Influence of chlorine poisoning of copper/alumina catalyst on the selective hydrogenation of crotonaldehyde

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The effect of the presence of chlorine on the activity and selectivity of a Cu/Al_2O_3 catalyst has been examined for the selective hydrogenation of an αβ unsaturated aldehyde, crotonaldehyde. Cu/Al_2O_3 in the absence of chlorine poisons produced 1-butanol almost exclusively, whereas catalysts pre-dosed with a suitable amount of chlorine compound (CCl_4, $CHCl_3$ and CH_2Cl_2) shifted the product distribution towards formation of butanal. The poisoning effectiveness increased in the order $CCl_4 < CHCl_3 < CH_2Cl_2 \ll CH_3Cl$ and methyl chloride was found to totally deactivate the catalyst. The most significant enhancement in butanal selectivity was observed with CCl_4 and CH_2Cl_2. The effect of chlorine as a poison is in contrast to the effect of sulphur which enhances formation of crotyl alcohol and the origins of these effects are discussed.

Keywords: Copper/alumina; crotonaldehyde hydrogenation; selectivity (butanal); chlorine poisoning

1. Introduction

The control of reaction selectivity has become an increasingly important topic in recent years. Particular interest has been applied to the control of hydrogenation of αβ unsaturated aldehydes, e.g. crotonaldehyde. A number of studies have focused attention on the hydrogenation of these compounds to the corresponding unsaturated alcohol. Initial approaches have utilised supported metal catalysts in which the support is considered to play an important role in controlling catalyst morphology. For example, a number of catalysts have been found to show improved selectivity for the hydrogenation of the carbonyl bond in preference to the carbon–carbon double bond: $Ni/Cu/Al_2O_3$ [1], Pt/TiO_2 [2], $Pt/Fe/SiO_2$ [3] and Cu/Cr_2O_3 [4]. Most recently, Marinelli et al. [5] have shown that Pt catalysts can also give enhanced reac-

tion selectivity in this reaction when Ge, Ga or Sn additives are present. In a previous study [6], we have shown that partial poisoning of supported copper catalysts with thiophene gives a marked enhancement in the selectivity for crotyl alcohol from crotonaldehyde hydrogenation. In this study we now present our initial results for the partial poisoning of a supported copper catalyst with chloro-compounds and demonstrate that a distinctly different effect can be observed.

2. Experimental

2.1. CATALYST PREPARATION

Supported copper catalyst precursors were prepared by adding γ-alumina (Condea SCF, Puralox SCFa 140, 136 $m^2\ g^{-1}$) to an aqueous solution containing an appropriate amount of copper nitrate (Aldrich 99.99%) so as to yield 5 wt% Cu metal. The slurry was stirred at 80°C and evaporated to a thick paste then dried (110°C, 16 h) and calcined (450°C, 16 h) to convert the nitrate to the oxide. Temperature-programmed reduction of the calcined 5% Cu/Al_2O_3 precursor using 5% hydrogen in helium diluent showed that reduction of the oxide to the metal occurred at 210–220°C and hence 210°C was selected as the reduction temperature. The catalyst sample (100 mg) was loaded into a fixed-bed microreactor and reduced in situ in hydrogen (3.6 $\ell\ h^{-1}$) at 210°C for 2 h and subsequently the temperature was decreased to 150°C. The Cu surface area determined using the standard nitrous oxide adsorption method was 22 $m^2\ g^{-1}$ for the nm poisoned catalyst.

2.2. CATALYST EVALUATION

The vapour phase hydrogenation of crotonaldehyde (>99% purity, Aldrich) was investigated using a continuous flow fixed-bed reactor at atmospheric pressure. Crotonaldehyde was introduced via a calibrated syringe pump and vaporised in a preheated reactor inlet tube. Hydrogen was utilised as a carrier gas and a H_2/crotonaldehyde ratio of 14/1 was used in all studies. Chlorided catalysts were prepared by injection of chlorine containing compounds (CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl) directly onto the reduced catalyst in a hydrogen carrier gas. Product separation and analysis was achieved using on-line gas chromatography. The experimental errors associated with the conversion and selectivity data reported in this paper are ca. ±1%.

