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Low-Temperature Ethylene Oxyhydrochlorination: Effects of Supports and Promoters on the Mobilities of Active Species in $CuCl_2$ Catalysts

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The mobilities of active species in γ-Al_2O_3-supported $CuCl_2$–KCl–$LaCl_3$ at a low temperature typical of oxyhydrochlorination of ethylene (498 K) have been studied in a fluidized bed lab reactor. Copper chloride and KCl are mobile under reaction conditions and in a C_2H_4/N_2 atmosphere, whereas $LaCl_3$ is not. No mobility is observed in air or in HCl/air. It is suggested that the mobile species is cuprous. Mobility studies performed with catalysts supported on SiO_2, α-Al_2O_3, and γ-Al_2O_3 in reducing atmospheres show that copper chloride is not mobile on SiO_2 and α-Al_2O_3. Results of selective extractions with acetone, XRD, and TPR show that a strong salt–support interaction occurs in γ-Al_2O_3-, compared to α-Al_2O_3- and SiO_2-supported copper chloride. Either promoter separates the $CuCl_2$ from the γ-Al_2O_3, but does not affect the mobility of the species on this oxide. Lanthanum chloride increases the activity with no effect on the apparent activation energy. It counteracts the adverse effect of KCl which is not a promoter since it causes a decrease in the activity up to 525 K. The promotion of KCl occurs at higher temperatures. This behavior is due to an increase in the apparent activation energy with the addition of KCl. © 1995 Academic Press, Inc.

INTRODUCTION

Since the discovery that copper chloride catalyzes the conversion of hydrogen chloride to chlorine in the Deacon process, a great deal of effort has been made to understand the mechanism involved and to improve the efficiency of the catalysts by the addition of promoters. Much work has also been done on the related reactions methane oxyhydrochlorination (OXHC) and ethylene OXHC (1–4).

Despite the different temperature ranges in which these reactions are carried out—473–573 K for ethylene OXHC, 623–723 K for methane OXHC/Deacon—the same promoters are used, i.e., potassium chloride and rare-earth chlorides (3). This is somewhat surprising since the state of the active species and the mechanisms involved are believed to be different. Based on the phase diagram (5) one would expect $CuCl_2$–CuCl to be molten (or partially molten) in methane OXHC/Deacon and in a solid state in ethylene OXHC. The addition of potassium chloride allows the chloride mixture to be partially molten at ethylene OXHC reaction temperatures (5), although some authors believe that even at 573 K it is still in the solid state when supported (6). With regard to the mechanisms, it is generally agreed that for methane OXHC the chlorination involves gas-phase chlorine (7). For ethylene OXHC the belief is that the chlorination occurs on the surface with cupric chloride as the chlorinating agent (8), although the possibility of chlorine being the chlorinating agent has not been discarded (9).

Because of the liquid nature of the copper species at CH_4/Deacon OXHC reaction temperatures, the redistribution of the melt during the reaction might affect the catalytic activity. One of the roles assigned to the rare-earth chlorides is to prevent agglomeration. In an electron microscopy study of copper chloride/potassium chloride mixtures supported on low-area Al_2O_3 and TiO_2, the mobility of clusters leading to agglomeration at temperatures above 673 K was observed (10). Upon addition of cerium chloride the catalysts had a decreased tendency to agglomerate.

Another role assigned to a rare-earth chloride ($LaCl_3$), related to the mobility of species, was the inhibition of segregation in copper chloride–potassium chloride catalysts at high temperature (11).

Since it has been claimed that at low temperature the segregation leading to deactivation occurs (12), the initial purpose of this work was to determine if lanthanum chloride would play the same role in ethylene OXHC. With that goal in mind, the mobility of the species was studied under reaction conditions.

The active species were supported on γ-Al_2O_3 since this is the more common support according to the literature (4).

As a consequence of the results obtained in the pursuit of the goal mentioned above, the mobility under conditions other than reaction and on different supports, as well as the effects of the promoters on the catalytic activity, was also studied.

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EXPERIMENTAL

Catalysts Preparation and Characterization

Catalysts containing Cu, Cu–K, Cu–La, and Cu–K–La were prepared following the incipient wetness procedure. In every case, the aqueous solution containing the species to be deposited was added dropwise while the support was continuously stirred. The liquid-to-solid ratio was 0.4 ml/g. After impregnation the samples were dried in an oven at 393 K for 2 h and kept in a dessicator. The support used was high purity γ-Al_2O_3 (CONDEA CHEMIE, 190 m2/g, particle size <44 μm). Samples containing only copper, supported on α-Al_2O_3, obtained by high-temperature treatment of the γ-Al_2O_3, and on SiO_2 (Davison, Grade 62, 340 m^2/g, particle size 74 $\mu m < D < 88$ μm) were also prepared following the same procedure.

