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Thermal Properties of Cobalt and Molybdenum Containing Citrate Systems

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Abstract

Citrate complexes of transition metals, namely cobalt and molybdenum, used as active components in the synthesis of catalytic systems supported on alumina for hydrotreatment of heavy oil fractions have been studied. Cobalt nitrate hexahydrate and polyoxomolybdate (molybdenum blue) obtained by mechanical activation of molybdenum disulphide (MoS_2) powder were used as initial compounds. Thermogravimetric analysis of the samples was carried out during their heating from 25 to 750°C at a rate of 15°C/min in air. Thermogravimetric analysis shows that the order in which the active components are introduced significantly affects the thermal stability of the sample. Despite the general similarity of the profiles, a shift of the temperature range of citrate complex decomposition is observed, depending on the order of active components introduction. Presumably, this may be due to the different degrees of Mo and Co availability for the formation of compounds with citrate ligands. It is shown that the most thermally stable system is the one in which the Co-containing component and citric acid are introduced first, and then the alcohol solution of molybdenum blue; the least stable system is the reverse one, in which the alcohol solution of molybdenum blue is introduced first, then citric acid and the Co-containing component are added.

Keywords: Co–Mo/Al_2O_3, citrate complexes of transition metals, polyoxometallate compounds, molybdenum blue, heat treatment

INTRODUCTION

At present, the production of fuel distillates that meet modern standards (Class 5 or EURO-5) in our country is provided mainly (by about 70 %) through the use of imported catalytic systems [1–4]. The absence of technologies for obtaining competitive domestic catalysts for the processes of upgrading and processing hydrocarbon raw materials creates a potential threat of dependence of the Russian oil refining industry on the foreign market of catalysts [4]. One of the key directions of progress in this area is the development of highly active components and/or precursors capable of maintaining their qualities for a long time during the processing of heavy and extra heavy oils. The use of such systems will allow a significant increase in processing depth and will involve heavier types of raw materials.

In this regard, an urgent problem is the development of new methods for the synthesis of competitive domestic catalytic systems for secondary processes of oil and petroleum products refining (for example, hydrocracking, hydrotreatment, hydroisomerisation).

In modern catalysts for hydroprocessing, the following combinations of metals on porous support are most often used: Ni and W, Co and W, Ni

and Mo, Co and Mo. Aluminium oxide (γ-Al_2O_3 modification) is widely used as a support. One of the common methods for increasing the activity of Co(Ni)–Mo(W)/γ-Al_2O_3 compositions is the use of new starting metal compounds that are active elements. Thus, the use of promising polyoxomolybdate compounds, molybdenum blue, as precursors of the active phase to replace the traditional ammonium paramolybdate (source of Mo) is of particular interest. Since molybdenum blue has not actually been used as components of catalysts for hydroprocessing, questions regarding the effect of drying and heat treatment stages remain open.

The goal of the work was to study the features of thermal decomposition of cobalt- and molybdenum-containing citrate systems.

EXPERIMENTAL

The reagents used as initial components for the synthesis of Co–Mo-containing systems were: cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, analytically pure reagent grade), citric acid ($C_6H_8O_7 \cdot H_2O$, chemically pure grade), commercial pseudoboehmite (AlOOH, Ishimbay Specialised Catalyst Plant), and ethanol (chemically pure grade). Molybdenum blue (a source of Mo) was obtained according to the original procedure described in [5]: commercially available molybdenum disulphide (MoS_2) powder of Molysulfide® grade was subjected to mechanical activation in a ball mill for 8 h. After the stage of mechanical activation, ethanol is added to the formed MoS_2, which results in the formation of a solution of molybdenum blue in ethanol. To prepare the support (γ-Al_2O_3), pseudoboehmite was calcined in air at 550 °C for 4 h. The systems containing Co and Mo were prepared using the traditional method of incipient wetness impregnation of the support by varying the order of components introduction: simultaneous introduction of active components into the support (K-1 sample); sequential introduction of active components into the support: first, the Mo-containing compound, then the Co-containing one (K-2 sample), and vice versa (K-3 sample). After impregnation, the samples were dried at room temperature in air flow. Thus prepared systems were characterised using the following investigation methods: integrated thermal analysis (thermogravimetry/differential thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC)), IR spectroscopy, and X-ray phase analysis (XPA).

