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THERMAL DECOMPOSITION AND CREATION OF REACTIVE SOLID SURFACES

III. Analysis of chromia precursors

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Three chromia precursors, namely CrO_3, $(NH_4)_2Cr_2O_7$ and chromia gel, were subjected to thorough thermal analysis by means of TG and DTA. The thermal decomposition products obtained by calcination of these precursors at various temperatures (150–500°) for 5 h were investigated by infrared and X-ray techniques. The results obtained allowed a thorough physicochemical characterization of the intermediate steps and products throughout the thermal decomposition.

Chromia is well known as a powerful redox catalyst [1, 2]. It occurs with various water contents, as amorphous or crystalline [3], mesoporous or microporous [4], with various surface concentrations of coordinatively unsaturated Cr^{3+} and O^{2-} [1], and with no excess oxygen or with various kinds of excess oxygen [5].

Earlier investigations performed in this laboratory [6–8] and others [9–11] have shown that the adsorptive and redox-catalytic properties of chromia are controlled primarily by both the nature and the concentration of surface Cr—O species. Since in most of these investigations the catalysts were obtained via the thermal decomposition of relevant inactive precursors, various correlations between the surface properties of the products, the thermal pretreatment conditions imposed and the nature of the precursors have plausibly been set up [6–9, 11].

The thermal genesis of chromia has been under continuous debate with regard to the stoichiometry of the complex series of disproportionation reactions involved and the physicochemical identity of the intermediates [12–17]. Therefore, the present investigation was undertaken to yield further insight into the thermal

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decomposition reaction pathways of three of the widely-adopted chromia precursors (namely, CrO_3, $(NH_4)_2Cr_2O_7$ and chromia gel) using thermogravimetric, differential thermal, X-ray diffraction and infrared absorption techniques.

Experimental

Chromia gel (CG) was prepared and then dried as detailed earlier [18]. Preliminary water content measurements showed that the dried gel was almost pentahydrated, i.e. $Cr_2O_3 \cdot 5 \cdot 2H_2O$. Chromium trioxide (CO) and ammonium dichromate (ADC) were high-purity (99.9%) Merck products. The samples used for the X-ray and ir investigations were obtained by calcination of the respective precursor at various temperatures (150–500°) for 5 h. For simplicity, these calcination products are presented in the text by the designatory letters of the respective precursor, followed by the calcination temperature in parentheses. For example, CG(150) represents chromia gel calcined at 150° for 5 h, CO(220) represents CrO_3 calcined at 220° for 5 h, and ADC(400) represents $(NH_4)_2Cr_2O_7$ calcined at 400° for 5 h.

Thermogravimetric (TG) and differential thermal (DTA) curves were automatically recorded over a wide range of temperatures (RT–1200°), at a low rate of heating (5 deg/min) and in a dynamic atmosphere of air (20 ml/min), using small portions of the test sample (10–15 mg), as described earlier [19]. X-ray (XRD) and ir (IRA) investigations on the precursors and their decomposition products (150–500°) were performed according to Fahim et al. [18].

Results and discussion

Thermal analysis of chromium trioxide (CO)

The TG curve in Fig. 1A shows that CO decomposes in two steps. The first, at about 220–375°, is accompanied by a 16.0% weight loss, whereas the second, at 385–415°, brings the total weight loss up to 22.5%. The corresponding DTA curve, Fig. 1A reveals an endothermic process in the immediate vicinity of the first decomposition step, at 200°, followed by a strong composite exothermic effect of three components, at 250°, 330° and 390°. There is a second endothermic effect in a temperature range (465–500°) well beyond the completion of the second decomposition step. At $>$500–1200°, the final product obtained at 415° suffers neither a significant weight loss ($<$1.0%) nor a physical change.