The nominal content of copper and potassium was 5 and 1%, respectively (according to (6) the optimum contents for γ-Al203-supported Cu–K catalysts), and variable (0.5, 1.2, 2.5, 5, and 10%) for lanthanum. Accordingly, the molar ratios were 0.32 for K/Cu and 0.045, 0.11, 0.23, 0.46, and 0.92 for La/Cu. The catalysts are identified by the species present and by the lanthanum nominal content. For example, CuK2.5La stands for a catalysts containing Cu, K, and 2.5% La. The metal contents were determined by atomic absorption analysis in a Varian AA 1475 spectrophotometer.

X-ray diffraction measurements were made with a Varian PW1799 diffractometer with Cu–K radiation and scanned at a rate of 0.035°/min (in 2Θ).

Temperature-programmed reaction (TPR) determinations were carried out in a temperature-programmed reduction/reaction system described elsewhere (9). Briefly, the reactor is a Pyrex 0.6-cm-o.d. glass tube. The amount of catalyst used was 0.04 g and it was held in place by glass wool plugs. The gas mixture used was 5% H_2 in Ar at a flow rate of 30 cm^3/min, and the heating rate was 6.5 K/min.

To determine the relative strengths of salt–support interactions in the catalysts, the amounts of copper remaining in 0.4-g samples after extraction with 150 ml of acetone in a soxhlet (20 cycles) were measured [see (11) and references cited therein].

Mobility Studies

The mobility measurements were performed at atmospheric pressure in glass flow reactors. A flow diagram of the reaction system is shown in Fig. 1.

All elements in the reaction system are made of Pyrex or Teflon except the on–off and regulating flow valves, made of stainless steel.

One of the reactors (3 cm o.d., 60 cm long) has a 4.5-cm-long preheater section filled with glass beads followed by a fritted disk that supports the catalytic bed and acts as a distributor of the reactant mixture. The glass beads were treated in aqua regia, thoroughly washed, and dried at 793 K in air before use. An internal coaxial thermowell (0.4 cm o.d.) allows temperature readings along the catalytic bed. The reactor is in close contact with a brass cylinder (10 cm o.d., 65 cm long) heated by eight Hotwatt cartridges. The temperature is controlled by a temperature controller within ±1 K. The upper part of the reactor, 17.5 cm long and with a larger diameter (12 cm o.d.) to prevent catalyst losses, was kept at 393 K by a heating tape. A condenser at the exit of the reactor, kept at 278 K by a circulating refrigerating unit, allows liquid samples to be collected. Samples of the feed and the gaseous and liquid effluent streams can be obtained from sampling points conveniently located (see Fig. 1). The bed temperature is measured with a type J thermocouple located in the reactor thermowell. Small (<2 K) axial temperature gradients were observed in the catalytic bed under reaction condition. No axial gradients were observed otherwise.

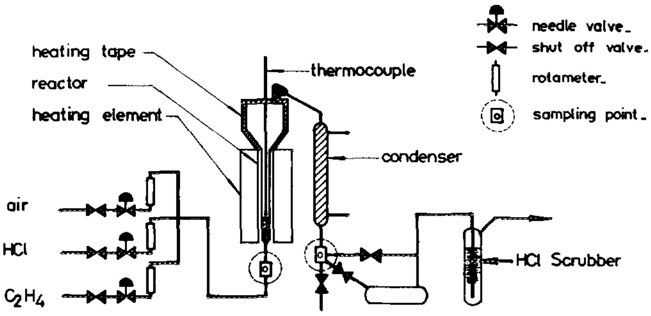

FIG. 1. Flow diagram of the reaction system.

A smaller reactor was also used (2.3 cm o.d., 25 cm long; upper part, 7 cm o.d., 7.5 cm long). The heating device is similar to that described above. The temperature was monitored by a $\frac{1}{32}$-in. stainless-steel shielded J thermocouple, introduced into the reactor through a septum located in the upper part. After determination of the temperature, the thermocouple was removed from the bed.