Integrated thermal analysis was carried out with the help of a synchronous thermoanalyser STA 449C Jupiter (Netzsch, Germany), which involves simultaneous measurement of the mass (TG/DTG) and thermal fluxes (DSC), combined with a quadrupole mass spectrometer QMS 403 C Aeolos (Netzsch) for the analysis of gases evolved during sample heating. The sample was heated from 50 to 750 °C at a rate of 15 °C/min in the dynamic atmosphere of air (gas flow rate 30 mL/min).

To investigate by means of IR Fourier transform spectroscopy with the help of a Nicolet 5700 infrared spectrometer (Thermo Fisher Scientific, USA), the samples were pressed in discs with spectrally pure KBr. The portions of the substance and the matrix were the same in all experiments; each spectrum was obtained as a result of 64 scans within the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

The X-ray phase analysis was carried out using a D8 Advance powder diffractometer (Bruker, Germany) equipped with a unidimensional detector Lynx-Eye and a K_β-filter with CuK_α-radiation. Recording was performed within the angle range $10° < 2\theta < 86°$. The refinement of the structural parameters was carried out over powder diffraction patterns according to the Rietveld method using Topas 4.2 software.

RESULTS AND DISCUSSION

Results of thermal analysis

Thermal analysis of K-1, K-2 and K-3 samples (Fig. 1) proceeds in the oxidative medium and starts from sample dehydration at a temperature above 100 °C.

One can see in the TG curves that the total mass loss for K-1, K-2, K-3 samples was 30.78, 39.31 and 27.84 %, respectively. The removal of adsorbed water proceeded up to 200 °C, and the largest amount of water was determined for K-2 sample – 16.69 %. However, in general, the relative difference between mass loss values due to water removal was insignificant for the samples under investigation (for K-1 – 12.20 wt. %, K-2 – 16.69 %, K-3 – 14.95 %).

The most interesting temperature range is 220–240 °C, within which the main decomposition reactions of cobalt- and molybdenum-containing compounds proceed. In the case of K-1 and K-2 samples, decomposition occurs at temperatures of 215 and 220 °C, respectively, while in

the case of K-3, it takes place at a higher temperature, 240 °C, which may be evidence of the higher thermal stability of the supported compounds. Within the temperature range 245–317 °C, a small peak is observed on the DRG curve; its position is determined by the order in which the components are introduced. This may be connected either with the most strongly sorbed water or with other effects, such as the formation of citrate complexes differing from each other in composition and stability [6]. However, to make more precise statements, additional investigations are necessary.

Comparison between the DTG curves of the samples under investigation (see Fig. 1) reveals that the rates of mass change for samples K-1 and K-2 are close to each other. The profiles of the DTG curves of these samples look similar, the only difference is a more clearly pronounced peak in the region of 250 °C for the K-2 sample, while for K-1 the corresponding peak looks like an inflection. For the K-3 sample, the highest rate of mass loss was observed in the region of 100 °C (higher than that for K-2 by 24 %, and higher than that for K-1 by 50.9 %). The mass loss corresponding to the decomposition of supported compounds occurs for K-2 sample within a broader temperature range (a broader peak on the DTG curve) in comparison with the observed ranges for K-1 and K-3. For the latter sample, the maximum of the peak on the DTG curve was shifted to a higher temperature – 240 °C, and its mass loss within this range was only 5 %.

