

Thermal and spectroscopic studies of chromium chromate hexahydrate – a likely composition for redox surfaces of calcined chromia catalysts

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Abstract

Invoked by the possibility that chromium chromate species might constitute the surface composition of calcined chromia catalysts, a commercial $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ compound was examined by thermogravimetry and differential scanning calorimetry in different reactive gas atmospheres. The principle goal was a proper assessment of its thermal and chemical stabilities with the hope of making an objective judgment on current environmental reservations about industrial applications of calcined chromia catalysts, owing to volatility of $\text{Cr}^{\text{IV}}\text{-O}$ species. On the basis of the thermal analysis results, the chromate compound was calcined at some selected temperatures in the range from 150°C to 1000°C. The solid products were, then, subjected to X-ray powder diffractometry and spectroscopies of infrared absorption and UV–Vis diffuse reflectance. The results have shown the parent bulk chromate to dehydrate completely near 300°C and to decompose into chromate-covered $\alpha\text{-Cr}_2\text{O}_3$ particles at 450–1000°C, encompassing formation of noncrystalline polychromate ($\text{Cr}_{1+x}\text{O}_{4+3x}^{2-}$) and nonstoichiometric $\gamma\text{-Cr}_2\text{O}_{3+x}$ bulk phases. In the presence of hydrogen atmosphere, the dehydration is intercepted by an immediate reduction, however the eventual product (α -chromia) remained chromate covered to 1000°C. The high-temperature thermal and chemical stabilities thus revealed for the dispersed chromates are attributed to electronic interactions with nearby $\text{Cr}^{\text{III}}\text{-O}$ species dwelled in a crystalline lattice. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Calcined chromia catalysts, whether supported or unsupported, perform actively in redox reactions [1]. Their surfaces comprise variously structured chromate species ($\text{Cr}_{1+x}\text{O}_{4+3x}^{2-}$), viz. monomeric or polymeric [2,3], and crystalline or noncrystalline [4,5]. Charac-

terization studies [4–6] have brought about enough evidence that interaction species involving $\text{Cr}^{\text{VI}}\text{-O}$ and nearby $\text{Cr}^{\text{III}}\text{-O}$ species generate the surface mobile-electron environment [7] necessitated by redox reactions [8]. The establishment of such interaction species on $\alpha\text{-Cr}_2\text{O}_3$ particles has been postulated [9,10] to improve the thermal and chemical stabilities of the chromate. Thus, the current environmental reservation about industrial utilization of calcined chromia catalysts [11,12] may be alleviated.

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The present paper presents and discusses results of thermal and spectroscopic studies of a commercially available chromium chromate hexahydrate, viz. $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$. The work was invoked by the possibility that the compound could represent a likely composition for $\text{Cr}^{\text{III}}\text{--Cr}^{\text{VI}}$ interaction species generated on calcined chromia catalysts. The investigation undertaken was designed to monitor the thermal and chemical stabilities of the test material to high temperature treatments in different reactive gas atmospheres.

2. Experimental

2.1. Materials

The chromium chromate hexahydrate, $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$, was a greenish yellow, finely divided AR-grade product of F.E. Decker (England). It was heated in a stream of N_2 or H_2 (40 ml/min) at different temperatures in the range from 150°C to 1000°C for 3 h, and in a stream of oxygen (40 ml/min) in the range from 600°C to 1000°C for 3 h. The applied temperatures were chosen on the basis of thermal analysis results (vide infra), in order to warrant decomposition of the chromate. The decomposition product in N_2 at 350°C was found to assume an O/Cr atomic ratio (≈ 2.5) very close to that (≈ 2.4) expected for anhydrous $\text{Cr}_2(\text{CrO}_4)_3$, by a preliminary ICP analysis using a GBC Integra XM sequential inductively coupled plasma spectrometer. Gases used were 99% pure products of the Industrial Gases (Cairo/Egypt); N_2 and H_2 were made to pass through appropriate oxisorb traps prior to application.

