FORMATION OF Cr(II) SPECIES IN THE H_2/CrO_3 SYSTEM
Parameter control

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Abstract

The thermal behaviour of CrO_3 on heating up to 600°C in dynamic atmospheres of air, N_2 and H_2 was examined by thermogravimetry (TG), differential thermal analysis (DTA), IR spectroscopy and diffuse reflectance spectroscopy (DRS). The results revealed three major thermal events, depending to different extents on the surrounding atmosphere: (i) melting of CrO_3 near 215°C (independent of the atmosphere), (ii) decomposition into $Cr_2(CrO_4)_3$ at 340–360°C (insignificantly dependent), and (iii) decomposition of the chromate into Cr_2O_3 at 415–490°C (significantly dependent). The decomposition $CrO_3 \rightarrow Cr_2(CrO_4)_3$ is largely thermal and involves exothermic deoxygenation and polymerization reactions, whereas the decomposition $Cr_2(CrO_4)_3 \rightarrow Cr_2O_3$ involves endothermic reductive deoxygenation reactions in air (or N_2) which are greatly accelerated and rendered exothermic in the presence of H_2. TG measurements as a function of heating rate (2–50°C min^{-1}) demonstrated the acceleratory role of H_2, which extended to the formation of Cr(II) species. This could sustain a mechanism whereby H_2 molecules are considered to chemisorb dissociatively, and then spill over to induce the reduction. DTA measurements as a function of the heating rate (2–50°C min^{-1}) helped in the derivation of non-isothermal kinetic parameters strongly supportive of the mechanism envisaged.

Keywords: Cr(II), chromium trioxide, kinetics, reduction, thermal analysis

Introduction

In view of their activity in ethylene polymerization reactions (Philips catalyst for high-density polyethylene), chromia-based cayalysts have stimulated research interest during the past three decades [1]. A large amount of research work has been devoted not only to the polymerization activity, but also to other applications of industrial importance, e.g. dehydrogenation and dehydration of primary and secondary alcohols [2] to produce aldehydes, ketones and alkenes. Catalytic oxidation of light alkanes [3] form natural gas to form industrially important chemicals, and the dehydrogenation of isobutane to isobutene [4] for MTBE synthesis, have also been considered. Chromia has recently been tested as a soot oxidation catalyst [5], a combustion catalyst [6], and an oxidation catalyst for alcohol in the gas phase [7].

Environmentally, chromia catalysts exhibit pronounced activities towards the decay and destruction of many harmful pollutants: (i) the decomposition of certain halogenated hydrocarbons, even at low temperatures [8], (ii) the oxidation of CO to CO_2 [9], and the reduction of NO with NH_3 [10].

Chromium trioxide is frequently used as a precursor for the synthesis of chromia catalysts [4, 8, 9, 11–14]. During the preparation, in an oxidizing atmosphere, CrO_3 provides the catalyst surface with CrO_4^{2-} species. For certain catalytic reactions, the reduction of a Cr–oxygen species is crucial for the required activity, e.g. for ethylene polymerization. CO has been used as the reducing agent [9, 13], and Cr(II) species have been detected in the reduced catalysts. Due to the instability of Cr(II) species, the catalyst is reduced in situ with CO. Bensalem *et al.* [13], using in situ diffuse reflectance spectroscopy, have reported that reduction with CO is accompanied by the formation of CO, carboxylate and possibly carbonate surface species. Consequently, reduction with H_2 may be advantageous over reduction with CO in this regard; IR spectroscopy [15] of H_2-reduced α-Cr_2O_3, could reveal the formation of Cr(II) species. The TPR methods [16, 17] have only a limited ability to detect Cr(II) species in such a complex system.

On the other hand, appropriate control over the reduction parameters, e.g. the heating rate, may influence the reduction behaviour and help to achieve the formation of a definite reduction state. These parameters were the object of some recent published work [18, 19]. For instance, the heating rate has been found [18] to determine the reduction products of WO_3, and fast heating is responsible for the decomposition of chromium nitrate into Cr_2O_3, without the formation of CrO_2 [19].