According to DSC data (Fig. 2), for all samples at 100 °C, similar values of endothermic effects due to the loss of adsorbed water were determined. Within the temperature range 215–300 °C, a clearly pronounced strong *exo*-effect is observed, with a maximum at 260 and 280 °C for K-1 and K-3, respectively, corresponding to decomposition of the supported Co- and Mo-containing compounds.

Unlike for K-1 and K-2 samples, there is a peak in the region of 318 °C on the DSC curve of K-3 sample. This peak corresponds to the endothermic process accompanied by mass loss. This may be due to the final removal of the most strongly bound water [7].

So, it is shown on the basis of the data of thermal analysis that changes in the order of metal introduction affect the nature of thermal genesis of the catalysts, which is likely due to the changes in the composition and properties of supported compounds. They decompose at 220 °C, and the temperature rise leads to the complete decomposition of initial citrate complexes. The data obtained by means of thermal analysis are in good agreement with the results of mass spectrometric analysis.

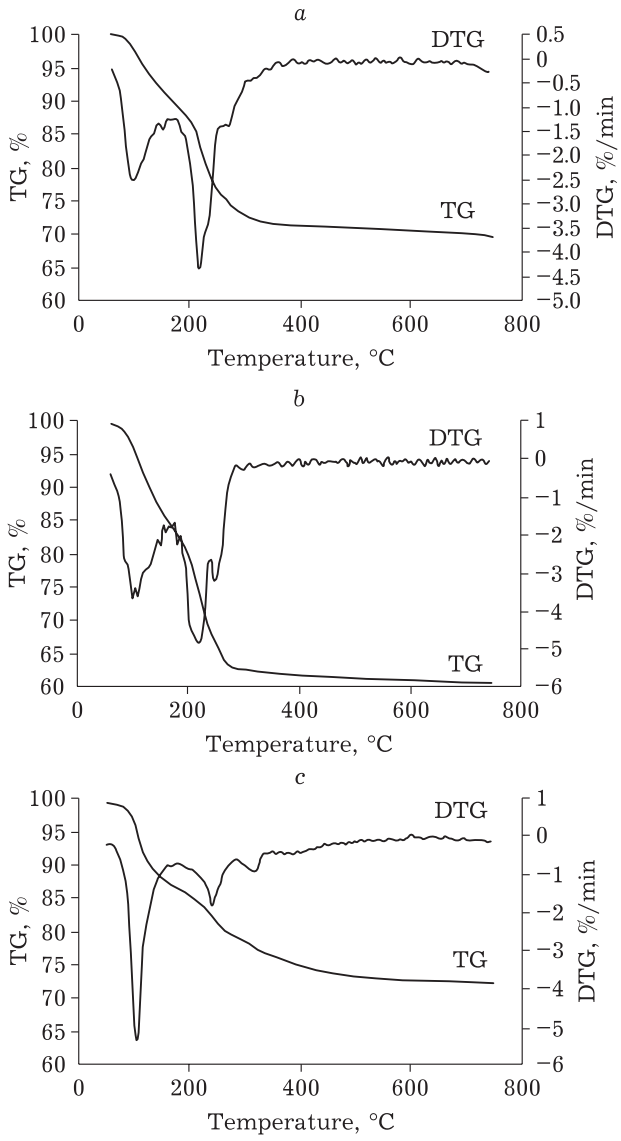

Fig. 1. Thermogravimetric curves (TG/DTG) of the prepared systems in air: samples K-1 (*a*), K-2 (*b*) and K-3 (*c*).

