.33	0	0.03
TPR2 (H/Cr)	0.21	0.24	0.28
TPR2 (H/Cr) $\cdot \text{m}^{-2} \times 10^3$	1.2	2.1	3.2

gives the change of the fluorination activity, of the reversible chromium species (TPR2) over a chromium (III) oxide prepared by dehydration of the hydroxide at 380°C under a nitrogen flow ($\text{Cr}_2\text{O}_3\text{-N}_2\text{-}380^\circ$) and fluorinated for two different times (2 h and 70 h). When the degree of the fluorination of the catalyst (F/Cr) increases, the specific area and the fluorination activity decrease. We can also notice that the nonprefluorinated chromium (III) oxide and the chromium (III) oxide fluorinated 2 h (F/Cr = 0.6) have similar activity. We observed in a previous paper (9) that the activation period during the fluorination of $\text{CF}_3\text{CH}_2\text{Cl}$ was very brief when no preliminary fluorination of the catalyst was performed. After this period the nonfluorinated catalyst and the fluorinated (2 h) catalyst had similar catalytic activity. A preliminary fluorination of the catalyst surface is necessary for it to be active for the fluorination of $\text{CF}_3\text{CH}_2\text{Cl}$.

In every case (F/Cr = 0.6 or 1.6), the fluorination of the catalyst with HF reduces the chromium species on the surface (TPR1 = 0), but the total amount of the reversible chromium sites is not modified. However, an increase of the amount of reversible oxidized chromium sites per unit surface can be observe while the intrinsic activity decreases.

Figure 1 shows the profile of TPR2 for chromium oxide with different degrees of fluorination. We observe that

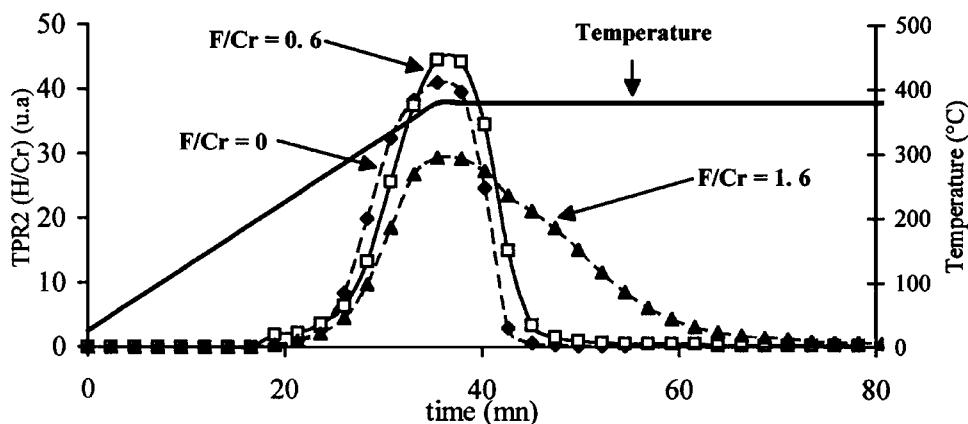


FIG. 1. Profiles of the temperature of the second reduction (TPR2) with the degree of fluorination of the chromium oxide (prepared by activation of the chromium hydroxide at 380°C under nitrogen).

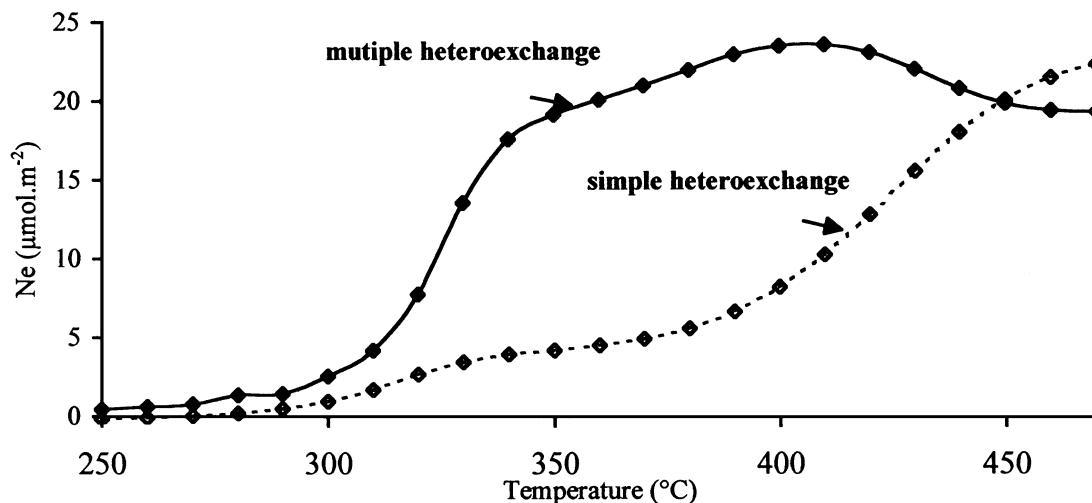


FIG. 2. Dioxygen exchange by simple and multiple heteroexchange over chromium (III) oxide (prepared by activation of the chromium hydroxide at 380°C under nitrogen) at different temperatures.