In the mobility measurements under reaction conditions, the contents of light gases (CO, CO_2, O_2, N_2, C_2H_4) were determined in a HP 5890 GC equipped with column-switching valves and thermal conductivity detection following separation in a Porapak S and MS columns operated at 363 K. The compositions of the liquid effluents (0.5 h collection time, after 8 h under reaction conditions) were determined in a second HP 5890 GC with flame ionization detection following separation in a CP Sil 8CB column with programmed temperature. To determine the chlorinated compounds present in the gaseous effluent, a third HP 5890 GC with flame ionization detection following separation in a CP Sil 5CB column operated at 343 K was used in some measurements for balancing purposes. The carbon balances were within ±5%. All chromatographs were coupled with HP 3392 electronic integrators.

The mobility runs involving the larger reactor were carried out at 498 K for 24 h under reaction conditions (feed molar ratios $C_2H_4:HCl:O_2 = 1:1.8:0.9$; total flow rate, 355 ml/min) and also in air (flow rate, 220 ml/min), in a HCl/air mixture (feed molar ratio HCl:air = 1:10; total flow rate, 210 ml/min), and in an C_2H_4/N_2 mixture (feed molar ratio $C_2H_4:N_2 = 1:10$; total flow rate, 210 ml/min). In every case the bed, in the regime of fluidization, was composed of 100 g of catalyst and 10 g of the γ-Al_2O_3 used as support but with a larger particle size ($74\ \mu m < D < 100\ \mu m$).

After the runs in which HCl was involved, the bed was kept under flowing air at the same temperature for 2 h in order to stripp off the HCl. No catalyst agglomeration was observed with the exception of a portion near the fritted disk.

Mobility measurements in catalysts with differents lanthanum loadings and catalysts on different supports were performed in the smaller reactor. The copper-containing fraction (9 g) was taken to 498 K under flowing nitrogen. After verification of good fluidization, the bare fraction (9 g) was added and a proper mix was verified. The runs were then carried out at the same temperature for 24 h in an C_2H_4/N_2 mixture (feed molar ratio $C_2H_4:N_2 = 1/10$; total flow rate, 210 ml/min). In every case, a good fluidization was observed after the runs.

After a mobility run, the fractions with different particle size were separated by sieving using a Ro-Tap testing sieve shaker, and the content of Cu, K, or La in each fraction was determined.

Catalytic Activity Measurements

The catalytic activity measurements were carried out in the small reactor previously described. To work in the low-temperature region (458–513 K) and keep the conversion below 15%, the amount of catalyst used was 3 g. It was diluted with 10 g of α-Al_2O_3 prepared by high-temperature treatment of the γ-Al_2O_3 used as support.

The total flow rate of reactants was 220 ml/min and the molar ratios were $C_2H_4:HCl:O2 = 1:1.8:1.1$. In every case the bed was taken to the reaction temperature under flowing air.

Materials Used

Anhydrous hydrogen chloride (acetylene, 1500 ppm w/w, main impurity) and ethylene (99.95% w/w) were supplied by Monomeros Vinilicos S.A. Air (99.9% w/w) and nitrogen (99.998% w/w) were supplied by La Oxigena S.A.

RESULTS

Tables 1–3 show the metal contents of the different catalysts used in this study. The amounts of Cu extracted with acetone in some samples are shown in Fig. 2. It can be seen that only 15% of Cu is removed when the support is γ-Al_2O_3, whereas it is easily removed when the support is SiO_2 or γ-Al_2O_3, indicating a very small salt–support interaction in these cases. It can also be seen that upon addition of either promoter the fraction of copper removed increases.

TABLE 1

Metal Contents in Catalyst Used in Mobility Measurements under Reaction Conditions[a]

Catalyst	Cu (%)	K (%)	La (%)
Cu	5.2	—	—
Cu*K*	5.3	1.0	—
Cu1.2La	5.2	—	1.2
Cu*K*1.2La	5.4	1.0	1.3

[a] For all the catalysts listed the support was γ-Al_2O_3.

Figure 3 shows the results of XRD measurements of catalyst on different supports. It can be seen that $Cu_2(OH)_3Cl$ (paratacamite) is present in the γ-Al_2O_3-supported copper chloride but absent in α-Al_2O_3– and SiO_2-supported catalysts in which $CuCl_2$ and $CuCl_2 \cdot 2H_2O$ are present. The involvement of basic OHs from the γ-Al_2O_3 in the formation of paratacamite has been suggested in a study of copper chloride–support interaction (13). It was also shown in that study that γ-Al_2O_3, SiO_2, and α-Al_2O_3 could be arranged in that order regarding stability of the complexes formed in the preparation.

The presence of XRD peaks indicate that copper chlorides are not well dispersed on the supports. The particle sizes, estimated from the broadening of the diffraction lines using the Scherrer equation (14) were 150, 150, and 260 Å for copper chloride supported on γ-Al_2O_3, SiO_2, and α-Al_2O_3, respectively.

