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MECHANISM AND KINETICS OF THERMAL DECOMPOSITION OF AMMONIACAL COPPER OXALATE CHROMATE

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A complex precursor of composition Cu/Cr=1 has been synthesized, dissolving copper oxalate and ammonium dichromate in aqueous ammonia followed by evaporation and drying. The thermal decomposition of the precursor has been studied in different environments, air/argon. In air, overlapping decomposition of the complex and simultaneous oxidation of the products of decomposition (oxidative decomposition) occur in four steps and the overall process is highly exothermic, whereas the process completes in two stages only in argon preventing oxidation of the products and so resulting negligible heat of decomposition. The elemental analysis and thermogravimetric measurements suggest the stoichiometric formula of the precursor to be $CuNH_3C_2O_4NH_4CrO_4$. The precursor is termed as ammoniacal copper oxalate chromate (ACOC).

The products of decomposition resulted in different environments have been characterized by X-ray diffraction and particle size analysis. Bi-dispersed particles of $CuO \cdot CuCr_2O_4$ (Adkins' catalyst) are obtained in air while mono-dispersed particles of $Cu \cdot CuCr_2O_4$ (novel Adkins' catalyst) result in argon environment.

The decomposition kinetics of ACOC in argon environment has been found to be zero order and first order for the first and second steps respectively. The values of activation energy corresponding to the first and second step have been found to be 87.63 and 250.36 kJ mol^{-1}, respectively.

Keywords: *Adkins' catalyst, copper chromite precursor, mechanism and kinetics, thermal analysis*

Introduction

Copper catalysts containing chromia are used in several industrially important reactions such as hydrogenation, dehydrogenation, oxidation, alkylation, etc. In an earlier paper [1] the advantages of using an ammoniacal complex of copper oxalate chromate as a precursor in the preparation of catalysts has been demonstrated. It has been shown that using such a precursor followed by its thermal decomposition in an inert atmosphere highly active and novel catalysts can be developed. One of the important features of such catalysts is that the pre-reduction step is eliminated which is otherwise an essential and very sensitive step of in situ reduction of the conventional catalysts. A catalyst thus prepared has been found to be more active than an industrial catalyst in dehydrogenation of alcohol. Thus, the thermal decomposition of the complex precursor is one of the important steps in the preparation of the active catalysts. It is desirable to understand the decomposition process as well as the factors influencing the morphology of the resulting catalysts.

Thermal analyses of copper oxalate [2, 3], copper amino oxalate [4], copper chromate [5], basic cupric ammonium chromate (BCAC) [6] and Cu/Ni/Cr hydrotalcites [7] have been well studied. Dollimore in a recent review [8] pointed out that in the early publications the interaction of the oxalate upon decomposition with the atmosphere had been neglected whilst as a generalization it might be said that many recent publications did not pay enough attention to the morphological form of the material. Impregnation of copper with chromia on supports through an ammoniacal solution is advantageous because it results in uniform dispersion [9]. As the thermal decomposition of the complex precursor has not been thoroughly studied before, the present work has been undertaken to determine the stoichiometric formula of the complex precursor and to investigate the influence of the experimental conditions on the mechanism and kinetics of the decomposition process and also on the morphology of the resulting catalysts. This was done to understand the formation of copper catalysts containing chromia in different environments of air and argon. The results of this work should be helpful in design and development of copper catalysts containing chromia.

Experimental

Sample preparation

Thermal decompositions of ammonium dichromate [10, 11] and copper amino oxalate [4] in an inert environment have been found to be exothermic and endo-

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thermic, respectively. Also they decompose almost in the same temperature range. These observations of contrary nature of thermal decomposition of the two compounds led to the design and synthesis of a complex precursor, such that the net heat of decomposition of the same in an inert environment is negligible. The precursor was synthesized, dissolving ammonium dichromate in ammoniacal solution of copper oxalate in a Cu/Cr atomic ratio of 1:1 followed by evaporation on a steam bath and finally drying at 378 K in an oven for 5 h. No precipitation occurred during dissolution of ammonium dichromate. The dried greenish colored complex was stored in a desiccator over anhydrous calcium chloride. The homogeneous complex precursor is soluble in aqueous ammonia. All analytical grade chemicals were used in the synthesis of the sample.