3. Results and discussion

Crotonaldehyde was hydrogenated over chlorided and non-chlorided Cu/Al_2O_3 at 150°C and WHSV = 1.2 h^{-1}, and the results showing the effect of increased reaction time are given in table 1. In the absence of chlorine butanol was

Table 1
Hydrogenation of crotonaldehyde over Cu/Al_2O_3 catalyst modified with chloro-compound [a]

Time on line (min)	% Conversion	Product selectivity (%)			
		crotyl alcohol	butanal	butanol	condensation by-product [b]
unchlorided					
15	100	1.0	0.3	95	3.7
30	100	1.0	1.0	98	–
60	100	1.0	22.0	77	–
120	100	1.0	49.0	50	–
180	100	1.0	55.0	43	–
1 μl CCl_4/100 mg catalyst					
15	71.4	0.4	59.8	38.8	1.1
30	18.6	6.8	88.3	4.0	0.9
60	13.4	8.0	88.6	1.8	1.6
90	9.3	8.4	87.6	1.5	2.6
120	6.1	8.9	85.6	1.3	4.3
180	1.7	9.7	74.5	–	15.8
1 μl $CHCl_3$/100 mg catalyst					
15	54.0	2.5	58.4	36.6	2.6
30	11.1	6.6	81.4	6.9	5.2
60	3.8	10.2	80.0	2.1	7.8
90	2.9	9.9	77.4	2.4	10.2
120	2.5	7.7	80.5	2.9	8.9
180	1.5	7.1	72.1	3.3	17.5
1 μl CH_2Cl_2/100 mg catalyst					
15	4.1	10.0	78.4	3.4	8.3
30	2.9	8.3	79.6	2.8	9.3
60	1.8	7.7	74.2	2.8	15.3
90	1.6	7.0	72.8	2.4	17.7
120	1.5	5.8	73.6	2.4	18.2
180	1.3	5.3	71.0	2.5	21.2
0.4 ml CH_3Cl					
15	0	–	–	–	–
30	0	–	–	–	–

[a] 150°C, crotonaldehyde WHSV 1.2 h^{-1}.
[b] Aldol condensation products.

the major reaction product, particularly for the fresh catalyst, as the catalyst deactivated butanal also became a major product, but the selectivity only reached 55% even after 180 min reaction time. Butanol can be formed via two parallel pathways and hence three possible hydrogenation products can be formed: butanol, butanal

and crotyl alcohol. The effect of pre-treatment of the catalyst with chlorine containing compounds (CCl_4, $CHCl_3$, CH_2Cl_2) is to enhance significantly the selectivity to butanal. In particular, sustained high selectivities to butanal were observed throughout the reaction period. Chloriding does lead to a significant loss of catalyst activity as would be expected from the known effect of chlorine compounds on copper catalysts. The poisoning effect of CH_xCl_y compound investigated on crotonaldehyde conversion increased in the order $CCl_4 < CHCl_3 < CH_2Cl_2 << CH_3Cl$. In particular, CH_3Cl was found to completely deactivate the catalyst. However, it is important to note that during the early part of the reaction prior to significant deactivation, the yield of butanal is markedly enhanced on chloriding, indicating that the chlorine is positively affecting the rate of formation of butanal and inhibiting the subsequent hydrogenation of the carbonyl group. For example, chloriding with 1 μl CCl_4 gives a yield of 16.4% at 30 min time-on-stream at 150°C, whereas the unchlorided catalyst gives a yield of only 1% at comparable reaction conditions and time. It is therefore apparent that the chloride surface promotes the hydrogenation of the carbon–carbon double bond while inhibiting the hydrogenation of the carbonyl group.

