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High-Temperature Oxychlorination Catalysts: Role of $LaCl_3$ as an Inhibitor of the Segregation of Active Species during Heating/Cooling Cycles

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The effects of heating/cooling cycles on the structure and catalytic properties of $CuCl_2$–KCl catalysts supported on Al_2O_3 and SiO_2 have been studied. It is demonstrated that after the catalysts are heated to 673 K and cooled to room temperature, an irreversible segregation of K and Cu occurs. X-ray diffraction (XRD), differential thermal analysis (DTA), electron paramagnetic resonance (EPR), and scanning electron microscopy (SEM) analysis have experimentally confirmed the proposed segregation. This segregation process appears to be the main cause of the deactivation observed on SiO_2-supported $CuCl_2$–KCl catalysts for the CH_4 oxychlorination reaction after a heating/cooling cycle. On γ-Al_2O_3 the situation is somewhat different. Due to the strong affinity of Cu for the Al_2O_3 support a surface Cu oxychloride species is stabilized and the segregation process is consequently enhanced. However, the deactivation is not evident on this catalyst because the stabilized surface Cu oxychloride species has its own catalytic activity. On the other hand, when La is added to the $CuCl_2$–KCl catalysts a significant improvement in activity, which is maintained over a heating/cooling cycle, is observed. This promoter effect may be ascribed to the action of La as an inhibitor of K–Cu segregation.

INTRODUCTION

Catalytic oxychlorination of methane can be carried out at temperatures above 650 K in the presence of supported molten alkali, rare earth, and copper chloride mixtures (*1–4*). The alkali chloride plays an important role in these supported catalysts. Among the several advantages in using KCl as a promoter, the most prominent one is the depression of the melting point of the salt mixture. This depression allows the mixture to be partially or totally molten under reaction conditions (*5*, *6*). In previous work (*7*, *8*) we have correlated the catalytic activity with the physical state of the catalyst. Taking into account that when a molten phase is present the evolution of chlorine atoms is high (*5*, *6*), we have proposed that, in such cases, the oxychlorination reaction proceeds via a gas-phase mechanism initiated by chlorine atoms evolved from the melt. But, on the other hand, when the temperature falls to the point at which the entire mixture is in the solid state, the evolution of chlorine drastically decreases and so the reaction must proceed via a surface mechanism. In agreement with this hypothesis it was shown that the addition of alkali has a promoter effect on activity only when the catalyst comprises a molten phase. Otherwise, it merely acts as a site-blocking moiety (*7*).

Due to their potential importance in industrial operations, we have been interested in elucidating the effects of heating/cooling treatments on the catalytic properties of supported catalysts and the role played by promoters during these treatments. Thermodynamics predicts that on cooling a mixture from a totally molten state, a temperature is reached at which the system enters the two-phase region. Depending on the composition of the mixture, one of the components will start to come out of the solution, while the solution will

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become richer in the other component. Therefore, at the end of the cooling process the constituents of the mixture may become physically separated. In a homogeneous bulk mixture, this process can be reversed by raising the temperature to its starting value. However, in a supported $CuCl_2$–KCl catalyst the high dispersion of the salt and the presence of the support may alter the reversibility of the process. We have previously demonstrated (*8–10*) that $CuCl_2$ may react with the oxide support. This reaction would contribute to effect an irreversible segregation. A comparative study of $CuCl_2$ supported on several oxides showed that the strength of the salt–support interaction follows the sequence γ-Al_2O_3 > TiO_2 ≫ SiO_2 (*9, 10*). Thus, we can expect that the segregation of Cu from K will be more marked on γ-Al_2O_3 than on the other supports.

As will be shown here, this behavior can be modified by the use of La, which would act as an inhibitor of the segregation process. La has been proposed as an additive in different patents (*11–13*) although its role is not clearly understood. In a recent work (*8*), we reported a synergistic effect of the promoter action of KCl and $LaCl_3$. It was observed that the addition of $LaCl_3$ to KCl–$CuCl_2/SiO_2$ catalysts resulted in a marked improvement in activity and in maintenance of activity over several heating/cooling cycles. The nature of this ability is discussed in this paper.

EXPERIMENTAL

Catalyst Preparation

We prepared a series of $CuCl_2$–KCl (two-component catalysts) and $CuCl_2$–KCl–$LaCl_3$ (three-component catalysts) supported on SiO_2 (Aerosil 380, 380 m^2/g) and γ-Al_2O_3 (Degussa C, 100 m^2/g). The supports were impregnated with aqueous solutions of appropriate $CuCl_2$ + KCl and $CuCl_2$ + KCl + $LaCl_3$ concentrations to yield 7 wt% nominal Cu content and nominal molar ratios for K/Cu of 1.0 and for La/Cu of 0.5. In every case, the liquid-to-solid ratio was 5 ml/g. Each sample was then dried in air at room temperature and further dried in an oven at 373 K for 2 h. The resulting Cu content was determined by atomic absorption analysis performed in a Varian AA 375 spectrometer. We identify the catalysts according to the support, the nominal Cu content, and the additives used. For example, A7KLa stands for a γ-Al_2O_3-supported 7 wt% nominal Cu catalyst promoted with K and La. The characteristics of the catalysts investigated are summarized in Table 1.

TABLE 1

Identification of the Catalysts Investigated

Catalyst	Support	Cu (%)	Nominal K/Cu	Nominal La/Cu
A7K	γ-Al_2O_3	6.6	1.0	0.0
A7KLa	γ-Al_2O_3	6.6	1.0	0.5
S7K	SiO_2	6.5	1.0	0.0
S7KLa	SiO_2	6.5	1.0	0.5

Catalyst Characterizations

Each catalyst was characterized by selective extractions with solvents, differential thermal analysis (DTA), powder X-ray diffraction (XRD), electron paramagnetic resonance spectroscopy (EPR), and electron scanning microscopy with elemental analysis microprobe (SEM-EDAX). Selective extractions of the supported salts with HNO_3 and acetone were conducted at room temperature as a fresh sample and after a heating/cooling cycle. In this treatment, the samples were heated at 673 K for 1 h and then cooled to room temperature under a pure N_2 flow. According to Avila *et al.* (*14*) and Valle *et al.* (*15*) and as we noted in a previous work (*9*), the fraction extracted with acetone represents the agglomerated phase of $CuCl_2$ which has not been stabilized by the support. On the other hand, the amount extracted with HNO_3 corresponds to the total Cu content.

