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Characterization by Temperature-Programmed Reduction and by Temperature-Programmed Oxidation (TPR–TPO) of Chromium (III) Oxide-Based Catalysts: Correlation with the Catalytic Activity for Hydrofluoroalkane Synthesis

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The catalytic activity of chromium (III) oxide for the fluorination of CF_3CH_2Cl (HCFC 133a) is proportional to the number of reversibly oxidized sites. The proportionality coefficient depends on the atmosphere employed during the pretreatment of the catalyst. The temperature-programmed reduction and temperature-programmed oxidation experiments constitute a simple technique that allows the number of reversibly oxidized chromium atoms to be measured. The method of preparation of the chromium hydroxide has little effect on the catalytic properties of chromium (III) oxide. The activation atmosphere and the temperature are essential parameters in the formation of chromium (III) oxide from hydroxide. Indeed, the most active chromium (III) oxide for the fluorination of CF_3CH_2Cl is obtained by thermal treatment of hydroxide at 380°C under nitrogen.

INTRODUCTION

The alternatives to chlorofluorocarbons (CFC) at present are hydrofluoroalkanes and/or hydrochlorofluoroalkanes. Their preparation involves a F to Cl exchange and requires a catalyst (1, 2). The fluorination agent used is hydrogen fluoride, and the reaction is carried out either in the liquid phase (3–5) or in the gas phase. In the latter case, a metal or an oxide deposited (or not) on a support is used as a heterogeneous catalyst (6–8). As yet the only way to compare the performances of the catalysts is by the results of catalytic testing and few correlations with bulk or surface physicochemical characteristics have been proposed. Nevertheless, it is essential that these correlations be established in order to acquire better knowledge as a basis for the formulation of new catalysts.

We are studying the selective fluorination of CF_3CH_2Cl into CF_3CH_2F in the presence of chromium (III) oxide-based catalysts (9–14). The reaction involved is

$$CF_3CH_2Cl + HF \rightleftharpoons CF_3CH_2F + HCl,$$

with

$$CF_3CH_2Cl \rightleftharpoons CF_2{=}CHCl + HF$$

as a main by-product reaction. We have characterized the catalysts in parallel by temperature-programmed reduction and oxidation (TPR–TPO) (15, 16). The reactions involved are

$$2Cr^nO_{n/2} + (n-3)H_2 \rightarrow Cr_2O_3 + (n-3)H_2O \qquad TPR_1$$

$$zCr_2O_3 + z(x-3)/2\ O_2 \rightarrow 2zCr^xO_{x/2} \qquad TPO$$

$$2zCr^xO_{x/2} + z(x-3)H_2 \rightarrow zCr_2O_3 + z(x-3)H_2O \qquad TPR_2,$$

with $n > 3$, $x \leq 6$, and $0 < z \leq 1$ (z represents the part of chromium reversibly oxidizable after the first reduction (TPR1)).

We present in this paper the first correlation between catalytic activity and redox properties of chromium (III) oxide(s) deduced from TPR–TPO experiments.

EXPERIMENTAL

Preparation and Thermal Treatment of the Catalysts

Chromium (III) oxide was prepared by dehydration of chromium hydroxide obtained by the addition of an ammonia solution (5 *M*) to a solution of chromium nitrate (0.5 *M*). As the structure of chromium hydroxide depends on the precipitation method (17–19), the two following methods were used.

Method no. 1. The precipitation at constant pH consisted in pouring simultaneously the chromium nitrate and the ammonia solutions so as to maintain a pH of around 7 ± 1.

Method no. 2. The precipitation at increasing pH (pH

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4–8) was obtained by adding ammonia at a uniform rate (20 cm^3 min^{-1}) to the chromium nitrate solution.

For both these methods of preparation the final pH was 7.5 and the hydroxide formed was constantly stirred and heated at 80°C for 1 h to complete the precipitation. The hydroxide thus obtained was then filtered and washed three times successively with hot distilled water (80°C). It was then dried in an oven at 90°C for 16 h and submitted to thermal treatment in a flow regime (under nitrogen, hydrogen, or in air) between 300 and 500°C min^{-1} for 8 h. The chromium (III) oxide formed was cooled under the same vector gas. Solids prepared by methods 1 and 2 will be designated respectively as samples 1 and 2.