The results of XRD measurements on promoted cata-

TABLE 2

Metal Contents in Catalysts Used in Mobility Measurements in C_2H_4/N_2 Atmosphere

Catalyst	Support	Cu (%)	K (%)	La (%)
Cu	γ-Al_2O_3	5.5	—	—
Cu/α-Al_2O_3	α-Al_2O_3	5.2	—	—
Cu/SiO_2	SiO_2	5.4	—	—
Cu*K*2.5La	γ-Al_2O_3	4.1	1.0	2.3
Cu*K*5La	γ-Al_2O_3	4.2	1.0	4.8
Cu*K*10La	γ-Al_2O_3	3.9	0.9	9.8
Cu	γ-Al_2O_3	4.1	—	—
5LaSi	SiO_2	—	—	5.0
10LaSi	SiO_2	—	—	9.7

TABLE 3

Metal Contents in Catalysts Used in Catalytic Activity Measurements[a]

Catalyst	Cu (%)	K (%)	La (%)
Cu	4.6	—	—
Cu*K*	4.6	1.0	—
Cu0.5La	4.7	—	0.4
Cu1.2La	4.4	—	1.3
Cu2.5La	4.6	—	2.5
Cu*K*0.5La	4.6	0.9	0.5
Cu*K*1.2La	4.4	0.9	1.2
Cu*K*2.5La	4.3	0.9	2.5

[a] For all catalysts listed, the support was γ-Al_2O_3.

lysts supported on γ-Al_2O_3 are shown in Fig. 4. It can be seen that the band due to paratacamite in γ-Al_2O_3-supported catalysts is absent upon addition of potassium and decreases its size upon addition of lanthanum. At La/Cu molar ratios similar to K/Cu molar ratios the band is absent. These results show that one of the roles of La, as well as K, is to increase the initial dispersion of the species since bands other than those of the support are not present.

Figures 5 and 6 show the results of TPR measurements of the fresh catalysts. It can be seen in Fig. 5 that the peaks due to the two-step reduction of the cupric species (9) are shifted to higher temperatures in α-Al_2O_3- and SiO_2-supported compared to γ-Al_2O_3-supported copper chloride. The same effect is observed upon addition of either promoter (see Fig. 6).

The results of the mobility studies of γ-Al_2O_3-supported CuK1.2La catalyst, carried out in the large reactor, are shown in Fig. 7. Measurements involving only Cu, CuK, and Cu1.2La were performed for comparison purposes. It can be seen that copper is mobile under reaction conditions, and the mobility is not altered by the presence of either potassium or lanthanum or both. It can also be seen that potassium is mobile as well but lanthanum is not. The transfer does not occur in air or in HCl/air but it does in C_2H_4/H_2.

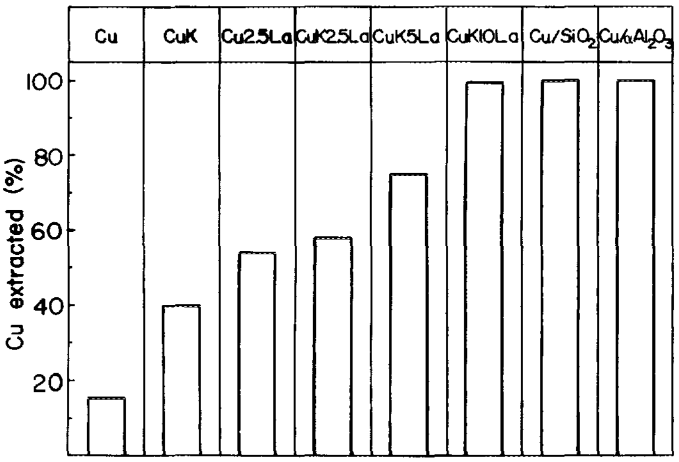

FIG. 2. Amounts of copper extracted with acetone in unpromoted and promoted γ-Al2O3-supported copper chloride catalysts and in unpromoted α-Al_2O_3- and SiO_2-supported copper chloride catalysts.