2.2. Thermal analyses

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out by heating (at 5°C/min) in different dynamic atmospheres of O_2 , N_2 and H_2 (40 ml/min), using Shimadzu stand alone TGA-50H and DSC-50 analyzers (Japan) equipped with a model Chromatopac C-R4AD data handling system. It is worth noting, however, that due to using copper seats for the sample cells, DSC measurements were not conducted in O_2 atmosphere. Comparably small weights of test samples (10–15 mg) were used,

and highly sintered $\alpha\text{-Al}_2\text{O}_3$ (Shimadzu) was the thermally inert reference for DSC measurements. The heat of transition (28.24 J/g) of pure indium (Johnson Matthey, UK) at 157°C was adopted for DSC chart calibration.

2.3. X-ray diffractometry and spectroscopic analyses

X-ray powder diffractometry (XRD) was carried out on a model PW1700 Philips diffractometer (UK) with Ni-filtered CuK_α radiation (35 kV; 30 mA; $\lambda = 1.5418 \text{ \AA}$). The diffractometer was operated with 20° diverging and receiving slits at a scan rate of 2°/min, and a continuous intensity trace was recorded as a function of 2θ . Test samples, ground to a particle size of $\leq 44 \mu\text{m}$ and packed into the well of sample holders, were mounted in a horizontal position. Diffraction patterns (I/I^0 vs. d -spacing) derived from the recorded diffractograms were compared with ASTM standards for phase composition identification purposes.

Infrared absorption spectroscopy (IR) was performed with a model 559P ratio recording Perkin-Elmer spectrophotometer (UK). The spectra were taken from KBr-supported disks of test samples (ex-situ heated) over the frequency range from 4000 to 400 cm^{-1} at a resolution of 5 cm^{-1} .

UV-Vis diffuse reflectance (DR) spectra were recorded over the wavelength range from 800 to 200 nm on a model 2100 double-beam Shimadzu spectrophotometer (Japan) equipped with a diffuse reflectance attachment and a data station. Specpure BaSO_4 (Shimadzu) was the reference material adopted. The DR spectra were not used for quantitative measurements; therefore, they are not represented in units of the Kubelka-Munk function [13].

3. Results and discussion

3.1. Thermochemical stability

Fig. 1 compares TG curves obtained for $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ in differently reactive gas atmospheres; namely oxidative (O_2), inert (N_2) and reducing (H_2) atmospheres. DSC curves, which were obtained only in N_2 and H_2 atmospheres, are also given in Fig. 1. It is obvious from the results that in O_2 or N_2 the parent chromate decomposes at 60–390°C

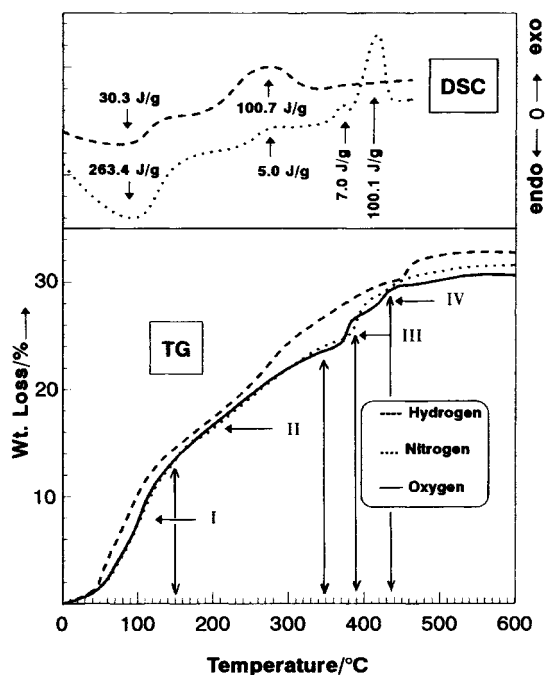


Fig. 1. TG and DSC curves obtained by heating $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ at $5^\circ\text{C}/\text{min}$ in the different dynamic (40 ml/min) gas atmospheres indicated.