The DTA thermograms were obtained under pure flowing N_2 in a Du Pont 990 calorimeter, at a heating rate of 20 K/min. The corresponding support was used as a reference. Each sample was analyzed in two heating/cooling cycles from room temperature up to 673 K. The X-ray diffraction patterns were obtained in a Rigaku diffractometer (Cu$K\alpha$ radiation, 20 mA, and 40 kV). The scanning rate was 2°/min (range $10° < 2\theta < 80°$). The catalysts were analyzed as fresh samples and after the previously described heating/cooling cycle. The crystalline phases were identified by comparison with reference materials and literature indexes (*16, 17*). EPR spectra were obtained in a Brucker spectrometer, operated at X-band frequency, at room temperature. SEM-EDAX studies of powdered samples were conducted in a Phillips SEM 505 EDAX 9100 electron microscope.

To study the mobility of Cu over the support surface an aliquot of S7K catalyst was placed in a Pyrex tube preceding a 4.5-cm bed containing one of the two supports investigated. After 2 h at the desired temperature (670 K) under vacuum (10^{-3} Torr) the tube was cut into several 1.5-cm-long segments. The concentrations of Cu and K in each segment were determined by atomic absorption. Before each run, the supports were treated with distilled water and dried in air at room temperature.

Catalytic Activity Tests

The catalytic activity of the samples for the CH_4 oxychlorination reaction was determined in a spherical 60-cm^3 Pyrex flask operated as an isothermal batch reactor. Reactant mixtures were prepared in a second flask connected to the reactor. The temperature in the reactor was measured with a glass-covered chromel–alumel thermocouple, placed close to the catalyst bed, and it was controlled by an electronic temperature controller. For each activity determination, the reactor containing 5.5 mg of fresh catalyst was evacuated using a mechanical pump while the temperature was increased up to 380 K. The sample was then pretreated in a gaseous HCl–O_2 mixture ($HCl : O_2$ 2 : 1; total pressure: 300 Torr) at the reaction temperature (670 K) for 30 min. Subsequently, the reactant mixture ($CH_4 : HCl : O_2$ 5 : 2 : 1) was introduced and the reaction was allowed to take place at an initial total pressure of 700 Torr. After a given time the reaction was quenched by suddenly cooling the reactor. A fresh sample was used for each run. To study the effect of heating/cooling cycles on activity, after each first 20-min reaction period the catalyst was cooled to room temperature and heated again at 670 K under vacuum for 30 min before a second 20-min reaction period. The products were analyzed by gas chromatography. As the conversions reached during the activity determinations were low, the products were mainly methyl and methylene chloride. Anhydrous hydrogen chloride, pure oxygen (La Oxigena), and natural gas (97% methane), purified through activated carbon and molecular sieve traps, were used as reactants.

RESULTS

Extraction Analysis

Figure 1 shows the amount of Cu extracted by acetone and by HNO_3 from catalysts A7K and S7K, as fresh samples and after a heating/cooling cycle in a pure N_2 flow. The data are expressed as [% Cu extracted by HNO_3 − % Cu extracted by acetone)/% Cu extracted by HNO_3] × 100. This ratio represents the fraction of Cu which has been anchored to the oxide carrier and cannot be extracted by acetone. For the Al_2O_3-supported catalyst the fraction of Cu anchored to the support significantly increases after the heating/cooling cycle. Over the SiO_2 support the nonextractable fraction is very small for both fresh and treated catalysts. In previous works (*7, 9*) we demonstrated that under our preparation conditions the interaction between SiO_2 and $CuCl_2$ is very weak. Therefore, even the small fraction retained by the support should rather be ascribed to Cu trapped into macropores of the oxide carrier than to any salt–support interaction.

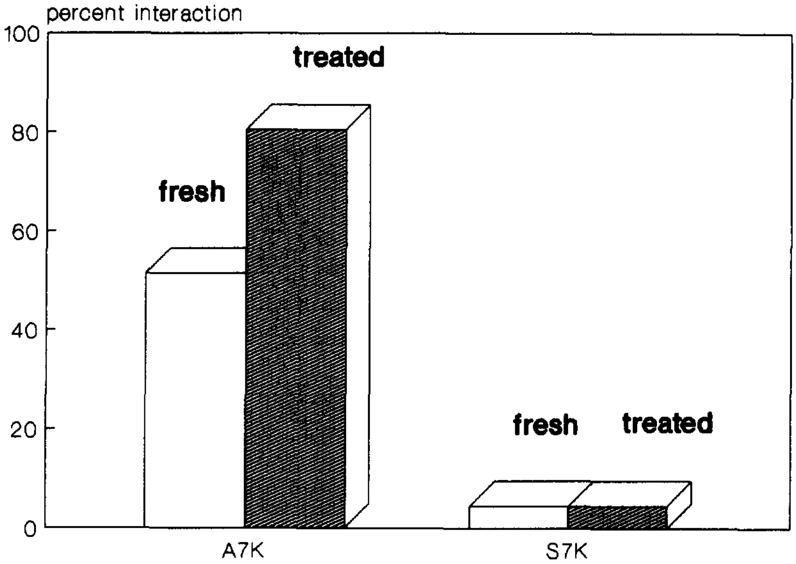

FIG. 1. Percentage of Cu which has interacted with the support and cannot be extracted by acetone for $CuCl_2$–KCl/Al_2O_3 and $CuCl_2$–KCl/SiO_2 catalysts. The data are expressed as [(Cu extracted by HNO_3 − Cu extracted by acetone)/Cu extracted by HNO_3] × 100. Open bars, fresh samples; cross-hatched bars, samples treated with a heating/cooling cycle in pure N_2 flow.

We have also used atomic absorption analysis to study the mobility of Cu ions over the two supports. In Fig. 2 we show the amount of Cu that migrated through SiO_2 and γ-Al_2O_3 over a 2 h at 673 K under vacuum. Bar 1 corresponds to the concentration of Cu ions in the segment used as a source (30 mg of catalyst S7K). The subsequent bars represent the Cu concentrations in the consecutive segments following the source. We can see that on SiO_2, significant amounts of Cu could be detected up to the last segment of the bed. The K/Cu ratio dropped from 1.1 in the first segment to 0.57 in the last one. In contrast, on γ-Al_2O_3 only potassium ions were detected in the last segment as the Cu concentration dropped to approximately zero before the third segment. This experiment is evidence of the different abilities of the two supports to stabilize the Cu ions and of a K/Cu segregation process that can take place on the two-component catalysts at 673 K.

Thermal Analysis

DTA thermograms of all the samples analyzed exhibited two zones of endothermic peaks. As we described in previous works (*7–9*), the low-temperature region (room temperature-450 K) corresponds to processes related to the evolution of water, while the high-temperature region (above 500 K) involves melting processes of the supported salt particles. In this paper we concentrate on the high-temperature region. As shown in Table 2, more than one endothermic peak appeared in the first heating cycle for most of the catalysts investigated. As mentioned above, the melting point of the chloride mixtures decreases with alkali concentration. Accordingly, and as previously shown (*7*), the lower-temperature peaks in this region can be ascribed to K-rich phases and the higher-temperature ones, to K-lean phases.

