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Stabilization of the Active Phase by Interaction with the Support in $CuCl_2$ Oxychlorination Catalysts

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Salt–support interactions have been studied on unpromoted $CuCl_2$ catalysts supported on γ-Al_2O_3, TiO_2, and SiO_2. Selective extraction by solvents and thermal analysis have been used to probe the extent of interaction, which follows the sequence: $Al_2O_3 > TiO_2 > SiO_2$. It also increases with copper chloride dispersion. The experimental results can be explained in terms of the formation of a regenerable active phase on the support surface. This species is formed on Al_2O_3 and TiO_2 but it is not on SiO_2. The interacting phase can resist deactivation while the surface of the noninteracting particles is rapidly reduced to CuCl rending them inactive. © 1986 Academic Press, Inc.

INTRODUCTION

It is widely recognized that the support plays a decisive role in the catalytic behavior of supported $CuCl_2$ oxychlorination catalysts used for production of chloromethanes, chlorobenzene and chloroethylene (*1*). However, most of the studies on the subject have been carried out using potassium and lanthanum chloride promoters which may mask the support effect. In the catalytic reaction scheme the most generally proposed chlorinating agent is chlorine, which is evolved from $CuCl_2$ in a Deacon process step (*2*). In this way, $CuCl_2$ is reduced to CuCl which has to be oxidized and then rechlorinated by O_2 and HCl, respectively, which are fed in a HCl : O_2 ratio of about one. The K and La chlorides are believed to promote the regeneration step during this catalytic cycle by effecting the formation of a $(CuCl)_n$ complex which can be easily oxidized and subsequently chlorinated to $CuCl_2$ (*3*). In addition, they lower the melting point of the copper chloride mixture. Thus, under reaction conditions the copper chloride particles are at least partially melted. Accordingly, the regeneration is favored because both the Cu^+ reoxidation rate and the mass transport rate are increased.

If promoters were not to be used, the surface $CuCl_2$ layers would be gradually reduced to CuCl which in turn is not easily oxidized. Therefore, it would appear that without promoters the catalyst would be rapidly deactivated by the formation of a CuCl film on the surface of the $CuCl_2$ particles.

We attempt to demonstrate that an interaction with the support may create a distinct surface species which would not be deactivated during the reaction and so the activity could be maintained even though promoters were not present. In this paper we describe a comparative study of the salt–support (γ-Al_2O_3, SiO_2, and TiO_2) interactions occurring during three important stages of the catalyst life: impregnation, thermal treatment, and reaction (oxychlorination of methane).

EXPERIMENTAL

A series of supported $CuCl_2$ catalysts was prepared on three different supports: titania TiO_2 (Degussa P 25, 50 m^2/g), silica

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TABLE 1

Catalyst	Support	Amount of Cu (g/g cat.) extracted by		Cu-acet./Cu-HNO_3	DTA peak II/peaks(I+II)
		HNO_3	Acetone		
1A	γ-Al_2O_3	0.012	0.00053	0.046	0.00
2A		0.020	0.00432	0.216	0.23
5A		0.046	0.02649	0.569	0.27
10A		0.098	0.05998	0.612	0.56
1T	TiO_2	0.009	0.00225	0.250	0.00
2T		0.019	0.01011	0.505	0.15
4T		0.040	0.03550	0.887	0.35
10T		0.096	0.08611	0.897	0.50
1S	SiO_2	0.010	0.00491	0.474	0.00
2S		0.022	0.01501	0.682	0.00
4S		0.045	0.36172	0.804	0.35

SiO_2 (Aerosil, 200 m^2/g, and γ-alumina Al_2O_3 (Degussa C, 100 m^2/g). The supports were impregnated with aqueous solutions of appropriate $CuCl_2$ concentrations in order to yield (dry basis) catalysts with Cu contents ranging from 1 to 10%. Subsequently, the catalysts were dried in air at room temperature.

In Table 1 the catalysts are identified by Cu content and type of support, e.g., 4T means a TiO_2-supported $CuCl_2$ catalysts with 4% Cu.

Each catalyst was characterized by selective extraction with acetone and nitric acid. These extractions were conducted at room temperature. According to Avila *et al.* (*4*) and Valle *et al.* (*5*) the fraction extracted with acetone represents the agglomerated phase of $CuCl_2$ which has not reacted with the support while the amount extracted with nitric acid corresponds to the total copper content. Quantitative analysis of Cu in the extraction solutions was performed in a Hewlett–Packard atomic absorption spectrometer.