Direct observation on the visible physical changes taking place throughout the decomposition indicated the following: Solid CO melts at 200°; the liquid increases

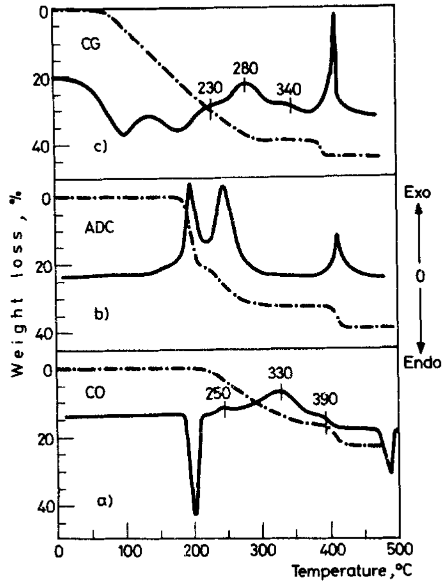

Fig. 1 TG and DTA curves for CrO_3 (A), $(NH_4)_2Cr_2O_7$ (B) and chromia gel (C). Heating rate: 5 deg/min

in viscosity at 230°, commences effervescence at 250°, and suddenly solidifies at *ca.* 290°, giving a dark-brown material. According to Rode [12], the composition of the liquid is in the range CrO_3—$CrO_{2.96}$, the increase in viscosity is due to a simultaneous polymerization process, and the effervescence is a result of oxygen loss to give a compound of composition $CrO_{2.96}$ (i.e. chromium decachromate, $Cr_2(Cr_{10}O_{31})_3$). It is also believed that the formation of this compound is responsible for the exothermic component at 250° [12]. However, the weight loss at 250° (10.0%), as determined from the TG curve (Fig. 1A), rather points to the composition $CrO_{2.5}$, i.e. $Cr_2O_5 \simeq CrO_2 \cdot CrO_3$.

Within this context, the XRD results, compiled in Table 1, for CO(250) indicate a trace coexistence of CrO_2 with the dominating CrO_3. The relevant ir spectrum (Fig. 2) manifests marked changes about the characteristic band structure of the parent oxide [CO(RT)]; these are the absorptions at 985, 870, 680, 540 and 420 cm^{-1}, assigned respectively to symmetric and antisymmetric terminal Cr = O stretches, antisymmetric Cr—O—Cr stretches, symmetric Cr—O—Cr stretches, and Cr = O bending vibrations [20]. Since CrO_3 is known for its chain structure [21], the emergence of such structural features must signify compatibly the formation of 3-dimensional complex chromium oxypolyanions [20].

The strong exothermic effect peaking at 330° (DTA, Fig. 1A) has been considered by Rode [12] to correspond to the formation of chromium dichromate,

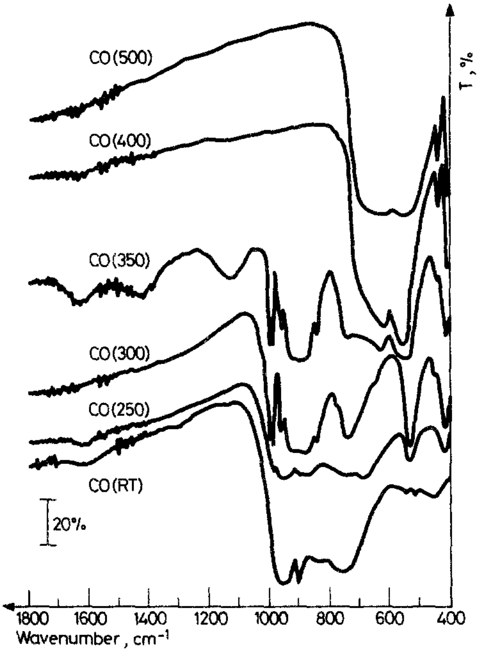

Fig. 2 ir spectra for CrO_3 (RT) and its decomposition products at the temperatures indicated for 5 h

$Cr_2(Cr_2O_7)_3 = CrO_{2.625}$. Park [16, 17], however, has claimed the formation of a double compound of Cr(III) and Cr(VI) oxides having the composition $Cr_5O_9 \simeq 2Cr_2O_3 \cdot CrO_3$. Although the XRD results given (Table 1) for CO(300) and (350) confirm the coexistence of CrO_3 and Cr_2O_3, calculations based on the accompanying weight loss (14.0%) at 330° (Fig. 1A) suggest the formation of a compound having the composition $CrO_{2.20}$ (i.e. $Cr_2(CrO_4)_3$). This excludes the formation of Cr_5O_9, where the corresponding composition should have been $CrO_{1.8}$. The ir spectrum exhibited in Fig. 2 for CO(300) displays a well-defined band structure very analogous to that reported for heavy-metal monochromates [22]. On the other hand, the spectrum given for CO(350) (Fig. 2) manifests clear evidence of the coexistence of a Cr_2O_3-like structure, i.e. absorptions at 620, 550 and 443 cm^{-1} [23].

