

## Fluorinated $\gamma$ -Alumina. Catalytic Fluorination of 1,1,1-Trichloroethane at Ambient Temperature

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$\gamma$ -Alumina, fluorinated with sulphur tetrafluoride followed by treatment with 1,1,1-trichloroethane, behaves as a catalyst for the room temperature fluorination of  $\text{CH}_3\text{CCl}_3$  with anhydrous HF, giving a mixture of chlorofluorohydrocarbons.

The promotion of Lewis acidity on a  $\gamma$ -alumina surface by chlorination with carbon tetrachloride or carbonyl chloride is well established.<sup>1,2</sup> 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.

$\gamma$ -Alumina chlorinated with  $\text{CCl}_4$  or  $\text{Cl}_2\text{CO}$  has no ability to

**Table 1** Composition of the organic products (mole %)<sup>b</sup> from the catalytic fluorination of CH<sub>3</sub>CCl<sub>3</sub><sup>a</sup>

Run	CH <sub>3</sub> CCl <sub>3</sub>	CH <sub>2</sub> =CCl <sub>2</sub>	CH <sub>3</sub> CCl <sub>2</sub> F	CH <sub>3</sub> CClF <sub>2</sub>	CH <sub>3</sub> CF <sub>3</sub>
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

<sup>a</sup> Reaction conditions: 2 h at room temperature, Monel metal vessel, mole ratio CH<sub>3</sub>CCl<sub>3</sub> to HF = 3:1 Catalyst prepared from calcined (523 K)  $\gamma$ -alumina treated with SF<sub>4</sub> (F content = 3.7 mg atom g<sup>-1</sup>) then CH<sub>3</sub>CCl<sub>3</sub> as described in the text. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the liquid mixture.

isomerize but-1-ene at room temperature but isomerisation occurs when but-1-ene is exposed to  $\gamma$ -alumina which has been fluorinated with OCF<sub>2</sub> 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.<sup>3</sup>

Hydrolysis of F<sub>2</sub>CO on the surface of calcined  $\gamma$ -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<sub>3</sub> or NH<sub>4</sub>F,<sup>4</sup> has been noted previously. The reaction between Cl<sub>2</sub>CO and calcined  $\gamma$ -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<sub>2</sub>CO and in-plane bridging oxygens.<sup>2</sup>

Surface Lewis acidity has been probed by the dehydrochlorination behaviour of 1,1,1-trichloroethane. The behaviour of CCl<sub>4</sub>- or Cl<sub>2</sub>CO-chlorinated  $\gamma$ -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.<sup>5</sup> Dehydrochlorination of CH<sub>3</sub>CCl<sub>3</sub> 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  $\gamma$ -alumina nor  $\gamma$ -alumina halogenated with HCl, OCF<sub>2</sub> (at either 298 or 500 K) or anhydrous HF has any dehydrochlorinating ability towards CH<sub>3</sub>CCl<sub>3</sub> at room temperature.

Hydrolysis of sulphur tetrafluoride on calcined  $\gamma$ -alumina, giving F<sub>2</sub>SO and SO<sub>2</sub>, is rapid at room temperature, and is very exothermic. Treatment of calcined (523 K)  $\gamma$ -alumina

(0.5 g) with three successive aliquots of SF<sub>4</sub> (1 mmol) under static conditions at room temperature for 2 h, followed by CH<sub>3</sub>CCl<sub>3</sub> (3 mmol) at room temperature for 1 h results in the formation of CH<sub>2</sub>=CCl<sub>2</sub>, laydown of purple oligomeric material on the surface, and a mixture of chlorofluorohydroethanes, CH<sub>3</sub>CCl<sub>2</sub>F, CH<sub>3</sub>CClF<sub>2</sub> and CH<sub>3</sub>CF<sub>3</sub>. This surface is a catalyst for the room-temperature fluorination of CH<sub>3</sub>CCl<sub>3</sub> by anhydrous HF which gives a mixture of CH<sub>3</sub>CCl<sub>3-n</sub>F<sub>n</sub>, *n* = 0–3, and some CH<sub>2</sub>=CCl<sub>2</sub>, Table 1. Fluorination of CH<sub>3</sub>CCl<sub>3</sub> 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<sub>2</sub>Cl<sub>6-n</sub>F<sub>n</sub>, *n* = 3 or 4, on fluorinated chromia.<sup>6</sup>

The dehydrochlorination of CH<sub>3</sub>CCl<sub>3</sub> at SF<sub>4</sub>-fluorinated  $\gamma$ -alumina indicates that strong Lewis acid sites, analogous to those formed using CCl<sub>4</sub> or Cl<sub>2</sub>CO,<sup>2</sup> are present. An additional treatment of calcined  $\gamma$ -alumina with SF<sub>4</sub>, then CH<sub>3</sub>CCl<sub>3</sub>, as described above, results in further fluorination since F<sub>2</sub>SO and SO<sub>2</sub> are both observed. Dehydrochlorination of CH<sub>3</sub>CCl<sub>3</sub> occurs on this surface but no fluorinated organic products are formed. Evidently fluorination with SF<sub>4</sub> 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<sub>3</sub>CCl<sub>3</sub>. Too much HF must be avoided, for example a mole ratio of HF to CH<sub>3</sub>CCl<sub>3</sub> 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  $\gamma$ -alumina which has been fluorinated by SF<sub>4</sub> or chlorinated by CCl<sub>4</sub> or Cl<sub>2</sub>CO is blocked by the HF treatment. However, treatment with HCl has no effect.

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