The catalysts were further characterized by differential thermal analysis (DTA). These experiments were carried out under pure nitrogen flow in a Du Pont 990 DTA-DSC calorimeter. In order to eliminate from the thermograms those peaks due to thermal processes occurring on the supports, the same oxide used as support in the catalyst sample was employed as a reference. Previously, it was wetted and dried in the same way as the catalyst, so similar moisture contents may be expected in the bare support used as a reference and in the support of the catalyst under investigation. Thus, only the thermal processes related to the copper chloride phases are detected because those processes related to the support itself are subtracted.

Relative activities of the various catalysts were measured in a pulse reactor.

About 0.5 g of fresh catalyst were used in each run. The catalyst was maintained at 633 K in a HCl/O_2 stream. The flow rate was kept at 100 cm^3/min and the HCl/O_2 ratio at 5/100. After stabilizing the system for 30 min, a 2-ml CH_4 pulse was injected into the HCl/O_2 stream. The products were analyzed in a Perkin–Elmer F11 gas chromatograph equipped with a 6-ft. column filled with Porapak Q and operated at 423 K.

RESULTS

Selective Extraction Analysis

The amounts of Cu extracted by acetone

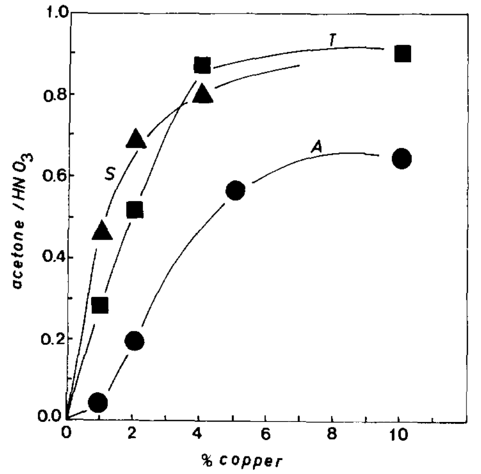

FIG. 1. Ratio of the amount of Cu extracted by acetone to that extracted by HNO_3 as a function of Cu content in the catalyst. The different symbols represent the supports used: ●, γ-Al_2O_3; ■, TiO_2; and ▲, SiO_2.

and by nitric acid for each fresh catalyst are summarized in Table 1. Figure 1 shows these data expressed as the ratio of the Cu concentration in the acetone extraction solution (Cu-acet.) to the Cu concentration in the NO_3H extraction solution (Cu-NO_3H) as a function of total Cu content, determined by the extraction with NO_3H. The observed trend for the three supports indicates that the fraction of Cu which has not interacted with the oxide carrier (Cu-acet./Cu-NO_3H) increases with Cu content for the three supports investigated. However, the extent of interaction is much greater on the γ-Al_2O_3 support than on the others.

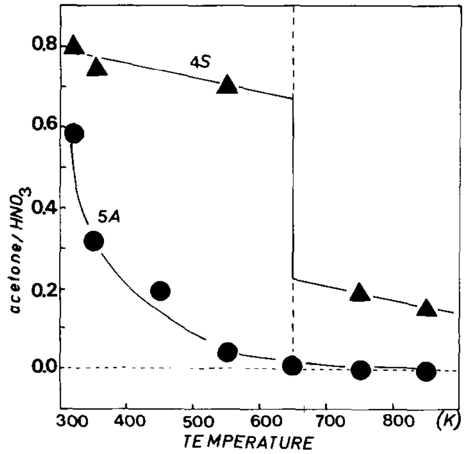

FIG. 2. Ratio of the amount of Cu extracted by acetone to that extracted by HNO_3 as a function of temperature of activation. The dashed line indicates the onset of Cl_2 and HCl evolution. 4S = $CuCl_2/SiO_2$ (4.5% Cu), 5A = $CuCl_2$/γ-Al_2O_3 (4.6% Cu).

To study the effect of the thermal activation as a function of temperature, the extraction analysis was performed on two typical catalysts (4S, 5A) after heating in pure N_2 flow at several temperatures. Figure 2 shows the (Cu-acet./Cu-NO_3H) ratio as a function of temperature of activation. Remarkably different trends are observed for the two catalysts. The silica-supported catalyst maintains almost the same (Cu-acet./Cu-NO_3H) ratio up to about 650 K but at this temperature a sudden drop is evident. By way of contrast, the alumina-supported catalyst shows a monotonic decay for the whole temperature range.