In the present work, the reduction of CrO_3 with H_2 was investigated. Different heating rates were applied, in order to establish conditions that might promote the production of Cr(II) species. Thermal analysis and some other physico-chemical techniques were used to probe the reduction course.

Experimental

Chromium oxide, CrO_3, was a pure product of Riedel-de Haen AG (Hannover, Germany). To ensure the purity of the gases used (H_2, N_2 and air), specific purification techniques (mainly dehydration and/or deoxygenation) were applied to each gas. In a dynamic atmosphere (30 ml min^{-1}) of H_2, thermogravimetry (TG) and differential thermal analysis (DTA) were carried out at different heating rates (2–50°C min^{-1}) with a 30-H Shimadzu thermal analyzer (Japan). For comparison purposes, TG and DTA curves were also measured in flowing air and N_2 at a heating rate of 20°C min^{-1}. The Kissinger equation, $\ln(\beta/T^2)= -(\Delta E/R)/T+\ln(AR/\Delta E)$, where β and T are the heating rate and the DTA peak temperature, respectively, was adopted for kinetic analysis [20]. ΔE, the activation energy for each thermal event, was computed. A model 2100 Shimadzu UV-Vis spectrophotometer was used to measure the diffuse reflectance spectra. For IR measurements, a 580B Perkin Elmer double beam spectrophotometer was used.

Results and discussion

The TG and DTA curves monitoring the course of reduction of CrO_3 in H_2 (HTG) at $20°C$ min^{-1} are given in Fig. 1. For comparison, the curves relating to the thermal behaviour of the test material in air and in N_2 ($20°C$ min^{-1}) are also presented. The HTG curve displays two distinct mass loss steps, denoted as event II and event IV. An additional gradual and very weak mass loss step (event V) could also be seen. These three steps were revealed by DTA to be exothermic, and maximized at 360, 415 and $570°C$. The DTA curve resolves a very sharp and strong mass-invariant endothermic event (I) at $215°C$. Direct observation of the visible changes taking place throughout this temperature range showed that CrO_3 melts at $215°C$.
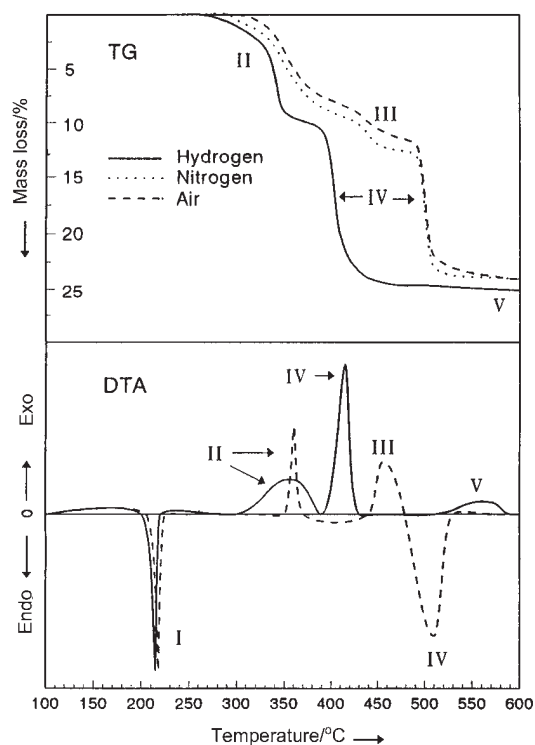

Fig. 1 TG and DTA curves of CrO_3 measured at $20°C$ min^{-1} in H_2, N_2 and air atmospheres