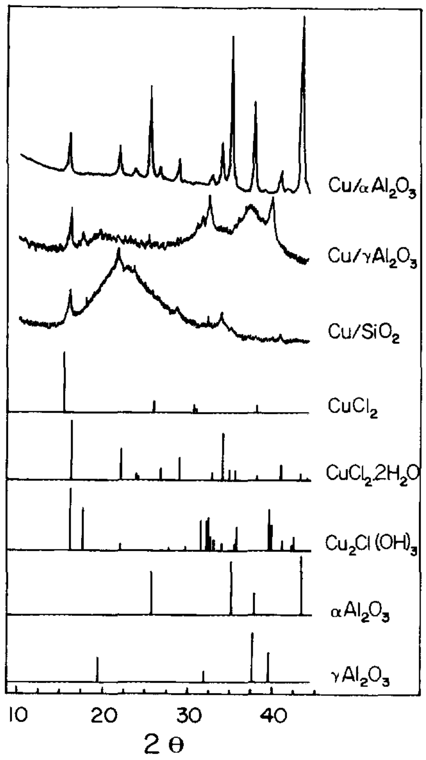

FIG. 3. X-ray diffraction patterns of unpromoted copper chloride supported on different oxides.

Considering that mobility is observed in a C_2H_4/N_2 mixture in which the cupric species is reduced to cuprous, and that under reaction conditions this species is also present, the results suggest that the mobile species is cuprous.

Table 4 shows the contents of C_2H_4, O_2, CO, and CO_2 (in moles percent) in the effluent gases and the composition of the liquid organic phase (in parts per million), measured during the mobility runs under reaction conditions. As mentioned in the literature (4, 6, 15) a decrease in combustion due to the presence of potassium is observed. The result obtained with the Cu–La catalyst indicates that lanthanum might play a similar role. With regard to the liquid organic phase, it can be seen that potassium causes an increase in the selectivity to EDC but lanthanum does not.

Since the bare Al_2O_3 was a small fraction (10%) of the bed, it was possible that only those species present on the outer portion of the catalyst particles were involved in the

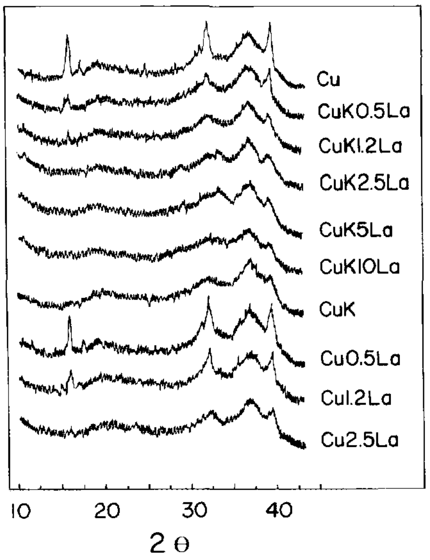

FIG. 4. X-ray diffraction patterns of γ-Al_2O_3-supported unpromoted and promoted copper chloride catalysts.

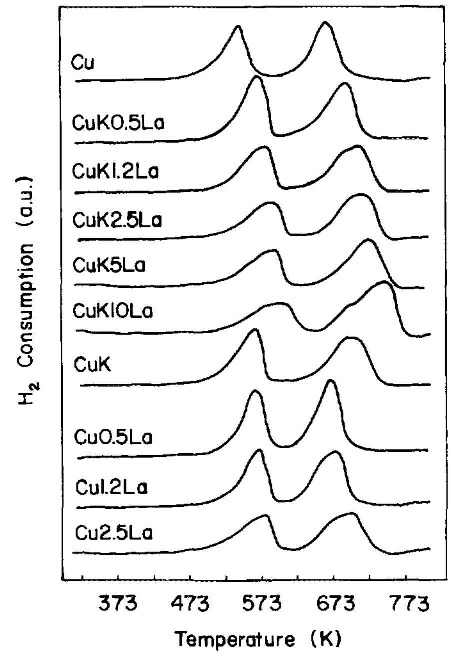

FIG. 6. TPR profiles of unpromoted and promoted γ-Al_2O_3-supported copper chloride catalysts.

transfer. To determine if copper species deposited in the center of the particles of the support were also involved, the studies of the effects of lanthanum content, or the support, on the mobilities were carried out using a catalyst/bare support ratio equal to 1. These studies were performed under reducing conditions since the mobilities under these, and under reaction conditions, were similar. The small reactor was used for this purpose. To compare with the large reactor, a mobility run with the Al_2O_3-supported CuK1.2La under reaction conditions was carried out in the small reactor. A similar result, not shown, was obtained.