Chromium (III) Oxides Characterization

The chromium (III) oxides prepared in this way were characterized by their BET area, by their XRD structure, and by TPR–TPO.

BET area. The adsorption of nitrogen took place on a sample (100–200 mg) previously degassed at 350°C. The apparatus used was a FlowSorb 2300 (Micrometrics).

X-ray diffraction. The apparatus used was a DACO-MP diffractometer monitored by a microcomputer.

Temperature-programmed reduction and oxidation. This method consisted in measuring the amount of hydrogen or oxygen consumed during reduction or oxidation of the catalyst subjected to an increase in temperature. In these techniques, reactions were carried out in a pulse regime by injecting calibrated pulses of hydrogen or oxygen on to the catalysts at regular intervals and observing the fraction of the pulse not consumed by the solid on a recorder coupled to a catharometer detector.

Catalytic Fluorination

The fluorination of CF_3CH_2Cl was carried out at 380°C under atmospheric pressure in a fixed-bed flow reactor. First the oxide was fluorinated *in situ* by HF for 2 h at 380°C. The reactant CF_3CH_2Cl was then injected into the reactor in the presence or in the absence of hydrogen fluoride. The general operating conditions of fluorination of CF_3CH_2Cl were temperature = 380°C, catalyst weight = 50 mg, contact time = 0.01 s, HF/HCFC133a = 4 (HCFC 133a = CF_3CH_2Cl).

The catalytic activity was measured over a prefluorinated (2 h) chromium oxide and after 2 h reaction with CF_3CH_2Cl.

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

All the experiments on the characterization of different chromium oxides were carried out twice; the precision was about 10%.

RESULTS

The catalytic properties of chromium oxide (isomerization, dehydrogenation reactions, etc.) depend largely on the method of preparation and activation (18). For fluorination reactions these parameters do not seem to have been greatly studied. We have moreover made the hypothesis that the fluorinating activity of the catalyst could depend on a certain mobility of the surface fluorinated species, themselves dependent on the mobility of surface oxygen species. We have therefore attempted to estimate this mobility by studying the reducibility and the oxidizability of these substances.

To this end two chromium hydroxides were prepared by the two different methods presented earlier. They were activated thermally at between 300 and 500°C under nitrogen or hydrogen or in air. We then looked at the effect of these parameters on the chromium oxide activity for the fluorination of CF_3CH_2Cl as well as on the redox properties of these oxides.

Effect of the Pretreatment Temperature of Chromium Hydroxides

Figure 1 shows the effect of the pretreatment temperature on the BET surface area of chromium (III) oxide obtained from samples 1 and 2 of chromium hydroxide.

Irrespective of the method of preparation of the chromium hydroxide (samples 1 and 2), when the activation temperature increases, the specific area of the corresponding oxide decreases. However, the main differences between these catalyst samples can be observed for activation temperatures in the 350 to 400°C range. Indeed the chromium (III) oxides prepared at constant

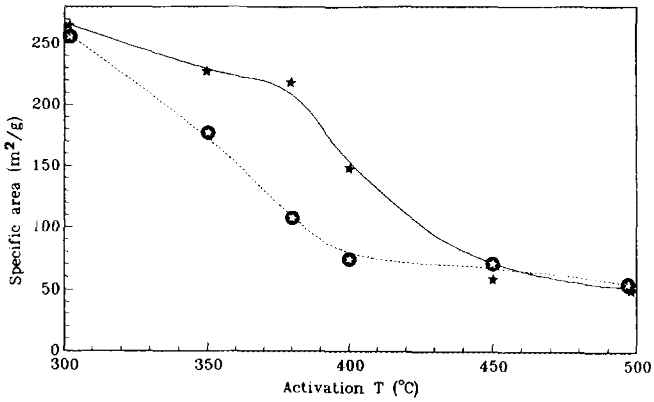

FIG. 1. Effect of pretreatment temperature (under nitrogen for 8 h) on the specific area (m^2/g) of the chromium (III) oxide obtained from two samples of hydroxide: (○) Sample 1, (★) Sample 2.

