

DTA ANALYSIS OF THE SYSTEM CARRIER-CuCl₂, KCl Part II.

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Catalysts of the type carrier-CuCl₂, KCl differing in the temperature at which they were obtained and after the ethene oxychlorination process were analyzed thermogravimetrically. Catalysts after the oxychlorination process differed in total salt content and in the molar ratio of CuCl₂ to KCl. A number of endothermic processes were observed in the DTA curves, the extents of these varying with change in the temperature at which the catalysts were obtained and in the catalyst composition.

It has been suggested [1] that the carrier surface takes part in the formation of probably K₂CuCl₃ in the active phase of ethene oxychlorination catalysts. It has been noted [1] that the interaction with the carrier leads to changes in composition in the mixture of CuCl₂ and KCl after impregnation of the carrier. As concerns ethene oxychlorination, it is very important to recognize the structure of the active phase of the catalysts under the oxychlorination process conditions. In the present work, thermal analyses were performed on the catalysts of ethene oxychlorination which differed in the temperature at which they were obtained, and thermogravimetric analyses of the catalysts were performed directly after their use in the oxychlorination process. The catalysts after ethene oxychlorination differed in the mass of the active phase and in the molar ratio of CuCl₂ to KCl.

Experimental

The investigation involved catalysts obtained in a pseudofluid carrier system in the apparatus described in [2]. Constant impregnation conditions identical to those [1] were applied to all catalysts, which differed in total

content of CuCl_2 and KCl , or in the molar ratio of CuCl_2 to KCl . Three catalysts differed in the temperature at which they were obtained. The thermogravimetrically analyzed catalysts are listed in Table 1.

Table 1. Set of thermogravimetric data after impregnation (A) and after oxychlorination process (B)

Catalyst Number	A			B		
	Salt contents	Molar ratio	Impregnation temp.,	Salt contents,	Molar ratio	Impregnation temp.,
	%	Cu/K	K	%	Cu/K	K
4	22.10	0.768	423			
4	22.10	0.768	393			
4	22.10	0.768	378			
1				19.89		
2				25.42	0.768	378
3				33.27		
4				22.10		
5					0.691	
6				22.10	0.845	378
7					0.922	378

Catalysts after oxychlorination were earlier used in a concrete process of ethene oxychlorination at 623 K for 1.5 h, using the reactant flow method ($\text{C}_2\text{H}_4:\text{O}_2:\text{HCl} = 1:0.5:2$). The catalysts were heated at 673 K for 1.5 h before the reaction, in a continuous flow of HCl and O_2 in the same ratio as used in the oxychlorination process. The oxychlorination apparatus was described in [3, 4]. Catalysts after oxychlorination were quickly cooled to room temperature and thermogravimetrically analyzed. The same sample of catalysts No. 2 and No. 4 as in the first (after oxychlorination) thermogravimetric analyses were again thermogravimetrically analyzed. Thermogravimetric analyses were performed with a derivatograph (MOM, Budapest, Hungary) within the temperature range 293-773 K. The catalysts uniformly weighed 1.328 g, with the same granulation (0.02-0.06 cm) and degree of sample compaction. The measurement conditions were constant and identical to those in [1].

Results

The thermal curves of catalyst No. 4 after impregnation at 378 K were reported in [1]. Figure 1 shows the thermal curves of catalyst No. 4 obtained at an impregnation temperature of 423 K. Disappearance of the endothermic effects with minima at 498-518 K and 573-593 K was observed in the DTA curve (Fig. 1) relative to the curve relating to 378 K [1]. The DTA

