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Destruction of chlorinated methanes by catalytic hydrolysis

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CH_2Cl_2, $CHCl_3$ and CCl_4 react with water vapour to give $CO_2 + HCl$ over γ-Al_2O_3, TiO_2 (rutile) and other acidic oxide catalysts; high conversions are obtained between 673 and 773 K. Rates are proportional to concentration of chlorinated methane and are inhibited by high concentrations of water; they are described by a Langmuir–Hinshelwood rate expression.

Keywords: chloroform; chlorinated methanes; alumina; titania; acidic oxides

1. Introduction

A large number of chlorinated molecules are environmental hazards by reasons of their toxic and sometimes carcinogenic effects on living organisms. There is therefore a need for a cheap and effective means for their destruction by conversion into less harmful products that are readily recovered: transformation into $CO_2 + HCl$, both easily caught by wet-scrubbing, is the obvious solution. A number of papers have appeared in recent years, canvassing methods for the catalysed destruction of chlorinated molecules: these include (i) dehydrochlorination [1], (ii) hydrogenolysis [2] and (iii) oxidation [3–5]. The first two methods have used catalysts (either basic or metallic) that are poisoned by HCl, and will leave a residual hydrocarbon that may indeed be less obnoxious than the reactant. Most attention has however been given to the possibility of destruction by oxidation.

It is somewhat strange that this should be so, because it is immediately apparent that molecules containing more Cl atoms than H atoms cannot be wholly converted by air to HCl, and there is a risk amounting to a near certainty that even more toxic products such as Cl_2 and $COCl_2$ will be formed. It seems obvious that what is required is the hydrolysis of the carbon–chlorine bonds, with the formation of HCl and some intermediate C_1 species that will quickly convert to $CO_2 + H_2O$. Some years ago we naively tried to supply additional H atoms as short-chain alkanes (propane + butane, i.e. Calor Gas), and this was effective [6]: we later came to realise that the alkanes were being oxidised over the Pt catalyst to $CO_2 + H_2O$, and that it was the water that was the effective reactant, causing hydrolysis of the chlorinated molecules. The heat of reaction was sufficient to maintain the catalyst at a temperature such that high conversions were obtained, without the need for external heating. We have carried out further work on this system [7], and it will be reported elsewhere: we now summarise work performed with acidic oxide catalysts containing no metal, and using water vapour as the destructive agent.

2. Experimental

Reactions were performed in a fixed-bed flow-system at atmospheric pressure, using ~ 5 g catalyst: the flow-rates used were: 250 $cm^3\ min^{-1}$; N_2, 60 $cm^3\ min^{-1}$ plus amounts of water vapour and of chlorinated methane as determined by the temperatures of saturators. Evolved HCl was dissolved in water and estimated by titration with NaOH using methyl orange as indicator. The chlorinated methanes (CH_2Cl_2, $CHCl_3$ and CCl_4) were analysed using a 2m Poropak Q column at 210°C.

Catalysts included γ-Al_2O_3 (Alcoa F-1), SiO_2 (Merck 40), TiO_2 rutile (Tioxide International plc) and SiO_2–Al_2O_3 cracking catalyst. A number of SiO_2-supported oxides were prepared by grafting; supported Al_2O_3, B_2O_3, SnO_2, Ga_2O_3, In_2O_3 and TiO_2 were obtained by reaction of the corresponding chlorides with surface silanol groups. All materials were characterized by N_2 physisorption, XPS, laser Raman spectroscopy etc.