The results of the mobility studies of copper catalyst on different supports can be summarized as follows: copper is transferred from γ-Al_2O_3 particles to γ-Al_2O_3 particles but not from α-Al_2O_3 particles to α-Al_2O_3 particles or from SiO_2 particles to SiO_2 particles. No transfer is observed from γ-Al_2O_3 particles to α-Al_2O_3 particles, from γ-Al_2O_3 particles to SiO_2 particles, and from α-Al_2O_3 particles to SiO_2 particles. In the opposite cases the transfers occur, although in a small amount from SiO_2 particles to α-Al_2O_3 particles. These results indicate that cuprous chloride wets γ-Al_2O_3, but not α-Al_2O_3 or SiO_2. This suggests that regardless of the initial dispersion on γ-Al_2O_3, copper chloride will be dispersed under reaction conditions. This is not true for the other supports.

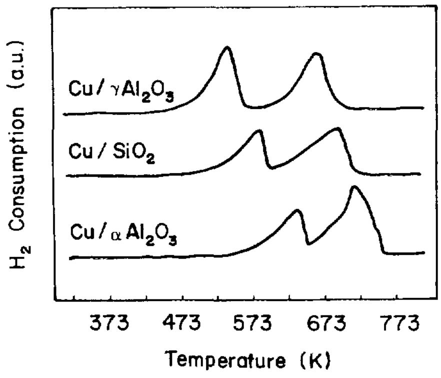

FIG. 5. TPR profiles of unpromoted copper chloride supported on different oxides.

About half of the copper deposited on γ-Al_2O_3 particles was transferred to the bare γ-Al_2O_3 particles, indicating that the transference is not limited to those copper chloride particles deposited on the outer portion of the support particles.

The catalysts were white after the mobility runs, indicating the reduction to cuprous chloride, which is transparent. Upon exposure to air at room temperature, no change in color was observed in SiO_2- and α-Al_2O_3-supported samples but a change to green was seen on γ-Al_2O_3-supported catalysts indicating oxidation of the Cu(I) species to Cu(II). Results of TPR measurements in samples exposed to air after the mobility runs, not shown here, confirmed the presence of only cuprous species on SiO_2 and α-Al_2O_3 and cupric species on γ-Al_2O_3. The stabilization of cuprous chloride on SiO_2 has been reported [see (9) and references cited therein].

To see whether high local temperatures due to reaction between cupric chloride and ethylene were partly responsible for the transfer, an experiment was performed in which

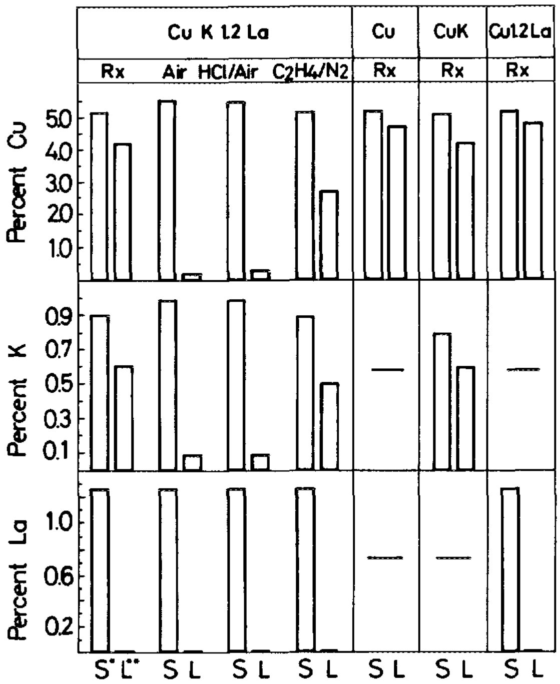

FIG. 7. Mobilities of species in promoted and unpromoted γ-Al_2O_3-supported copper chloride catalysts, at 498 K under different conditions. (*) Small particles (<44 μm); (**) large particles (>74 μm).

a γ-Al_2O_3-supported copper chloride catalyst was treated in ethylene, flushed with N_2, and then the bare γ-Al_2O_3 with larger particle size was added and kept 24 h at 498 K in flowing N_2. Forty-three percent of the copper chloride was transferred to the bare γ-Al_2O_3 particles, indicating that high local temperatures due to reaction are not necessary.

Figure 8 shows the results obtained in the mobility runs with catalysts with different lanthanum content. These results confirm that copper in contact with lanthanum moves to a γ-Al_2O_3 surface.

In order to determine whether copper chloride on γ-Al_2O_3 moves onto lanthanum chloride particles, measurements of mobilities from γ-Al_2O_3-supported copper chloride to SiO_2-supported lanthanum chloride with 5 and 10% La were performed. Silica was chosen because no transfer from γ-Al_2O_3-supported copper chloride to SiO_2 was observed. The amount of copper transferred (not shown) increased with the amount of lanthanum on SiO_2, indicating that the cuprous species on the γ-Al_2O_3 surface does move onto lanthanum chloride.