Differential Thermal Analysis

A typical DTA thermogram obtained under pure N_2 flow is shown in Fig. 3. Two endothermic peaks are evident, one at 390 K (peak I) and the other at 420 K (peak II). The relative magnitudes of peak I and peak II vary for the catalyst series. Ratios of the areas under each peak for the various cata-

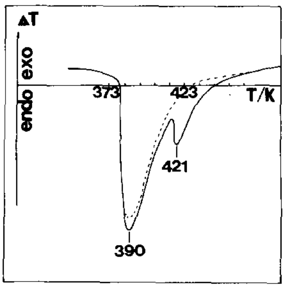

FIG. 3. Typical DTA thermogram obtained under pure N_2 flow. The dashed line represents the thermogram of the same catalyst after washing with acetone.

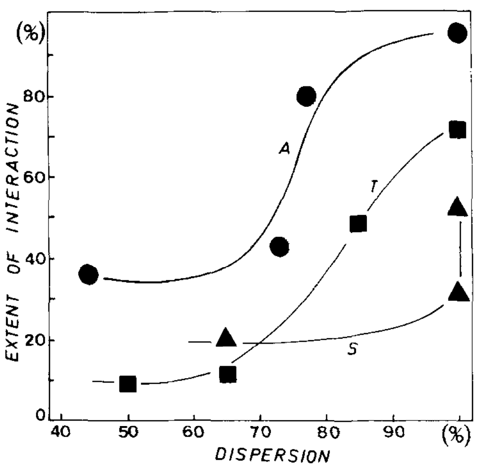

FIG. 4. Extent of salt–support interaction determined by selective extraction and expressed as 1-(Cu-acet./Cu-HNO_3) as a function of salt dispersion determined by DTA and expressed as peak I/(peak I + peak II). The different symbols represent the supports used: ●, γ-Al_2O_3; ■, TiO_2; and ▲, SiO_2.

lysts are summarized in Table 1. The observed trend indicates that the (peak II/peak I) ratio increases with Cu content in every case. We believe that both peaks are related to H_2O evolution. Peak I would be due to surface H_2O desorption and peak II to interstitial H_2O freed from the $CuCl_2$ particles. In order to check for these assignments we performed the same DTA experiment on pure $CuCl_2 \cdot 2H_2O$ crystals. In this case the thermogram only showed the peak II. On the other hand, samples previously heated to 500 K and exposed to moist air, only showed peak I. Finally, as shown in Fig. 3, samples previously washed with acetone only showed peak I because acetone selectively extracts the three-dimensional, noninteracting phase, which is responsible for the evolution of interstitial H_2O.

Accordingly, the ratio of the area under peak I to the total area under peaks I and II may be considered as a relative measure of the copper chloride dispersion because, it would represent, at least qualitatively, a surface-to-volume ratio. Therefore, we can combine the results from selective extraction analysis with those from DTA to picture the extent of salt–support interaction as a function of salt dispersion. This is shown in Fig. 4 as 1-(Cu-acet.)/(Cu-NO_3H) vs peak I/(peak I + peak II).

Activity Tests

Figure 5 shows the total CH_4 conversion obtained for each consecutive injection on three low-Cu-content catalysts (1A, 1S, 1T). The alumina-supported catalyst presented a significant initial conversion which was maintained over the subsequent injections indicating that the active phase was completely regenerated after each pulse. Contrarily, the silica-supported catalyst exhibited a relatively high initial conversion but it dropped to zero after the first two pulses. On the other hand, the catalyst supported on TiO_2 showed a low initial activity but gradually increasing after each pulse. After four injections it reached a constant conversion level.

Figure 6 shows the evolution of conversion for higher Cu content catalysts (5A, 4S, 4T). These catalysts have a much larger fraction of $CuCl_2$ particles than the low Cu content ones. In the previous section we have shown that the larger particles do not strongly interact with the support and as a

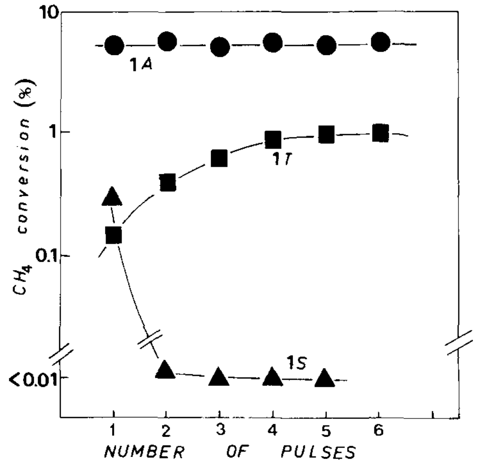

FIG. 5. Evolution of total CH_4 conversion to chloromethanes with the number of consecutive methane pulses on 1% Cu content catalysts. The different symbols represent the support used: ●, γ-Al_2O_3; ■, TiO_2; and ▲, SiO_2.

