

# Thermoanalytical investigations on supported chromia catalysts

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## Abstract

Ceria- and titania-supported chromia catalysts were prepared by wet impregnation technique and their thermal stability as well as redox behaviour were examined by evolved gas analysis (EGA), thermogravimetric analysis (TGA) and temperature programmed reduction (TPR). EGA of previously calcined samples of ceria- and titania-supported chromia samples indicate the absence of bulk like behaviour due to interaction between chromia and support. Evolution of peak corresponding to mass of 44 at multistages suggests the heterogeneous nature of the surface. TG analysis under isothermal conditions suggests that the interaction is greater in ceria-supported catalytic systems. It is also observed from TG studies that the nature, population and strength of the hydroxyl groups are the determining factors for the effective interaction between active chromia phase and the support phase under severe operating conditions. TPR of ceria-supported chromia catalysts show the stabilisation of two kinds of species on the support; the first type (Peak B) being thermally stable chromate species which are reoxidisable, and the second type (Peak A) is thermally unstable species (bulk like aggregates) which are not reoxidisable after reduction or thermal decomposition. TPR studies collectively advocate the predominant prevalence of bulk like “aggregates” rather than anchored chromate species with the formation of polymeric species on increasing the chromia content.

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## 1. Introduction

Supported chromia catalysts have extended a significant contribution to the industrial catalysis, since the discovery of alumina-supported chromia system for dehydrogenation reactions by Frey and Huppke [1]. Of the various supports employed, silica [2], alumina [3] and zirconia [4,5] have been found to have contributed

considerably in various industrially important catalytic processes. The basis for the activity of chromium in such a wide spectrum of reactions is due to the variability of oxidation states, coordination environments and degree of polymerisation of chromium oxide species. This variability is especially pronounced on the surface of solid supports [6]. Thus, knowledge on the surface chemistry of chromium in inorganic oxides is of key importance in environmental sciences and heterogeneous catalysis. Of late titania-supported chromia system had also been explored for its applicability in selective catalytic reduction (SCR), as titania is claimed to stabilise amorphous chromia on its surface [7,8]. Moriceau et al. [9,10] have examined the ceria-supported chromia system and reported the catalytic activity of the system towards dehydrogenation

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of isobutane. Despite the number of investigations carried out on these systems, there are certain points on the nature of active sites such as coordination environment, molecular and chemical state of the chromia species which are still a matter of debate [6].

The analysis of thermal behaviour of the supported chromia phase reveals the enhanced stability of the surface chromia species [11]. Moreover, the redox behaviour of the supported chromia phase differs remarkably from the bulk phase [12,13]. Thus it is reasonable to believe that the higher thermal stability of the surface chromia would resolve the issue of health hazards associated with employing  $\text{Cr}^{6+}$  in catalytic processes. The modified behaviour of the supported chromia phase in relation to its bulk counterpart is due to the esterification process taking place between the hydroxyl groups of the support and the chromia active phase [14,15].

Thermoanalytical techniques have been successfully employed in comprehending the thermal stability of the active and support phases. These are well-documented in the literature [16–20]. In the present investigation, we endeavour to examine the thermal and redox behaviour of the supported chromia phase on ceria and titania supports by means of thermoanalytical techniques such as evolved gas analysis (EGA), thermogravimetric analysis (TGA) and temperature programmed reduction (TPR).

## 2. Experimental

### 2.1. Preparation of catalysts

All the catalysts were prepared by wetness impregnation method using titania and ceria as supports and aqueous  $\text{CrO}_3$  as precursor. The impregnated catalysts were dried at 393 K for 12 h and calcined at 573 K for 2 h. The dried samples will be hereafter referred to as the “fresh” catalysts. The ceria-supported chromia catalysts prepared will be denoted as “CrCe X” and titania-supported catalysts as “CrTi X” where X is the loading of chromia ( $\text{CrO}_3$ ) expressed in wt.%.

### 2.2. Pretreatment of commercial samples

The commercial samples of  $\text{CeO}_2$  (CDH) and  $\text{TiO}_2$  (Baker analysed) as received were digested with dilute

$\text{H}_2\text{SO}_4$  in order to clean the surface, washed with distilled water and then dried at 393 K for over night. The samples thus treated were used for preparation of catalysts.