showing two weight loss (WL) steps: a fast, endothermic step-I ($\text{WL} \approx 12\%$; $T_{\text{max}} = 70^\circ\text{C}$) occurring at $60\text{--}120^\circ\text{C}$, followed by a slower, exothermic step-II ($\text{WL} \approx 11\%$; $T_{\text{max}} = 250^\circ\text{C}$) at $120\text{--}370^\circ\text{C}$. Step-I occurs similarly in H_2 , but step-II is overlapped by another WL-step commencing near 230°C . The DSC indicates that the amount of heat absorbed by step-I is very much suppressed in H_2 ($\Delta H = 263.4$ (N_2) and 30.3 (H_2)), however the heat released by step-II is considerably increased ($\Delta H = 5.0$ (N_2) and 100.7 (H_2)).

Further heating up to 450°C results in WL-processes that seem to be dependent on the surrounding atmosphere (Fig. 1). In O_2 , two successive WL-steps occur at $370\text{--}450^\circ\text{C}$: step-III, $\text{WL} = 2.5\%$ and $T_{\text{max}} = 390^\circ\text{C}$; and step-IV, $\text{WL} = 3.0\%$ and $T_{\text{max}} = 440^\circ\text{C}$. These two steps are shown by the corresponding DSC curve to be exothermic in nature. In N_2 , the weight loss pertaining to step-III is almost doubled in magnitude ($\sim 6\%$), whereas that accompanying step-IV is halved ($\sim 1.5\%$). However, the cumulative weight losses in O_2 and N_2 are very close, viz. 31%

and 32% , respectively. In H_2 , step-III seems to be that overlapping with step-II. Thus, it is enhanced to commence at a much lower temperature (250°C instead of 370°C in O_2 or N_2). Step-IV is slightly retarded in H_2 to maximize at 460°C , and the cumulative weight loss assumes the highest magnitude of ca. 33% . However the most remarkable difference is that in H_2 the exothermic nature of step-IV is no longer visible. The heat released while the occurrence of step-III seems to overlap with that of step-II ($T_{\text{max}} = 250^\circ\text{C}$), in presence of H_2 .

Molecular stoichiometry calculations based on the parent molecular formula ($\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$) and the weight losses determined imply that the endothermic step-I and -II involve complete elimination of the 6 mol of water of hydration (cumulative $\text{WL}_{\text{obs}} \approx 23\%$, cumulative $\text{WL}_{\text{calc.}} \approx 20\%$) as well as a minor oxygen release. Oxygen release from simple chromates results in the formation of polychromates ($((1+x)\text{CrO}_4^{2-} \rightarrow \text{Cr}_{1+x}\text{O}_{4+3x}^{2-} + x\text{O}$) [14], which, in turn, decompose reductively to form Cr_2O_3 as the eventual product [15]. The exothermic step-III and -IV end up by making the cumulative weight loss come to $31\text{--}33\%$, which meets very well with the complete conversion of $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ into Cr_2O_3 (cumulative $\text{WL}_{\text{calc.}} = 32.1\%$). Thus, the anhydrous chromate, $\text{Cr}_2(\text{CrO}_4)_3$, is decomposed to produce Cr_2O_3 via formation and subsequent decomposition (step-III) of polychromate species. The increase in the weight loss accompanying step-III, from 3% in O_2 to 6% in N_2 , may presume that the product is largely nonstoichiometric and contains a varying amount of excess oxygen ($\text{Cr}_2\text{O}_{3+x}$) depending on the heating atmosphere. A similar nonstoichiometric Cr_2O_3 was encountered by Ellison et al. [4,5] and identified as being $\gamma\text{-Cr}_2\text{O}_{3+x}$. Thus, step-IV involves the elimination of excess oxygen and formation of largely stoichiometric Cr_2O_3 . The corresponding large exotherm (Fig. 1) is analogous to that marking the crystallization into $\alpha\text{-Cr}_2\text{O}_3$ [16].