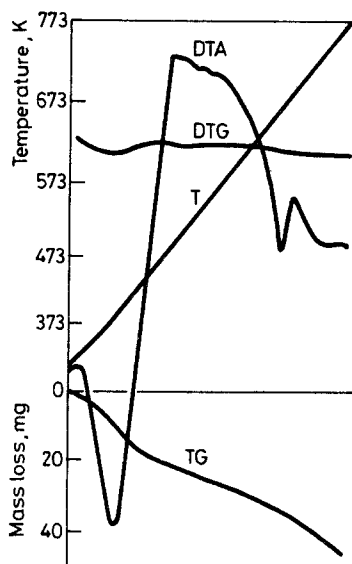


Fig. 1 TG, DTG and DTA curves of a catalyst number 4 obtained at 423 K

curve (Fig. 1) also revealed an intensive endothermic effect due to the loss of water from the carrier [5] and a well outlined endothermic effect with minimum at 663 ± 5 K. Figure 2 shows the distribution of the peak areas in the DTA curves with minima at 498-518 K, 573-593 K and 663 ± 5 K, as a function of the impregnation temperature of the carrier during preparation of the catalysts of the type carrier- CuCl_2 , KCl. Figure 2 demonstrates that the areas of the endothermic effects with minima at 498-518 K and 573-593 K are markedly reduced in the DTA curves of the catalysts obtained above 378 K. The area of the endothermic effect with minimum at 663 ± 5 K slightly increases with increase of the temperature of catalyst preparation. Figure 3 shows the thermal curves of catalyst No. 4 after ethene oxychlorina-

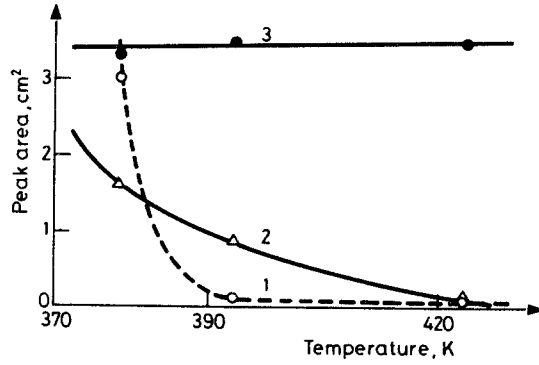


Fig. 2 Variation of the area of the endothermic effects at 498-518 K (Curve 1), at 573-593 K (Curve 2), at 663 ± 5 K (Curve 3) as a function of temperature of their obtaining

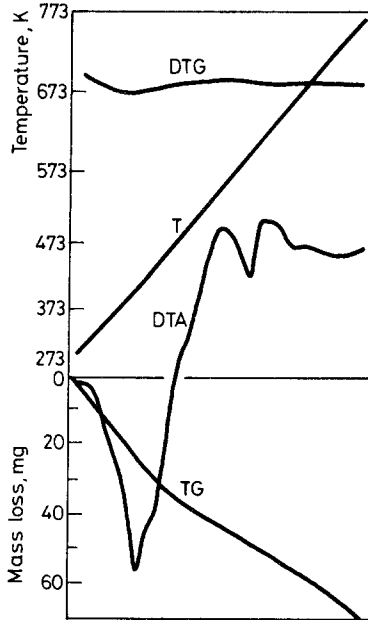


Fig. 3 TG, DTG and DTA curves of a catalyst number 4 after oxychlorination process

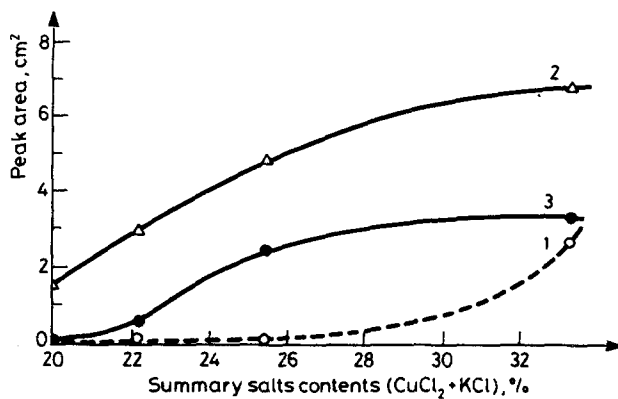


Fig. 4 Variation of the area of the endothermic effects at 498 K (Curve 1), at 603 K (Curve 2), at 663 \pm 5 K (Curve 3) as a function of summary salts contents in the catalysts after oxychlorination process

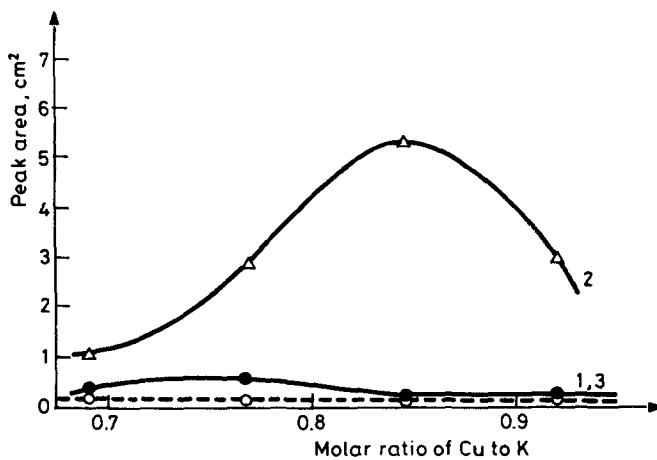


Fig. 5 Variation of the area of the endothermic effects at 498 K (Curve 1), at 603 K (Curve 2), at 663 \pm 5 K (Curve 3) as a function of the molar ratio of Cu to K in the catalysts after oxychlorination process