### 2.3. Characterisation of materials

The chemical analysis of  $\text{Cr}^{6+}$  was carried out based on the property that water removes  $\text{CrO}_3$  from the support [2]. The estimation was carried out using spectrophotometric technique as the same is reported to be highly suitable for the estimation of chromium catalysts [21]. The details of the procedure are given elsewhere [22].

The temperature programmed study was carried out between 323 and 673 K by monitoring the evolved gases using quadrupole mass filter (Balzers GAM 442 gas analyser) at a scanning rate of  $10^\circ$  per cycle. The sensitivity of the technique is confined to the species having ion current as low as  $10^{-14}$  A under the pressure in the order of  $1.3 \times 10^{-4}$  Pa. As the system works under vacuum, the temperature of the peaks was not compared with the results of the work carried out under ambient conditions. Consequently, the analysis is made carefully by making a relative comparison over the samples. The vacuum chamber is baked for at least 4 h before every measurement, at a scanning rate of  $10^\circ$  per cycle in order to ensure the absence of any other species evolved from the previous sample. The samples that were considered for the study were pure  $\text{CrO}_3$ , commercial and homemade  $\text{CeO}_2$ ,  $\text{TiO}_2$ , CrCe and CrTi samples of various loading of  $\text{CrO}_3$ .

TG analysis was carried out under isothermal conditions by holding the sample at 323 K for 30 min of duration prior to the temperature scanning. Then it was followed by heating the sample from 323 to 773 K at a heating rate of  $100^\circ$  per minute and holding the sample at 773 K for 60 min. Weight losses of the pure  $\text{CrO}_3$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$  and supported chromia catalysts were calculated under the identical experimental conditions. From the weight loss, for the supported and unsupported oxides, the factor  $\alpha$  which is a measure of interaction strength between active phase and oxide support can be calculated [12].

Thermogram was also recorded in continuous mode for the pure supports at equal intervals of temperature from 673 to 1473 K, and the percentage weight loss has been calculated. Almost same quantities of

the support samples have been used (around 47 mg) for the TGA measurement. From the values of the percentage weight loss, the hydroxyl content in millimoles per gram of the support was found out. In order to compare the hydroxyl content of the supports of different surface area, the same was normalised to the unit surface area and expressed as hydroxyl population per  $\text{nm}^2$  [12].

TPR studies were carried out using a conventional flow system with test samples of about 0.17 g placed into a quartz microreactor in a 5%  $\text{H}_2/\text{He}$  flow [Model: Auto Chem 2910, Micrometrics, USA]. Prior to a TPR experiment, the samples were pretreated *in situ* with He at a flow rate of 50 ml/min at 423 K for 2 h. In a typical TPR experiment, the reaction temperature was linearly increased up to 1073 K at the heating rate of  $20^\circ$  per minute and the hydrogen concentration was continuously measured using a thermal conductivity detector. The flow rate of the individual gases were regulated by mass flow controllers. The samples used

for the TPR studies are bulk  $\text{Cr}_2\text{O}_3$  and supported chromia catalysts of various chromia loading calcined at 573 K for 2 h. The BET surface area and pore volume were calculated for pure ceria and supported chromium catalysts of various loading using Carlo Erba sorptometer. Prior to the surface area measurement the samples have been degassed at 393 K.

### 3. Results

The EGA pattern of bulk  $\text{CrO}_3$  has been recorded and the profile is shown in Fig. 1. The peak observed between 473 and 543 K corresponding to mass of 52 along with the corresponding isotopic peaks is assigned to chromium ions detected as  $\text{Cr}^+$  due to the decomposition of  $\text{CrO}_3$ . The evolution of species of mass 16 and 32 between the same temperature range are attributed to the atomic and molecular oxygen species, respectively. The differential scanning