The segregation phenomenon mentioned above may be indirectly evidenced through analysis of the consecutive DTA cycles. The changes in position and in relative area of the high-temperature region peaks observed between consecutive cycles are summarized in Table 2. For catalyst S7K the area corresponding to the melting of the K-rich phase in the first heating cycle was

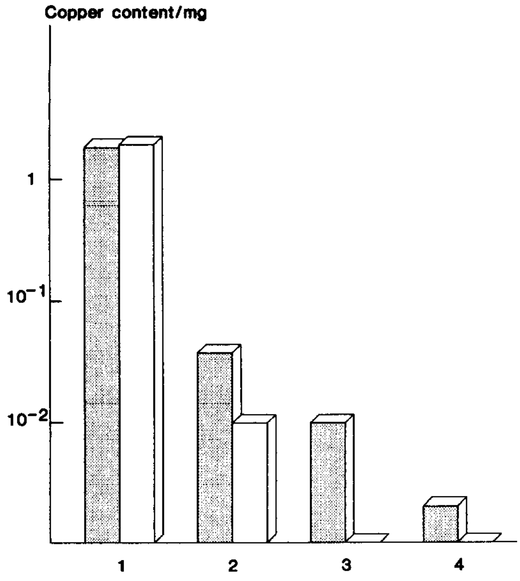

FIG. 2. Amount of Cu (mg) that migrated from a S7K source through consecutive segments of support bed after 2 h at 673 K under vacuum. Open bars, Al_2O_3 bed; shaded bars, SiO_2 bed.

much larger than the other. During the second heating cycle this catalyst showed an increase in the size of the higher-temperature peak and a shift to lower temperature of the lower-temperature peak. On the other hand, catalyst A7K exhibited only one endothermic peak in the melting region investigated. It was observed that during the second heating cycle, this peak shifted to higher temperatures while its intensity decreased.

The three-component catalysts show an important difference. As opposed to the two-component catalysts the relative area of the melting peak appearing at about 600 K is significantly increased during the second cycle. These results indicate that the amount of salt melting during the second cycle for La-containing catalysts is significantly greater than that during the first cycle.

X-ray Diffraction

Diffraction patterns corresponding to catalysts S7K, A7K, and A7KLa as fresh samples and after a heating/cooling cycle are shown in Figs. 3, 4, and 5, respectively. The presence of $CuCl_2$, KCl, and double salts of the type $KCuCl_3$ and K_2CuCl_4 (*16*, *17*) was evidenced in all the samples investigated. Free $LaCl_3$ was detected in catalyst A7KLa.

As shown in Figs. 3 and 4, when catalysts A7K and S7K were heated at 673 K and then cooled, an increase in the maxima corresponding to KCl and the double salt K_2CuCl_4 was observed. It must be pointed out that this increase was much more marked for KCl. For catalyst S7K an increase in the maximum corresponding to $CuCl_2$ was also observed. This increase was

TABLE 2

Consecutive DTA Heating/Cooling Cycles

Catalyst	First heating cycle		Second heating cycle	
	Peak position/K	Relative area	Peak position/K	Relative area
S7K	605	83	595	42
	655	17	655	56
A7K	519	100	571	56
S7KLa	602	77	601	153
	617	23	642	20
A7KLa	591	11	601	142
	621	74	—	—
	631	15	—	—

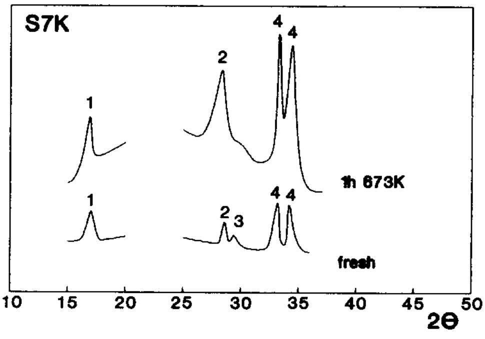

FIG. 3. X-ray diffraction patterns of catalyst S7K as a fresh sample and after a heating/cooling cycle. (1) $CuCl_2$, (2) KCl, (3) $KCuCl_3$, (4) K_2CuCl_4.

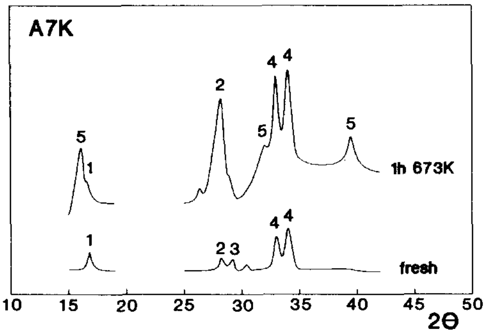

FIG. 4. X-ray diffraction patterns of catalyst A7K as a fresh sample and after a heating/cooling cycle. (1) $CuCl_2$, (2) KCl, (3) $KCuCl_3$, (4) K_2CuCl_4, (5) $Cu_2(OH)_3Cl$.

not evident for catalyst A7K, which in turn, after the thermal treatment, exhibited the appearance of clear maxima corresponding to an oxychloride of the type $Cu_2(OH)_3Cl$.

Catalyst A7KLa exhibited a rather different behavior. On one hand, the growth of the signal corresponding to KCl following the thermal treatment was not as marked as for the two-component catalysts. On the other hand, a clear increase in the signal of the double salt $KCuCl_3$ was observed. Finally, this catalyst did not show the appearance of the peaks ascribed to the Cu oxychloride species which were clearly evident for catalyst A7K after the thermal treatment.

Paramagnetic Resonance Electron

EPR spectra of catalysts S7K, A7K, and A7KLa are shown in Figs. 6, 7, and 8, respectively. The three fresh catalysts (Figs. 6a, 7a, and 8a) showed a symmetrical signal. It is observed that catalyst S7K kept the symmetry of the signal even after the heating/cooling cycle (Fig. 6b). By contrast, a clear change in the symmetric signal following the thermal treatment was observed for catalyst A7K (Fig. 7b). It must be noted that this change did not occur for the three-component catalyst. The spectrum of the thermally treated A7KLa catalyst (Fig. 8b) showed a broad symmetric signal.

In previous work (*8*, *10*) we identified two different EPR signals in $CuCl_2$ catalysts and related them to different environments of the Cu(II) ion. First, we ascribed an asymmetric signal, typically observed for the low-Cu-content Al_2O_3-supported catalysts, to isolated Cu(II) ions interacting with the support through surface oxygen atoms. That signal could be associated with an axially symmetric environment of the Cu(II) ion, with two components of the g tensor equal ($g_{xx} = g_{yy} = g_{\perp}$) and one different ($g_{zz} = g_{\parallel}$) (*18*).