The enhancement conceded by step-III in H_2 atmosphere may imply a direct reduction of the anhydrous chromate (product of step-II) into Cr_2O_3 . The maintenance of step-IV in H_2 atmosphere may presume that the reduction product is still nonstoichiometric, i.e. $\gamma\text{-Cr}_2\text{O}_{3+x}$. However, the absence of a corresponding exotherm in the DSC curve (Fig. 1) may suggest that the product is not completely converted into the

crystalline α -phase in the temperature range examined.

Summing up, $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ is dehydrated in two steps (I and II) on heating up to 300°C , irrespective of the surrounding atmosphere. Then, the anhydrous chromate is polymerized prior to decomposition into the highly oxidized $\gamma\text{-Cr}_2\text{O}_{3+x}$ phase at 390°C (step-III). The extent of oxidation of the product is optimized in O_2 atmosphere as compared to N_2 . However, the decomposition process (step-III) is surpassed by a direct reduction of the anhydrous chromate in H_2 atmosphere. The reduction product appears to be the oxidized $\gamma\text{-Cr}_2\text{O}_{3+x}$ phase. Irrespective of the gas atmosphere, $\gamma\text{-Cr}_2\text{O}_{3+x}$ is decomposed into largely stoichiometric Cr_2O_3 at $420\text{--}450^\circ\text{C}$. The eventual chromia seems to crystallize progressively into the α -phase in O_2 or N_2 , but not in H_2 .

3.2. Decomposition product analysis

3.2.1. XRD

XRD results (Fig. 2) indicate that neither the hydrated, nor the anhydrous chromate (product of step-II, Fig. 1), assumes a crystalline bulk structure. It was not until the temperature exceeded 300°C that diffraction patterns were observed. The diffraction pattern obtained for the decomposition product at 350°C , which displays stronger peaks for the product in N_2 (and O_2) than in H_2 atmosphere, is closely similar to the standard pattern (ASTM 6-0504) of $\alpha\text{-Cr}_2\text{O}_3$. Thus, formation of Cr_2O_3 during polymerization of chromates, e.g. $2\text{Cr}_2(\text{CrO}_4)_3 \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_7)_2 + 2\text{Cr}_2\text{O}_3 + 2\text{O}_2$, can be confirmed. Also, H_2 -reduction of chromates into Cr_2O_3 can be confirmed.

3.2.2. IR

IR spectra taken from $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ and its decomposition products in O_2 atmosphere were largely similar to the spectra shown in Fig. 3 for decomposition products in N_2 . The spectra exhibited by the decomposition products in H_2 are demonstrated in Fig. 4. The results brought about support the above-presented and discussed results of the following:

1. Complete dehydration of the parent chromate in steps I and II, as shown by the elimination of the relevant $\delta\text{-H}_2\text{O}$ band (at 1640 cm^{-1}) on heating up to 350°C .

