Catalytic conversion of CCl_2F_2 on a γ-Al_2O_3 catalyst

T.N. Bell

Department of Chemistry, Simon Fraser University, Burnaby,
British Columbia, Canada V5A 1S6

P. Kirszensztejn and B. Czajka

Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

Received 26 November 1993; accepted 5 October 1994

Reaction of hydrogen with CCl_2F_2 has been studied on a γ-Al_2O_3 catalyst at 300°C. Pure γ-Al_2O_3 appears to be unselective in the catalytic conversion of CCl_2F_2, however, halogenated alumina showed high activity in a reaction leading to the formation of disproportionation products.

Keywords: CFCs; catalytic hydrogenolysis; alumina

1. Introduction

Replacement of halogen atoms in CFCs by H through catalytic hydrogenolysis, is one route to the conversion of CFCs to compounds of much reduced stratospheric ozone depletion potential or which are ozone benign.

The reactions involving the production of chlorofluorocarbon alternatives are produced by complex catalytic chemical processes, involving a number of reactions such as hydrogenation, dehydrohalogenation, hydrodehalogenation, and halogen exchange, which reactions are very often accompanied by isomerization, disproportionation and elimination reactions. Very often during the catalytic conversion of CFCs, many of these reactions occur together, and this leads to difficulty in interpretation of the mechanism. The starting materials (halocarbons) as well as products (HCl or HF) formed during the reaction, may interact with the catalyst metal, and also with the catalyst support, and this adds to the complexity of these processes.

Much of the information on this subject can only be gleaned from the patent literature [1–3]; only a small amount has been published as regular papers. Recently, Manzer and Rao summarized much of this information in an elegant review [4].

One aspect of the use of oxide catalysts which has been observed on alumina, silica–alumina or zeolites is the enhancement of catalytic activity through the incorporation of fluorine in some form on the surface. This causes the lattice polarization to be enhanced due to the electronegativity of F, and results in the enhancement of the acidity of both protonic (Brønsted) and non-protonic (Lewis) sites.

Our interest is in the hydrogenolysis of the carbon–halogen bond with particular reference to CFCs and halons, and involves the catalyst $Pt/\gamma\text{-}Al_2O_3$. Some work has already been reported [5–8] and this present paper is concerned with the reaction of the alumina support with CCl_2F_2 (CFC 12). The study includes the influence of halogenation of the Al_2O_3 on the conversion of CCl_2F_2.

2. Experimental

The $\gamma\text{-}Al_2O_3$ used was obtained by the hydrolysis of aluminum isopropoxide. In order to convert small amounts of bayerite that may have formed during the hydrolysis into boehmite, the suspension was aged at room temperature for one week [9]. The aluminum hydroxide was then washed thoroughly with water and filtered, then dried at 100°C for 5 h. Finally, the support material was obtained by heating the dried material for 24 h in air at a temperature of 500°C.

All the reactions studied were carried out in a series of stainless steel glass lined tubular reactors (operated under continuous flow conditions). Each reactor held 5.00 g of 0.35–0.80 mesh alumina. The reactor was heated in a cylindrical resistance oven. Average temperature fluctuations at the external wall of the reactor were ±5°C for fixed temperature control settings. Gases were delivered to a mixing chamber through a flow valve, and flow controllers calibrated for the gases used. A separate flow controller was used to control the flow of the feed gas mixture through the reactor, at a pressure inside the reactor of 1.05 atm. A multi-port sampling valve and loop assembly were used to sample the reactor feeds and products formed during the reaction. Reactants and products were analyzed using a Perkin-Elmer 900 gas chromatograph equipped with a thermal-conductivity detector, and a 2.4 m column packed with 5% Fluorocol on Carbopack B, and maintained at 50°C. The GC was connected with a Hewlett-Packard HP-3396 Series II integrator. Additional analysis was through a HP GCMS model No. 18001A with electron ionization detector.

Contact times (c/t) are defined as (catalyst volume)/(reactor gas flow rate at STP). For most experiments the reactions were carried out with contact times ~ 13 s.

Unless otherwise mentioned, the ratio between H_2 and CCl_2F_2 was 6 : 1 (vol.). All alumina samples were pretreated with H_2 (300°C for 5 h), as a standard procedure for treating catalysts in this present specific study.

The gases CCl_2F_2 and H_2 were used as received from commercial sources, however, for some experiments the CCl_2F_2 consisted of contaminated material recovered from old refrigerators and contained water, oil and acid. These contaminants were easily removed by passage over molecular sieve, and the results obtained with the resultant CCl_2F_2 were indistinguishable to those obtained from pure material.

3. Results and discussion

The reaction of CCl_2F_2/H_2 1 : 6 mixtures when passed over γ-Al_2O_3 at 300°C is complex.

