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INFLUENCE OF ADDITIVES ON THE DTA CURVES OF THE SYSTEM $CuCl_2$ - KCl

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Mixtures of CuCl and KCl containing the additives $MgCl_2$, NaCl or CsCl were heated at 473 K in air atmosphere, and then subjected to DTA analysis in the temperature range 293–773 K. The molar ratio of Cu to K in the mixtures varied from 0.5 to 1.0. The influence of the additives on the DTA pictures of the $CuCl_2$–KCl system was observed.

DTA analysis of the system $CuCl_2$–KCl has been reported [1]. However, the phase changes in the system $CuCl_2$–KCl have not been described equivocally. Accordingly, studies of the ethylene oxychlorination mechanism [2–4], the constitution of the liquid phase of the ethylene oxychlorination catalyst [1, 5], and the influence of the carrier on the constitution of the system $CuCl_2$–KCl [6, 7] are being continued.

The present work involved thermogravimetric investigations of the system $CuCl_2$–KCl (molar ratio of $CuCl_2$ to KCl from 0.5 to 1.0) containing additives of $MgCl_2$, NaCl or CsCl, within the temperature range 293–773 K. It was assumed that these additives would influence the $CuCl_2$–KCl phase changes, especially since the CsCl–KCl catalyst [8], catalytic additives of Mg [9] and the negative influence of Na on the catalyst efficiency [10] are known.

Experimental

To prepare the additive-containing $CuCl_2$–KCl system, dihydrous copper(II) chloride, potassium chloride, hexahydrous magnesium chloride, sodium chloride, and caesium chloride (POCh, Gliwice) were used.

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Weighed quantities of the salts, in appropriate proportions, were dissolved in distilled water, the solutions were evaporated to dryness and the residues were roasted at 473 K for 2 h in air atmosphere. After cooling down to room temperature, the samples were crushed and ground, and subjected to thermogravimetric analyses. Mixtures with molar ratios of $CuCl_2$ to KCl of 0.5; 0.614; 0.692; 0.768; 0.845; 0.922 and 1.0 containing 0.5; 1.0, 3.0 and 10% by weight of the additives were prepared as described above.

Thermogravimetric analyses were performed with a derivatograph (MOM, Budapest, Hungary) within the temperature range 293–773 K. The measurement conditions were as follows: constant sample mass 0.600 g, corundum crucible, air atmosphere, Al_2O_3 as reference material, heating rate 5 deg/min, sensitivity DTA 1/5, sensitivity DTG 1/10, and sensitivity TG 200 mg.

Results

Only selected curves are reported here. Common DTG, TG and T curves have been drawn in the Figures to make them more readable, as the lines were almost identical.

Figure 1 shows the endothermic effects in the DTA curves of the investigated samples with $MgCl_2$ when the molar ratio of Cu to K in the samples was 0.692.

The curves reveal changes in the areas of the endothermic effect, with a minimum at 573–583 K. On increase of the $MgCl_2$ content of the mixtures, the above endothermic effect also increased. The area of the endothermic effect with minimum at 603–618 K gradually increased. The influence of the $MgCl_2$ content on the area of the endothermic effect with minimum at 533–543 K was observed.

Figure 2 demonstrates the full disappearance of the endothermic effect with peak at 573–583 K even at 3% $MgCl_2$ in the mixtures. Increase of the $MgCl_2$ content up to 10% did not cause changes in the shape and quantity of the endothermic effect with peak at 603–618 K. Also, for instance, the changes were observed in the DTA curves of the mixtures with a Cu to K molar ratio of 0.5 and containing $MgCl_2$, and these were compared with those for the mixture of $CuCl_2$ and KCl alone.

Figure 3 demonstrates the changes in the shape of the endothermic effect with peak at 603–618 K as a result of NaCl addition to the mixtures of $CuCl_2$ and KCl.