At the same time, we have ascribed a symmetric signal, which is representative of a spherical symmetry with the three principal components of the g tensor equal ($g_{xx} = g_{yy} = g_{zz} = g_{iso}$), to Cu(II) ions which do not interact with the support. This signal is typical of high-Cu-content SiO_2-supported catalysts. For those catalysts, such as A7K, which exhibited contributions of both asymmetric and symmetric signals, the symmetric one could be selectively removed by washing with acetone. This fact demonstrates that this signal is indeed related to Cu(II) ions which did not interact with the support. For instance Fig. 7c shows the spectrum of a thermally treated A7K sample washed with acetone. It can be seen that the only signal remaining after the

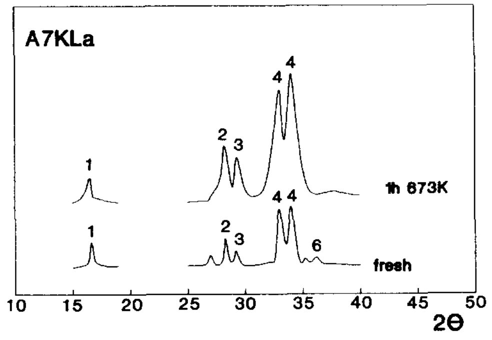

FIG. 5. X-ray diffraction patterns of catalyst A7KLa as a fresh sample and after a heating/cooling cycle. (1) $CuCl_2$, (2) KCl, (3) $KCuCl_3$, (4) K_2CuCl_4, (6) $LaCl_3$.

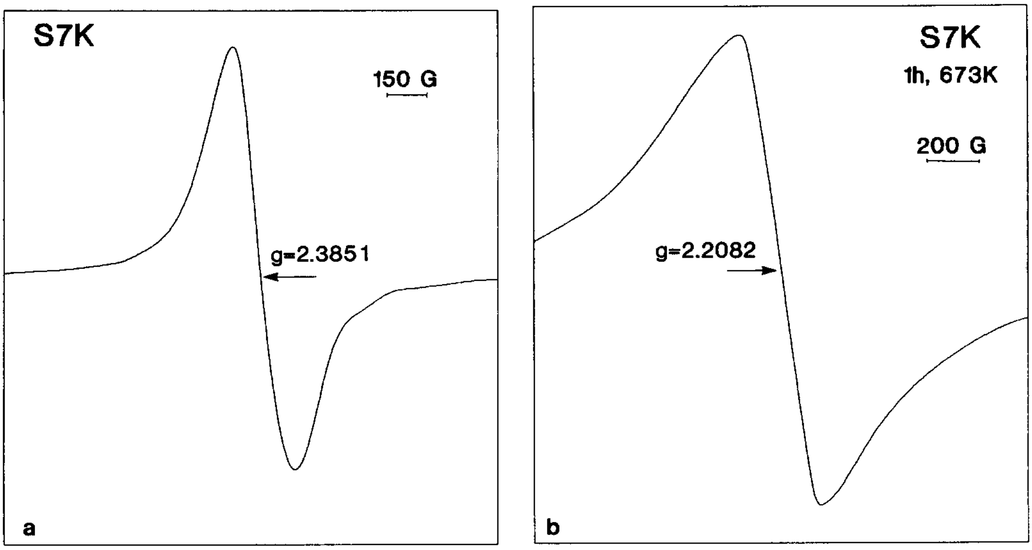

FIG. 6. EPR spectra of catalyst S7K as (a) a fresh sample and (b) after a heating/cooling cycle.

washing is the asymmetric one, related to Cu(II) ions stabilized by the oxide carrier. Similar assignments for symmetric and asymmetric signals have previously been given by other authors (*19–23*).

Table 3 summarizes the corresponding values of ∂H and *g* factors for each case. The broadening observed after the thermal treatment can be attributed to the evolution of water from the samples. Water acts as a "spin diluent" in fresh samples. So that the time constant of the spin–spin relaxation process, which is inversely proportional to ∂H (*18*), has a higher value in water-containing samples than in samples without water.

TABLE 3

EPR Data of the Samples Investigated

Sample	Treatment	∂H (Gauss)	g_{iso}	$g_{\parallel}$	$g_{\perp}$
A7K	Fresh samples	175.9	2.3455		
S7K		225.0	2.3851		
A7KLa		225.0	2.3214		
A7K	1 h at 673 K	370.0		2.2763	2.0614
S7K		309.7	2.2082		
A7KLa		421.4	2.2572		
A7K	1 h at 673 K, acetone washed	168.7		3.0846	2.2627

Electron Scanning Microscopy and Elemental Analysis

Figures 9 and 10 show the SEM micrographs of catalyst A7K before and after the heating/cooling cycle, respectively. The fresh sample exhibits a high density of amorphous agglomerates while the thermally treated sample shows an increase in the degree of crystallinity. These observations are in line with the pronounced increases in XRD intensities observed after the thermal treatment. As determined by EDAX, the K/Cu atomic ratio for the crystalline zones in both samples was about 0.7.

Micrographs of catalyst A7KLa before and after the thermal treatment are shown in Fig. 11 and 12, respectively. Two different zones are clearly evident, a well-ordered crystalline phase which exhibits a K/Cu ratio of about 1.6 and a low La content and an amorphous zone which is rich in La and has a lower K/Cu ratio. For comparison, we have included in Fig. 13 a micrograph of a thermally treated Al_2O_3-supported sample with the same Cu and La

