Ethene Chlorination and Oxidative Coupling over Supported Mono- and Bi-metallic Chloride Catalysts

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Temperature-programmed reduction of metal chlorides upon silica, alumina, and titania supports using ethene produces chloroethene and 1,2-dichloroethane, together with rather unexpectedly, 1,1-dichloroethane and benzene in yields which differ from one metal chloride to another; results suggest the involvement of novel · · H/Cl · · exchange and oxidative-coupling reactions and also suggest that this technique of ethene titration may be of value in characterising the active sites in chloride catalysts and catalytic precursors.

The present work involves the passage of a gaseous reductant alkene (here ethene) over a sample (100 mg) of the supported metal chloride catalyst, which had been flushed for 0.5 h in flowing He, in a flowing stream of 1% ethene in He (BOC, 101 kPa, 40 cm^3 per min) while this was being heated from 298 to 773 K at 5 K per min. Products were analysed by g.c. and mass spectral methods. This technique is between temperature-programmed-reduction and -titration (t.p.r. and t.p.t.) methods and it was felt that the analysis of product distributions as a function of temperature might provide more information than isothermal measurements. Temperature-programmed methods are increasingly used for catalyst characterisation and this might provide a useful extension to these methods, enabling *in situ* characterisation of phases active in oxychlorination. It was possible to separate the main products, *i.e.* 1,2-dichloroethane (1,2-DCEA), 1,1-dichloroethane (1,1-DCEA), chloroethene (CEE), and ethene (EE), chromatographically; product identification was confirmed by mass spectroscopy. Some samples produced an additional g.c. peak which was found by mass spectroscopy to be due to benzene (B). The g.c. was calibrated for all products.

Table 1. Yields of different products in ethene temperature-programmed titration.

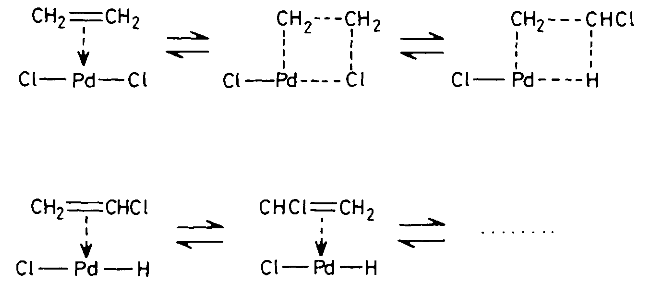
			Molecules per 1000 Cu atoms (temp./K of maximum rate)		
Catalyst[a]	% Metals	Precursor salt	1,2-DCEA	1,1-DCEA	CEE
Cu/A	4.2	$CuCl_2$	0.53 (513)	—	NA (623)[b]
Cu/S	3.8	$CuCl_2$	1.13 (493)	—	NA (623)
Cu/T	4.2	$CuCl_2$	1.56 (493)	—	NA (718)
Cu–Pd/A	3.8–0.46	$CuCl_2/H_2PdCl_4$	0.207 (546)	0.024 (498)	0.082 (468)
Cu–Pd/A	4.0–0.99	$CuCl_2/H_2PdCl_4$	0.226 (478)	0.033 (463)	0.115 (448)
Cu–Pd/A	4.0–1.97	$CuCl_2/H_2PdCl_4$	0.199 (481)	0.036 (468)	0.130 (453)

[a] $CuCl_2{\cdot}2H_2O$ (AnalaR, >98% purity) and $PdCl_2$ (Specpure, Johnson Matthey) were used as aqueous solutions to prepare catalysts, the latter as H_2PdCl_4. Boehmite (A; Norton SA6373, >99.85% alumina, 0.6 $cm^3\ g^{-1}$ pore volume), silica (S; Davison 923, >99.6% purity, 0.38 $cm^3\ g^{-1}$ pore volume), and titania (T; Degussa P25, 78% anatase and balance to 99.5% purity given by rutile, 3.8 $cm^3\ g^{-1}$ pore volume) were impregnated with these solutions to give monometallic or bimetallic chlorides. [b] NA indicates product area not assessed because of its small size. Average crystallite sizes of Cu^{2+} phases on A, S, and T supports were determined by *X*-ray powder diffraction line broadening to be 60—70 nm.

Table 2. Relative rates of formation of benzene per metal atom* catalysed by alumina-supported metal chlorides containing 5 wt % metal at the optimum temperature for each catalyst.[a]

$FeCl_3$ 1.14*	$CoCl_2$ 1.00*	$NiCl_2$ 2.86*	$CuCl_2$ 1.71*
$RuCl_3$ 871*	$RhCl_3$ 2171*	H_2PdCl_4 529*	— —
— —	$HIrCl_4$ 771*	H_2PtCl_6 480*	$HAuCl_4$ 34.3*

[a] Prepared using the incipient wetness technique and Norton SA6373 alumina.