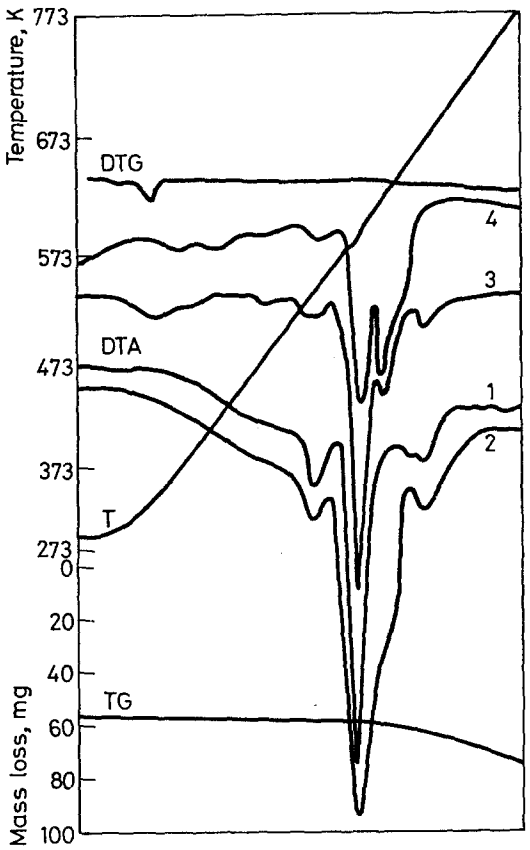

Fig. 1 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 473 K for 2 h. Molar ratio of Cu to $K = 0.692$.
Curve - 1 - mixture of $CuCl_2$ and KCl; 2 - mixture of $CuCl_2$ and KCl with 1% $MgCl_2$; 3 - mixture of $CuCl_2$ and KCl with 3% $MgCl_2$; 4 - mixture of $CuCl_2$ and KCl with 10% $MgCl_2$

The area of the endothermic effect with peak at 603–618 K gradually decreased to zero on increase of the NaCl content of the mixtures of $CuCl_2$ and KCl. The changes in the endothermic effects with peak at 573–583 K and with peak at 533–543 K were observed. A similar phenomenon was observed for the mixtures of $CuCl_2$ and KCl with CsCl (Fig. 4).

In the DTA curves of all analysed mixtures containing the additives $MgCl_2$, NaCl or CsCl, all the endothermic effects reported in [1] were observed. New endothermic effects were not detected.

Discussion

The DTA curves of the system $CuCl_2$–KCl with molar ratios of Cu to K of from 0.5 to 1.0 reveal endothermic effects with peaks at 533–543 K, 603–618 K and 673–693 K [1]. The thermogravimetric results presented in this work are quantitatively the same those described in [1]. In the DTA curves, the peaks have identical temperatures to those reported in [1]. The processes recorded in the DTA curves of the mixtures with $MgCl_2$, NaCl or CsCl appear to be identical to those observed in [1]. The results obtained here show that the addition of $MgCl_2$ to the investigated mixtures shifts the DTA picture towards that for higher molar ratios of Cu to K in the mixtures and