The mass losses caused by events II and IV were 9.5 and 24%, respectively. The former loss, which also occurs (9.4%) in air and N_2 atmospheres through events II and III, can not be attributed either to the formation of Cr_2O_5 (8%) or to the formation of Cr_4O_9 (12%) [21, 22]. Stoichiometric calculations attributed event II to the formation of a compound of composition Cr_5O_{12} (experimental mass loss 9.6%). The compound which should contain Cr(III)– and Cr(IV)–oxygen species corresponds to

chromium chromate, $Cr_2(CrO_4)_3$. The formation of $Cr_2(CrO_4)_3$ during the thermal decomposition of CrO_3 in air has been discussed previously [11]. The formation of $Cr_2(CrO_4)_3$ in air and in N_2 (Fig. 1) may help to demonstrate that event II is solely thermally induced, without a significant role played by the H_2 atmosphere.

In contrast, event IV, the second mass loss process, was markedly enhanced in H_2. The determined loss of 24% corresponds to the formation of Cr_2O_3 (experimental mass loss=24%). This loss is fairly close to those determined in N_2 and in air. Previous XRD measurements proved that the decomposition product in this step in air is solely α-Cr_2O_3 [11, 22]. However, the DTA curves (Fig. 1) reveal two major differences: (i) the character of this step (event IV) in N_2 and in air is endothermic, whereas in H_2 it is exothermic, and (ii) the DTA peak is shifted from 510 in air to 415°C in H_2.

These results emphasize the reductive role of H_2 after event II. This may suggest that, in this temperature range of event IV, H_2 contributes to the deoxygenation process. The reductive influence seems to be responsible for exothermic event V, which was observed only in H_2 (Fig. 1). The exothermic nature of event IV may reveal H_2-deoxygenation involving lattice oxygen of the freshly resulting Cr_2O_3. A limited reduction of Cr(III) to Cr(II) species might therefore have occurred, at least in the surface layer.

Effect of heating rate on Cr(II) formation

Figure 2 presents TG curves measured for CrO_3 in H_2 at different heating rates (2–50°C min^{-1}). Data relating to the DTA peaks at different heating rates are given in Table 1. The Kissinger plot [20] for such peak data is depicted in Fig. 2. Activation energies (ΔE) and frequency factors derived from this plot for each thermal event are included in Table 1. Figure 2 permits two observations:

1. Events II and IV increasingly overlap with decreasing rate of heating.

2. Event V, which is predicted to involve the formation of Cr(II) species, is reinforced and clearly restructured into different processes at low heating rates. At a heating rate of 2C° min^{-1}, the total mass loss determined amounts to 27%, which indicates a reduction of about 40% of the Cr(III) to Cr(II).

Table 1 DTA peak temperatures (°C) at different heating rates in H_2 atmosphere, the corresponding activation energies (kcal mol^{-1}) and frequency factors

Event	2°C min^{-1}	10°C min^{-1}	20°C min^{-1}	50°C min^{-1}	ΔE	ln$A$
	DTA peak temperatures/°C					
I (endo)	200	210	215	222	66.6	62.4
II (exo)	300	310	360	390	24.0	11.5
IV (exo)	358	415	415	435	35.0	18.15
V (exo)	510	540	570	600	46.6	20.4

The above results reveal that the reductive role of H_2 is greatly enhanced at low heating rates. Thus, a dissociative adsorption of H_2 may be envisaged over surface coordinately unsaturated sites, prior to its reaching the lattice oxygen. Low heating
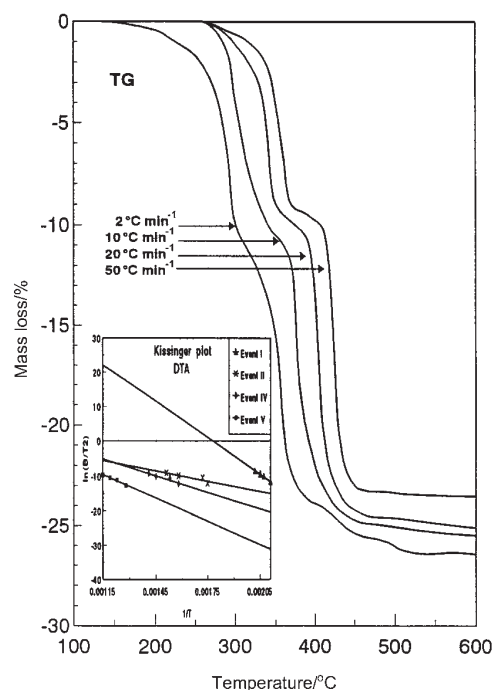
Fig. 2 TG curves measured for CrO_3 in H_2 30 ml min^{-1} at the indicated heating rates. The Kissinger plot for the corresponding DTA peaks is also given (lower part). H_2 atmosphere 30 ml min^{-1}