Methods

Elemental analysis

The composition of the elements present in the precursor was determined by a Perkin-Elmer 2400 CHN elemental analyzer and by a Perkin-Elmer 373 atomic absorption spectrophotometer.

Thermal analysis

The curves were recorded on a Stanton Redcroft STA-781, simultaneous thermal analysis system in still air and argon flow of 40 $cm^3 min^{-1}$ at a heating rate of 10 $K min^{-1}$. Platinum sample pan and α-Al_2O_3 as reference were used. Sample of particle size 100–200 mesh and mass of 12–15 mg were taken. The sample was thoroughly dried before analysis.

Phase and morphological analyses

X-ray powder diffraction spectra of the samples were obtained in a Seifert, Model ID 3000 diffractometer (Germany) using CuK_α radiation to identify the phases present. Morphological studies include particle size analysis and BET surface area. The particle size analysis was carried out using toluene as a dispersant media with the help of a Micron Photosizer, SKC-2000, Seishin (Japan).

Results and discussion

Elemental analysis of the precursor

The composition of carbon, hydrogen, nitrogen, copper and chromium in the precursor are given in Table 1. Composition of oxygen was determined by the difference and it was found to be equivalent to the carbon and chromium content in the sample as C_2O_4 and CrO_4. The experimentally found N/H ratio works out to be 4.07 (from the percent composition), which agrees well with the theoretical value of 4.00 if N and H are present as both NH_3 and NH_4. Further, it is evident from Table 1 that the results of mass losses by thermogravimetry in argon environment (51.18%) and by the elemental analysis (50.82) are consistent. These observations suggest a chemical composition of the precursor closely approximating the formula, $CuNH_3C_2O_4NH_4CrO_4$, and it is termed as ammoniacal copper oxalate chromate (ACOC). The results are reproducible for three samples prepared under identical conditions. The complex precursor ACOC is stable under ambient conditions.

Table 1 Elemental analysis of copper amino oxalate chromate

Element	Composition/%	
	theoretical	experimental
carbon	7.93	7.87
hydrogen	2.31	2.21
nitrogen	9.25	8.99
copper	21.01	21.23
chromium	17.19	17.37
oxygen (by difference)	42.31	42.33
N/H ratio		
experimental		4.07
theoretical in (NH_3+NH_4)		4.00
Decomposition loss/%		
thermal analysis in Ar		51.18
thermal analysis in air		48.56
element analysis [C+H+N+3/4O]		50.82

Mechanism of thermal decomposition of ACOC

In description of thermal decomposition it is necessary to consider mechanism prior to development of an equation. The results of TG, DTA and DTG of the precursor are shown in Fig. 1. The results clearly show a remarkable effect of the two different environments in which ACOC is decomposed. Three overlapping steps followed by fourth non-overlapping step of decomposition of ACOC in air (Fig. 1a) can be visualized, whereas the decomposition in argon atmosphere (Fig. 1b) seems to complete in two steps only. The DTA peak temperatures of the various steps of decomposition are given in Table 2. Many complicated reactions occur on heating the precursor, the intermediate products are very difficult to postulate without any in situ analysis. Although the intermediate steps are distinct in air but their exact positions are difficult to locate on TG curve because of the simultaneous decomposition and oxidation reactions (oxidative decomposition), as evidenced by the overlapping DTG and DTA peaks (Fig. 1a).