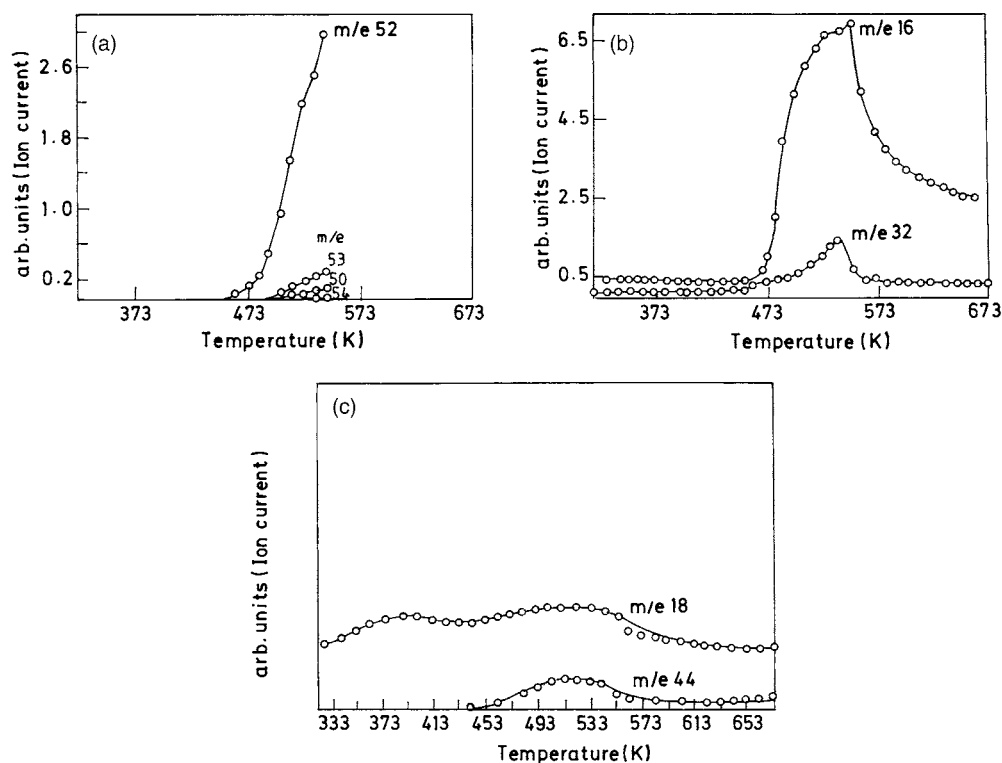


Fig. 1. EGA profiles as a function of temperature for bulk  $\text{CrO}_3$  (fresh).

calorimetric (DSC) profile recorded for bulk  $\text{CrO}_3$  shows an endothermic peak at 473 K corresponding to the melting point of  $\text{CrO}_3$  and is in agreement with the literature [23]. The curve corresponding to mass of 18 denotes the physisorbed water desorbing around 373–533 K due to the presence of moisture, as chromia is hygroscopic in nature. Desorption of water can also be attributed to the surface dehydroxylation occurring at higher temperature. The pattern corresponding to mass of 16 signifies the evolution of oxygen due to the thermal decomposition of chromia and surface dehydroxylation occurring at the support surface.

Fig. 2(a) and (b) shows the evolved gas profiles of pure  $\text{CeO}_2$  (comm.) and fresh  $\text{CrCe}$  8 (comm.) catalyst, respectively. EGA profile shows peaks corresponding to mass 16, 44 and 52 and are ascribed to the atomic oxygen, carbon dioxide and chromium in the gas phase, respectively. In addition, the EG analysis of supported chromia samples after calcination did not show peak corresponding to mass of 52.

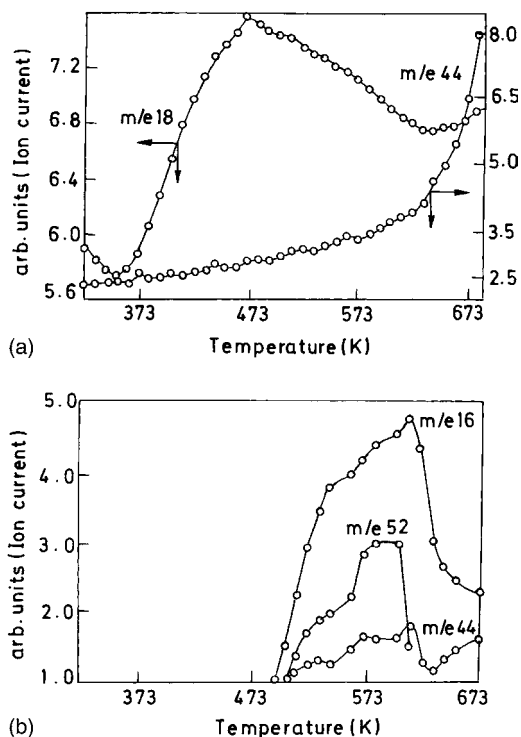


Fig. 2. EGA profiles as a function of temperature for (a) pure  $\text{CeO}_2$  (comm.) and (b)  $\text{CrCe}$  8 (comm.).