Scheme 1

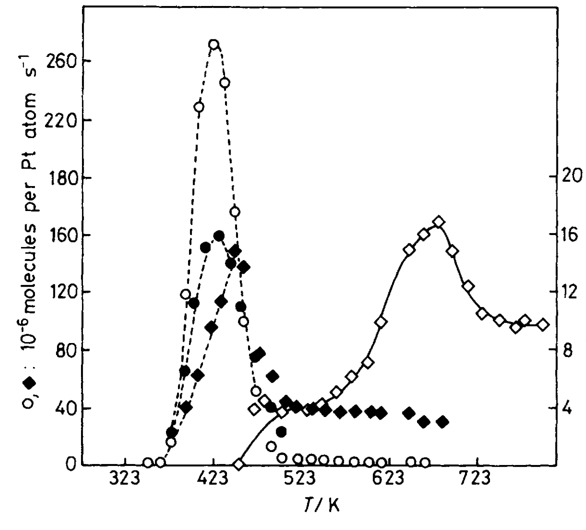


Figure 1. Temperature-programmed ethene titration of H_2PtCl_6 upon Al_2O_3 in 5 wt % Pt producing 1,2-DCEA (○), 1,1-DCEA (●), CEE (◆), and B (◇).

Tables 1 and 2 indicate the catalysts prepared and subsequently titrated with ethene as described above and also the results obtained in terms of the extent of formation of different products and the temperature at which these products appeared at a maximum rate. Figure 1 illustrates the results obtained in terms of the alumina-supported H_2PtCl_6.

There are a number of points concerning these results. First, only two products were observed for the monometallic Cu^{2+} chloride catalysts: 1,2-DCEA at low temperatures and CEE at higher temperatures. Both products are those seen in oxychlorination catalysis.[1] However, the free energy of formation of 1,2-DCEA is favourable for reduction of CuCl at all titration temperatures (and very unfavourable for formation from $CuCl_2$ sites). Hence it appears that the peak area of this product may reflect the concentration of surface Cu sites in the +1 state; clearly Table 1 suggests that their concentration is very small. T.p.r. with hydrogen has already shown that the vast majority of the Cu in these samples is divalent.[2] It is interesting that the concentration of such sites suggested here by total 1,2-DCEA yields is 2—3 times greater upon silica and titania than upon alumina; this is possibly a reflection on the extent to which these supports promote copper reduction. On the other hand the free energy change producing CEE is only favourable above about 600 K if the reactant site is $CuCl_2{\cdot}2H_2O$; titration results suggest that such phases exist in the present Cu catalysts (see Table 1). *X*-Ray powder diffraction reveals the hydrated dichloride on silica and titania, but the hydroxy-chloride $Cu_2(OH)_3Cl$ upon alumina. Therefore temperature-programmed reductive titration with ethene appears to be able to characterise the sites in such supported chloride catalysts whose presence is not revealed by traditional hydrogen t.p.r.[2]

Secondly, it is noteworthy that the addition of increasing amounts of Pd^{2+} chloride (presumably locked in a monodispersed state in the Cu^{2+} structures) produces increased concentrations of 1,1-DCEA. In addition CEE is produced at lower temperatures (about 450 K, where traditional dehydrochlorination of 1,2-DCEA can be ruled out) than with the monometallic Cu^{2+} catalysts. This suggests a C–H · · Cl–Cu–Cl exchange producing C–Cl · · H–Cu–Cl and thence HCl and Cu^0. This is novel and potentially useful in activation of alkanes.[3] Pd addition reduces the extent of formation of 1,2-DCEA.

Thirdly, monometallic Pd chlorides behaved very differently from the above bimetallic catalysts (which suggests that the bimetallic chlorides must indeed be microscopically homogeneous and not simple chloride mixtures with any degree of separation). It is important to note that Pd catalysts produced both B and CEE and so did other transition metal chloride phases as shown in Table 2; this formation of B is novel. Although its formation might make the net free energy change more negative and hence the formation of CEE and 1,2-DCEA even more thermodynamically favourable over the metal chlorides, the fact that benzene is produced at temperatures below CEE on some chlorides (*e.g.* Rh) but above CEE on others (*e.g.* Pt) suggests that the mechanism involved is not simple trimerisation of ethyne produced by dehydrochlorination of CEE on the catalyst. Table 2 shows that the supported Rh chloride showed the greatest activity towards B; its activity towards B formation and CEE formation was tested isothermally at 453 and 723 K respectively. Activity declined no faster than for many metal-catalysed hydrocarbon reactions. Previously, direct B formation from ethene[4] and ethyne[5] has only been reported on zero-valent metal surfaces. There is no clear trend of these relative benzene turnover numbers with the heat of dissociation of the metal chlorides or the metal–chloride bond strength.

It appears that temperature-programmed methods of analysing ethene–MCl_x interactions can probe the active surface sites in a manner not possible by traditional hydrogen t.p.r.[6] The results suggest that $C–H \cdot \cdot Cl–M–Cl$ exchanges producing C–Cl might be catalysed selectively (*i.e.* 1,2-DCEA and 1,1-DCEA can be produced on different surfaces) (Scheme 1). This may be useful in the direct formation of chlorocarbons[3] and in activating alkanes. The oxidative coupling of ethane to form benzene on such surfaces is also an important finding. It suggests that modifying oxychlorination technology could yield both chlorocarbons by exchange (rather than addition plus dehydrochlorination) and aromatic compounds by oxidative coupling. Further work on catalysis on chlorides will amplify this.

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