3. Results

Table 1 gives the rates at 623 K and the Arrhenius parameters derived in the specified temperature ranges for the hydrolysis of $CHCl_2$, $CHCl_3$ and CCl_4 over γ-Al_2O_3 and TiO_2 (rutile). The activities of these two catalysts at this temperature are about the same, and reactivity of the chlorinated molecules increases with the number of Cl atoms. With γ-Al_2O_3, conversions close to 100% were observed at 623 K for CCl_4, at 677 K for $CHCl_3$ and at 760 K for CH_2Cl_2. Rates were proportional to chlorinated methane concentration and were inhibited by increasing H_2O concentration (see fig. 1 from an example). HCl continued to be evolved long

Table 1
Rates and kinetic parameters for the catalysed hydrolysis of chlorinated methanes (P_{CM} = 36.2 Torr) [a]

Catalyst	Reactant	$P(H_2O)$ (Torr)	r^{623}	E (kJ mol^{-1})	T range (K)	ln A
Al_2O_3	CH_2Cl_2	32	1.1	58.1	613–673	0.15
	$CHCl_3$	32	2.9	85.3	606–655	6.02
	CCl_4	75	3.6	85.8	597–663	6.34
TiO_2	CH_2Cl_2	167	0.35	74.0	625–708	1.74
	$CHCl_3$	108	1.3	58.6	607–667	0.03
	CCl_4	85	2.8	53.5	598–638	−0.14
SiO_2–Al_2O_3	CCl_4	377	2.6	79.1	505–533	4.70
Al_2O_3/SiO_2	CCl_4	430	13.5	81.2	532–588	6.77

[a] Rate at 623 K (r^{623}) and A in units of mol min^{-1} g^{-1}; linear Arrhenius plots within T range.

after the flow of the chlorinated molecule was stopped; the amount released depended on the previous conditions of use, and the rate of its formation increased with temperature and with water vapour pressure.

High activities were also shown by the amorphous SiO_2–Al_2O_3 cracking catalyst (see table 1; 71% conversion at 546 K) and by the sample of Al_2O_3/SiO_2 prepared by grafting (see also table 1; 86% conversion at 623 K). Both of these materials had much higher surface areas than the γ-Al_2O_3 (respectively 600 and 630 m^2 g^{-1} compared to 250 m^2 g^{-1}), although some loss of surface area occurs during use. To a first approximation, activity is determined by the number of surface Al^{3+} ions per g; SiO_2 (700 m^2 g^{-1}) is virtually inactive.

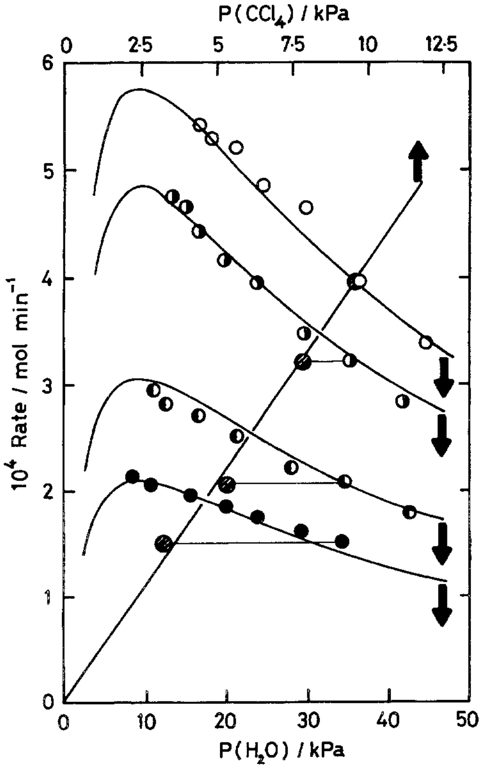

Fig. 1. Variation of rate of hydrolysis of CCl_4 on Al_2O_3/SiO_2 catalyst at 565 K with H_2O vapour pressure at various CCl_4 pressures: (○) 9.6 kPa; (◑) 7.8 kPa; (◐) 4.8 kPa; (●) 3.2 kPa. The hatched points show the dependence of rate on CCl_4 pressure at an H_2O pressure of ~ 34.6 kPa.