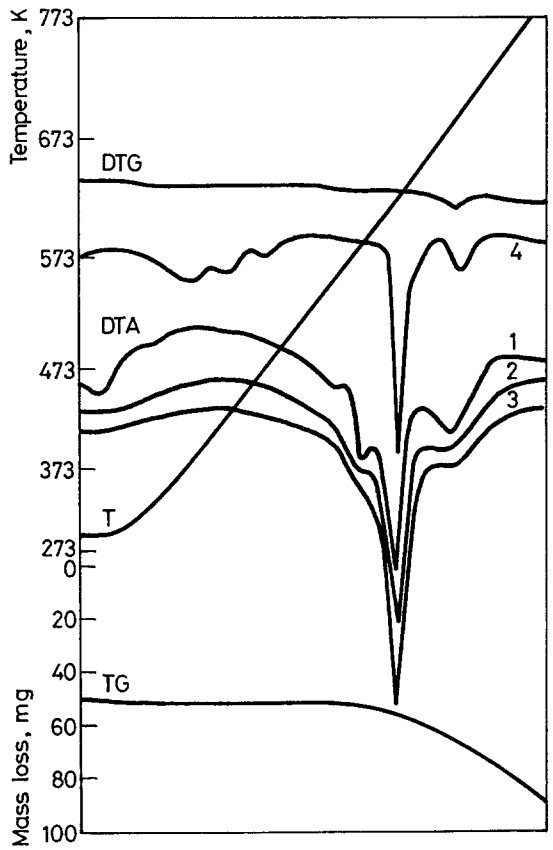

Fig. 2 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 473 K for 2 h. Molar ratio of Cu to $K = 0.922$.
Curve - 1 - mixture of $CuCl_2$ and KCl; 2 - mixture of $CuCl_2$ and KCl with 1% $MgCl_2$; 3 - mixture of $CuCl_2$ and KCl with 3% $MgCl_2$; 4 - mixture of $CuCl_2$ and KCl with 10% $MgCl_2$

does not influence the quantity and quality of the change at 603–618 K (Cu to K = 1.0). These observations together indicate that $MgCl_2$ stabilizes the combination formed in the 603–618 K change. The addition of NaCl or CsCl to the mixtures of $CuCl_2$ and KCl shifts the DTA picture towards that for

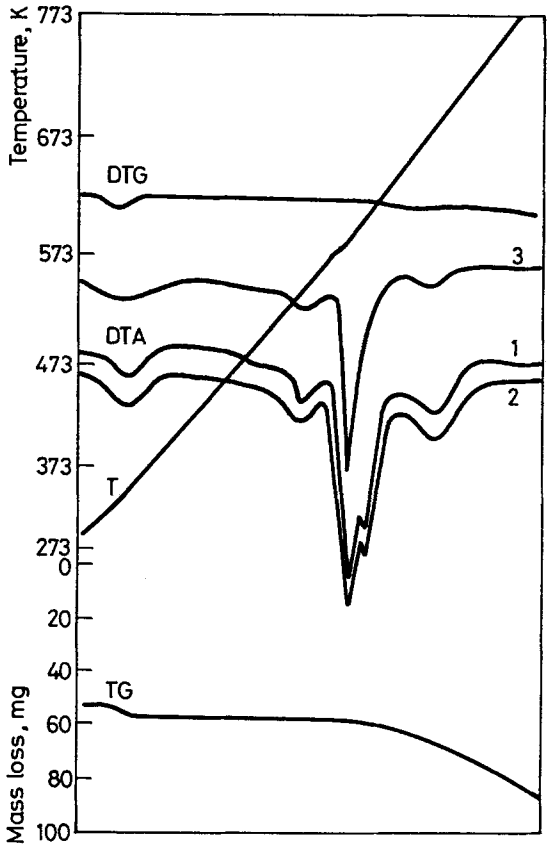

Fig. 3 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 473 K for 2 h. Molar ratio of Cu to $K = 0.768$.
Curve - 1 - mixture of $CuCl_2$ and KCl; 2 - mixture of $CuCl_2$ and KCl with 1% NaCl; 3 - mixture of $CuCl_2$ and KCl with 3% NaCl

smaller molar ratios of Cu to K in the mixtures and does not influence the change at 573–583 K (Cu to K = 0.5). Thus, it may be suggested that NaCl and CsCl destabilize the combination formed in the 603–618 K change or play the same role as KCl in the mixtures of $CuCl_2$ and KCl. The influences of NaCl and CsCl on the DTA curves of the investigated mixtures appear comparable. Accepting the ionic constitution of $CuCl_2$ and KCl mixtures [5],