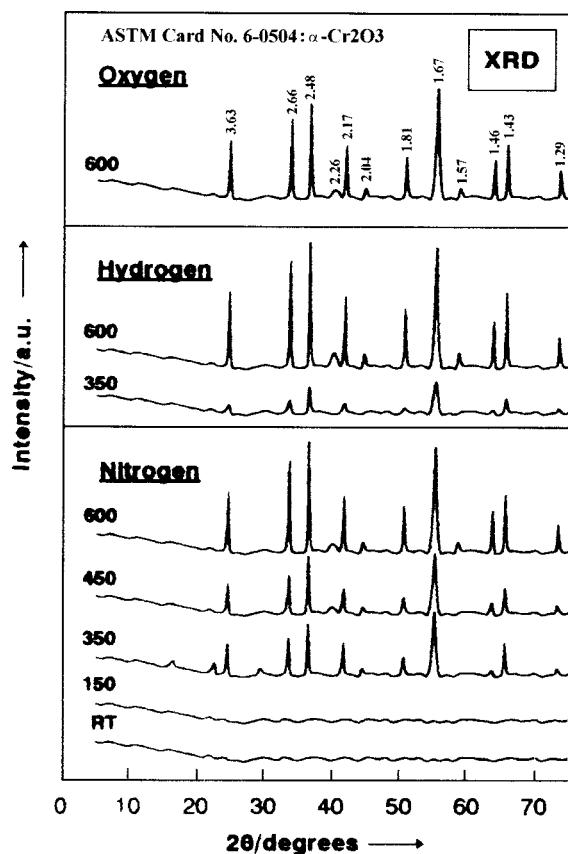


Fig. 2. X-ray powder diffractograms ($\text{CuK}\alpha$ radiation) for $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ (RT) and its decomposition products at the temperatures and atmospheres indicated. Numerals marking the diffraction peaks are the corresponding d -spacings (in Å).

2. Persistence of the chromate structure to heating in N_2 (or O_2) up to 250°C , but in H_2 some considerable changes to the IR band structure of the chromate (at $1000\text{--}400\text{ cm}^{-1}$ [17]) are observed, following heating at 200°C ; thus, the reduction of the chromate in H_2 commences effectively at a lower temperature than implied from the TG curves (Fig. 1).
3. At 350°C the spectra display bands confirming the formation of polychromates (at $1000\text{--}700\text{ cm}^{-1}$ [18]), Cr_2O_3 (at $600\text{--}400\text{ cm}^{-1}$ [19]) and charged molecular oxygen species (at $1200\text{--}1100\text{ cm}^{-1}$ [20]) that are most likely associated with the formation of $\gamma\text{-Cr}_2\text{O}_{3+x}$; these bands being more resolved in N_2 (or O_2) than in H_2 (Fig. 4).

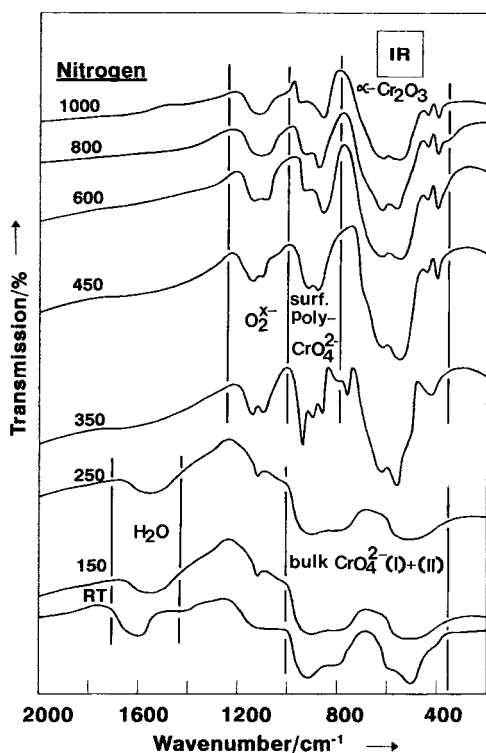


Fig. 3. IR transmission spectra taken from $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ and its decomposition products obtained by heating in N_2 (or O_2) at the temperatures indicated.

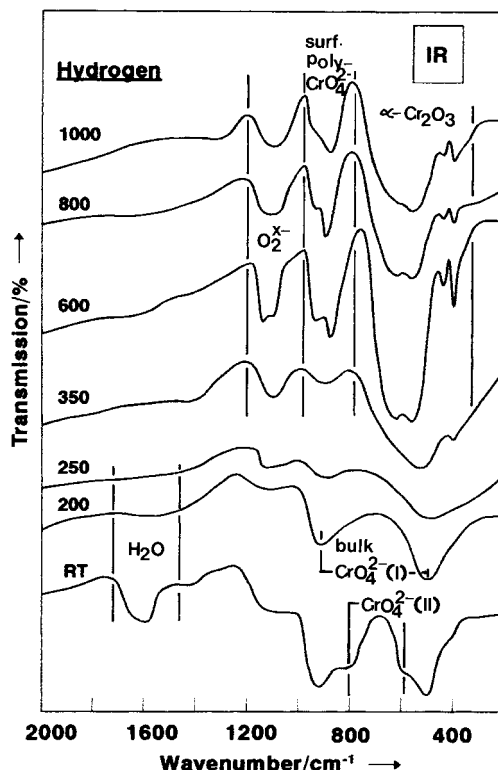


Fig. 4. IR transmission spectra taken from $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ and its decomposition products obtained by heating in H_2 at the temperatures indicated.