The effect of level of the chlorine containing compound was investigated for CH_2Cl_2 and the results are shown in fig. 1. It is clear that increasing the level of

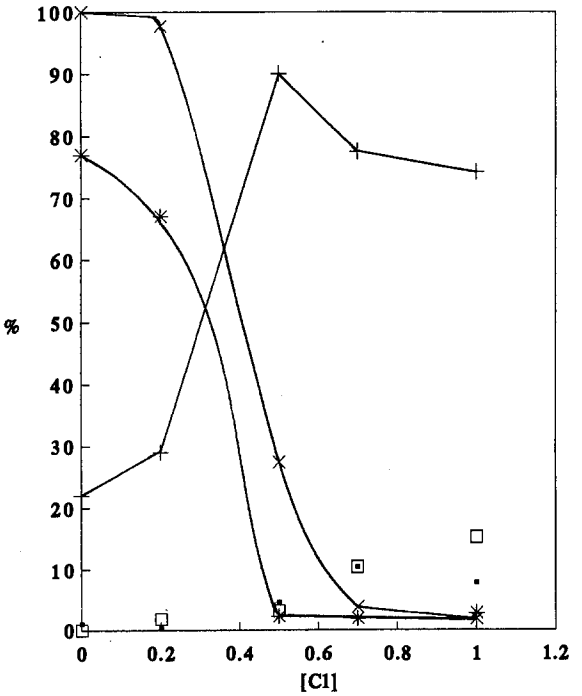

Fig. 1. Effect of amount of CH_2Cl_2 on Cu/Al_2O_3 catalyst performance. Temperature of chloriding 150°C, WHSV = 1.2 h^{-1}, time-on-line 60 min. (■) Crotyl alcohol; (+) butanal; (*) butanol; (□) aldol condensation by-products; (×) crotonaldehyde conversion; [Cl] = μl CH_2Cl_2.

CH_2Cl_2 significantly affects conversion, but the selectivity to butanal is $\geqslant 80\%$ for $\geqslant 0.5\,\mu l\ CH_2Cl_2/100\,mg$ catalyst.

The data presented in the time-on-line studies (table 1) does not permit comparison of product selectivities for chlorided and non-chlorided catalysts at comparable conversions, since the non-chlorided catalyst gave 100% crotonaldehyde conversion at the conditions examined (150°C and WHSV = $1.2\ h^{-1}$). A series of experiments were therefore carried out with the non-chlorided catalyst at 150°C and varying crotonaldehyde WHSV and the variation of product selectivity with conversion is shown in fig. 2. The data presented are for 60 min time-on-line to ensure that the selectivity is obtained for similar levels of catalyst deactivation. It is clear that as the crotonaldehyde conversion is decreased, the selectivity to butanal and to a lesser extent crotyl alcohol both increase and the selectivity to butanol is decreased. This is expected, since at low conversions it can be anticipated that the intermediate hydrogenation products will be formed. The data obtained from chlorided catalysts at 150°C and 60 min time-on-line is also presented in fig. 2. When comparisons are made at equivalent conversions it is apparent that chloriding with CCl_4 and CH_2Cl_2 gives catalysts with significantly enhanced butanal selec-