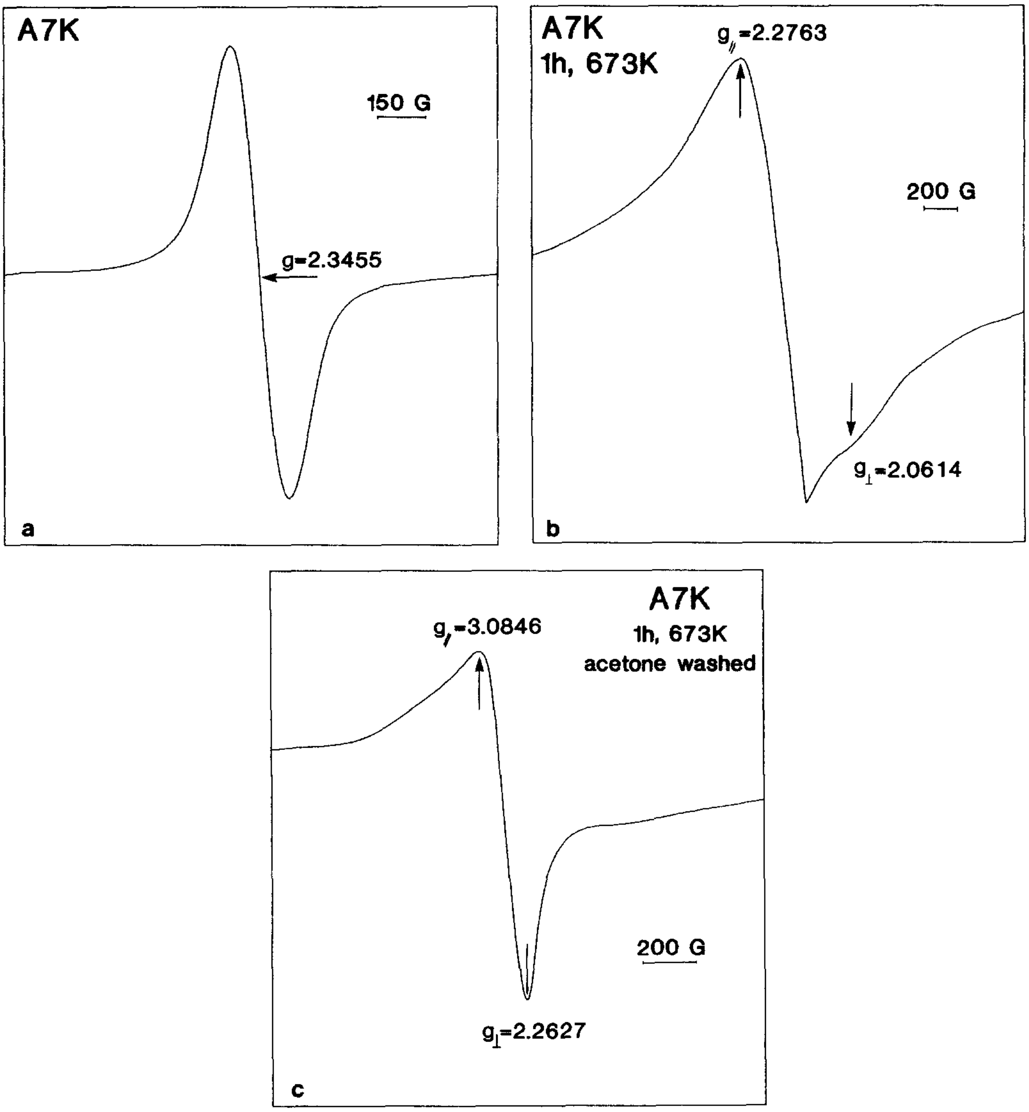

FIG. 7. EPR spectra of catalyst A7K: (a) fresh sample; (b) after a heating/cooling cycle; (c) sample b washed with acetone.

contents as A7KLa, but without K. The lack of crystalline formations is clearly evident on this sample.

Catalytic Activity

Figure 14 shows the total CH_4 conversions obtained for the Al_2O_3- and SiO_2-supported catalysts in the CH_4 oxychlorination reaction. The open bars represent the levels of conversion reached after a first 20-min reaction period at 670 K after a 30-min treatment in $HCl–O_2$ mixture at the same reaction temperature. It is evident that the addition of La causes an increase in activity for all the catalysts investigated. On the other hand, the level of activity exhibited in a second reaction period at 670 K is also shown in Fig. 14 as hatched bars. It must be noted that before this second run the catalyst had been cooled in the reaction mixture

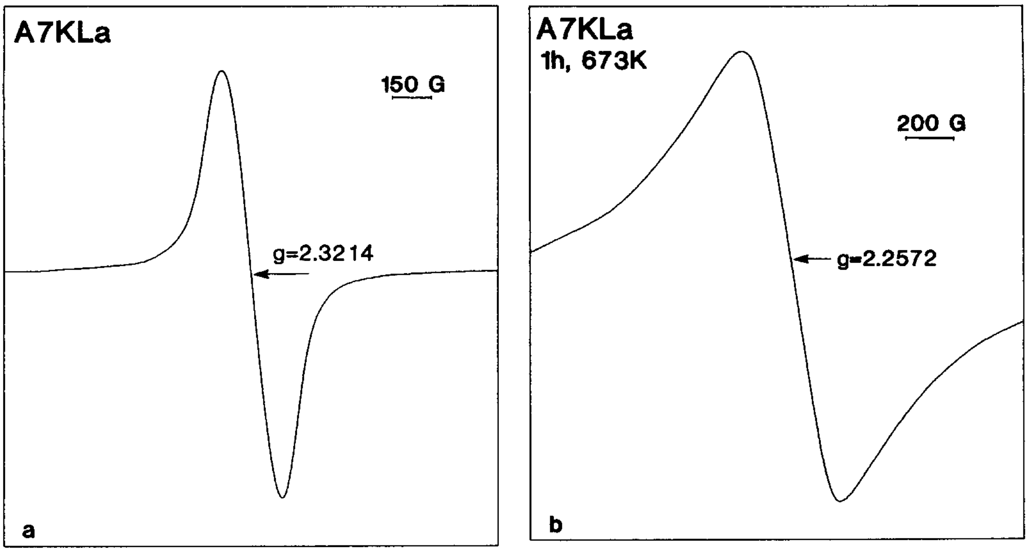

FIG. 8. EPR spectra of catalyst A7KLa: (a) fresh sample; (b) after a heating/cooling cycle.

from 670 K to room temperature. A pronounced decrease in activity during the second cycle is observed for catalyst S7K, almost no change for S7KLa, and an increase for A7K and A7KLa. As demonstrated by atomic absorption analysis on the used catalysts, no significant losses of Cu occur during the reaction period. Therefore, the observed deactivation cannot be attributed to volatilization of the active phase.

DISCUSSION

We interpret our results in terms of the irreversible segregation observed to occur after a heating/cooling cycle in the two-component catalysts. The addition of $LaCl_3$ as a copromoter appears to inhibit this phenomenon, and be responsible for the maintenance of activity after consecutive heating/cooling cycles in the three-component catalysts.

As was previously mentioned, the double salt formation caused by the addition of KCl to $CuCl_2$-supported catalysts lowers the melting point of the Cu chloride mixtures, allowing the catalysts to be molten under reaction conditions (*5*, *6*). Considering the phase diagram of the system KCl–$CuCl_2$ (*5*), we can expect that for K/Cu molar ratios ranging between 0.7 and 2.5 the mixture at 670 K will be totally molten. Even though the K/Cu ratio used in the preparation of the catalysts was 1.0, the distribution of Cu and K is not homogeneous (*7*) so that zones with different K/Cu ratios are expected to be present in the catalysts. When the temperature is lowered, and depending on the K/Cu ratio, the phase diagram predicts that the system may enter a two-phase region. When the K/Cu ratio is higher than that of the eutectic, i.e., about 1.5, KCl and K_2CuCl_4 start to come out of the liquid mixture while the liquid becomes richer in Cu until it reaches the composition of the eutectic. Analogously, in the case that the K/Cu ratio is lower than 1.5, the cooling causes the separation of a solid phase rich in $CuCl_2$ and $KCuCl_3$ and a liquid phase which becomes richer in K until the composition of the eutectic is reached. In this way, after a heating/cooling cycle a two-component catalyst will exhibit a segregation of K and Cu.