To further determine the role of lanthanum chloride, the activities of promoted catalysts were measured.

Figure 9 shows the results of activity measurements expressed as molecules of C_2H_4 converted per total Cu atoms per second. It can be seen that the addition of lanthanum causes an increase in activity without affecting the apparent activation energy. It can also be seen that, in this range of temperature, potassium does not promote the activity but decreases it.

DISCUSSION

The larger amount of copper extracted with acetone in promoted catalyst shown in Fig. 2 indicates that upon addition of either promoter the effect of the support decreases. In accordance with this, the disappearance of the band due to paratacamite in γ-Al_2O_3-supported catalysts upon addition of either promoter is observed (see Fig. 4). The detachment of the cupric species from the γ-Al_2O_3 surface upon addition of potassium chloride or lanthanum chloride is also suggested by the similar behavior in the TPR results between promoted catalysts and α-Al_2O_3- and SiO_2-supported catalysts. In catalysts in which a weak salt–support interaction occurs, shifts of the TPR peaks to higher temperature are observed.

The inhibition of the effect of the support by the addition

TABLE 4

Composition of Liquid and Gas Effluents of the Reactor in the Mobility Measurements under Reaction Conditions (Values in ppm v/v and Mole Percent)[a]

Organic compound	Catalyst			
	Cu	Cu*K*	Cu1.2La	Cu*K*1.2La
	Liquid phase (ppm)[b]			
C_2H_4	7	16	0	64
C_2H_3Cl	14	5	0	12
C_2H_5Cl	6	5	8	4
$C_2H_2Cl_2$	664	237	685	233
C_4H_6Cl	174	0	0	0
1,1-EDC[c]	44	41	43	40
CCl_4	1643	2229	440	3110
$CHCl_3$	1132	1362	322	1434
C_2HCl_3	762	907	1024	968
C_2Cl_4	10794	8043	7585	8914
$C_2H_3Cl_3$	11634	7240	11202	8489
$C_2H_2Cl_4$	4052	1363	8416	1459
Unknown	477	390	355	459
1,2-EDC[c]	96.9	97.8	97.0	97.5
	Gas phase (%)			
C_2H_4	2.1	4.6	1.4	4.0
O_2	3.7	9.5	10.1	8.5
CO	2.3	0.5	1.3	0.7
CO_2	5.2	1.7	2.4	2.1

[a] *T*, 498 K; feed molar ratios $C_2H_4:HCl:O_2 = 1:1.8:0.9$; total flow rate, 355 cc/min.

[b] 0.5 h collection time after 8 h under reaction conditions.

[c] EDC, ethylene dichloride.

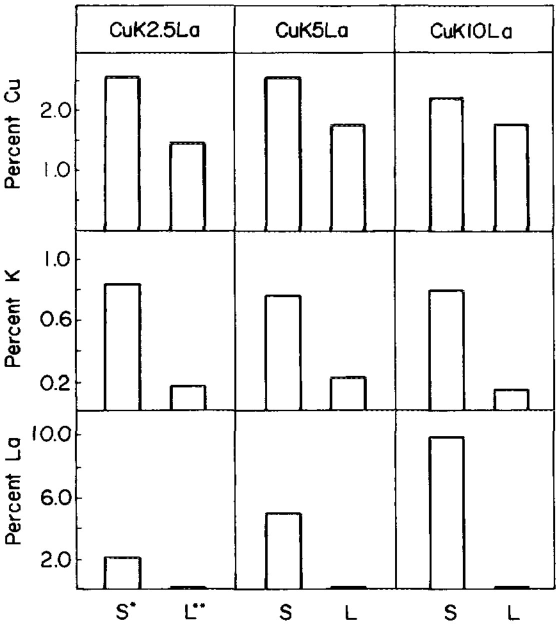

FIG. 8. Effect of lanthanum content on the mobilities of species in Al_2O_3-supported Cu*K*La catalysts at 498 K in C_2H_4/N_2 atmosphere. (*) Small particles (<44 μm); (**) large particles (>74 μm).

of potassium or lanthanum has been also observed in SiO_2-supported cuprous chloride (9).

The addition of either promoter leads to better initial dispersion. The reason for the better dispersion might be different. The absence of XRD bands due to lanthanum chloride, together with the lack of mobility of this promoter (see Fig. 7), suggests that lanthanum chloride is well dispersed and in direct contact with the support. The detachment of copper from the surface must be the result of copper located totally or partially on top of lanthanum. In agreement with this model, the catalytic activity of copper chloride increases with the addition of lanthanum without change in the apparent activation energy (see Fig. 9), indicating that the number of active sites but not the type of sites is modified (increased).