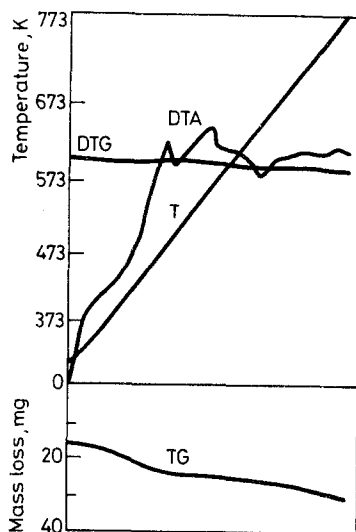


Fig. 6 TG, DTG and DTA curves of a catalyst number 4 after oxychlorination process obtained during secondary thermogravimetric analysis

tion. Above 473 K, the DTA curve revealed a slight endothermic effect with minimum at 498 K, a well outlined endothermic effect with minimum at 603 K, and a very small endothermic effect with minimum at 663 ± 5 K. The distribution of the peak areas in the DTA curves above 473 K for the catalysts after oxychlorination which differed in the contents of CuCl_2 and KCl displayed an increase in the areas of the three endothermic effects with minima at 498, 603 and 663 ± 5 K, together with an increase in the total content of the two salts in the catalysts after oxychlorination. The areas of the first and third endothermic effects are minimal in the DTA curves of the catalysts which contain up to 22.10 % CuCl_2 and KCl . The area of the endothermic effect with minimum at 663 ± 5 K quickly increases with the content of the two salts above 22 % and the area of the endothermic effect with minimum at 498 K quickly increases with the content above 26 %. At the same time, in curves 2 and 3 the occurrence of inflexion points is observed for contents about 26 %. Figure 5 presents the distribution of the areas of the endothermic effects with minima at 498, 603 and 663 ± 5 K in the DTA curves of the catalysts after oxychlorination which differed in the molar ratio of CuCl_2 to KCl . In the DTA curves of the catalysts containing 22.10 % of active salts with different molar ratios of CuCl_2 to KCl , there were practically no endothermic effects with minima at 498 K or 663 ± 5 K. Figure 5

demonstrates that the area of the endothermic effect with minimum at 603 K (curve 2) is the largest at a Cu to K molar ratio of 0.845. Figure 6 shows the thermal curves of catalyst No. 4 after oxychlorination of ethene in the second thermogravimetric analysis. All three endothermic effects which occurred in the DTA curves of the catalysts after impregnation [1] are present (Fig. 6).

Discussion

The variation in the areas of the endothermic effects above 473 K in the DTA curves of the catalysts differing in the temperature at which they were obtained supports the suggestion in [1] about the probable formation of K_2CuCl_3 in the active phase of the oxychlorination catalysts due to the interaction of the carrier surface with the mixture of $CuCl_2$ and KCl . The DTA curves of the catalysts obtained at 393 K and 423 K exhibit practically minimal endothermic effects, with minima at 498-518 K. For the catalysts obtained at these temperatures, the contact time of the aqueous solution of $CuCl_2$ and KCl with the carrier surface is considerably reduced in comparison to this time in the case of catalyst No. 4 obtained at 378 K. The area of the endothermic effects with minimum at 573-593 K, which is probably connected with melting of the eutectic K_2CuCl_4 - $KCuCl_3$ [6], also decreases markedly with increase of the temperature of catalyst preparation above 393 K. This may result from the fact that at an impregnation temperature of 393 K, and much more so at 423 K, the mixture of $CuCl_2$ and KCl without carrier forms the phase system $KCuCl_3$ - KCl , and not K_2CuCl_4 - KCl - $KCuCl_3$ [7, 8]. The non-parallel character of curve 3 relative to curves 2 and 1 (Fig. 2) indicates that a phase change at $663 \pm K$ is not consecutive to changes at 498-518 K and 573-593 K. The shape of the DTA curves of catalysts after oxychlorination suggest that there is significant unification of the active mass of the catalysts under the ethene oxychlorination conditions, and the endothermic effect with minimum at 603 K, in agreement with results in [6], may be attributed to the melting of K_2CuCl_4 . Unification of the active phase of the catalysts under the oxychlorination conditions is probably a result of consecutive reactions with chloride anion in accordance with the reactions described by Fontana *et al.* [6], $CuCl_4^{2-}$ being formed in the reaction:



