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DTA ANALYSIS OF THE SYSTEM CARRIER-$CuCl_2$, KCl. PART II

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DTA analysis of carrier-$CuCl_2$, KCl catalysts with total active salt contents of from 17.68 to 33.27%, and with Cu:K molar ratios of from 0.691 to 0.922, revealed a number of endothermic processes within the temperature range 293-773 K. The extents of these processes depended on the total salt content and the Cu:K molar ratio. The influence of the carrier on the active phase constitution was observed.

Data on the structure of a mixture of copper and potassium chlorides under the conditions of the oxychlorination reaction are not available in the literature. Neither is the structure of these mixtures known in phase areas through which they have to pass until the reaction temperature is reached [1, 2]. Investigation of the structure of the active phase of the ethene oxychlorination catalyst of the type carrier-$CuCl_2$, KCl is complicated, due to the presence of the carrier. It has been found that the nature of the carrier exerts a significant influence on the efficiency of the ethene oxychlorination catalyst [3-5]. However, the exact form of this influence is unknown. The current discussion is concerned with the presence of monovalent copper inside the active phase of catalysts of type carrier-$CuCl_2$, KCl [6-9], and the effects of the carrier surface on the active phase and structure of the catalyst [10-12]. Thus, little is known about the exceptional applicability of the natural carrier with the trade-name "Florida" for the production of a catalyst for the process of ethene oxychlorination [13]. On an industrial scale, this carrier has found application in many vinyl chloride production plants.

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In the present work, thermogravimetric analyses were performed on ethene oxychlorination catalysts based on the "Florida" carrier, which differed in the mass of the active phase, and in the molar ratio $CuCl_2$:KCl. The system of salts $CuCl_2$ and KCl on the carriers α-Al_2O_3, γ-Al_2O_3 and silica gel was investigated thermogravimetrically earlier [14, 15].

Experimental

The investigation was concerned with catalysts obtained in a pseudo-fluidal carrier system in the apparatus described in [16]. Optimal constant impregnation conditions were applied to all catalysts, which differed in total content of $CuCl_2$ and KCl at a constant molar ratio $CuCl_2$:KCl of 0.768, or which differed in the molar ratio $CuCl_2$:KCl at a fixed total salt content of 22.10%. The temperature of impregnation was 378 K, and the dropping rate of the aqueous solution of the mixture of $CuCl_2$ and KCl was 2.75 cm^3/min, the volume of the dropped solution being 200 cm^3 per 100 cm^3 of the carrier. Full characteristics of the carrier are given in [17]. The set of catalysts after impregnation are given in Table 1.

Table 1 Set of catalysts after impregnation

Catalyst No.	Series	Total active salt content, %	Molar ratio of Cu to K	Imregnation temperature, K
1		17.68		
2		19.89		
3	1	22.10	0.768	378
4		25.42		
5		33.27		
6			0.691	
7	2	22.10	0.845	378
8			0.922	

Thermogravimetric analyses were performed with a derivatograph (MOM, Budapest, Hungary) within the temperature range 293-773 K. The measurement conditions were as follows: heating rate 2.5 deg/min, air atmosphere, platinum crucible, Al_2O_3 as reference material, sensitivity DTA 1/1, sensitivity DTG 1/3, sensitivity TG 200 mg. The weight of catalyst was always 1.328 g, the granulation was -0.02: -0.06 cm and the degree of sample compaction was also constant. The application of the maximally feasible sensitivity, DTA 1/1, led to well marked peaks in the DTA curves (in comparison with the peaks obtained in [14, 15]). However, this required many preliminary analyses to determine the optimal mass of the analysed samples of the carrier and the catalyst, as well as the mass of the reference material, so that the whole run of the DTA curves might be recorded with sharply outlined peaks.

Results

The thermal curves of the carrier used for the preparation of the catalysts is presented in [17]. Figure 1 shows the thermal curves of catalyst no. 3. In all the DTA curves of the catalysts after impregnation, the analysis

