Fluorinated γ-Alumina. Catalytic Fluorination of 1,1,1-Trichloroethane at Ambient Temperature

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γ-Alumina, fluorinated with sulphur tetrafluoride followed by treatment with 1,1,1-trichloroethane, behaves as a catalyst for the room temperature fluorination of CH_3CCl_3 with anhydrous HF, giving a mixture of chlorofluorohydrocarbons.

The promotion of Lewis acidity on a γ-alumina surface by chlorination with carbon tetrachloride or carbonyl chloride is well established.[1,2] Carbonyl fluoride does not behave in an analogous fashion but promotes Brønsted acidity. A search for fluorinating agents capable of generating strong Lewis acid sites has led to the discovery of a novel, heterogeneous catalytic reaction in which 1,1,1-trichloroethane is converted to a mixture of chlorofluorohydrocarbons at room temperature.

γ-Alumina chlorinated with CCl_4 or Cl_2CO has no ability to

Table 1 Composition of the organic products (mole %)[b] from the catalytic fluorination of CH_3CCl_3[a]

Run	CH_3CCl_3	$CH_2{=}CCl_2$	CH_3CCl_2F	CH_3CClF_2	CH_3CF_3
1	76.9	4.5	7.2	7.6	3.6
2	68.7	5.3	24.3	1.4	0.35
3	76.5	0.5	22.5	0.75	trace
4	85.0	0.3	12.7	1.1	1.0
5	95.0	trace	4.0	0.75	0.75

[a] Reaction conditions: 2 h at room temperature, Monel metal vessel, mole ratio CH_3CCl_3 to HF = 3 : 1 Catalyst prepared from calcined (523 K) γ-alumina treated with SF_4 (F content = 3.7 mg atom g^{-1}) then CH_3CCl_3 as described in the text. [b] Determined by ^1H NMR analysis of the liquid mixture.

isomerize but-1-ene at room temperature but isomerisation occurs when but-1-ene is exposed to γ-alumina which has been fluorinated with OCF_2 or chlorinated with anhydrous hydrogen chloride. The former surface is more selective for the isomerisation of but-1-ene to but-2-ene, a reaction which is known to be dependent on Brønsted acidity.[3]

Hydrolysis of F_2CO on the surface of calcined γ-alumina is rapid at room temperature and the increased Brønsted acidity of the surface appears to be due to the hydrolysis product HF. Promotion of Brønsted acidity by other fluorides, for example BF_3 or NH_4F,[4] has been noted previously. The reaction between Cl_2CO and calcined γ-alumina is minimal at room temperature. At 500 K surface chlorination produces both Brønsted and Lewis sites. The former are derived from the hydrolysis product HCl and we have suggested that the latter result from a direct reaction between Cl_2CO and in-plane bridging oxygens.[2]

Surface Lewis acidity has been probed by the dehydrochlorination behaviour of 1,1,1-trichloroethane. The behaviour of CCl_4- or Cl_2CO-chlorinated γ-alumina towards 1,1,1-trichloroethane at room temperature is analogous to that observed previously using the strong Lewis acid, solid anhydrous aluminium(III) chloride.[5] Dehydrochlorination of CH_3CCl_3 occurs rapidly at room temperature to give 1,1-dichloroethene and HCl. 1,1-Dichloroethene undergoes further reaction on the surface to give a purple, oligomeric, organic layer. Neither calcined γ-alumina nor γ-alumina halogenated with HCl, OCF_2 (at either 298 or 500 K) or anhydrous HF has any dehydrochlorinating ability towards CH_3CCl_3 at room temperature.

Hydrolysis of sulphur tetrafluoride on calcined γ-alumina, giving F_2SO and SO_2, is rapid at room temperature, and is very exothermic. Treatment of calcined (523 K) γ-alumina (0.5 g) with three successive aliquots of SF_4 (1 mmol) under static conditions at room temperature for 2 h, followed by CH_3CCl_3 (3 mmol) at room temperature for 1 h results in the formation of $CH_2{=}CCl_2$, laydown of purple oligomeric material on the surface, and a mixture of chlorofluorohydroethanes, CH_3CCl_2F, CH_3CClF_2 and CH_3CF_3. This surface is a catalyst for the room-temperature fluorination of CH_3CCl_3 by anhydrous HF which gives a mixture of $CH_3CCl_{3-n}F_n$, n = 0–3, and some $CH_2{=}CCl_2$, Table 1. Fluorination of CH_3CCl_3 does not occur in the absence of a catalyst and the F-for-Cl halogen exchange reactions occur under conditions that are far milder than those usually required, for example for the vapour-phase catalytic fluorination of $C_2Cl_{6-n}F_n$, n = 3 or 4, on fluorinated chromia.[6]

The dehydrochlorination of CH_3CCl_3 at SF_4-fluorinated γ-alumina indicates that strong Lewis acid sites, analogous to those formed using CCl_4 or Cl_2CO,[2] are present. An additional treatment of calcined γ-alumina with SF_4, then CH_3CCl_3, as described above, results in further fluorination since F_2SO and SO_2 are both observed. Dehydrochlorination of CH_3CCl_3 occurs on this surface but no fluorinated organic products are formed. Evidently fluorination with SF_4 after the initial laydown of the purple oligomer does not produce the HF necessary for the halogen exchange reaction and HF must be supplied directly mixed with CH_3CCl_3. Too much HF must be avoided, for example a mole ratio of HF to CH_3CCl_3 of 1 : 1 with the other reaction conditions specified in Table 1 results in a far lower conversion. This is related to the observation that the dehydrochlorination behaviour of γ-alumina which has been fluorinated by SF_4 or chlorinated by CCl_4 or Cl_2CO is blocked by the HF treatment. However, treatment with HCl has no effect.

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