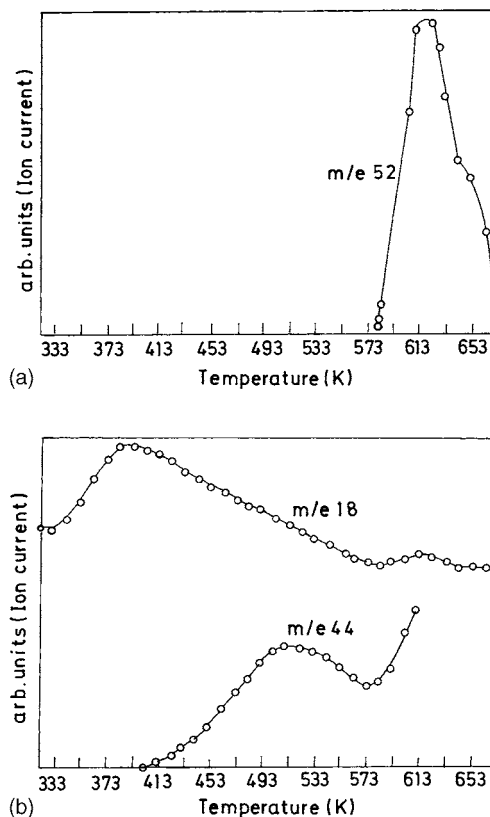


Fig. 3. EGA profiles as a function of temperature for fresh  $\text{CrTi}$  5 (comm.).

EGA profiles of fresh  $\text{CrTi}$  5 and  $\text{CrTi}$  10 (comm.) are shown in Figs. 3 and 4, respectively. Analysis of  $\text{CrTi}$  5 and  $\text{CrTi}$  10 (comm.) samples show the pattern corresponding to mass at 52, 44 and 18, whereas  $\text{CrTi}$  0.4 did not show the presence of peak corresponding to mass 52.

TG analysis was carried out based on the fact that the thermal event that has the closest relevance to the interfacial reactivity is the weight loss. Thus, a proposed degree of interaction strength in terms of the parameter  $\alpha$ , expressed as the relative change in percentage weight loss (WL), is calculated as the ratio of weight loss of supported catalyst ( $\text{WL}_S$ ) to that of the unsupported material ( $\text{WL}_{US}$ ). Here  $\text{WL}_{US}$  is the weight loss of the unsupported chromium compound ( $\text{CrO}_3$ ); this weight loss is 34.34% for  $\text{CrO}_3 \rightarrow \alpha\text{-Cr}_2\text{O}_3$ .  $\text{WL}_S$  is the weight loss of the supported chromium compound; this is the difference in weight

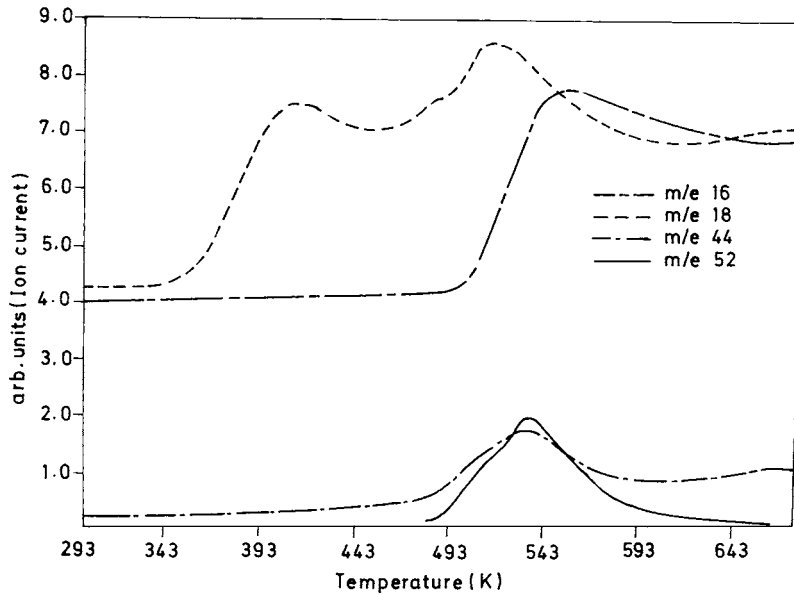


Fig. 4. EGA profiles as a function of temperature for fresh CrTi 10 (comm.).