SnO_2/SiO_2 and TiO_2/SiO_2 materials were prepared in various ways, and also showed good activity: some were stable, but in many cases volatile chlorides ($SnCl_4$, $TiCl_4$) were formed at high conversion and low H_2O concentration. The loss of the active component was acute when SiO_2-supported Ga_2O_3 and In_2O_3 were used.

4. Discussion

It is clear that under reaction conditions each of the chlorinated molecules converts the surface of the active component into a chlorided state, which when the reaction is stopped quite slowly reacts with water to form HCl and to regenerate an hydroxylated surface. The essential features of the reaction mechanism will therefore involve the disruption of the chlorinated reactant at a Lewis acid site, with formation of Cl–M bonds (M = Al, Ti etc.), the chemisorption of water at similar Lewis acid centres and its reaction with the Cl–M bond to form HCl. From the form of the kinetics, both reactants compete for the same sites, the water molecule more effectively. When the rate of formation of the Cl–M bonds is too high and the water vapour pressure too low, species such as Cl_2M and Cl_3M are formed, and may react further to give the gaseous metal chloride. The C_1 species, stripped of its Cl atoms, is presumed to react quickly with water or adsorbed hydroxyl groups to give CO_2.

We have tested the experimental results against the simplest possible rate expression, based on each reactant in undissociated form competing for a single type of site according to the Langmuir equation. Fig. 1 shows the observed variation of rate with water vapour concentration for four different pressures of CCl_4 at 565 K on Al_2O_3/SiO_2, together with calculated curves using constants b_c (the adsorption coefficient for CCl_4) = 1.81×10^{-4} kPa^{-1} and b_w (w = water) = 1.97×10^{-3} kPa^{-1}; the intrinsic rate constant is 2.60×10^{-2} mol min^{-1}. The agreement is very satisfactory. Also shown is the dependence of the observed rates on CCl_4 pressure when $P_w = 40$ kPa: as expected from its smaller adsorption coefficient, the rate is almost proportional to its pressure. The inhibiting power of water decreases with increasing temperature, as expected.

The apparent activation energy is generally a function of the water vapour pressure. For the Al_2O_3/SiO_2 catalyst, values measured between 529 and 565 K are as follows: at $P_w = 16.5$ kPa, $E_a = 73.4$ kJ mol^{-1}; at $P_w = 34$ kPa, $E_a = 81.6$ kJ mol^{-1}; and at $P_w = 51.3$ kPa, $E_a = 96.6$ kJ mol^{-1}. This variation is a direct consequence of the Temkin equation [8,9] which expresses how the apparent activation energy E_a has to be corrected for the enthalpies of adsorption ($-\Delta H$) of the reactants to obtain the true activation energy E_t. In the present case,

$$E_a = E_t - n_w \Delta H_w + n_c \Delta H_c \,,$$

where the n's are the orders of reaction: the positive sign before the last term signifies a decrease in θ_c with increasing temperature, while the negative sign before the previous term signifies that water desorption generates more vacant sites for adsorption of the other reactant, and hence allows the reaction to proceed even faster.

It should be easily possible to develop the reaction of hydrolysis of chlorinated molecules by acidic solids into a viable large-scales process for the treatment of potential environmental pollutants containing C–Cl bonds, and its extension to fluorinated molecules is conceivable, although the C–F bond is stronger. Efficient reaction, however, requires the supply of water vapour sufficient to prevent over-chloriding the surface, with its attendant risks; in view of the marked tendency for Al_2O_3 to retain chloride ion on its surface, as for example in petroleum reforming, it is a little surprising to learn that $-\Delta G°$ at 500 K for the reaction

$$2AlCl_3(l) + 3H_2O(g) \rightarrow Al_2O_3(s) + 6HCl(g)$$

is as much as 232.5 kJ mol^{-1}, corresponding to a value of K_p of 1.96×10^{24}. There are clearly dangers in extrapolating bulk thermochemical parameters to the behaviour of surfaces.

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