The initial conversion, initially 100%, decreases to a plateau level ~ 70%, in the first few hours. The gaseous products eventually settled to a reproducible plateau level after approximately 2 h. This plateau level was maintained for at least the next 30 h in the flowing gas stream, as can be seen from the data presented in fig. 1.

The main product of reaction was $CClF_3$ (60 mol%) with the additional main products being CF_4 and CCl_3F each around 10 mol% and CCl_4 30 mol%. We are grateful to Dr. L. Manzer (Dupont) for help in assigning these particular compounds.

Both HCl as well as HF were detected in the gaseous outflow from the reactor, and following dissolution of these products in water, our preliminary analyses shows that the ratio between Cl and F was about 15 : 1.

Experiments were carried out to try and determine if the causes for the high initial catalyst reactivity were different to those responsible for the plateau region.

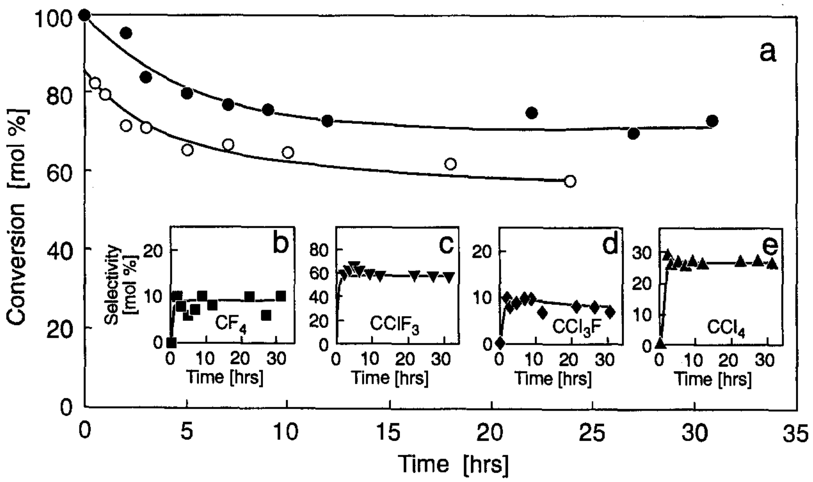

Fig. 1. Conversion of CCl_2F_2 over γ-Al_2O_3 and selectivities to particular products at 300°C (CCl_2F_2 : H_2 = 1 : 6) (solid data points). Same sample after 30 h reaction following H_2 treatment for 5 h at 300°C (open circles).

3.1. REGENERATION OF ALUMINA ACTIVITY

Following the long plateau region the sample of alumina was treated with H_2 alone for 5 h at 300°C, followed by restoration of the CCl_2F_2/H_2 mixture flow. The results are shown in fig. 2.

It is seen that a high initial regeneration reactivity (~ 85% conversion) was obtained which decreases with time as is observed with the original sample, and reaches a new plateau level ~ 60%. The extent of conversion is less (about 10%) than with the original sample, however, the conversion curve characteristics are the same.

In order to determine whether carbonaceous deposits affect the catalytic behavior, similar regeneration experiments were carried out where the catalyst from the plateau region was treated with air at 500°C for 5 h to remove any carbon deposit. This treatment converted the alumina, which was always blackened during reaction, to a grey white colour. This alumina was treated with H_2 at 300°C. The resultant regenerated alumina, yielded the same conversion curve characteristics and values as those obtained from simple H_2 regeneration treatment as described above. Thus, we conclude that carbonaceous deposits on the surface of the alumina do not affect its catalytic behavior for the reactions being investigated.

It is possible the high initial alumina activity is connected with a reaction involving halogenation of the surface resulting in catalyst activation.

In the present work, an X-ray diffraction analysis of the alumina sample following reaction, and also after hydrogen treatment, showed the presence of a distinct AlF_3 structure. No compound structure involving Cl species was observed.

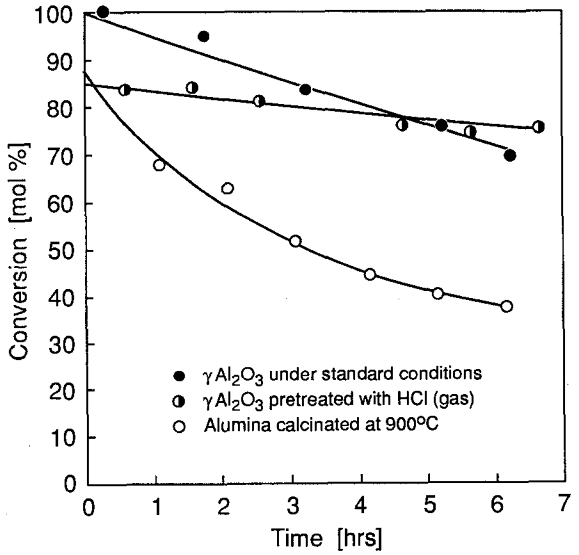

Fig. 2. Conversion of CCl_2F_2 over γ-Al_2O_3.