Table 1  
Degree of interaction strength ( $\alpha$ ) of supported chromia catalysts

Loading (% weight of CrO <sub>3</sub> )	1	1.4	2	4.0	5	8	10
Cr/CeO <sub>2</sub> (comm.)	0.55	1.3	1.8	4.0	5.6	9.3	11.8
Cr/TiO <sub>2</sub> (comm.)	–	–	3.7	–	10.5	11.8	–

loss of the supported chromium catalyst to the weight loss of the support alone. The  $\alpha$  values calculated for ceria (comm.) and titania (comm.) supported chromia systems according to the above equation are shown in Table 1.

Thermogravimetric analysis (TGA) has also been used to compute the hydroxyl density and the thermal stability of the hydroxyl groups of the supports employed using Eqs. (1) and (2) [24] as the hydroxyl chemistry of the supports is said to extend a significant consequence

$$\sigma \text{ (OH content)} = \left\{ \frac{((WL_0 - WL_T)/100)}{17} \right\} \times 1000 \text{ mmol OH g}^{-1} \quad (1)$$

where  $WL_0$  is the percentage weight loss at 1573 K and  $WL_T$  the percentage weight loss at a

given temperature.

$$\sigma' \text{ (OH population)} = \left\{ \frac{\sigma \times 6.02 \times 10^{20}}{S_{\text{BET}} \times 10^{18}} \right\} \text{ mmol OH/nm}^2 \quad (2)$$

on the distribution of the chromium species [25,26].

The gross hydroxyl density values computed for ceria and titania supports at the maximum temperature of 1573 K are shown in Table 2. TG analysis was also

Table 2  
Gross hydroxyl population of CeO<sub>2</sub> and TiO<sub>2</sub> supports

Properties	CeO <sub>2</sub> (comm.)	TiO <sub>2</sub> (comm.)
Surface area, m <sup>2</sup> /g	17	15
Total weight loss, %	1.18	1.17
OH population, mM/nm <sup>2</sup> ( $\times 10^{11}$ )	2.45	2.80

Table 3  
Change in hydroxyl population of the supports as a function of temperature

Temperature (K)	Hydroxyl population ( $\sigma'$ ) OH mM/nm <sup>2</sup> ( $\times 10^{11}$ )	
	CeO <sub>2</sub> (comm.)	TiO <sub>2</sub> (comm.)
773	1.79	1.32
873	1.66	0.96
973	1.66	0.85
1073	1.45	0.82
1173	1.20	0.80
1273	0.37	0.75
1373	0.25	0.63
1473	0.14	0.23

used to calculate the variation of hydroxyl population of the commercial ceria and titania supports at various temperatures and the results are shown in Table 3.

TPR measurements have been carried out for ceria- and titania-supported samples. Acquisition of TPR profile for pure Cr<sub>2</sub>O<sub>3</sub> also was made for the reference purpose and is shown in Fig. 5(a). It shows only a broad and diffuse reduction pattern around 733 K with almost negligible consumption of H<sub>2</sub> for  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>. Since ceria support shows reduction pattern only above 973 K, TPR profiles for ceria has not been obtained. Titania support is reported to exhibit a reduction pattern above 873 K and moreover the recorded TPR profiles of titania-supported catalysts do not exhibit the peaks above 873 K and are not presented.

TPR profiles recorded for CrCe (comm.) samples of loading 2, 5 and 8 wt.% are shown in Fig. 5(b)–(d). The analysis of TPR profiles of CrCe 2, CrCe 5 and CrCe 8 (comm.) samples show two well separated peak maxima; the intense feature (Peak A) at 640 K and the weaker one (Peak B) at 725 K. The peak temperature and the intensity of peak maximum at 725 K

appears to be unvarying with chromia content though the H<sub>2</sub> consumption does vary with the chromia content. Peak maximum and the corresponding amount of H<sub>2</sub> consumption for CrCe and CrTi samples are given in Table 4, respectively. It has been observed that with the increase in chromia content the low temperature maximum of Peak A shifts towards higher temperature. The peak maximum observed for CrCe 2 is at 568 K, whereas for CrCe 5 and CrCe 8 the peak maximum have been observed at 619 and 640 K, respectively. Moreover, for the chromia content of 8 wt.%, a shoulder at 823 K begins to grow.