4. Polychromate and charged molecular oxygen species persist against heating up to 1000°C , irrespective of the gas atmosphere; the same applies to Cr_2O_3 regardless of the modifications conceded by its characteristic band profiles in H_2 atmosphere.

Moreover, IR spectra reveal that the parent chromate comprises at least two different types of CrO_4^{2-} groups: type-I, bands at 950 and 560 cm^{-1} ; and, type-II, bands at 793 and 596 cm^{-1} [17]. They also show that it contains extra-lattice oxygen species, shoulder at $1200\text{--}1100\text{ cm}^{-1}$. The type-II chromate, which is rather dichromate like [16], is shown to be less stable to heating in H_2 atmosphere, the corresponding bands are eliminated at 200°C (Fig. 4). Type-I chromates persist until 250°C . The results also indicate that the eventual decomposition product of the parent chromate, i.e. product of step-IV near 450°C , consists dominantly of $\alpha\text{-Cr}_2\text{O}_3$ but not entirely. The IR bands

at $1200\text{--}800\text{ cm}^{-1}$, which are still observed in the spectra taken from the 1000°C decomposition products both in N_2 (or O_2) and H_2 , indicate the coexistence of noncrystalline polychromates and $\gamma\text{-Cr}_2\text{O}_{3+x}$ as bulk and/or surface structures.

3.2.3. DRS

UV-Vis DR spectra taken from the parent chromate and its decomposition products in N_2 (or O_2) and H_2 atmospheres are compared in Fig. 5. It is obvious that the spectra of the decomposition products in N_2 (or O_2) at $150\text{--}450^\circ\text{C}$ are similar to the spectrum taken from the parent chromate. The display absorption bands and shoulders at 230 , 270 , 350 and 390 nm , as well as a broad absorption extending over the wavelength range from 400 to 800 nm . The spectrum taken from the 600°C product is different; it resolves two absorption maxima at 460 and 600 nm . The absorption features displayed in the latter spectrum

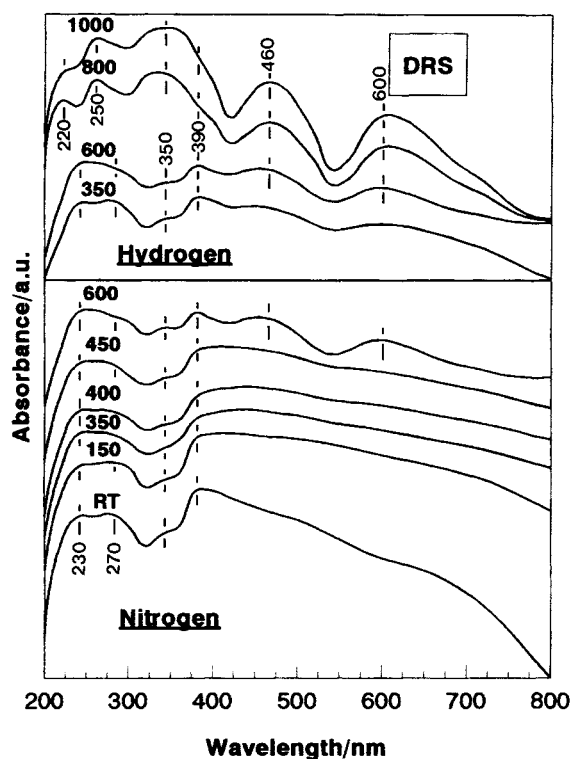


Fig. 5. UV-Vis DR spectra taken from $\text{Cr}_2(\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$ and its decomposition products obtained by heating at the temperatures and atmospheres indicated.

are similarly exhibited not only by the 600°C decomposition product in H_2 , but also by the 350°C product. The absorption bands at 230, 270, 350 and 390 nm are due to charge transfer and d–d transition interactions in mono- and polychromates [17,21]. The extended absorption over the low frequency region (400–800 nm) can be ascribed to the presence of different types of chromates (I and II) experiencing d–d electron exchange interactions with Cr^{III} ions [4,5]. Resolution of the two absorptions at 460 and 600 nm (Fig. 5) marks the contribution of $\alpha\text{-Cr}_2\text{O}_3$ particles [22].