The distribution of the areas of the endothermic effects in the DTA curves in Fig. 4 seems to confirm the occurrence of these consecutive reactions in the active phase of the catalysts after oxychlorination. The shapes of the curves in Fig. 4 suggest that there is a decomposition of the last-formed complex under the oxychlorination conditions. Decomposition is possible during the cooling of catalyst samples and during thermogravimetric analysis. The variation in the areas of the endothermic effect with minimum at 603 K in the DTA curves of the catalysts after oxychlorination, which differed in the molar ratio of Cu to K, is identical in shape to the efficiency curve for the same catalysts in the concrete ethene oxychlorination process [4] and to the curve for the areas of the endothermic effect with minimum at 498-518 K for the same catalysts after impregnation [1]. It has been suggested [1] that the efficiency of the catalyst of ethene oxychlorination depends on the capacity of the carrier to produce K_2CuCl_3 in the active phase of the catalysts. It may now be suggested that the efficiency of the catalysts of ethene oxychlorination depends on the quantity of $CuCl_4^{2-}$ formed under oxychlorination conditions, and the quantity of $CuCl_4^{2-}$ depends on the capacity of the carrier to produce K_2CuCl_3 in the active phase of the catalysts. The endothermic effect observed in the DTA curves of the catalysts after oxychlorination with minimum at 603 K originates from the phase change of the complex formed under the oxychlorination conditions. At the same time, it is not the same endothermic effect (simply shifted in temperature) as occurs in the DTA curves of the catalysts after impregnation with minimum at 573-593 K. The thermal curves in Fig. 6 support these two sentences. The shape of the DTA curve (Fig. 6) and the temperatures of the endothermic effects indicate that complexes formed in the active phase of the catalysts under the oxychlorination conditions must have decomposed during the first thermogravimetric analysis, the catalyst composition thereby becoming similar to that of the catalysts after impregnation. This would indicate that all reactions which lead to unification of the active phase of the catalysts under ethene oxychlorination conditions are reversible in nature.

Conclusion

It has been supported that, due to the "Florida" carrier surface, probably K_2CuCl_3 is formed in the active phase of the catalysts of type $CuCl_2$, KCl-carrier.

Increase of the impregnation temperature of the carrier above 393 K results in decay of the $K_2CuCl_4 \cdot KCuCl_3$ phase in the active mass of the investigated catalysts, which undergo endothermic changes at 573-593 K.

This investigation allows the assumption that the phase change of the active phase of the catalysts at 663 ± 5 K is not consecutive to the changes at 498-518 K and 573-593 K.

Unification of the active phase of the investigated catalysts takes place under the ethene oxychlorination conditions. Probably $CuCl_4^{2-}$ is formed on the surface of the catalyst carrier during this unification process. Under the ethene oxychlorination conditions, the active phase of the catalysts decompose via the reverse reactions to those in which they were obtained.

This investigation points to the dependence of the efficiency of the catalysts of ethene oxychlorination on the quantity of the active phase obtained under the conditions of this process, which undergoes endothermic change at 603 K. This quantity of the active phase seems to result intermediately from interaction of the carrier and the active phase of the catalysts under the conditions of their formation.

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Zusammenfassung — Bei verschiedenen Temperaturen hergestellte Katalysatoren des Types Carrier- $CuCl_2 \cdot KCl$ wurden nach dem Ethylen-Oxychlorierungsprozeß thermogravimetrisch untersucht. Die Katalysatoren unterschieden sich nach dem Oxychlorierungsprozeß sowohl in ihrem absoluten Salzgehalt als auch im Molverhältnis $CuCl_2$ zu KCl . Anhand der DTA-Kurven wurde eine Anzahl endothermer Vorgänge beobachtet, deren Ausmaß von der Katalysatorenzusammensetzung sowie davon abhängt, bei welcher Temperatur der Katalysator hergestellt wurde.