TPR investigations have been undertaken for CrTi 2 and CrTi 5 (comm.) and the profiles are shown in Fig. 6. It has been observed that the sample CrTi 2 exhibited a broad maximum around 591 K (Peak A) and the higher temperature maximum at 733 K (Peak B) is almost absent. On the other hand the TPR pattern of CrTi 5 consists of two peaks of less intense features; the first maximum shifting to 585 K and a broad maximum around 733 K.

## 4. Discussion

### 4.1. Evolved gas analysis

The EGA and DSC results agree with each other in that the evolution of peak corresponding to mass of 52 is due to the decomposition of bulk chromia. Moreover, it is known from the literature that the melting point of bulk chromia is 473 K. Consequently, it begins to decompose into Cr<sub>2</sub>O<sub>3</sub> and O<sub>2</sub> at 533 K [23]. The decomposition of bulk chromia can be found from the evolution of atomic and molecular oxygen species in the same temperature range between 473 and 543 K in EGA profile (Fig. 1) with the corresponding peaks

Table 4  
TPR and the respective hydrogen consumption values for supported chromia catalysts (commercial)

Sample	Peak A		Peak B	
	Temperature maximum (K)	H <sub>2</sub> consumption (mM/g)	Temperature maximum (K)	H <sub>2</sub> consumption (mM/g)
CrCe 2	568	–	722	0.149
CrCe 5	619	0.417	726	0.176
CrCe 8	640	1.109	725	0.096
CrTi 2	591	0.076	–	–
CrTi 5	585	0.064	733	–

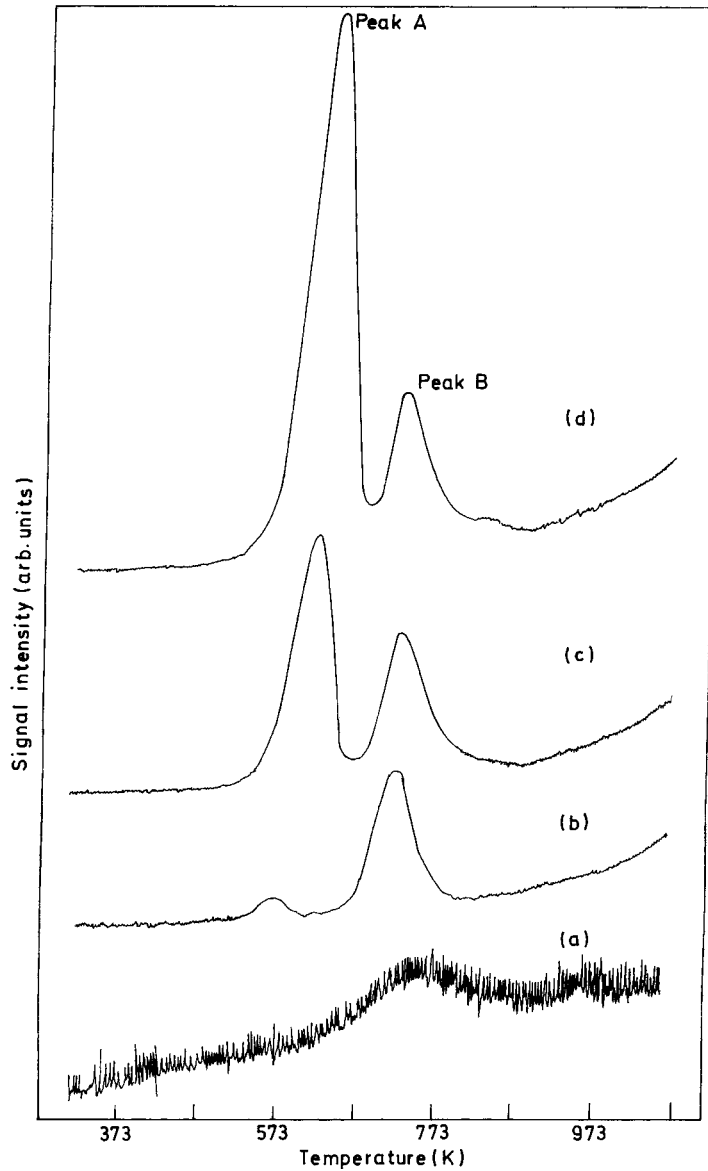


Fig. 5. TPR profiles of CrCe (comm.) (a) bulk  $\text{Cr}_2\text{O}_3$ , (b) CrCe 2, (c) CrCe 5, (d) CrCe 8.

observed at mass 16 and 32, respectively. In addition, the isotopic peaks of mass 52 confirm the presence of chromium. These observations together confirm the presence of  $\text{Cr}^+$  species in the gas phase due to the decomposition of bulk  $\text{CrO}_3$  exhibiting bulk like behaviour.