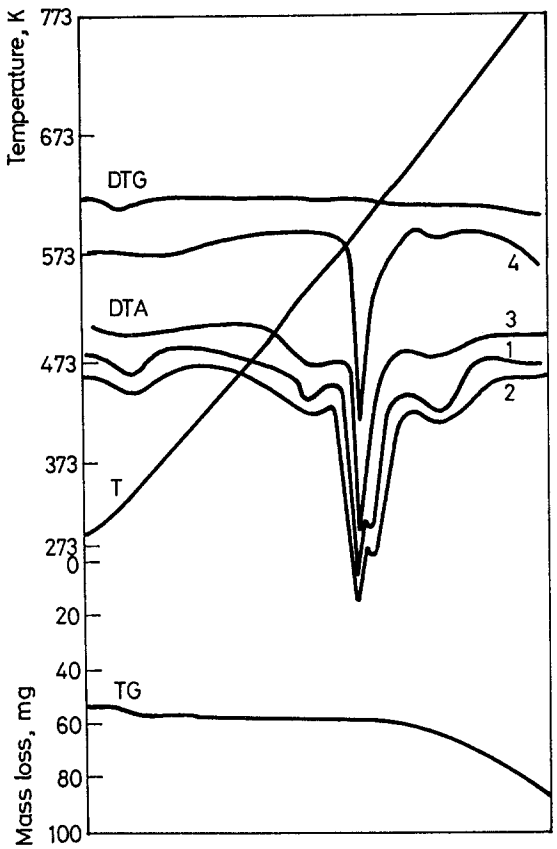

Fig. 4 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 473 K for 2 h. Molar ratio of Cu to $K = 0.768$.
Curve - 1 - mixture of $CuCl_2$ and KCl; 2 - mixture of $CuCl_2$ and KCl with 1% CsCl; 3 - mixture of $CuCl_2$ and KCl with 3% CsCl; 4 - mixture of $CuCl_2$ and KCl with 10% CsCl;

it may be suggested that the differences in the electropositivities of sodium, potassium and caesium are too small to be the reason for the changes in the DTA pictures of the investigated mixtures. It may also support the finding that Na, K, and Cs do not participate in the process of obtaining equilibrium between the ions [5].

Conclusion

The mixtures of $CuCl_2$ and KCl studied here, containing $MgCl_2$, NaCl or CsCl as additives, undergo endothermic processes at 533–543 K, 573–583 K, 603–618 K and 673–693 K. The same processes have been found for the mixtures without $MgCl_2$, NaCl and CsCl.

$MgCl_2$ probably stabilizes the combination formed at 603–618 K in the mixtures of $CuCl_2$ and KCl.

NaCl and CsCl play the same role as KCl, or destabilize the combination formed at 603–618 K in the investigated mixtures.

The differences in the electropositivities of sodium, potassium and caesium are too small to cause the changes in the DTA pictures of the mixtures investigated here. Equally, sodium, potassium and caesium may not participate in the attainment of equilibrium between the ions.

References

1 Z. Czarny and K. Zurowski, J. Thermal Anal., 32 (1987) 1387.
2 N. Todo *et al.*, J. Chem. Soc. Japan, Ind. Chem. Sec., 69 (1966) 1463.
3 K. Miyauchi *et al.*, J. Chem. Soc. Japan, Ind. Chem. Sec., 71 (1968) 695.
4 A. M. Zernosiek *et al.*, Kinet. Katal., 12 (1971) 407.
5 C. M. Fontana and E. Gorin, Ind. Eng. Chem., 44 (1952) 363.
6 J. Blanco *et al.*, Proc. Vth Intern. Congr. Catalysis, Miami Beach, 1972, p. 905.
7 R. L. Dotson, J. Catal., 33 (1974) 210.
8 Eur. Pat. Appl., EP 62320 (1982).
9 Pat. USA, 3969424 (1976).
10 Engineer's Inform., Wloclawek Oxychlor. Plant, 1990.

Zusammenfassung – Gemische aus $CuCl_2$ und KCl wurden mit Zusätzen von $MgCl_2$, NaCl oder CsCl bei 473 K in Luft erhitzt und dann im Temperaturbereich 293–773 K einer DTA-Untersuchung unterzogen. Das Molverhältnis Cu:K variierte in den Gemischen zwischen 0.5 und 1.0 . Es wurde der Einfluß der Zusätze auf den Verlauf der DTA-Kurven des Systemes $CuCl_2$–KCl untersucht.