consequence we could expect that during the reaction they would rapidly deactivate because they would undergo an irreversible surface reduction. That was indeed the case, as evidenced by a significant decay in conversion observed for catalysts 5A and 4T after several pulses compared to the activity maintenance observed on low-Cu-content 1A and 1T catalysts. Therefore, on the high-Cu-content alumina-supported catalysts two opposing processes take place during the reaction: regeneration of the interacting phase and particle agglomeration leading to deactivation. In the case of titania-supported catalysts, the two competitive processes occurring as the reaction proceeds are the formation of the regenerable species and the salt agglomeration, resulting in the appearance of the maximum shown in Fig. 6.

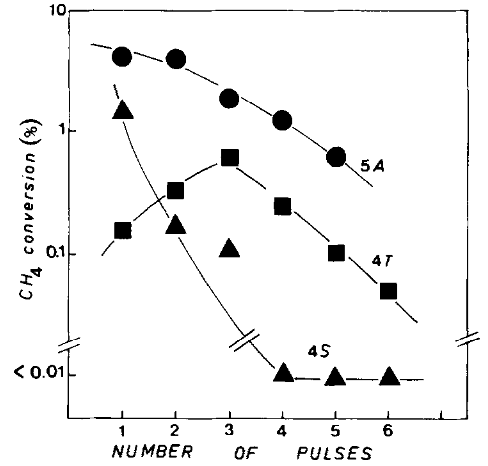

FIG. 6. Evolution of total CH_4 conversion to chloromethanes with the number of consecutive methane pulses on 4–5% Cu content catalysts. The different symbols represent the support used: ●, γ-Al_2O_3; ■, TiO_2; and ▲, SiO_2.

The silica-supported 5S catalyst showed the same rapid deactivation observed for the low-Cu-content 1S catalyst. In both cases the $CuCl_2$ particles were rapidly reduced, becoming inactive after the first few pulses.

DISCUSSION

We can interpret our results in terms of salt–support interactions occurring during the different steps investigated: impregnation process, activation treatment, and CH_4 oxychlorination reaction.

Impregnation Process

The strength of interaction between the aquo–chloro complex of Cu and the support surface during the impregnation seems to follow the sequence: $Al_2O_3 > TiO_2 > SiO_2$.

Figure 1 might indicate that at high Cu contents the interaction on silica is stronger than on titania. However, if this comparison is made at similar salt dispersions (see Fig. 4) the proposed sequence is valid for all the catalysts investigated.

The strong initial interaction on γ-Al_2O_3 may be explained in terms of a hydrolytic adsorption process described by Brunelle for the impregnation of CuC_2 on γ-Al_2O_3 (*6*). This author has proposed that the hydrolytic adsorption leads to the formation of a dispersed phase, fixed to the surface. Simultaneously, an agglomerated $CuCl_2$ phase is formed by a liquid phase reaction of complex ions in the vicinities of the surface followed by precipitation on the support. These two competitive mechanisms yield a given ratio of interacting to noninteracting phases depending on several factors such as concentration and pH of the impregnating solution, type of oxide support, etc.

Our results indicate that among the supports investigated, γ-Al_2O_3 has the highest capacity for exchanging surface hydroxil groups with the aquo-ligands of the Cu complex. This ability would be less marked on the TiO_2 support, although its relative surface area has to be taken into account when comparing absolute amounts of copper chloride retained on each support. Finally, SiO_2 appears to be the most inert support during the impregnation process.

Obviously, the observed trend may not be generalized for all aluminas, titanias or silicas. Different preparations and pretreatments of the supports may alter the degree of interaction. For instance, Blanco *et al.* (*7*) have shown that the temperature of pretreatment of the alumina carrier strongly affects the catalytic behavior of $CuCl_2$ oxychlorination catalysts.

The different adsorption capacities of the three supports investigated may be related to their different zeta potential curves. While the γ-Al_2O_3 and the TiO_2 supports are amphoteric oxides whose isoelectric points are reported to lie at pH values of 9.0 and 6.6, respectively (8), the SiO_2 support is a more acidic oxide having its isoelectric point at pH = 2.0. Considering that the pH of the impregnating solution was about 4, we can expect that the copper complex could react readily with the more basic OH groups on the γ-Al_2O and TiO_2. In agreement with our results, Baiker and Holstein (*9*) have recently described the impregnation of copper chloride on alumina considering two types of copper species: one formed by rapid irreversible immobilization and one formed by precipitation. These two species were evidenced by TPE measurements, which exhibited two significant maxima for the H_2 consumption rate. Their relative intensity varied with Cu content.