rates, of course would facilitate the occurrence of such a process, particularly if it is succeeded by a spillover of the hydrogen atoms to sites to be reduced.

Table 1 shows that event I has an activation energy of 66 kcal mol^{-1}, which agrees very well with that determined for CrO_3 in the air atmosphere [20]. Table 1 also reveals that the activation energy for event II, which is mainly a thermal decomposition, is obviosuly lower than the energies derived for events IV and V. The latter two events involve reduction by H_2 to the lower valencies, Cr(III) and Cr(II). It is evident that reduction to Cr(II) (event V) is more difficult than reduction to Cr(III) (event IV).

Reduction intermediates

Attempts to separate reduction intermediates after the first reduction step failed to produce them in a pure state or form. The diffuse reflectance spectrum (Fig. 3) of the resulting (green) compound displays characteristic absorption bands in the charge transfer region (<400 nm) and in the d–d transition region (>400 nm). These bands are well known and have previously been reported [1, 11] for chromia, Cr_2O_3. Moreover, the IR spectrum (not included) also depicts the characteristic absorption bands reported [21] for Cr_2O_3. As discussed above, this reduction step (event II) is mainly accompanied by strong exothermic effects. The heat evolved from such effects triggers and accelerates the dissociative
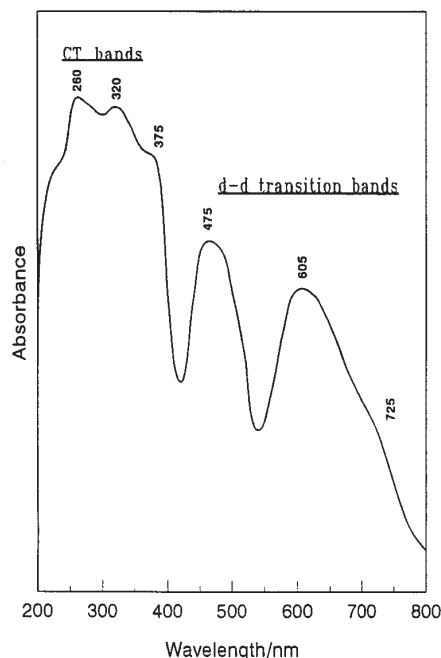
Fig. 3 DRS spectrum of the H_2-decomposition product of event II.
Calcination temperature: 250°C; atmosphere: flowing hydrogen

adsorption of hydrogen and facilitates the following reduction process. A similar effect has been previously reported by Maciejewski *et al.* [10].

Conclusions

From the above-mentioned and discussed results, the following conclusions may be drawn:

1. In H_2 atmosphere, the behaviour of CrO_3 is different from that in air or N_2 atmospheres. The decomposition course starts mainly as a thermal effect (events I and II), and the reductive chemical parameter then dominates at higher temperatures (events IV and V), through the dissociative adsorption of hydrogen.

2. Low heating rates support the formation of Cr(II) species, by providing the dissociative hydrogen adequate time to spill over and reduce the nearby reducible chromium ions.

3. Separation of the H_2-reduction intermediate of event II is a difficult task, where the exothermic effects allow the role of reductive hydrogen to be more operative.

4. A study of this system, H_2/CrO_3, under isothermal conditions, and also in situ measurements to specify the different reduction stages and to verify Cr(II) formation, are crucial demands.

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