In a homogeneous bulk mixture the initial liquid phase can be restored by increasing the temperature to its starting value. How-

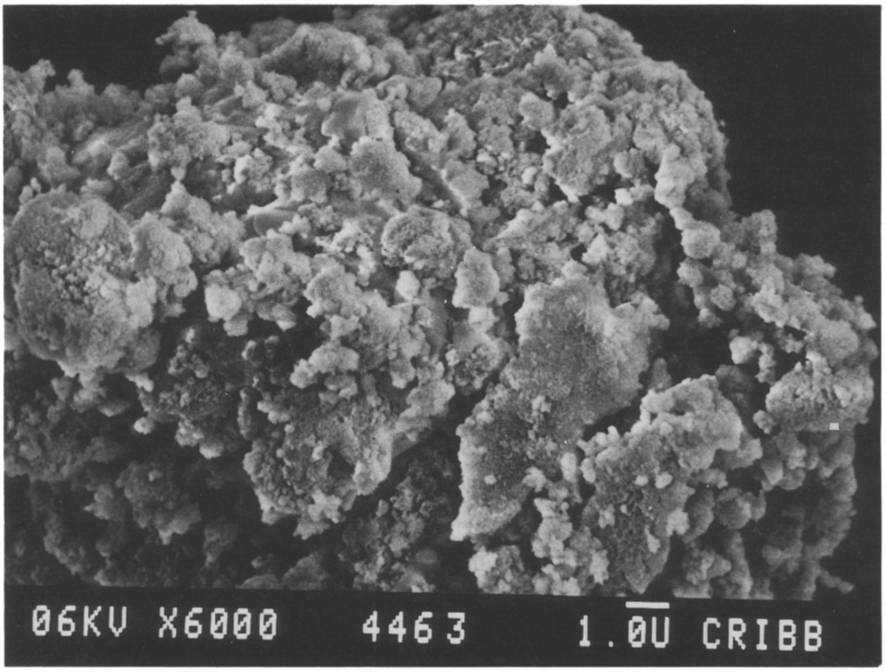

FIG. 9. SEM micrograph of a fresh A7K sample. Bar = 1 μm.

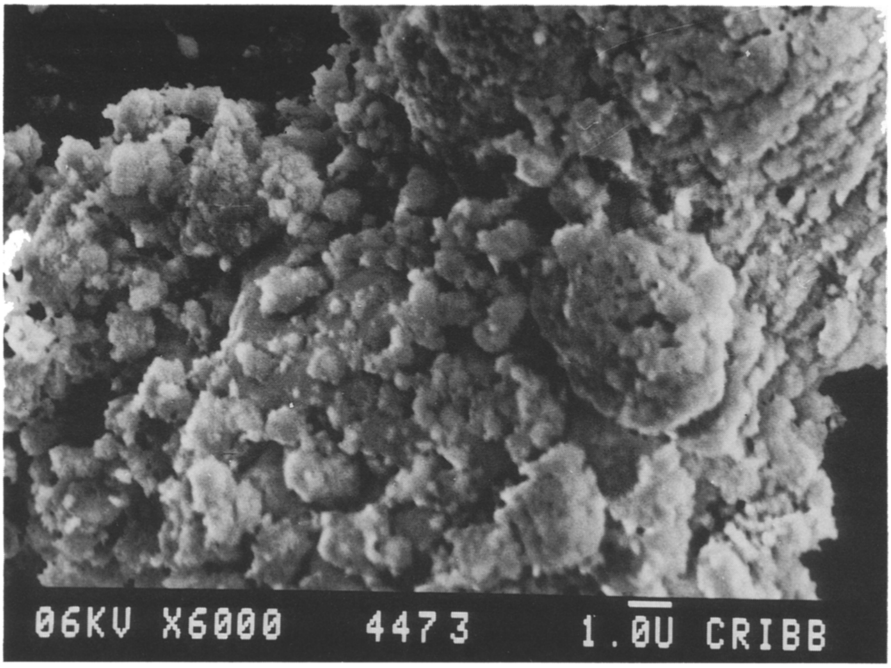

FIG. 10. SEM micrograph of catalyst A7K after a heating/cooling cycle. Bar = 1 μm. Note the increase in crystallinity compared with Fig. 9.

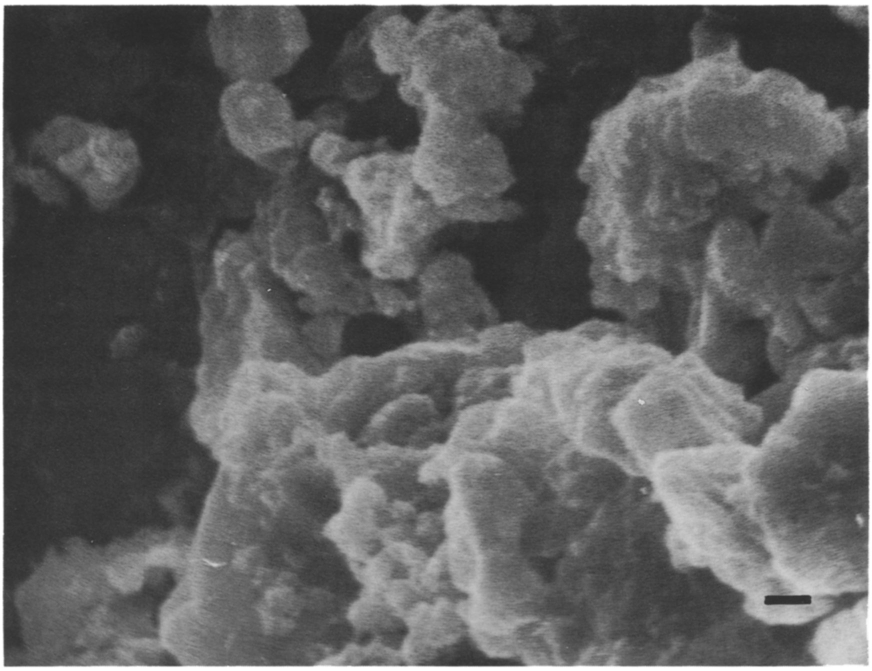

FIG. 11. SEM micrograph of a fresh A7KLa sample. Bar = 2 μm.