A chemical analysis of the alumina composition immediately following reaction showed that both Cl and F were present in significant amounts but after H_2 regeneration the Cl content had significantly declined relative to the F content.

A similar observation has been reported by Adkins and Davis [10]. They found that on a Pt–Sn/Al_2O_3 catalyst, an intense chloride peak (chlorine added during the metals impregnation) was observed in the ESCA spectra for unreduced samples, and that this peak disappeared after chemical reduction with H_2. Their chemical analysis, however, showed Cl^- to be present in the bulk of the alumina even after H_2 treatment.

We propose that the reaction of alumina with CCl_2F_2, results in, initially, fluorination and chlorination of the surface, and that this halogenation produces an active catalytic surface. The Cl content of the surface is itself reactive and may be removed by H_2 treatment at 300°C.

3.2. PRETREATMENT WITH HCl (GAS)

If the above proposal is correct, it should be possible to halogenate an alumina sample with a Cl source such as HCl gas. This was done (HCl, 1 h, 300°C, flow 15 ml/min) after which the residual HCl was displaced with He followed by the standard CCl_2F_2/H_2 mixture.

The subsequent conversion results shown in fig. 2 are compared with CCl_2F_2 conversion using a fresh untreated alumina sample. A significant difference is observed with the HCl treated sample behaving from the beginning as if it were already in the plateau region (~ 80% conversion), while the non-HCl treated alumina showed 100% initial conversion falling to the 80% level after ~ 4–5 h.

These results are in accord with there being two processes occurring: (1) a rapid early halogenation of Al_2O_3, (2) a steady conversion to disproportionation products of CCl_2F_2.

We suggest the requirement for disproportionation is the formation of an active halogenated surface, and the results with HCl alone and the regeneration experiments with H_2 suggest that activation by Cl is an important process. Certainly, it would appear that Cl is a more labile system than F, which is stabilized as AlF_3 on the alumina.

The product distribution (selectivity) obtained for HCl treated alumina is given in fig. 3 (note CCl_4 was not measured). The selectivities (based on moles CFC converted and moles of each product formed), are similar to those obtained on γ-Al_2O_3 itself in the plateau section of the conversion curve. There seems to be a difference in the reaction time for a particular product to appear, again probably due to the fact that halogenation is a necessary prerequisite for the conversion of CCl_2F_2 to gaseous products, and thus product formation is delayed when fresh untreated Al_2O_3 is used.

Also in fig. 2 is presented the results of conversion carried out on γ-alumina calcinated at a temperature of 900°C for a 6 h period. Under these conditions alumina

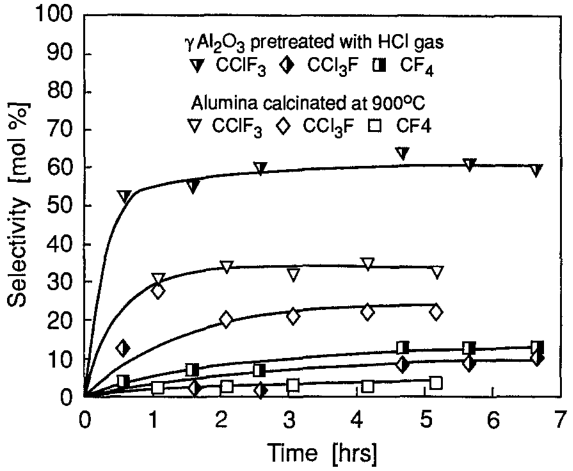

Fig. 3. Product selectivity from CCl_2F_2 conversion on alumina.

loses almost all its surface OH groups and is converted to α-Al_2O_3. This particular structure results in a diminished conversion of CCl_2F_2 to around half that obtained with the low temperature calcinated alumina. The fall-off in conversion in the initial stages of reaction displays similar shape characteristics which suggests that even in the absence of OH groups, a process involving halogenation of the alumina surface may also occur. This is in agreement with the model of Kerkhof et al. [11] involving the incorporation of fluorine on an alumina surface, showing that halogens cannot only substitute surface OH groups, but also the O groups which are present. The nature and distribution of these phases depends not only on the applied fluorinating agent, but also on the temperature at which the catalysts have been treated [11,12].

It should be kept in mind, however, that the observed decrease of the extent of conversion, can also be attributed to a decrease of the specific surface area of samples calcinated at higher temperatures.

The yield of $CClF_3$ on high temperature calcinated alumina (OH surface free) is significantly lower (by a factor approximately 2), over that obtained (again after a short, 3–4 h, initial period) for the HCl treated (fig. 3), or the normal treated alumina (fig. 1c). The CCl_3F formed, however, is considerably higher. Thus the temperature of calcination appears to play a significant role in the product selectivity.