Results of mass spectrometric analysis

The mass spectra of K-1 and K-2 samples are presented in Fig. 3. The composition of the products emitted in the gas phase corresponds to NO_2, NO, H_2O and CO_2, recorded from the ion current of NO_2^+, NO^+, H_2O^+ and CO_2^+. The spectra shown in Fig. 3, *a*, *d* illustrate that nitrogen-containing gases NO and NO_2 (m/z = 30 and 45, respectively), as well as CO_2 (m/z = 44), are emit-

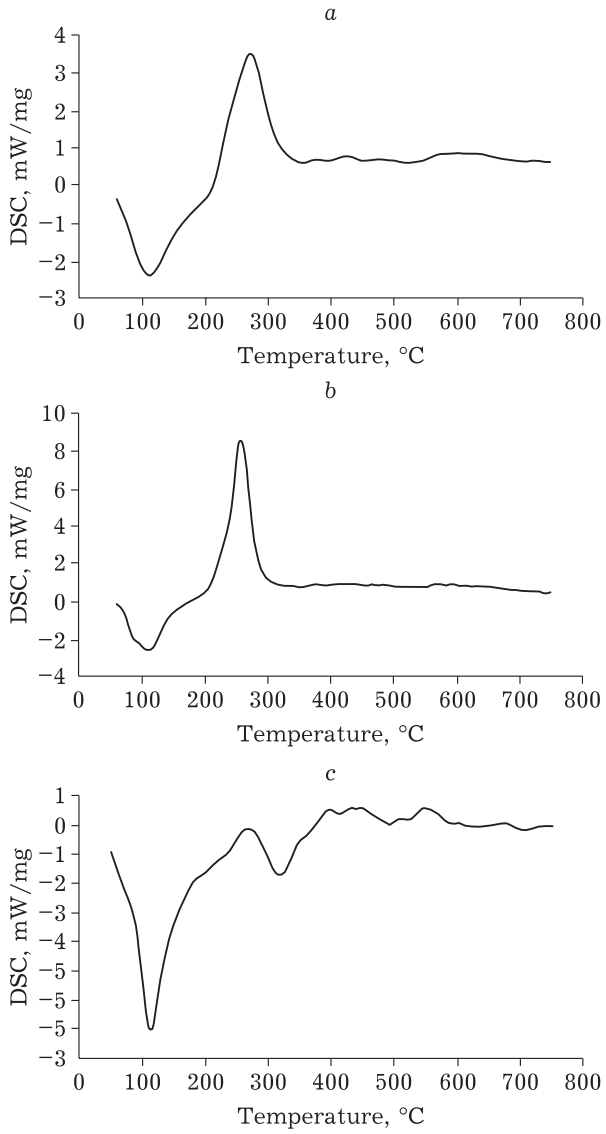

Fig. 2. DSC profiles of samples K-1 (*a*), K-2 (*b*) and K-3 (*c*).

ted within the range 195–250 °C. The evolution of nitrogen oxides is connected with the processes of cobalt nitrate decomposition. The evolution of CO_2 in the region 175–270 °C is evidence of the gradual decomposition of the citrate complex [8]. The mass spectrum with m/z = 44 (CO_2^+) corresponds to the evolution of CO_2, and has a relatively symmetrical configuration with the maximum at 240 °C, which is in agreement with the data of TG, DTG and DSC, where large mass losses are observed, with a high rate and large *exo*-effect. In Fig. 3, *c*, a peak in the region of 100 °C is observed, which is evidence of water evolution.

Thus, it may be concluded that the order in which the active components are introduced has a substantial effect on thermal and chemical properties of the catalytic systems.

Results of IR spectroscopy

The IR spectra of the K-1 sample after drying at 25 °C and calcining at 400 °C are shown in Fig. 4.