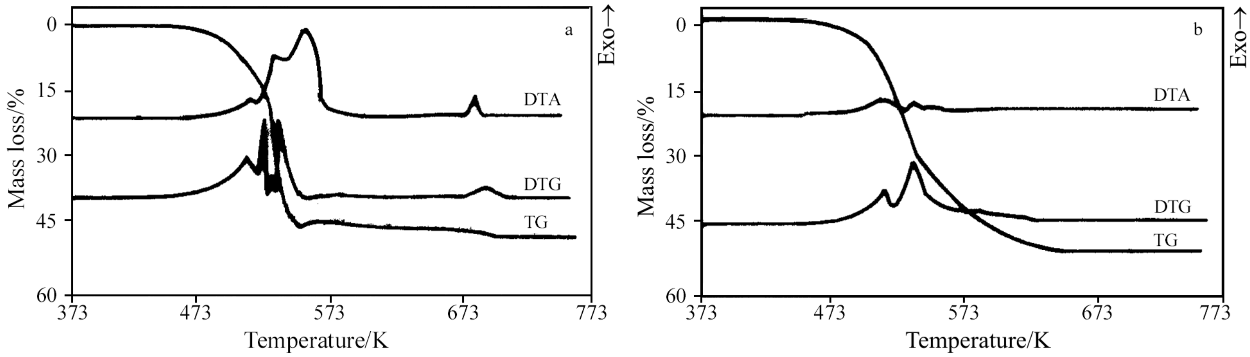

Fig. 1 Curves of ACOC: heating rate 10 K min^{-1} in a – static air and b – argon flow

The TG curve in air (Fig. 1a) shows a continuous loss in mass of the sample up to 44.36% followed an increase in the mass thereby decreasing the percentage loss to 44.00%. Since the increase in mass was observed in the presence of oxygen, this would be ascribable to the oxidation of the resulting solid product. Further loss in mass of the sample occurs with increasing temperature to a final value of 48.56% suggesting the formula of the solid product to be $CuOCu{\cdot}Cr_2O_4$, known as Adkins' catalyst (theoretical loss 48.58%). The overall decomposition of ACOC in air can be exemplified by the following equation:

$$2CuNH_3C_2O_4{\cdot}NH_4CrO_4+2O_2 \rightarrow CuOCuCr_2O_4+4CO_2+2N_2+7H_2O \qquad (1)$$

The oxidative decomposition path followed is violent and highly exothermic as shown by the first three overlapping DTG and DTA peaks (Fig. 1a). Corresponding to the fourth step of transformation in air a sharp exotherm appears at 687 K on DTA curve. The decomposition of the chromate content of ACOC and the simultaneous auto-catalytic oxidation of the decomposition products in air are highly exothermic reactions. The exothermic chromate decomposition and violent oxidations, especially at the temperature of decomposition, completely overwhelm the endothermic deammoniation of the precursor.

The TG curve in argon (Fig. 1b) shows an appreciable initial decomposition of ACOC followed by short induction period and the acceleratory and decay periods. A gradual loss in mass of the sample occurs to a final value of 51.18% suggesting the final product to be $CuCuCr_2O_4$, known as active reduced Adkins' catalyst (theoretical loss 51.23%). The overall decomposition of ACOC in argon can be represented as follows:

$$2CuNH_3C_2O_4{\cdot}NH_4CrO_4 \rightarrow Cu{\cdot}CuCr_2O_4+2NH_3+N_2+4CO_2+4H_2O \qquad (2)$$

The decomposition path followed in argon is slower and controlled than oxidative decomposition. Argon environment prevents exothermic oxidation of released ammonia as well as of the resulting solid products of decomposition of ACOC, leading negligible heat of decomposition as can be seen from DTA curve (Fig. 1b). This avoids the large exotherms present during the decomposition of ACOC in air. The exotherms is still present but offset by the endothermic deammoniation of the precursor in argon.

An interesting observation is that corresponding to the fourth step of decomposition of ACOC in air around 687 K, there is no such transformation in argon atmosphere and the process completes in two steps only. The plausible explanation of this has been given in the next section of phase identification of the samples. A comparison of the intensities of the exotherms shows that in air it is several times larger than in argon. Therefore, decomposition of ACOC in air causes substantial heating of the solid product.