The ir spectrum given in Fig. 2 for the product obtained via the second rapid exothermic decomposition step (at 385–415°), CO(400), shows only the absorptions characteristic of the Cr_2O_3-like structure. The XRD results, given in Table 1, also support the above contention. The accompanying weight loss (22.5%) is slightly less than that expected for the transformation of CrO_3 to Cr_2O_3 (24.0%). It suggests a composition ($CrO_{1.6}$) similar to that earlier reported for the γ-$Cr_2O_{3.2}$ phase [6]. Such a highly nonstoichiometric phase can be plausibly considered to be

Table 1 X-ray analysis results on the decomposition products obtained by calcination of the chromia precursors at different temperatures (150–500°) for 5 h

Precursor	Chromium trioxide CO			Ammonium dichromate ADC				Chromia gel CG			
Phases identified calcination temperature °C	CrO_3	CrO_2	Cr_2O_3	ADC	CrO_3	CrO_2	Cr_2O_3	CrOOH	CrO_3	CrO_2	Cr_2O_3
150	—	—	—	—	—	—	—	← am →			
200	—	—	—	—	m	—	j	← am →			
220	—	—	—	—	m	—	j	← am →			
250	d	t	—	—	—	—	—	m	—	—	—
270	—	—	—	—	t	—	d	—	—	—	—
300	j	—	m	—	—	—	—	m	m	m	m
350	m	—	j	—	—	—	s*	—	m	t	j
400	—	—	s*	—	—	—	s	—	t	—	d
500	—	—	s	—	—	—	s	—	—	—	s

t = trace, m = minor, j = major, d = dominating, s = sole, am = amorphous
* highly strained structure

responsible for the notable lattice distortion revealed by the ir spectrum of CO(400) and confirmed by further XRD calculations (lattice strain parameter calculated according to ref. [6].

The final endothermic effect at 490°, accompanied by an insignificant weight loss (< 1.0%), has been considered to correspond to the formation of α-Cr_2O_3 [12]. Consistent results are given by the ir (Fig. 2) and XRD (Table 1) investigations of CO(500). Nevertheless, an earlier investigation [6] and results reported by Ellison and Sing [11] confirm the persistence of extralattice oxygen up to a much higher temperature (1200°), at least at the surface.

Thermal analysis of ammonium dichromate (ADC). The TG and DTA curves, given in Fig. 1B, show that ADC decomposes in three exothermic steps: at

185–215°, 230–315°, and 395–425°. The first is rapid and accompanied by a strong sharp exothermic effect. The weight loss (22.5%) is slightly higher than that (20.6%) anticipated theoretically for the transformation of $(NH_4)_2Cr_2O_7$ to CrO_3, which has repeatedly been reported to occur throughout this step [16, 24–26].

Despite several studies, ADC decomposition via this first step (185–215°) remains unclear. For instance, early investigations [25, 26] claimed the formation of CrO_3 as a consequence of the elimination of NH_3, by a proton transfer-type mechanism, followed by H_2O molecules. Recent mass-spectrometric gas analysis results [17], however, have indicated that at this stage (200°) the evolved gases consist of about 52% N_2O, 21% N_2, 26% H_2O and free NH_3 of less than 1%. This has been attributed to the autocatalytic oxidation of NH_4^+ ions on simultaneously generated CrO_3 surfaces as soon as the decomposition proceeds to give the other gaseous components. Although it was therefore expected that Cr(VI) ought to be reduced to give lower oxides, X-ray analysis of a decomposition product obtained by calcination of ADC at 240° for several hours has been reported [16, 17] to indicate the formation of CrO_3 as main product. In contrast, our ir (Fig. 3) and XRD (Table 1) analysis results for ADC(200) and (220) manifest clear evidence of the major existence of a highly distorted Cr_2O_3-like structure (cf. the ir spectrum of CO(400), Fig. 2), togethr with CrO_3 species and surface species of NH_4^+ (absorption at 1400 cm^{-1} (20)) and H_2O (absorption at 1640 cm^{-1}).