The absorption peak at 1629 cm^{-1} points to the bending vibrations of water molecules, while a neighbouring peak with a rather low intensity at 1720 cm^{-1} relates to the stretching vibrations of carbonyl groups in citric acid residue [9]. A broad absorption band (a. b.) within 2500–3700 cm^{-1} with maxima at 3420 and 3260 cm^{-1} is evidence of the presence of a free OH group [10]. This is caused by the high concentration of OH groups on the surface of the support, as well as by the presence of intra-cluster water (for example in $Co(NO_3)_2 \cdot 6H_2O$) and aqua-ligands. The structure of the carbon framework in citrate complexes is confirmed by the a. b. at 2900 cm^{-1}, where the bands corresponding to the stretching vibrations of C_{sp^3}–H bond are overlapped by the a. b. of the OH group. An intense peak observed in all three samples at 1384 cm^{-1}, coupled with the a. b. of medium intensity near 830 cm^{-1}, confirms the presence of nitro group in cobalt nitrate [11], while a peak at 1384 cm^{-1} provides evidence of the bending vibrations of CH_2-groups [12]. A broad a. b. with a maximum at 634 cm^{-1} evidences the presence of vibrational motions of the Mo–O bond [13], and vibrational motions of Al–O and Al–O–Al bonds [14].

Comparing the IR spectra of the K-1 samples dried at 25 °C and calcined at 400 °C (see Fig. 4), one can see that the intensity of the absorption bands related to the OH groups has decreased substantially after calcining, which confirms the removal of a part of water during thermal treatment. The partial presence of water may be explained by the fact that chemically sorbed water did not evaporate because more energy is necessary to remove it.

The absorption bands corresponding to the nitro group have disappeared completely after calcining of the K-1 sample (see Fig. 4). Thus, it may be concluded that nitrogen was eliminated from the active component by 400 °C. According to the results of thermogravimetric mass spectrometry, complete decomposition of citrate complexes may be assumed.

Results of X-ray phase analysis

In the diffraction patterns of the K-1 sample dried at 25 °C (Fig. 5, curve *1*), a number of reflections within the angle range 18–70° over 2θ have been determined. The presence of a set of