the nonfluorinated catalyst and the fluorinated catalyst ($F/Cr = 0.6$) show similar behavior. The maximum reduction is obtained at a temperature of approximately 380°C. The reduction peak of the chromium oxide with the $F/Cr = 1.6$ ratio is larger than the others (corresponding to higher reduction temperatures). Chromium species are more difficult to reduce when the F/Cr ratio increases.

Isotopic Exchange of Oxygen Atom

The mobility of the oxygen atom over chromium oxides prepared by the activation of the hydroxide chromium at different temperatures (300–450°C) was measured by isotopic exchange $^{16}\text{O}/^{18}\text{O}$. The catalytic activity depends on the chemical properties of the oxides catalysts (9, 11, 12).

Figure 2 gives the number of ^{16}O exchanged within a 250–450°C temperature range. The oxygen exchange began at a temperature around 300°C and the two mechanisms (simple and multiple heteroexchange) could be observed. However, the main reaction was the multiple heteroexchange. The maximum difference between the two mechanisms was observed at 380°C.

Table 2 gives the rate of exchange R_e^0 and the number of atoms exchanged (N_e) at 380°C, for chromium oxides activated at different temperatures. The exchange rate and the number of oxygen atom exchanged for the multiheteroexchange reaction were more significant than with the simple heteroexchange reaction. These results are similar whatever the temperature of activation.

O_2/HF Exchange

The chromium (III) oxide is reduced after its fluorination by HF (TPR1 = 0) which could correspond to a loss of dioxygen. Table 3 gives the amounts of reversible and exchangeable HF and O_2 adsorbed, at 380°C on chromium

(III) oxide ($\text{Cr}_2\text{O}_3\text{-N}_2\text{-380}^\circ\text{C}$). After the two first cycles, HF/ O_2 ratio (which represents HF- O_2 exchange) is reproducible with ca 60% of reactants irreversibly adsorbed. This means that the adsorption of HF makes the adsorption of O_2 possible and vice versa. This exchange involves a O_2/HF ratio approximately equal to 2. This value is too high for any surface reaction as the one with H_2 and O_2 (temperature programmed reductions and temperatures programmed oxidations) to occur.

DISCUSSION

A detailed description of the catalyst surface for the fluorination of $\text{CF}_3\text{CH}_2\text{Cl}$ is not yet possible. However, the results obtained in this work (the fluorination of the catalyst

TABLE 2

Isotopic Exchange of Dioxygen and Catalytic Activity for Chromium (III) Oxides Prepared by Activation of the Chromium Hydroxide at Different Temperatures

Activation temperature (°C)	300	350	380	400	450
S (BET) ($\text{m}^2 \cdot \text{g}^{-1}$)	235	199	178	177	86
Activity ($\text{mmol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$)	33	44	55	54	35
Activity ($\text{mmol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$)	0.14	0.22	0.31	0.31	0.41
<i>Initial exchange rate</i> ($\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$):					
$^{16}\text{O}_2$	0.4	0.5	0.6	0.6	0.7
$^{18}\text{O}^{16}\text{O}$	0.3	0.4	0.3	0.3	0.2
Total	0.7	0.9	0.9	0.9	0.9
<i>N exchange</i> ($\mu\text{mol} \cdot \text{m}^{-2}$):					
$^{16}\text{O}_2$	19	25	19	23	18
$^{18}\text{O}^{16}\text{O}$	8	10	10	7	13
Total	27	35	29	30	31

and the role of the oxygen) may be used qualitatively. The fluorination of the chromium (III) oxide (Cr₂O₃-N₂-380) decreases its specific surface which could correspond to a partial αCr₂O₃ crystallized phase and Cr-F bond involved in CrF₃ formation determined by XPS (9). Total fluorination of the catalyst would lead to a CrF₃ catalyst structure which is not active for the fluorination reaction (9). For a weak F/Cr ratio (0.6 and 1.6) the total amount of reversibly oxidable sites is practically constant. However, the nature or the strength of these sites are modified when the degree of fluorination increases. In fact, chromium (III) oxide with high F/Cr = 1.6 ratio requires a higher temperature of reduction and this catalyst has a smaller activity. The presence of the αCr₂O₃ crystallized phase and Cr-F bond involved in CrF₃ formation would lead to chromium species more difficult to reduce (13). The most active catalysts for the fluorination of CF₃CH₂Cl are those which contain chromium atoms easily reduced by hydrogen (lower temperature of reduction).