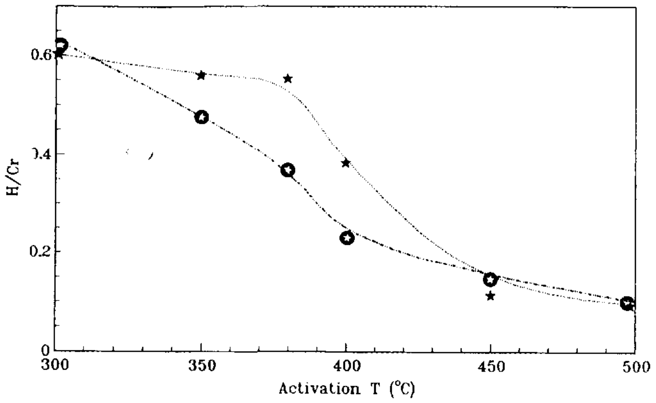

FIG. 2. Effect of the method of preparation of chromium (III) oxide on its oxidation state. Comparison between the chromium (III) oxides (samples 1 and 2) after activation under nitrogen between 300 and 500°C, characterized by TPR$_1$ (H/Cr): (○) Sample 1, (★) Sample 2.

pH (sample 1) have a smaller specific surface than those of the solids prepared with an increasing pH (sample 2).

A study using X-ray diffraction of the structure of chromium (III) oxides obtained after thermal treatment under nitrogen (sample 1 and 2) shows that they are amorphous up to 380°C. Between 380 and 400°C chromium (III) oxide crystallizes in the form of eskolaite with a rhombohedral structure. This crystallization varies little between 400 and 500°C. However, the size of the crystallites of chromium (III) oxides resulting from the first preparation method is smaller (between 50 and 100 Å) than that of chromium (III) oxide crystallites resulting from the second preparation method (between 100 and 150 Å).

These chromium (III) oxides (samples 1 and 2) were then characterized by TPR and TPO. The amount of hydrogen consumed during the reduction (TPR$_1$) represents the quantity of chromium in an oxidation state greater than III. TPO and TPR$_2$ (second reduction) make it possible to quantify the chromium capable of passing reversibly from an oxidized state into a reduced (redox chromium). The three reactions involved have already been described.

Figure 2 shows the change in the amount of hydrogen consumed by the chromium species during TPR$_1$ as a function of the activation temperature of the chromium hydroxides (samples 1 and 2).

The amount of hydrogen consumed during the first reduction decreases strongly when the activation temperature increases. This amount depends also on the chromium hydroxide preparation method. The most significant difference occurs at an activation temperature of 380°C. This difference is not observed for TPO and TPR$_2$. Indeed, results presented in Fig. 3 are almost identical whatever the preparation method.

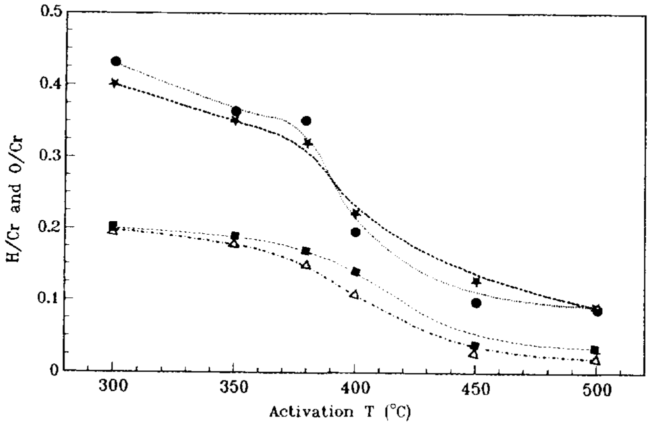

FIG. 3. Effect of the preparation method (1 and 2) of chromium (III) oxide on its redox properties. Comparison between the amounts of oxygen and hydrogen consumed during TPO (O/Cr) and TPR$_2$ (H/Cr), for chromium (III) oxides prepared from method 1 and 2 versus the activation temperature of the chromium hydroxide: (■) TPO Sample 1, (△) TPO Sample 2, (★) TPR$_2$ Sample 1, (●) TPR$_2$ Sample 2.

Effect of the Thermal Treatment under Nitrogen, Hydrogen, or in Air

The thermal treatment under flow conditions (nitrogen, hydrogen, or air) has a significant effect on the BET area of the chromium (III) oxide irrespective of the preparation method of the chromium hydroxide. Table 1 shows that at 380°C there is a difference in surface area between the solids obtained according to the two modes of preparation only after the treatment under nitrogen.