The contribution of $\alpha\text{-Cr}_2\text{O}_3$ is shown (Fig. 5) to be developed considerably following heating in H_2 at the high temperatures of 800°C and 1000°C. Moreover, the intensity ratio of the bands at 220 and 250 nm (I_{220}/I_{250}) is shown to decrease. The latter criterion can well be considered to mark the dominance of monochromates [21,22]. These results account for the reduction of the parent chromate.

Thus, DRS and IR results agree on the coexistence of $\alpha\text{-Cr}_2\text{O}_3$ and chromate species in the eventual decomposition product of the parent chromate, irrespective of the surrounding gas atmosphere. The DR band near 600 nm has been assigned to d–d interactions. The interacting species have been differently identified. While Mikolaichuk et al. [22] consider the interactions to involve nonoctahedral Cr^{III} , Weckhuyssen et al. [21] believe it to involve octahedral Cr^{III} . Ellison et al. [4,5], on the other hand, obtained experimental evidence from magnetic measurements to justify a different view invoking that the d–d interactions occur between $\text{Cr}^{\text{III}}\text{-Cr}^{\text{VI}}$ couples.

4. Conclusion

Calcination of unsupported or supported Cr^{III} compounds yields potential catalysts for redox processes [1]. The catalytic activity has been suggested to reside in chromium chromate like species established on surfaces of crystalline or noncrystalline Cr_2O_3 particles [4–6]. The required localized adsorption of reactants has been seen [6] to take place on coordinatively unsaturated Cr^{III} sites, and the electron availability to occur through electron-exchange interactions with nearby Cr^{VI} sites. Ellison et al. [4,5], in terms of results of systematic magneto-optical measurements, have also favored such a surface $\text{Cr}^{\text{III}}\text{-Cr}^{\text{VI}}$ mobile-electron phase to create the ideal environment in which not only the redox catalytic activity is maximized, but also the polymerization activity. However, industrialization of calcined chromia catalysts is hampered by strong environmental reservations [11] due to the high volatility of atmosphere detrimental $\text{Cr}^{\text{VI}}\text{-O}$ species [12].

The above presented and discussed results help in drawing the following relevant conclusions:

1. Anhydrous chromium chromate bulk compositions are thermally and chemically stable to heating up to 200°C.
2. In absence of a reducing atmosphere, the stability is extended to 350°C, where deoxygenation is triggered to result in the formation of bulk polychromates and noncrystalline Cr_2O_3 . Then, the bulk polychromates is decomposed into nonstoichiometric $\gamma\text{-Cr}_2\text{O}_{3+x}$ near 400°C, which loses the

excess oxygen near 450°C giving rise to crystalline α -Cr₂O₃ and noncrystalline chromate species. The dispersed chromates are electronically interacting with the nearby Cr^{III}-O species dwelled in crystalline lattice.

3. In presence of a reducing atmosphere, a some type of bulk chromates is reduced near 200°C, whereas another type persists up to 250°C. The reduction products of both types are noncrystalline γ -Cr₂O_{3+x} and crystalline α -Cr₂O₃. Near 450°C, the nonstoichiometric oxide is relieved of excess oxygen to form α -Cr₂O₃ and noncrystalline chromate species electronically interacting with the nearby Cr^{III}-O species.
4. The dispersed chromates thus established are chemically and thermally stable to heating in H₂, N₂ or O₂ atmosphere up to 1000°C.

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