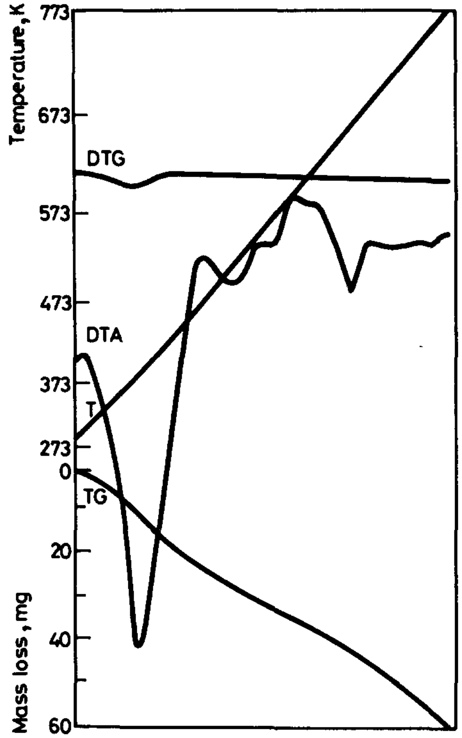

Fig. 1 TG, DTG and DTA curves of catalyst no. 3

revealed the occurrence of an intense endothermic effect with minimum at 383-393 K, due to the loss of water from the carrier, and the occurrence of three endothermic effects in the temperature ranges 483-543 K, 543-603 K and 603-683 K. The positions of the minima of the first two peaks exhibited some variation, e.g. 518 and 573 K, respectively, for catalyst no. 1, and 498 and 593 K for catalysts nos 4 and 5 and catalyst nos 7 and 8, respectively. The temperature of the third peak was constant for all the analysed catalysts, at 663 ± 5 K. A continuous mass loss was observed in the TG curves of all the catalysts. Figure 2 shows the peak areas of the DTA curves

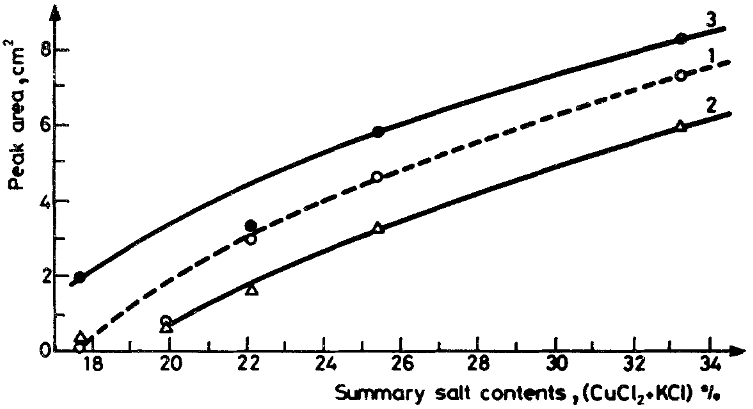

Fig. 2 Variation of the peak areas of the endothermic effects at 498-518 K (curve 1), 573-593 K (curve 2) and 663 ± 5 K (curve 3), as a function of the total salt content in the catalysts

above 473 K for the catalysts of the first series, with increase of the contents of $CuCl_2$ and KCl. The analysis demonstrated an almost linear increase in the areas of all three endothermic effects in the DTA curves, i.e. the effects with minima at 498-518 K, 573-593 K and 663 ± 5 K. At the same time, it is evident that the area increment curves of the investigated effects have a parallel character with respect to each other. Figure 3 depicts the peak areas of the same three endothermic effects as a function of the molar ratio $CuCl_2$:KCl (series 2). The curves of the areas of the endothermic effects with minima at 573-593 K (curve 2) and 663 ±5 K (curve 3) rise slightly with increase of the molar ratio $CuCl_2$:KCl. On the other hand, the curve of the areas of the endothermic effects with minima at 498-518 K (curve 1) passes through a maximum at a $CuCl_2$:KCl molar ratio of about 0.8.

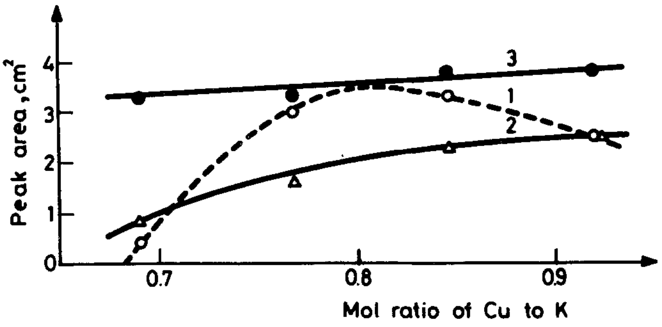

Fig. 3 Variation of the peak areas of the endothermic effects at 498-518 K (curve 1), 573-593 K (curve 2) and 663 ± 5 K (curve 3), as a function of the molar ratio Cu:K in the catalysts

Discussion

The continuous mass loss observed in the TG curves is caused primarily by the loss of water from the carrier [17]. Too high a dilution of the active phase of the catalysts with the carrier did not permit recording of the probable mass loss from the active phase. In the DTA curves of the catalysts and the mixtures of $CuCl_2$ and KCl [2], three well outlined endothermic effects are observed in the temperature range 473-773 K. The minimum of the first endothermic effect is at 498-518 K for the catalysts, and at 533-543 K for $CuCl_2$ and KCl. As far as the catalysts are concerned, this may be attributed to the triple phase transition of K_2CuCl_3-KCl-$KCuCl_3$ (498 K) or the double transition of K_2CuCl_3-KCl (518 K) [1], whereas a triple transition of K_2CuCl_4-KCl-$KCuCl_3$ (540 K) [1] can occur at 533-543 K. It may be presumed that, due to the presence of the carrier, the compound K_2CuCl_3 is formed inside the active phase of the catalyst, in which the copper is present as Cu(I). This is probably due to the effect of the carrier surface area on the superimposed mixture of salts. The second endothermic effect, with minimum at 573-593 K, occurs in the DTA curves of both the catalysts and the salt mixtures [2]. It may be attributed [1] to melting of the eutectic K_2CuCl_4-$KCuCl_3$ or K_2CuCl_4-KCl. The third endothermic effect is observed for the mixtures of $CuCl_2$ and KCl [2] (peak temperature 603-618 K), but not for the catalysts. However, there is a third, exceptionally stable endothermic effect in the DTA curves of the catalysts, at 663 ± 5 K. It can be attributed to melting of the eutectic $CuCl_2$-CuCl, whose presence has been found analogously on the surface of silica gel in the catalyst system SiO_2-$CuCl_2$, KCl [15].