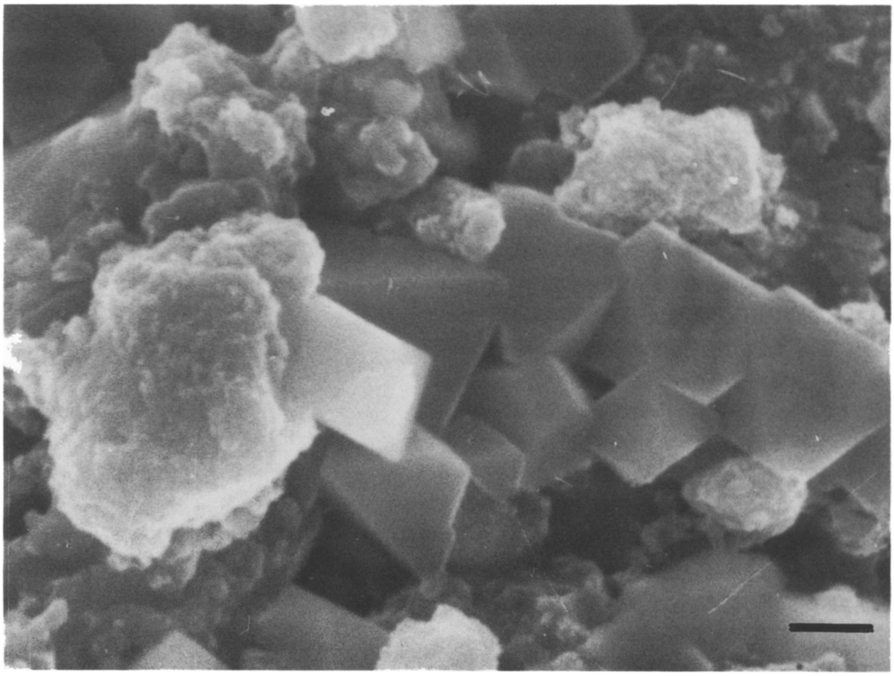

FIG. 12. SEM micrograph of catalyst A7KLa after the heating/cooling cycle. Bar = 1 μm. Note regular pyramidal crystalline formations which did not appear in Fig. 11.

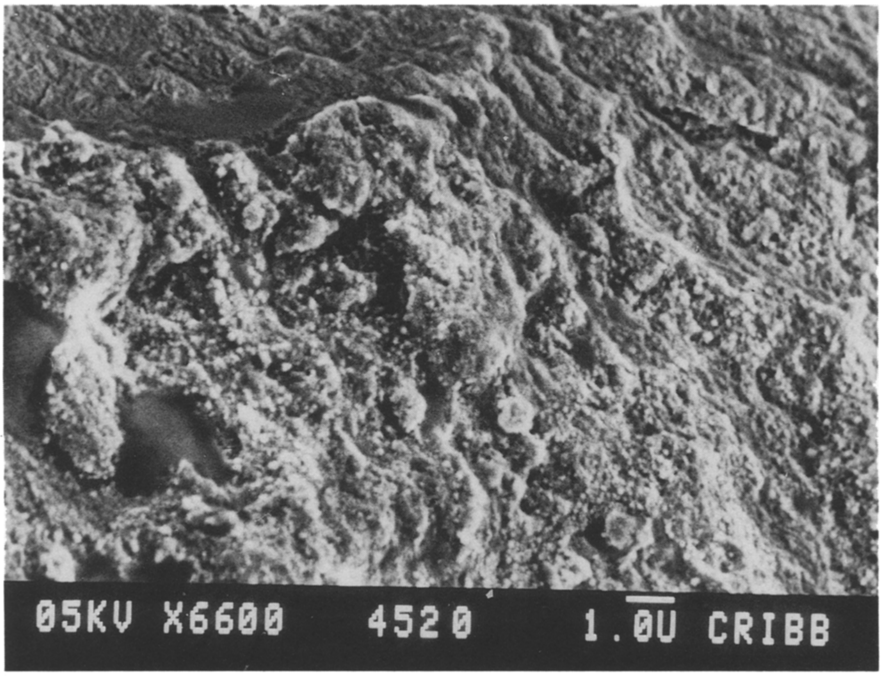

FIG. 13. SEM micrograph of $CuCl_2$–$LaCl_3/Al_2O_3$ catalyst after the heating/cooling cycle. Bar = 1 μm. Note the lack of crystalline formations.

ever, when dealing with salt mixtures dispersed on a high-surface-area support, total reversibility may not be expected. For instance, in a combined DTA-XRD study, Conner *et al.* (*24*) observed the disappearance of crystalline $KCuCl_3$ double salts in

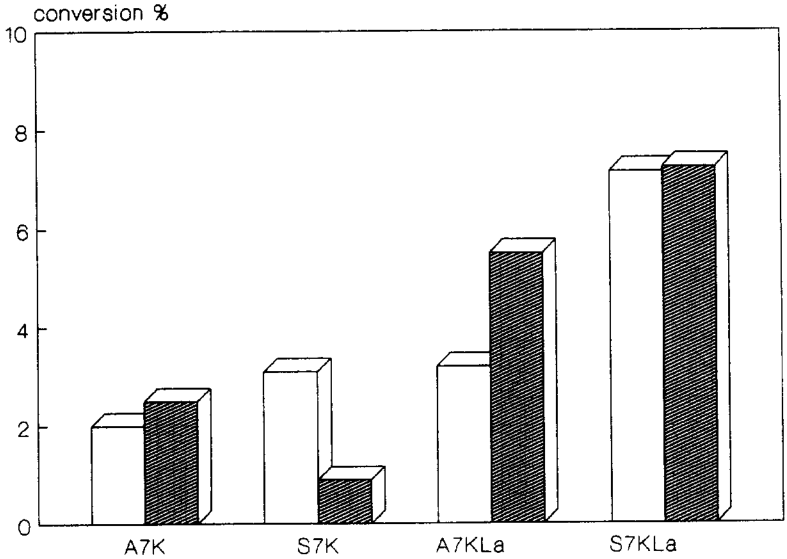

FIG. 14. Total CH_4 conversions obtained for the Al_2O_3- and SiO_2-supported catalysts in the CH_4 oxychlorination reaction. Open bars, first 20-min reaction period at 670 K; crosshatched bars, second 20-min reaction period at 670 K.

the heating cycle which do not reappear in the subsequent cooling cycle. Likewise, in the case of our S7K catalyst, a clear segregation is evidenced by the marked increase in the amount of crystalline KCl detected by X-ray diffraction. Other evidence of this segregation is given by the results of consecutive DTA cycles. During the second DTA cycle the K-rich phase was richer than in the first cycle. This was indicated by a shift of the corresponding melting peak to lower temperatures. At the same time, the fraction of particles with low K/Cu ratios was larger during this second DTA cycle as indicated by the increase in the size of the peak.

This segregation has a strong influence on the loss of activity between consecutive heating/cooling cycles. We have previously demonstrated (*8–10*) that $CuCl_2$, free of K, deactivates rapidly as a result of an irreversible surface reduction. During the oxychlorination reaction, chlorine atoms evolve from the $CuCl_2$ particles, leaving a surface layer of CuCl which is not easily reoxidized. The presence of KCl promotes catalyst stability as it forms complex species with the CuCl salt which can be easily oxidized (*25*). Therefore, the decreased activity displayed by catalyst S7K during the second reaction period can be related to the proposed irreversible segregation. This segregation will cause most of the $CuCl_2$ to be physically separated from the KCl. As a result the catalysts will behave as unpromoted.