EGA shows a variety of species evolved during the temperature programmed study. Evolution of species corresponding to mass 44 can generally be ascribed to the desorption of adsorbed  $\text{CO}_2$  through several mechanisms leading to different carbonate-like species. In view of its basic character, ceria strongly adsorbs  $\text{CO}_2$

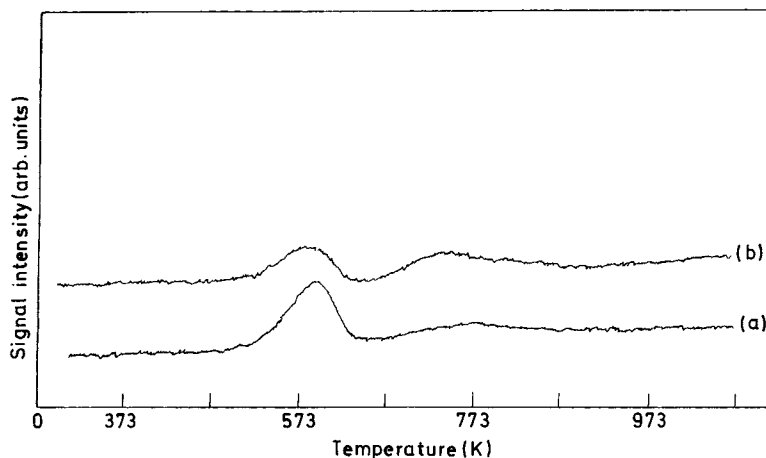


Fig. 6. TPR profiles of CrTi (comm.) (a) CrTi 2 (b) CrTi 5.

as carbonate entities on drying at 293 K under ambient conditions [27]. The analysis of EGA profile (Fig. 2(a)) shows that desorption of  $\text{CO}_2$  is gradual in  $\text{CeO}_2$  (comm.) support. On the other hand, CrCe 8 (comm.) sample show that at least two types of desorbed species can be distinguished; a strong chemisorption giving rise to surface species that need longer periods or higher temperatures to be desorbed and a weak chemisorption leading to surface species that are quickly removed at lower temperature. The fact that the desorption of  $\text{CO}_2$  is observed in stages at 513, 573 and 603 K, respectively, for fresh CrCe 8 (comm.), where as a gradual desorption of  $\text{CO}_2$  being observed in the above mentioned temperature range for pure ceria, suggests the existence of the surface heterogeneity in CrCe 8 (comm.) involving weak and strong chemisorption of  $\text{CO}_2$ . The strongly chemisorbed species can essentially be attributed to  $\text{Cr}_{\text{cus}}^{n+}-\text{O}_{\text{cus}}^{2-}$  (coordinatively unsaturated) couples, isolated cations and isolated anions [29]. Presence of  $\text{CO}_2$  can further be evidenced from the band at  $1383\text{ cm}^{-1}$  in FTIR spectrum [22].

The fact that desorption of  $\text{CO}_2$  is originated from coordinatively unsaturated chromium sites can further be comprehended from the similar pattern of evolution observed for species of mass 52, 16 and 44 for CrCe 8 (comm.) (Fig. 2(b)) under the temperature range studied. This fact has been further established by the spectroscopic studies carried out in our laboratory [28]. It is evident from the EGA profile of pure ceria that

considerable desorption of  $\text{CO}_2$  from its surface occurs only above 603 K. Consequently, it is concluded that the desorption of  $\text{CO}_2$  occurring at lower temperatures (513 and 573 K) are due to that adsorbed on chromium sites in various modes. The fact that  $\text{CO}_2$  is adsorbed over chromia crystallites is established by the band observed at  $1589\text{ cm}^{-1}$  is due to non-dissociatively adsorbed water and this in turn further substantiates the presence of coordinatively unsaturated chromium sites.