After calcination (activation under air) the BET areas are smaller and X-ray diffraction measurements show that these chromium (III) oxides are crystallized above 380°C, contrary to the chromium (III) oxides resulting from treatment under nitrogen or hydrogen.

Some experiments (BET and TPR–TPO) over a prefluorinated chromium oxide (activated at 380°C under nitrogen) were carried out. The fluorination pretreatment involved a partial reduction of oxide (very small TPR$_1$)

TABLE 1

Effect of the Thermal Treatment at 380°C under Nitrogen, Hydrogen, or Air on Specific Area of Chromium (III) Oxide Obtained from Chromium Hydroxide (samples 1 and 2)

	N_2	Air	H_2
Sample 1 BET surface (m^2/g)	107	41	203
Sample 2 BET surface (m^2/g)	218	44	221

TABLE 2

Catalytic Activity (in mmol h^{-1} $g_{cat.}^{-1}$) for CF_3CH_2Cl Fluorination over Chromium (III) Oxide Prepared from Chromium Hydroxide Activated under Nitrogen

Pretreatment temperature (°C)	Sample 1	Sample 2
350	111	130
380	98	104
400	60	48
450	39	25
500	30	16

and a decrease of the specific area (from 100 to 70 m^2/g). However, the TPR_2 was not affected by the fluorination pretreatment (the same TPR_2 was found for the chromium oxide and the prefluorinated chromium oxide).

Catalytic Properties in the Fluorination of 1,1,1-Trifluoro-2-chloroEthane (HCFC 133a)

Table 2 gives the catalytic activities of the chromium (III) oxides (samples 1 and 2) resulting from the thermal treatment under nitrogen for the fluorination of CF_3CH_2Cl.

Generally speaking, it should be noted that catalytic activities are similar for both preparation methods. Moreover, a significant decrease in the catalytic activity when the activation temperature of the chromium hydroxide increases can be also observed in both cases. The activities of the chromium (III) oxides, resulting from the thermal treatment under nitrogen, air or hydrogen of chromium hydroxide (sample 1) for fluorination of CF_3CH_2Cl, are presented in Table 3.

It is worth noting that

(i) Whatever the activation temperature, the best activities are obtained for the chromium (III) oxides which result from the thermal treatment of chromium hydroxide under nitrogen, then under hydrogen, and finally in air.

TABLE 3

Catalytic Activity (mmol h^{-1} $g_{cat.}^{-1}$) for the Fluorination of CF_3CH_2Cl of Chromium (III) Oxide as a Function of the Thermal Treatment (Nitrogen, Air, Hydrogen) of the Chromium Hydroxide

	Activation atmosphere		
Temperature (°C)	Nitrogen	Air	Hydrogen
350	111	6.2	77.8
380	98	17.2	57.3
400	60	22	54.3
450	39	17.6	22
500	30	—	—

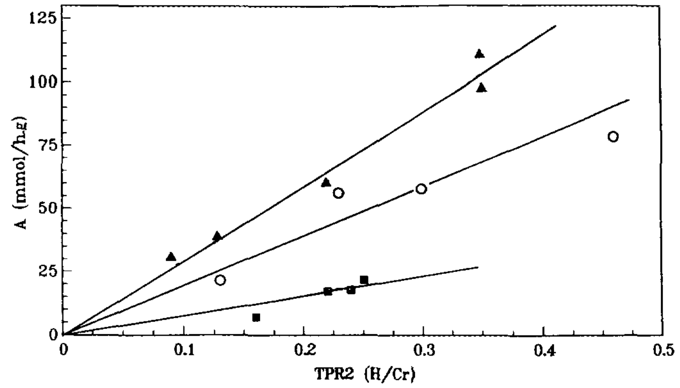

FIG. 4. Correlation between the activity of chromium (III) oxides (mmol h^{-1} g^{-1}) for the fluorination of CF_3CH_2Cl as function of their oxido-reducibility properties (H/Cr : TPR_2). Effect of pretreatment (nitrogen, air, hydrogen) of chromium hydroxide (sample 1) (T = 380°C, HCFC 133a/HF/N_2 = 1/4/5, contact time = 0.01 s): (▲) nitrogen, (○) hydrogen, (■) air.