In the case of Al_2O_3-supported catalysts a strong anchoring of Cu to the support may enhance the segregation. As indicated by the extraction analysis this anchoring is further favored by the thermal treatment at 673 K. Evidence of this interaction is the markedly different migration rate of Cu ions over Al_2O_3 compared to that over SiO_2. The EPR spectra further confirm these ideas. While the symmetry of the signal of the S7K catalyst (Fig. 6) does not change as a consequence of the thermal treatment, the spectrum of the A7K catalyst (Fig. 7) shows the appearance of an asymmetric signal which can be described as a superposition of symmetric and asymmetric contributions. As described above, these contributions were respectively ascribed to Cu(II) ions, which do not interact with the support, and Cu(II) ions, which do interact.

The Cu–Al_2O_3 interaction plays an important role in the segregation phenomenon. The stabilization of Cu species by the support enhances the removal of Cu ions from the salt mixtures. As shown in Fig. 3, XRD peaks corresponding to oxychloride species stabilized by the Al_2O_3 support become clearly evident as a consequence of the heating treatment on catalyst A7K. The first evidence for the enhancement of the K–Cu segregation in this catalyst compared to S7K comes from contrasting the increases in the amount of free KCl detected by XRD after the thermal treatment for both catalysts. It can be seen in Fig. 3 that this increase is more pronounced for the Al_2O_3-supported catalyst. At the same time, the increase in the maxima corresponding to the double salt K_2CuCl_4 for catalyst A7K is not as marked as for S7K. Additional evidence comes from comparing the rather different behavior of catalyst A7K during consecutive DTA cycles relative to that of S7K described above. Catalyst A7K showed the presence of only one melting peak, which shifted to higher temperatures in the second cycle. This can be explained in terms of the same two types of phases with varying K/Cu ratio previously proposed. The first phase would be a Cu-rich one stabilized by the Al_2O_3 support which would not melt in the temperature range investigated. The second would be a K-rich phase which in the second DTA cycle would have a K/Cu ratio exceeding the limit at which addition of K no longer diminishes the melting point of the mixture but instead starts raising it. The marked decrease in the area of the melting peak during the second cycle further confirms this picture.

Even though the segregation process is more marked on the Al_2O_3-supported catalyst than on the SiO_2-supported one, a decrease in catalytic activity was not observed for catalyst A7K, whereas it was clear for S7K. XRD and EPR results demonstrate that on catalyst A7K, the segregation phenomenon is accompanied by the formation of Cu(II) oxychloride species stabilized by the support. We have previously shown (*8, 9*) that such Cu(II) species has its own catalytic activity. Therefore, the observed increase in activity exhibited by this catalyst during the second run may be ascribed to the presence of this species.

The behavior of the three-component catalysts suggests that $LaCl_3$ acts as an inhibitor of the segregation phenomenon observed for the two-component catalysts. The diffraction patterns of catalyst A7KLa (Fig. 5) show that the K_2CuCl_4/KCl ratio changes little as a consequence of the thermal treatment, whereas it was drastically reduced for the two-component catalysts. Also, the signal corresponding to $KCuCl_3$ was more intense after the thermal treatment. But, in the case of the two-component catalysts it almost disappeared after heating. Furthermore, formation of the oxychloride, which would constitute additional evidence of the double salt dissociation on this support, was not detected in catalyst A7KLa. The absence of this species was further confirmed by EPR. Before and after the 1-h thermal treatment the spectra did not show any asymmetric contribution.

The sequential DTA experiments conducted on the three-component catalysts show that the heating/cooling cycle did not cause the segregation of ions described for the two-component catalysts. In both, Al_2O_3- and SiO_2-supported catalysts, the fraction of salt that melts at the lower temperature notably increased during the second cycle. This fraction could be associated with the well-defined crystalline phases shown in Fig. 12. These regular pyramidal crystals dominate on the three-component catalysts after the heating/cooling cycle and are shown to contain K, Cu, and moderate amounts of La. By contrast, as shown in Fig. 13, when only La and Cu are present no crystalline formations appear.

As shown in Fig. 14, the addition of $LaCl_3$ promotes both the activity and the maintenance of activity after a heating/cooling cycle. Considering the previously described effect of La on the stability of the K–Cu–Cl double salts, we propose that the maintenance of activity manifested by the La-promoted catalysts may be attributed to the action of La as an inhibitor of the segregation phenomenon, which as we noted in the previous section, appears as the main cause of deactivation of the two-component catalysts.

The effect of La is particularly clear in the SiO_2-supported catalyst, where no salt–support interaction contributes to maintain the activity. When no salt–support interaction occurs, the segregation process detected in the two-component catalysts must be related to the stability of the double salts. Some of the most important factors influencing the stability are polarization and ligand-field effects (*26*). In this way, an appropriate balance between electrostatic and steric factors may influence the catalyst stability. As a first approximation, the rate of dissociation of complex ions of the type MCl_4^{2-} into ions M^{2+} and Cl^- increases with the polarizing power of the associated cation. The polarizing power of cations appears to be proportional to $|Z|/r^2$, where Z is the cation charge and r its ionic radius (*26, 27*). The trend of dissociation increases moving up in the periodic table from Cs^+ to Li^+, as the polarizing power increases in this direction. Taking it into account, the trend to dissociation of the K–Cu–Cl double salts would be favored when K^+ is the associated ion to the $CuCl_4^{2-}$ anions.

On the other hand, La(III), which has a polarizing power higher than that of K^+ would avoid an excess of free chloride ions in the KCl–$CuCl_2$ melts, forming strong lanthanum chloride complexes (*25*). Therefore, La would decrease the concentration of anions available to draw back K from its association with the $CuCl_4^{2-}$ complex anions. Considering the high relative polarizing power of Nd^{3+}, Th^{4+}, and Mg^{2+}, a beneficial effect similar to that of La would be expected using some of these cations as copromoters.

CONCLUSIONS

The main conclusions of this work can be summarized:

When supported $CuCl_2$–KCl catalysts are thermally treated to high temperatures, i.e., 670 K, and subsequently cooled to room temperature, an irreversible segregation occurs.

On γ-Al_2O_3, where a surface Cu oxychloride species is strongly stabilized, the segregation process is enhanced as a result of this salt–support interaction.

The segregation process appears as the main cause of deactivation observed for the two-component catalysts after a heating/cooling cycle.

For the Al_2O_3-supported, two-component catalysts the deactivation is not evident due to the activity of the surface Cu oxychloride species itself.

The three-component catalysts, which contain La, exhibit an improved activity that is maintained over a heating/cooling cycle. This promoter effect may be ascribed to the action of La as an inhibitor of the dissociation of K–Cu–Cl double salts.

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