The differences in the thermal curves of the catalysts and mixtures of $CuCl_2$ and KCl point to the influence of the carrier on the structure of the mixture of salts. The linear increase in the area of the endothermic effects as a function of the content of the salts in the catalysts, and their parallel character with respect to each other (Fig. 2), indicate that in the range of salts superimposed on the carrier, the effects of the carrier on the active phase are of the same kind and the whole mass of the active phase is within their range. The distribution of the peak areas in the DTA curves of the catalysts with different molar ratio $CuCl_2$:KCl (Fig. 3) is different from that for the mixture of salts with identical molar ratio [2]. This confirms the earlier finding that the carrier used for the catalysts changes the composition of the salts with respect to the mixture of salts without a carrier but with identical molar ratio. This also indicates that the endothermic effects in the DTA curves of the catalysts concern other changes (with the exception of that at 573-593 K) than those observed in the DTA curves of the salt mixtures, and that they are not a result of temperature shifts of the endothermic effects in the DTA curves of the salt mixtures due to changes in the thermal conductivity of the samples. Curve 1 (Fig. 3) is almost identical in shape to the curve of the catalyst efficiency for the same molar ratio in a concrete process of ethene oxychlorination to 1,2-DCE [18]. This would suggest that the efficiency of the catalysts of ethene oxychlorination depends on the capacity of the carrier to produce (probably) K_2CuCl_3 inside the active phase of the catalyst. The lack of parallelism between curves 2 and 3 and curve 1 (Fig. 3) permits the assumption that the phase changes at 573-593 K and 663 ± 5 K are not consecutive to the change at 498-518 K, and it seems that they refer to a different part of the active phase of the catalyst's.

Conclusions

Within the temperature range 473-773 K, the active phase of the applied catalysts undergoes endothermic changes at 498-518 K, 573-593 K and 663 ± 5 K.

With the exception of the change at 573-593 K, these changes were not observed for the mixtures of $CuCl_2$ and KCl [2].

In accordance with the result of [1, 15], the following assignments are suggested: K_2CuCl_3-KCl and K_2CuCl_3-KCl-$KCuCl_3$: 498-518 K, K_2CuCl_4-$KCuCl_3$: 573-593 K, $CuCl_2$-CuCl: 663 ± 5 K.

It has been found that the "Florida" carrier influences the structure of the active phase of the catalysts of ethene oxychlorination of the type carrier-$CuCl_2$, KCl. The effects of the carrier are of the same kind throughout the whole range of salts superimposed on the carrier, and the whole mass of active phase is within the range of their activity.

Due to the effects of the carrier on the active phase of the catalysts, the composition of the complexes formed from $CuCl_2$ and KCl is changed after impregnation in comparison to the identical mixtures of salts without carrier.

The probable formation of K_2CuCl_3 inside the active phase of the catalysts results from the interaction of the mixture of $CuCl_2$ and KCl on the surface of the "Florida" carrier. The copper in K_2CuCl_3 is present as Cu(I).

These investigations indicate the dependence of the efficiency of the catalyst of ethene oxychlorination on the carrier's capacity to produce (probably) K_2CuCl_3 inside the active phase of the catalyst.

It may be assumed that the changes in the active phase of the catalysts at 573-593 K and 663 ± 5 K are not consecutive to a change at 498-518 K. Therefore, they may refer to the three different parts of the mass of the active phase of the catalysts.

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Zusammenfassung – Die DTA-Anlyse von Trägerkatalysatoren mit $CuCl_2KCl$ mit einem Aktivsalzgesamtgehalt von 17.68 bis 33.27% und einem molaren Verhältnis (Cu zu K) von 0.691 bis 0.922 zeigte, daß beim Erhitzen der Katalysatoren im Temperaturbereich von 293-773 K eine Reihe endothermer Vorgänge ablaufen. Die Größe dieser endothermen Effekte ist abhängig vom Aktivsalzgesamtgehalt und vom molaren verhältnis Cu:K. Der Einfluß des Trägermateriales auf die Konstitution der aktiven Phase wurde untersucht.