Phase identification of the samples

X-ray diffraction (XRD) studies on decomposed precursor, ACOC in air and argon are recorded to see the effect of the decomposition environments on the resulting phases of the catalysts. The decomposed samples at 700 K are removed from the decomposition reactor under inert atmosphere after cooling at room temperature and then used for XRD measurements. The results are given in Table 3 for samples obtained in air as well as in argon separately. The XRD data of the

Table 2 Thermogravimetric analysis of ACOC in still air and flowing argon

Decomposition step	In air				In argon	
	I	II	III	IV	I	II
DTA peak temperature/K	510 exo	538 highly exo	563 highly exo	687 exo	515 overall mild exo	547 overall mild exo
Experimental mass loss/%	–	–	–	48.56	–	51.18

Table 3 X-ray diffraction data of ACOC decomposed at 700 K in air and argon

ACOC decomposed in air				ACOC decomposed in argon			
Peak no.	d-value/Å	Relative intensity	Phase identified	Peak no.	d-value/Å	Relative intensity	Phase identified
1	3.631	66	Cr_2O_3	1	2.476	35	$Cu_2Cr_2O_4$
2	2.528	93	CuO	2	2.326	80	CuO
3	2.523	95	CuO	3	2.083	100	Cu
4	2.474	100	$Cu_2Cr_2O_4$	4	1.804	46	Cu
5	2.323	86	CuO	5	1.503	24	$CuCr_2O_4$
6	1.502	24	$CuCr_2O_4$				
7	1.376	18	CuO				

sample indicate that the decomposition of ACOC in air indicate the presence of CuO with other compounds such as $Cu_2Cr_2O_4$, Cr_2O_3 and $CuCr_2O_4$. According to the relative intensity, the major phases present in the sample are CuO and $Cu_2Cr_2O_4$, while $CuCr_2O_4$ is almost amorphous in nature. The data of the sample obtained in argon reveal the presence of Cu crystallites as well as of $Cu_2Cr_2O_4$ in addition to $CuCr_2O_4$.

The presence of Cr_2O_3 in the sample resulted in air is in accordance with the result of thermal analysis that the sharp exotherm around 687 K known as the 'glow up' phenomena [12] a characteristic of Cr_2O_3 observed on DTA curve (Fig. 1a). Whereas no such phenomena can be seen on DTA curve when ACOC is decomposed in argon (Fig. 1b). The XRD data also confirm that no free Cr_2O_3 is present in sample obtained in argon atmosphere. The XRD studies show the presence of $Cu_2Cr_2O_4$ in the samples obtained in both the environments. The formation of $Cu_2Cr_2O_4$ can occur by a disproportionation reaction between nascent copper crystallites formed in situ by ACOC decomposition and $CuCr_2O_4$, as suggested by Tonner [13] during reduction of the Adkins' catalyst:

$$Cu+CuCr_2O_4\rightarrow Cu_2Cr_2O_4 \tag{3}$$

The nascent Cu crystallites are in a state of high free energy and very large specific surface area. These particles achieve the stable state by loosing their excess free energy probably due to self-crystallization and also reacting with amorphous copper chromite as shown by above equation to form cuprous chromite crystallites of size distinguishable by XRD spectra. It appears that a fraction of nascent copper is immediately incorporated as $Cu_2Cr_2O_4$. The remaining most of the copper is left well dispersed and account for the X-ray observation in argon only.

Thus the phases identified are in accordance with the thermogravimetric analysis that decomposition of ACOC in air results, Adkins' catalyst ($CuO{\cdot}CuCr_2O_4$) and in argon reduced Adkins' catalyst ($Cu{\cdot}CuCr_2O_4$). Although the XRD spectra of the residue of ACOC decomposition at 700 K, indicate several phases, probably other phases are present in minute quantities. So that their effect on composition of the residue as determined from thermogravimetric analysis may not be significant, which form the basis of assigning composition of decomposed residues in both the environments.