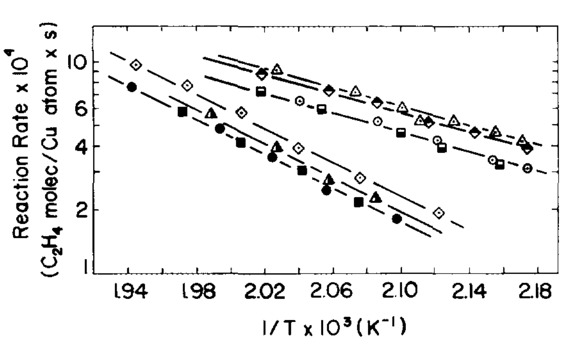

FIG. 9. Effect of promoters on the activity of γ-Al_2O_3-supported copper chloride catalysts. (⊙) Cu; (●) Cu*K*; (■) Cu*K*0.5La; (▲) Cu*K*1.2La; (◇) Cu*K*2.5La; (⬓) Cu0.5La; (⬙) Cu1.2La; (△) Cu2.5La.

In contrast, the mobility of potassium indicates that this promoter does not interact strongly with the support so the possibility of being on the surface of the copper chloride–potassium chloride particles cannot be discarded. The decrease in activity with change in the activation energy, suggesting that the type of sites are modified, further indicates that in this case copper chloride and potassium chloride are well interdispersed allowing potassium to be on the surface.

The results obtained in the mobility measurements under reaction conditions shown in Fig. 7 indicate that, in the temperature range of this study, the role of lanthanum is not to prevent segregation since it is not mobile under reaction conditions and does not prevent the mobilities of the other species. This is further confirmed by the results obtained on catalysts with different lanthanum contents (see Fig. 8).

The results show that copper chloride in contact with lanthanum chloride moves to a γ-Al_2O_3 surface, the fact that copper chloride also moves from γ-Al_2O_3 to lanthanum chloride, further indicates that lanthanum chloride does not play a role in mobility of γ-Al_2O_3-supported copper chloride at low temperature. The effect of lanthanum on mobility is probably important when the support is SiO_2 since copper chloride does not wet a bare SiO_2 surface, indicating that agglomeration might occur because it will not be dispersed under reaction conditions, but it wets lanthanum chloride so it is possible that agglomeration could be prevented if this promoter is present in a well-dispersed form.

Although in the presence of potassium chloride molten phases can exist in cupric–cuprous chloride mixtures at low temperature (5), the fact that copper without promoters is mobile on γ-Al_2O_3 (see Fig. 7) and the eutectic of the cupric–cuprous chloride mixture is 697 K, higher than the temperature used in this work, suggest that the mobility in this last case might be the result of a lower surface melting point.

With regard to the effect of lanthanum chloride and potassium chloride on the catalytic activity, the increase in activity with the addition of potassium observed in Refs. (6, 15) is caused by working at higher temperatures. As seen here and mentioned in Ref. (15), the apparent activation energy is increased by the presence of potassium. Up to about 525 K the effect of potassium is to decrease the activity but the opposite is true at higher temperatures. According to (4) a typical reaction temperature in industrial fluidized bed reactors is 498 K whereas up to 573 K can be observed in fixed-bed reactors (15). The results presented here indicate that under fluidized bed conditions a higher selectivity but lower activity should be found with potassium-promoted copper catalyst. Segregation would lead to an increase in activity and a decrease in selectivity because potassium would be removed from the surface.

The effect of lanthanum is to counteract the adverse effect of potassium on the activity at these low temperatures.

CONCLUSIONS

The effects of different amounts of $LaCl_3$ and 2% KCl on the activity and selectivity of 10% $CuCl_2$ supported on γ-Al_2O_3, as well as the mobility of species under different conditions, have been investigated. The main conclusions can be summarized as follows:

1. Copper and potassium are mobile under conditions of oxychlorination of ethylene at 506 K whereas lanthanum is not. Accordingly, lanthanum does not prevent segregation under these conditions.
2. The mobile copper species is cuprous.
3. Potassium chloride causes an increase in the apparent activation energy. In the range of reaction temperatures typical of industrial fluidized bed reactors (483–513 K) (4), KCl causes a decrease in the activity of $CuCl_2$ catalyst. The opposite is true at temperatures higher than 525 K.
4. Lanthanum chloride causes an increase in the activity without affecting the activation energy.

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