The mobility of oxygen was carried out by isotopic exchange. Two mechanism of exchange can be observed: the simple and the multiple heteroexchange, the main reaction being the multiple heteroexchange. The temperature of the activation of the hydroxide chromium does not modify the catalytic activity and the number of oxygen atoms exchanged.

Dioxygen-fluoride hydrogen exchange, measured by pulse chromatography can be observed. A O₂/HF ratio equal to approximately 2 was calculated but we have no explanation for this. This ratio could not solely be explained by the oxidation by O₂ and by the reduction by HF of the catalyst. The O₂/HF ratios, corresponding to a reversible adsorption or an O₂/HF exchange, are the same. The dioxygen

TABLE 3

O₂ and HF Uptake Reversible and Exchangeable over Chromium Oxide (Prepared by Activation of the Chromium Hydroxide at 380°C under Nitrogen)

	Total adsorbed (μmol)	Reversible adsorption		O ₂ /HF exchange	
		(μmol)	(%)	O ₂ /HF ratio	O ₂ /HF ratio
1st cycle of HF	46	30	65	16	2.3
1st cycle of O ₂	102	66	65	36	1.7
2nd cycle of HF	38	17	45	21	2.6
2nd cycle of O ₂	95	41	43	54	2.3
3rd cycle of HF	41	17	41	24	2.5
3rd cycle of O ₂	100	41	41	59	

Note. T = 380°C, mCr₂O₃ = 50 mg.

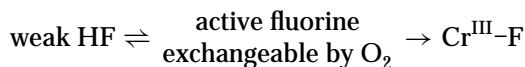
TABLE 4

Comparison between the Uptake of HF and of O₂ Measured during the First Cycles of Pulses and the Uptake of H₂ and of O₂ Measured during TPR and TPO

Catalyst	Cr ₂ O ₃ -N ₂ -380
TPR1 (H/Cr) · m ⁻² × 10 ³	1.9
TPO (O/Cr) · m ⁻² × 10 ³	0.67
TPR2 (H/Cr) · m ⁻² × 10 ³	1.2
1st cycle of HF (HF/Cr) · m ⁻² × 10 ³	0.39
1st cycle of O ₂ (O/Cr) · m ⁻² × 10 ³	1.7
2nd cycle of HF (HF/Cr) · m ⁻² × 10 ³	0.32

could be adsorbed on the catalyst surface without oxidation of the chromium atom. Table 4 gives the comparison between the uptakes of O₂ and of HF during the exchange and the uptakes of O₂ and of H₂ during the oxidation and reduction of the chromium (III) oxide. The HF uptake is smaller than that of H₂ uptake. HF reduces only a part of the sites reducible by H₂. But the O₂ uptake is more significant after the reduction of HF than after H₂. The hydrogen fluoride would modify the catalyst surface and would create oxygen adsorption sites.

We have shown that two types of HF are present at the catalyst surface; the first type is desorbed only by inert gas, whereas the second type is stable in the presence of inert gas and probably participates in the O₂/HF exchange and in the CF₃CH₂Cl fluorination. These two types of HF lead to a third type of HF which fluorinates irreversibly the catalyst (by the formation of Cr^{III}-F bond) and causes its deactivation (9, 23). These three types of HF are related and fluorinate the catalyst progressively (23).



The presence of oxygen, measured by O₂/HF exchange and by isotopic exchange, maintains the presence of the second type of HF (labile) without an irreversible fluorination of the catalyst. In fact, the presence of oxygen slows down the degree of fluorination of the catalyst.

APPENDIX

By using 4 moles of HF per mole of CF₃CH₂Cl, at 380°C, the CF₃CH₂Cl transformation involves two reactions, the fluorination reaction and the dehydrofluorination, which are thermodynamically limited. The value of the free enthalpy (Δ_RG°), of the formation enthalpy (Δ_RH°), and of the equilibrium constant (K_p) for each reaction were calculated with the theoretical values (24) and are reported in Table 5.

TABLE 5
Thermodynamic Calculated Values for the Reactions
of CF₃CH₂Cl in an Open System at 653 K

Reaction	$\Delta_R G^\circ$ (KJ mol ⁻¹)	$\Delta_R H^\circ$ (KJ mol ⁻¹)	$Kp \times 10^3$	Product (molar%)
Fluorination (Cl/F exchange)	27.7	29.7	6.1	CF ₃ CH ₂ F (14.2)
Dehydrofluorination (-HF)	34.4	131.9	1.2	CF ₂ =CHCl (1.2)

ACKNOWLEDGMENT

We thank the Elf-Atochem company for financial support.

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