Morphological characterization of the samples

It is apparent from the particle size distribution curves that the particles resulted by thermal decomposition of ACOC in air (Fig. 2a) are bi-dispersed with most probable sizes of 12 and 46 μm, and are larger than mono-dispersed particles with most probable size of 12 μm obtained in argon atmosphere. Also, the BET surface area (39.26 $m^2 g^{-1}$) of the particles resulting in argon is higher than that of air (28.73 $m^2 g^{-1}$). These differences in morphology of the particles produced under different conditions may be interpreted in terms of decomposition mechanism of ACOC. It is to be noted that the reduced form of Adkins' catalyst ($Cu{\cdot}CuCr_2O_4$) is the product of mild exothermic decomposition of ACOC in argon atmosphere, while Adkins' catalyst ($CuO{\cdot}CuCr_2O_4$) is the result of violent exothermic processes in air.

The exothermic processes of oxidative decomposition in air lead to substantial local over heating of the catalyst causing sintering and lowering of surface area. While in argon the oxidation of the released gaseous as well as of the solid product of ACOC decomposition is prevented, leading unusual morphology to the resulting catalyst particles.

Kinetics of the thermal decomposition of ACOC

Kinetics of decomposition of ACOC has been studied non-isothermally under conditions of sample temperature increasing at the rate of 10 K min^{-1} in a flowing atmosphere of argon. The following equation derived by Freeman *et al*. [14] is used to determine the activation energies and orders of decomposition steps.

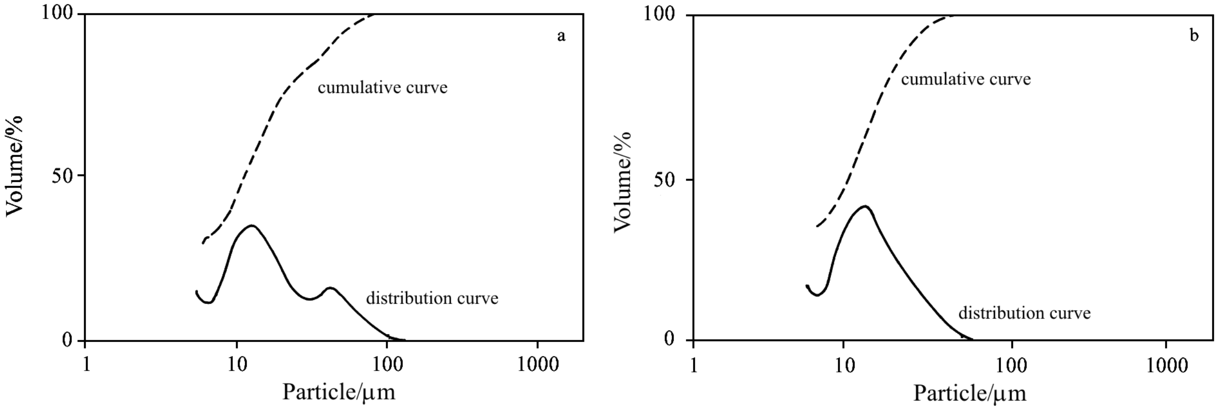

Fig. 2 Particle size distribution of the products of ACOC decomposition: a – in air and b – in argon