Activation Treatment

The differences observed in Fig. 2 for catalysts 4S and 5A can be ascribed to the different properties of the two supports. In the case of the γ-Al_2O_3-supported catalyst, the interaction is gradually enhanced as the temperature of activation increases. At lower temperatures, replacement of H_2O ligands by OH groups in the coordination sphere of Cu takes place. As the temperature is increased, a surface reaction between Cl^- ions and OH groups occurs leading to formation of Cu–O bonds and evolution of HCl, which has been experimentally verified. This sequence of ligand exchange strengthens the Cu–support interaction as temperature increases. A similar analysis of the $CuCl_2$–γAl_2O_3 system has been made by Zipelli *et al.* (*10*) from reflectance spectroscopy data.

On the other hand, in silica-supported catalysts whereas minimal initial interaction takes place, we note that the noninteracting (extractable) fraction is independent of the activation temperature. However, when this temperature is high enough (about 650 K) the $CuCl_2$ is decomposed to CuCl. Thus, the observed sudden drop in the extractable fraction has to be ascribed to the low solubility of CuCl in acetone, rather than to a salt–support interaction. This hypothesis has been confirmed by an EPR investigation (*11*).

Methane Oxychlorination Reaction

We believe that the three different behaviors observed for the different supports must be related to the existence of the proposed interacting phase which can be regenerated after each injection. According to Avila *et al.* (*4*) the fraction interacting with the alumina support would have a paratacamite structure ($Cu_2(OH)_3Cl$). The ability of γ-alumina in stabilizing this species can be ascribed to a more basic nature of this particular support with respect to $CuCl_2$ than SiO_2 or α-Al_2O_3. Our results would suggest that a similar surface complex should be formed during the reaction on the TiO_2 surface.

The effect of the reaction itself on the active phase–support interactions is a very important point which sometimes is not fully recognized. For instance, only a few among the numerous papers dealing with the well-known SMSI occurring in TiO_2-supported metal catalysts have mentioned that some reactions reverse the effects of the interaction (*12*). It would appear that in this case, the reaction itself promotes an interaction. However, we cannot postulate at the present a possible mechanism to support this hypothesis.

The silica support does not allow for the formation of the regenerable species. Thus, the catalyst loses its activity very rapidly as the $CuCl_2$ particles evolves chlorine atoms during the reaction leaving a surface layer of CuCl which is not easily reoxidated. Ohtsuka and Tamai (*13*) have observed a similar deactivation behavior for the catalytic oxychlorination of CH_4 on molten copper chloride as an insoluble inactive layer was formed on the surface of the $CuCl_2$ melt. X-Ray diffraction demonstrated that this layer was CuCl. On the other hand, Ng *et al.* (*14*) have found that the activity of $CuCl_x$ mixtures for oxychlorination and dehydrochlorination passes by two maxima at x values about 1.8 and 1.5. However, it decreases approaching to zero as x tends to one, evidencing the low activity of CuCl.

Avila *et al.* (*4*) have proposed that tridimensional $CuCl_2$ crystals in Al_2O_3-supported catalysts are inactive for benzene oxychlorination. From our point of view we would rather say that those crystals may have had an initial high activity but they became inactive after the first stages of reaction due to irreversible surface reduction of $CuCl_2$.

Our results suggest that when promoters are not used, γ-Al_2O_3-supported catalysts with low Cu content readily resist deactivation by generating a distinct surface species stabilized by the support. This conclusion is in line with previous studies (*15*) which indicate that γ-Al_2O_3 is preferred as support for oxychlorination catalysts. On the other hand, it might appear in conflict with a recent series of papers by Pieters *et al.* (*16*) who report that fumed silica showed to be the best support for methane oxychlorination. However, it must be noted that in Pieters' catalysts the active state of copper is Cu(I) instead of Cu(II) because the reaction mechanism does not involve a Deacon step as with conventional $CuCl_2$ catalysts. Thus, a good support in their case is one which stabilizes Cu(I) species while in our case the best support should stabilize Cu(II) species.

We conclude that salt–support interactions occurring on γ-Al_2O_3 and TiO_2 may lead to stabilization of regenerable Cu(II) species. Those interactions do not take place on SiO_2.

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