The results of a preliminary investigation of the reaction of CH_3Cl and CH_2Cl_2 with γ-Al_2O_3 shows that in these cases the initial conversion of the starting materials is much lower (25 and 75% respectively) in comparison to the corresponding results for CCl_2F_2, and after a few hours the conversion decreases to almost zero. The greater reactivity of CH_2Cl_2 over CH_3Cl follows a pattern in agreement with the results from the halogen replacement work of Buckman [13], and the conclusion of Gervasutti [14], that the CCl_2 moiety is a very reactive entity under hydrogenolysis conditions.

If our conclusions concerning the reasons for the sharp initial fall-off in conversion observed for CCl_2F_2 are correct, it would appear that the observed conversion of CH_3Cl and CH_2Cl_2 is connected only with the process of halogenation of the alumina surface. The resultant surface would appear not to be catalytically active to further reactions with the parent chlorocarbons CH_3Cl and CH_2Cl_2. It is interesting to note, however, that the alumina after treatment with either CH_3Cl or CH_2Cl_2 is active with respect to the conversion of CCl_2F_2. This aspect of the work is being investigated further.

Some experiments were carried out on the conversion of CCl_2F_2 in the absence of H_2. In order to simulate conditions in the presence of H_2, helium was substituted for H_2 to yield a mix CCl_2F_2/He 1 : 6. The results are shown in fig. 4. The first 8 h of reaction are similar to that for the system CCl_2F_2/H_2 but the catalyst activity declined significantly at greater times. The selectivity ratios are not significantly different to those obtained in the CCl_2F_2/H_2 case.

4. Conclusion

γ-alumina causes the disproportionation of CCl_2F_2 to products following halogenation of the surface. The presence of H_2 appears necessary to sustain the level of conversion to long times of reaction. Halogenating agents such as HCl and chloroalkanes are able to activate the alumina surface. The temperature of calcination is important in determining the reactivity of Al_2O_3 and its selectivity to products.

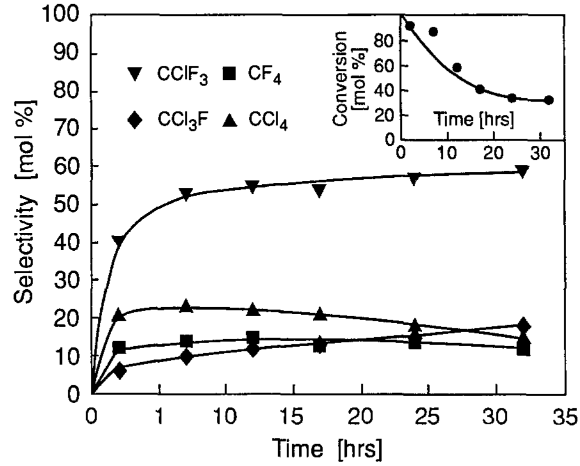

Fig. 4. Conversion of CCl_2F_2 on γ-Al_2O_3 and selectivities to products at 300°C in absence of H_2 (CCl_2F_2 : He = 1 : 6).

Acknowledgement

We are grateful for financial support from the British Columbia Science Council and to Dupont for providing technical information.

References

[1] C.S. Kellner and V.N.M. Rao; US Patent 4,873,381.
[2] L.B. Smith, US Patent 2,942,036.
[3] W.H. Manogue, V.N.M. Rao and F.J. Weigert, US Patent 5,030,372.
[4] L.E. Manzer and V.N.M. Rao, Adv. Catal. 39 (1993).
[5] P. Kirszensztejn, W. Przystajko and T.N. Bell, Catal. Lett. 18 (1993) 319.
[6] P. Kirszensztejn and T.N. Bell, Catal. Lett. 21 (1993) 371.
[7] T. Sheng, P. Kirszensztejn, T.N. Bell and I.D. Gay, Catal. Lett. 23 (1994) 119.
[8] M. Ahmed, T.N. Bell, P. Kirszensztejn and B. Marciniak, in: *Proc. Int. Conf. of Ozone Depleting Substances*, Whistler, September 1993.
[9] J. Medema, J. Catal. 37 (1975) 91.
[10] S.R. Adkins and B.H. Davis, J. Catal. 89 (1984) 371.
[11] F.P.J.M. Kerkhof, J.C. Oudejans, J.A. Moulijn and E.R.A. Matulewicz, J. Colloid Interf. Sci. 77 (1980) 120.
[12] S. Kowalak, Acta Chim. Acad. Sci. Hung. 107 (1981) 19.
[13] R.W. Buckman, US Patent 3,644,545.
[14] C. Gervasutti, L. Marongoni and W. Mara, J. Fluorine Chem. 19 (1981/82) 1.