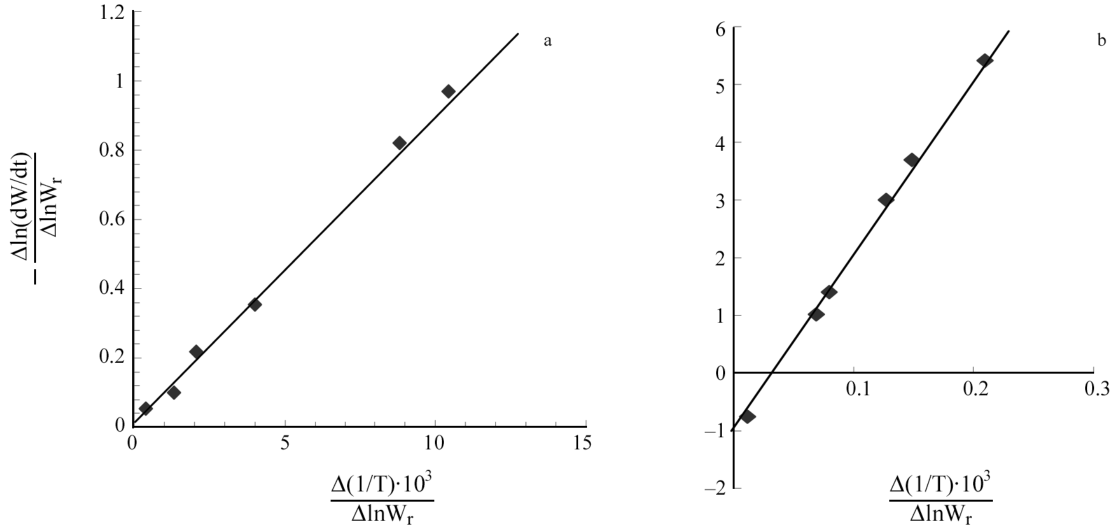

Fig. 3 Kinetics of non-isothermal decomposition of ACOC in argon, a – I step and b – II step

$$\frac{\Delta\ln(\mathrm{d}W/\mathrm{d}t)}{\Delta\ln W_r} = n - \frac{(E/R)\Delta(1/T)}{\Delta\ln W_r} \qquad (4)$$

where $W_r = W_c - W$, W_c is the mass loss at completion of reaction, W is the total mass loss up to time t, E is the energy of activation, R is the universal gas constant, T is the absolute temperature and n is the order of reaction with respect to reactant.

Figure 3 is a plot of $\Delta\ln(\mathrm{d}W/\mathrm{d}t)/\Delta\ln W_r$ *vs.* $\Delta(1/T)/\Delta\ln W_r$ for the two steps of decomposition of ACOC. The first step of decomposition corresponds to a mass loss of 19.17 percent and the second step to 51.18 percent. Values of $\mathrm{d}W/\mathrm{d}t$ and W_r are determined from the curves. The intercepts and slopes of the respective lines yield the values of the orders and energies of activation for the two decomposition reactions. The first and second steps of decomposition are found to be zero order and first order, respectively. The energies of activation are found to be 87.63 and 250.36 kJ mol^{-1} for I and II steps, respectively.

Conclusions

The stoichiometric formula, $CuNH_3C_2O_4NH_4CrO_4$ of the complex precursor, ACOC has been derived. The mechanism and kinetics of the thermal decomposition of ACOC have been established. The correct assessment of the kinetics of thermal decomposition of ACOC in air is difficult because of the complex and overlapping oxidative decomposition processes. Mild exothermic decomposition of ACOC results finely-divided mono-dispersed particles of active reduced Adkins' catalyst, $Cu\cdot CuCr_2O_4$ in argon. Violent exothermic decomposition of ACOC in air leads to bi-dispersed bigger particles and relatively lower specific surface area of Adkins' catalyst, $CuO\cdot CuCr_2O_4$.

Active conventional Adkins' catalyst is generally prepared by decomposition of basic copper ammonium chromate (BCAC) followed by reduction, which are highly exothermic processes. These exothermic processes cause sintering of the catalyst (loss of active area), smoothen down the edges, corners, etc. (decrease of density of active sites) and complicate pore structure (high diffusion resistance). On the other hand, mild exothermic decomposition of ACOC in an inert atmosphere causes busting of the original particles releasing more than 50% gaseous products, thereby producing open textured pores, and possessing high density of active sites catalyst. Thus, decomposition of the precursor in argon atmosphere results active catalyst bypassing reduction step, minimizing a process step, leading to saving of not only process time but also reducing and diluent gases.

Keeping in view above considerations, novel Adkins' catalysts could easily be prepared using ACOC as a precursor, which would reduce operational cost of catalyst reduction and other operational troubles.

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