The second exothermic decomposition step (at 230–315°) brings the total weight loss up to a value (32.4%) comparable to that anticipated theoretically for formation of the composition CrO_2. An X-ray analysis of the products obtained after calcination at a temperature where the second decomposition step is in progress (ADC(270)) and at another lying immediately beyond that range (ADC(350)) reveals the nonexistence of CrO_2 species, and the domination of a still highly strained Cr_2O_3 at the expense of the CrO_3 species. Consistent ir results are shown by the relevant spectra in Fig. 3. The gas analysis by Park [17] indicated consistently that this decomposition step involves the evolution of oxygen from the relatively unstable CrO_3.

Calculations based on the total weight loss (38.5%) completed via the final exothermic decomposition step (at 395–425°) suggest the composition $CrO_{1.5} \simeq Cr_2O_3$ for the product thus yielded. This suggestion is strongly supported by both the ir (Fig. 3) and the XRD (Table 1) results given for ADC(400) and (500), where the formation of highly stoichiometric α-Cr_2O_3 is clearly indicated. The formation of α-Cr_2O_3 at this stage can therefore be correlated with the drastic drop in the surface content of excess oxygen observed earlier at > 350° [6].

Thermal analysis of chromia gel (CG). The respective TG curve, given in Fig. 1C, shows that the pentahydrated chromia gel, $Cr_2O_3 \cdot 5 \cdot 2H_2O$, suffers a 39.0% weight loss in a single strong decomposition step with a moderate rate at 80–300°.

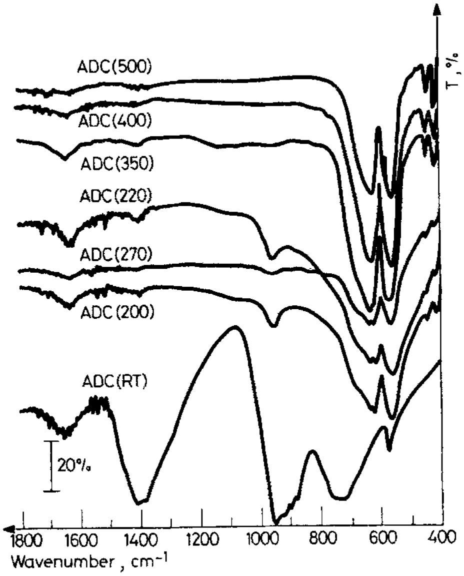

Fig. 3 ir spectra for $(NH_4)_2Cr_2O_7$ (RT) and its decomposition products at the temperatures indicated for 5 h

However, the corresponding DTA curve (Fig. 1C) manifests two endothermic effects, at 100° and 180°, and two exothermic ones, at 230° and 280°, and this reveals its composite nature. The TG curve further shows a following rapid exothermic decomposition step, at 380–390°, bringing the total weight loss up to 44.0%.

The early endothermic effect peaking at 100° (5.0% weight loss) is usually associated with the elimination of physisorbed water [6]. The succeeding endothermic effect centred around 180° (22.5% weight loss) has been found to correspond to the elimination of chemically bound water to give an intermediate trihydrate [3], i.e. $Cr_2O_3\cdot 3H_2O$. Water content measurement indicated that the amorphous (XRD) decomposition product CG(150) had an identical composition. The corresponding ir spectrum (Fig. 4), as compared to that given for the parent gel CG(RT), shows that the water thus eliminated was responsible for the absorption at 1450, 840 and 520 cm^{-1}. The last two absorptions are normally assigned to torsional oscillations of trapped water [27].

The exothermic effect located at *ca.* 230° (DTA curve) has been attributed by Carruthers and Sing [14] and Carruthers et al. [15] to the formation of CrOOH. Indeed, the total weight loss at 230° (TG curve) amounts to a value (30.4%) that agrees very well with that (30.7%) anticipated theoretically for the dehydration of $Cr_2O_3\cdot 5\cdot 2H_2O$ to give $Cr_2O_3\cdot H_2O \simeq 2CrOOH$. The dark-green decomposition product obtained at 250° gave rise to weak and fuzzy XRD lines, due to an immature nucleation of CrOOH microcrystallites on a gelatinous bed.