(ii) For each type of activation atmosphere of chromium hydroxide, the best catalytic activities are obtained for activation temperatures of 350 and 380°C; activities then decrease when the temperature increases.

(iii) If the variation of catalytic activity as a function of the amount of hydrogen consumed during TPR_2, is examined, a linear relationship is obtained for each pretreatment atmosphere whatever the activation temperature (Fig. 4) (20). A similar relationship is also obtained if the surface area is taken into account (Fig. 5).

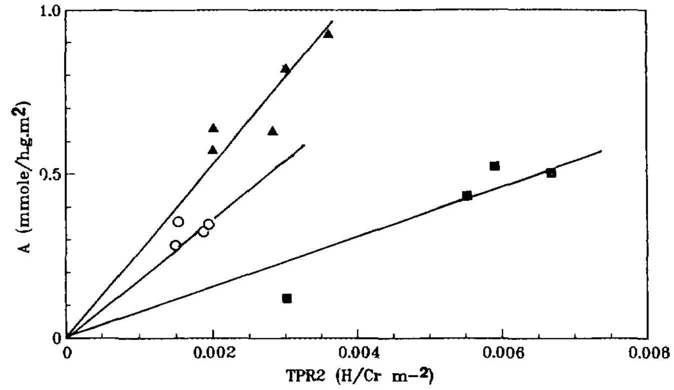

FIG. 5. Correlation between the activity of chromium (III) oxides (mmol h^{-1} g^{-1} m^{-2}) for the fluorination of CF_3CH_2Cl as function of their oxido-reducibility properties (H/Cr m^{-2} : TPR_2). Effect of pretreatment (nitrogen, air, hydrogen) of chromium hydroxide (sample 1) (T = 380°C, HCFC 133a/HF/N_2 = 1/4/5, contact time = 0.01 s): (▲) nitrogen, (○) hydrogen, (■) air.

TABLE 4

Measurement of Oxido–reducibility of Chromium (III) Oxide Depending on the Activation Atmosphere (Air, Hydrogen, Nitrogen) of the Chromium Hydroxide at 350°C Sample 1

Activation atmosphere	TPR_1 $(H/Cr)_1$	TPO_1 $(O/Cr)_1$	TPR_2 $(H/Cr)_2$	TPO_2 $(O/Cr)_2$
Nitrogen	0.47	0.19	0.35	0.18
Air	0.16	0.08	0.16	0.08
Hydrogen	0.17	0.25	0.46	0.21

DISCUSSION

The activation under nitrogen or hydrogen, or in air and the temperature of activation are key factors in the preparation of chromium (III) oxides.

The fluorination reaction of CF_3–CH_2Cl depends directly on reversibly oxidized chromium species in all catalysts. Results presented in Table 4 (where the successive redox measurements obtained with various chromium (III) oxides as a function of the activation atmosphere have been listed, show that there is a reversibility of the phenomenon whatever the activation atmosphere.

It can be seen from the results presented in Table 4 (which lists the successive redox measurements of different chromium (III) oxides pretreated in various atmospheres) that

(i) There is good reversibility of oxygen consumption. The ratio H/O is near 2 whatever the atmosphere of pretreatment.

(ii) The redox properties are greatly dependent on the pretreatment atmosphere.

As far as catalytic properties are concerned, there is a linear relationship between the activity and the hydrogen uptake during TPR_2 $[(H/Cr)_2]$. This proportionality depends on the atmosphere of pretreatment whatever the temperature of activation (Fig. 4). Therefore we can conclude that the fluorination reaction of CF_3CH_2Cl into CF_3CH_2F occurs on chromium species capable of being reversibly oxidized. They are formed during the preparation and especially during the pretreatment of the catalyst.

The increase in activity per unit surface area of working catalyst with a proportional increase in redox site population per unit area (Fig. 5) confirms the importance of this redox behavior.

Moreover, for a similar redox site concentration the activity depends on the pretreatment. This seems to indicate that when changing this pretreatment procedure the mobility of the exchangeable oxygen on the active sites is changed.

Finally, to our knowledge this is the first time that such a correlation between redox properties of oxides and catalytic properties in fluorination of chlorine compounds is established. Therefore such a simple redox method of characterization is of both fundamental and practical importance for the future. Work is in progress in order to identify the chromium species formed in each case and their reactivity with hydrogen fluoride during the activation procedure or the catalytic reaction.

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