Preparation of Substitutes for CFCs. Catalytic Properties of Chromia for Halogen Exchange involving Hydrogen Fluoride and Trifluorochloroethane

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The catalytic activity of chromia for F to Cl exchange in trifluorochloroethane is proportional to the number of chromium atoms which are reversibly oxidized.

The understanding of the behaviour of chromium(III) oxide in the fluorination of chloroalkanes is highly desirable since this oxide is used as a catalyst for the preparation of substitutes for CFCs. For example, one of the routes to hydrochlorofluorocarbons involves the vapour phase fluorination of 1,1,1-trifluoro-2-chloroethane (HCFC 133a) over chromia[1] [eqn. (1)].

$$CF_3CH_2Cl + HF \rightarrow CF_3CH_2F + HCl \qquad (1)$$

This Cl/F exchange is accompanied by dehydrofluorination to give $CF_2{=}CHCl$ (*ca.* 2%) and is also thermodynamically limited. At 380 °C the proportion of $CF_3{-}CH_2F$ (HFC 134a) is 20%. In order to achieve good productivity it is therefore necessary to have a very active catalyst.

We report that this catalytic activity is proportional to the number of chromium atoms which are capable of being reversibly oxidized. Chromium(III) hydroxide was the starting material for the preparation of the catalysts. To a 0.5 mol dm^{-3} chromium(III) nitrate solution, was added 5 mol dm^{-3} dm^{-3} aqueous NH_3.[2,3] The hydroxide was filtered, washed with warm distilled water and dried for 16 h at 90 °C. Samples of this hydroxide were dehydrated in nitrogen for 8 h at various temperatures between 350 and 450 °C. In total seven samples were prepared, and each of them was divided in two; one half for the measurement of catalytic activity and the other for redox properties.

Chromium(III) oxide (0.05 g) was diluted with Lonza graphite 28–42 mesh (11 g) and the catalytic fluorinations were carried out at atmospheric pressure and 380 °C (HCFC 133a : HF : N_2 = 1 : 4 : 5) in a stainless steel reactor, after pretreating the catalyst for 2 h at 380 °C with HF. There was no induction period. The duration of each experiment was 4 h during which time the conversion of HCFC 133a decreased from 14 to 11%. We speculate that this deactivation originates from the surface oligomerization of C_2F_2HCl.

In another set of experiments each of the above-mentioned samples was subjected to successive temperature programmed reduction (TPR1), temperature programmed oxidation (TPO)[4] and another programmed reduction (TPR2), between 20 and 380 °C, in a pulsed chromatograph. Ar or He was used as the carrier gas. For all the samples the uptake of hydrogen in TPR2 agreed with the uptake of oxygen in TPO, *i.e.* two hydrogen atoms for one oxygen per chromium atom (Table 1), except for the sample pretreated at 450 °C. This discrepancy

Table 1

Sample	Calcination temp./°C	H or O uptake/mol per mol Cr		
		TPR1	TPO	TPR2
1	350[a]	0.47	0.19	0.35
2	350[b]	0.52	0.18	0.36
3	380[a]	0.37	0.17	0.32
4	380[b]	0.51	0.15	0.35
5	400[a]	0.23	0.14	0.22
6	400[b]	0.33	0.10	0.20
7	450[a]	0.15	0.04	0.12

[a] Precipitation of chromium(III) hydroxide at constant pH. [b] Precipitation at increasing pH.

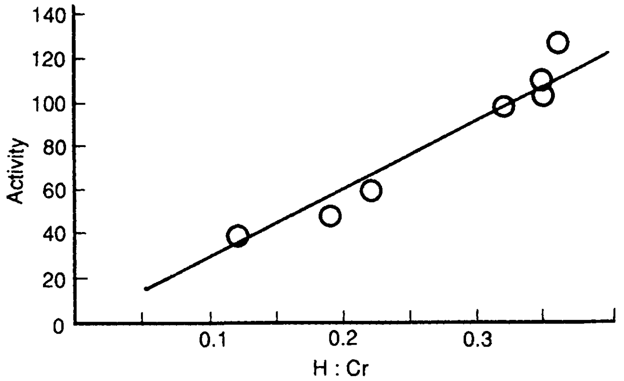

Fig. 1 Catalytic activity of Cr_2O_3. Conversion of HCFC 133a (mmol h^{-1} g^{-1}) *vs.* H : Cr in TPR2. T = 380 °C. HCFC 133a : HF : N_2 = 1 : 4 : 5. Contact time = 0.01 s.

arises from the uncertainty of the uptake of oxygen which is very small for that sample. The O : Cr and H : Cr ratios refer to bulk Cr.[5] We checked that this agreement lasted for many oxidation and reduction cycles. In a cycle including three TPO and four TPR, on the same sample, the H to O ratio was 2 ± 0.2.

These data show that the H : Cr ratio in TPR1 corresponds to the reduction of all the oxidized sites, and the H : Cr ratio in TPR2 measures the number of sites which are reversibly oxidized. Fig. 1 provides the relationship between the catalytic activity and H : Cr ratio in TPR2. The linear correlation indicates that the reversibly oxidized sites are involved in the fluorine for chlorine exchange. This titration appears to be an excellent method, fast and simple, for the characterization of fluorination catalysts.

Our experiments show also that the calcination temperature is a key factor for the formation of these sites. Nevertheless some other parameters may be important and they are currently under investigation in order to improve the properties of these catalysts.

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