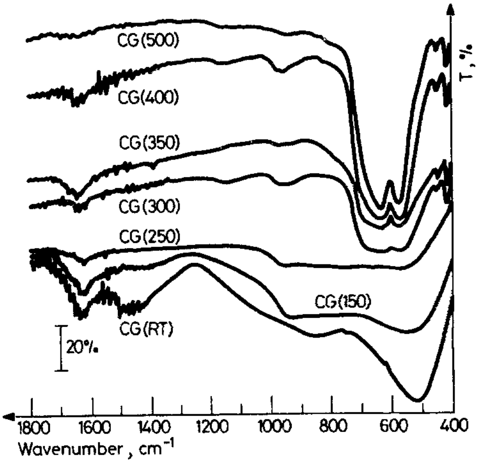

Fig. 4 ir spectra for chromia gel (RT) and its decomposition products at the temperatures indicated for 5 h

The broad exothermic effect centred around 280° has been reported to mark the surface oxidation of Cr^{3+} ions [14, 15]. The TG curve (Fig. 1C) indicates that this exothermic process is still accompanied by a decomposition process leading to a weight loss (10.4%) that agrees favourably with that expected for the topochemical oxidation reation [28]:

$$\tfrac{1}{2}\,O_2 + 2\ CrOOH \rightarrow 2CrO_2 + H_2O\ (10.7\%)$$

A reversible nature was earlier confirmed for this reaction [29], and it was explained on the basis of the close similarity between the structures of CrOOH (orthorhombic) and CrO_2 (tetragonal). The XRD results for CG(300) (Table 1) indicate the coexistence of CrO_2, CrO_3 and Cr_2O_3.

The following exothermic effect, at 340°, corresponds to a slight weight increase ($< 1.0\%$), denoting a progressive oxidation process. The XRD results given in Table 1 for CG(350) point to the formation of CrO_3 at the expense of CrO_2. In fact, the ir spectra of CG(300) and (350) (Fig. 4) display indications (absorptions at 1000–900 and 750–450 cm^{-1}) of the probable organization of CrO_3 and Cr_2O_3 in a chromium chromate-like structure.

The final rapid decomposition step at 380–390° (4.5% weight loss) is accompanied by an exothermic effect overlapped by a sharper one at 415°, corresponding to the calescence first observed by Berzelius [30]. It has been reported [15] that the decomposition of the higher oxidation states of chromium ions at 380–390° evolves an amount of heat high enough to trigger the exothermic crystallization of α-Cr_2O_3 at 400–420°. Consistent XRD (Table 1) and ir (Fig. 4) results were obtained from the products yielded at (CG(400)) and beyond (CG(500)) this stage.

Interestingly, the DT curve reported here for CG is quite different in character from those reported elsewhere [29] for CrOOH and CrO_2. Thus, the pronounced exothermic effect associated with the calescence phenomenon (at 415°) has not been observed in the course of the transformation of CrO_2 to α-Cr_2O_3. This is surprising in view of the appreciable oxidation which precedes the calescence exotherm when CG is heated in air. This again may suggest that, even under the most favourable conditions, the formation of CrOOH, CrO_2 and CrO_3 is restricted to a small proportion of the gel.

Correlating the catalytic results reported earlier [7, 8] with the findings of the present investigation, it is suggested that the creation of the Zener phase (coupled Cr^{3+}—Cr^{6+} ions), the active redox catalytic centres, is optimized at the surface, wherever the chromium chromate species form throughout the course of the thermal genesis of the catalysts.

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Zusammenfassung — Drei Vorstufen von Chrom(III)-oxid, nämlich CrO_3, $(NH_4)_2Cr_2O_7$ und Chrom(III)-oxidgel wurden mittels TA und DTA untersucht. Die bei 5-stündiger Temperung dieser Verbindungen bei verschiedenen Temperaturen (150–500 °C) erhaltenen Zersetzungsprodukte wurden IR-spectroskopisch und röntgendiffraktometrisch untersucht. Die erhaltenen Ergebnisse ermöglichen eine zuverlässige physikalisch-chemische Charakterisierung der im Verlauf der thermischen Zersetzung erfolgenden Teilschritte und entstehenden Zwischenprodukte.

Резюме — Методами ТА и ДТА изучены три исходные вещества: CrO_3, $(NH_4)_2Cr_2O_7$ и хромовый гель. Продукты термического разложения, полученные прокаливанием этих соединений при температурах 150–500° в течении 5 часов, были исследованы методом ИК спектроскопии и рентгеноструктурным анализом. Полученные результаты позволили провести физико-химическую идентификацию промежуточных и конечных продуктов разложения.