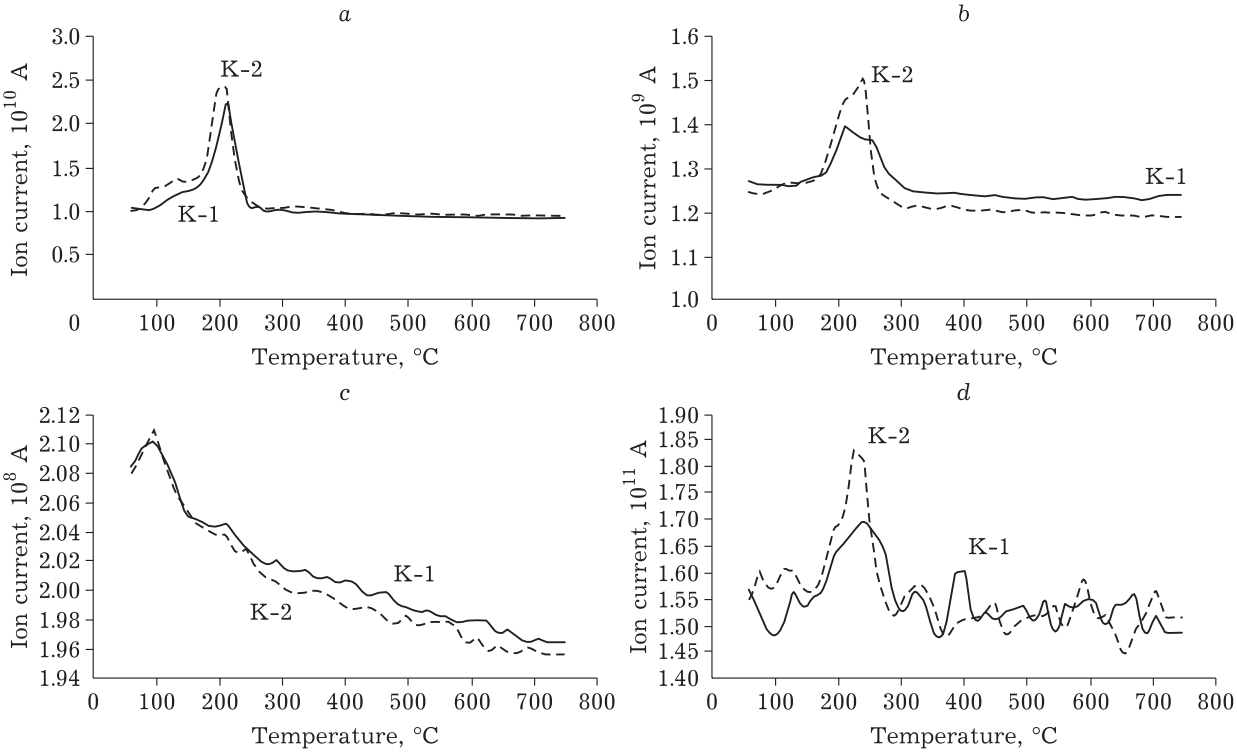

Fig. 3. Mass spectra of the products released from samples K-1 and K-2: NO^+ (*a*); NO^+_2–CO^+_2, m/z = 44 (*b*); H_2O (*c*); NO^+_2–CO^+_2, m/z = 45 (*d*).

low-intensity reflections at 19, 20, 23, 25, 26, 29, 30° over 2θ is evidence of the presence of cobalt nitrate phase ($Co(NO_3)_2 \cdot 6H_2O$) [PDF #12-0572]. A broad halo (rather well crystallised) within the angle ranges 43–49° and 64–70° over 2θ is evidence of the presence of aluminium oxide (γ-Al_2O_3) [PDF #01-1308]. In the diffraction patterns of the K-1 sample calcined at 400 °C (see Fig. 5, curve *2*), the disappearance of some reflections within the angle range 19–30° over 2θ is observed, which points to the complete removal of cobalt nitrate phase. Reflections that appear in the diffraction patterns at 24 and 26° over 2θ relate to the aluminium oxide phase (γ-Al_2O_3). In general, the regularities observed with the help of XPA agree well with the results obtained by means of thermal analysis.

CONCLUSION

It is revealed as a result of investigations that the order in which active metals are deposited affects the thermal properties of catalytic systems, the phase composition being liable to the effect of thermal treatment to a higher extent. The highest thermal stability is exhibited by the

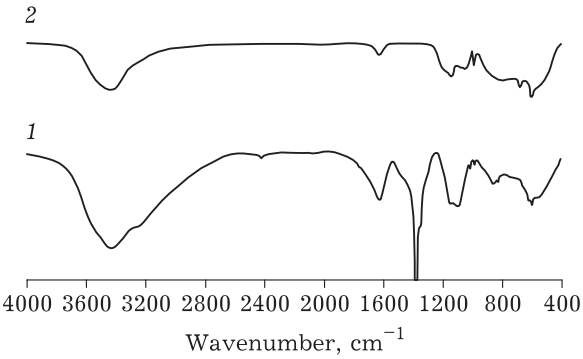

Fig. 4. IR spectra of K-1 sample: dried at 25 °C (*1*); calcined at 400 °C (*2*).

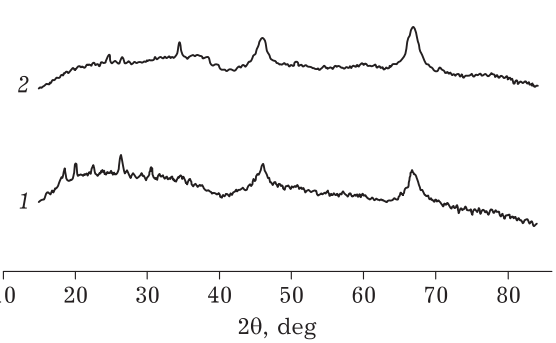

Fig. 5. X-ray diffraction patterns of K-1 sample: dried at 25 °C (*1*); calcined at 400 °C (2).

sample in which the cobalt-containing component was the first to be introduced, while the lowest stability is exhibited by the sample with the inverse order of components introduction (at first, molybdenum blue, and then the cobalt-containing reagent).

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