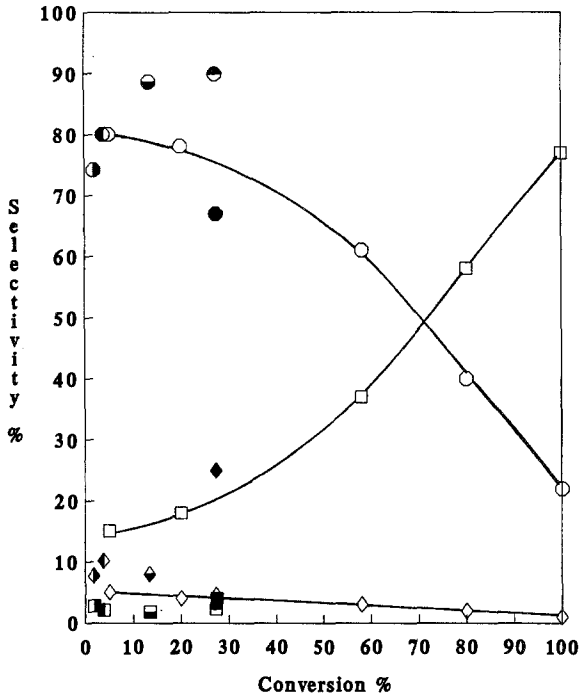

Fig. 2. Selectivity versus conversion at 150°C for crotonaldehyde hydrogenation, time-on-line 60 min. All catalysts; (○) butanal; (□) butanol; (◇) crotyl alcohol; open symbols = non-chlorided catalysts; chlorided catalysts: (◒) 1 μl CCl_4; (◐) 1 μl $CHCl_3$; (◑) 1 μl CH_2Cl_2; (◓) 0.5 μl CH_2Cl_2; (●) catalyst sulphided with 1 μl thiophene.

tivities. The effect is most marked for the catalyst initially chlorided with 0.5 μl CH_2Cl_2 for which the selectivity to butanal is enhanced to ca. 90%, whereas the unchlorided catalyst would give ca. 75% selectivity at this conversion. For comparison, the data for a catalyst pretreated under identical conditions with 1 μl thiophene and reacted at 150°, crotonaldehyde WHSV 1.2 h^{-1} are also given in fig. 2. For the sulphided catalyst, as noted previously [6] the selectivity to crotyl alcohol is significantly enhanced and the selectivities to butanal and butanol are much lower than those for the non-poisoned catalyst. This experiment demonstrates the clear differences in catalyst performance obtained for sulphided and chlorided catalysts. At low conversions (2–5%) it is apparent that chlorided catalysts also give a slight enhancement in selectivity for crotyl alcohol; however, this effect is not so pronounced as that observed with the sulphided catalysts.

The deactivation observed with increased reaction time (table 1) is due to deposition of carbonaceous residues on the catalyst surface. These are the results of the expected side reaction involving aldol condensations of the reactant and products. It is clear that for the unchlorided catalyst, the deposition of coke influences the product distribution and poisoning of the surface by coke also enhances butanal selectivity; however, significant selectivity to butanol is also observed and significantly high selectivities to butanal are not observed. Hence the effects on selectivity observed for chlorided catalysts are not due solely to coke deposition, since the effects are observed for short reaction times. For the non-chlorided catalyst, the rate of coke deposition is 2.5×10^{-2} mgC/(100 mg catalyst min) (150°C, WHSV = 1.2 h^{-1}), which is similar to that of a catalyst sulphided with 1 μl thiophene and tested under comparable conditions (2.8×10^{-2} mgC/(100 mg catalyst min). However, the chlorided catalysts exhibit an enhanced rate of coke deposition (3.7 ± 0.1 mgC/(100 mg catalyst min), in addition to significantly enhanced aldol condensation by-products (table 1). These by-products are not observed with the non-chlorided catalyst and are only observed to a minor extent for the sulphided catalyst. It is therefore apparent that chloriding leads to an enhanced rate of coke formation which is considered to be due to the increased formation of aldol condensation by-products, probably on chloride modified acid sites on the alumina support.

The effects on selectivity with chlorine containing poisons are in contrast to those observed for sulphur containing compounds with this catalyst system, eg. thiophene (fig. 2) [6] and SO_2 [7]. With partial sulphur poisoning the selectivity and yield of crotyl alcohol were enhanced, and detailed studies [8] have shown that the catalytic effect involves the formation of Cu^+ sites electronically promoted by adjacent sulphur atoms. Chlorine, being more electronegative than sulphur, would be expected to oxidise the catalyst surface significantly, and this may be the origin of the observed effects. In addition, the size differences of chlorine and sulphur may also be significant with respect to the creation of surface sites with specific geometries. At present no attempt has been made to optimise the selectivity effects observed with chlorine compounds, and it is clear that further detailed studies are

required to elucidate the mechanism of this effect. However, this study demonstrates that partial catalyst poisoning represents a valuable research approach for the control of reaction selectivity in heterogeneous catalysis.

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