The EGA profile for the fresh sample of CrCe 8 (comm.) presented in Fig. 2(b) shows the evolution of species corresponding to mass of 52, which is not observed when the sample is calcined at 573 K prior to the analysis. This can be due to the interaction (anchoring) of chromia with ceria support on calcination [29]. The FTIR results and differential thermal analysis (DTA) carried out in our laboratory for a supported chromium sample (CrCe 10) presented by us elsewhere [22,29] further supports the formation of dehydrated surface due to anchoring on calcination at 573 K.

The fact that the fresh sample of CrCe 5 (comm.) catalyst did not show the evolution of species of mass 52 indicates that the bulk like behaviour is pronounced when the loading of chromia exceeds 5 wt.%.

Similar EGA profiles for mass 52 have been observed for CrTi samples having 5 and 10 wt.% of chromia. Absence of peak corresponding to mass of 52 in EGA profile for 0.4 wt.% of chromia loading suggests



that at lower loading of chromia the free or loosely bound chromia is absent.

EGA profile further indicates that the desorption of CO<sub>2</sub> occurring in two stages. This observation suggests the presence of different binding sites. The weakly adsorbed CO<sub>2</sub> undergoes desorption around 483 K and the strongly adsorbed above 573 K and thus pointing towards the surface heterogeneity [30]. Useful information can be gained from careful inspection of the peaks corresponding to mass of 44 and 52 from EGA profile shown in Fig. 3. The peak corresponding to mass of 44 evolves between 523 and 603 K, whereas the peak corresponding to mass of 52 evolves between 613 and 663 K. This shows that CO<sub>2</sub> gets desorbed from the bare support surface between 523 and 603 K and the bulk like behaviour is manifested due to free chromia crystallites accumulated beyond the dispersion capacity of the support. On the other hand, the similar examination carried out on CrTi 10 sample shows the evolution of the peak maximum corresponding to mass 44 and 52 simultaneously at 533 K (Fig. 4). This may indicate that surface is covered to the maximum by chromia phase and desorption of CO<sub>2</sub> would have originated from the surface of the chromia crystallites. Vuurman et al. [25] have observed on CrTi system that even at coverages approaching monolayer, not all the surface hydroxyl groups are removed. Thus it is not appropriate to conclude at this instant that the surface is completely covered under given chromia content, without having ample evidence from the other surface techniques.

## 4.2. Thermogravimetric analysis

### 4.2.1. Chemical reactivity at the interface

The TG analysis carried out under isothermal condition focuses on modification of the chromium precursor as a result of interaction with given supports. It can be inferred from the ratio that the lesser the  $\alpha$  value, greater will be the chemical reactivity at the interface.

Thus comparison of  $\alpha$  values for both ceria and titania-supported catalysts suggest that the interaction is greater in ceria-supported catalytic systems. The probable explanation that can be offered for the above observation is that the chemical reactivity at the interface not only depends on the hydroxyl density but also on the nature of the hydroxyl groups. Ceria

being basic in nature, the interaction between chromia (acidic) and the support becomes stronger than titania as support. Moreover, the relative change in  $\alpha$  values with regard to the chromia content for CrCe (comm.) samples show a value  $\leq 1$  till CrCe 4. With the further increase in chromia content the ratio turns out to be greater than 1; this suggests the formation of bulk chromia “aggregates” above 4 wt.% of chromia content.

This result, to some extent supports the view established through spectroscopic investigations [28] that above 5 wt.%, three-dimensional dispersion of chromia begins. As a result the chemical reactivity at the interface decreases leading to the decomposition of bulk like “aggregates”. Similar explanation holds for TiO<sub>2</sub> (comm.) supported chromia system. Comparatively a larger increase in relative change in  $\alpha$  values with regard to chromia content in TiO<sub>2</sub> supported system suggests the lesser degree of chemical reactivity at the chromia–titania interface. EG analysis carried out in the current investigation also indicates that peak corresponding to mass of 52 could be seen even at lower chromia loading on titania-supported chromia samples in relation to ceria-supported ones. This means the incapability of titania support to form anchored chromates through interaction, whereas the interaction could be manifested through diffusion of chromium ions Cr<sup>3+</sup> in to anatase lattice as already noted by FT Raman studies in the literature [31].

The assumption behind this analysis is that only dehydroxylation occurs within the temperature range studied. It is observed in general that on increasing the temperature, the hydroxyl population diminishes at a different rate, owing to the surface dehydroxylation. It should be noted that apart from hydroxyl density, the strength of hydroxyl groups are also significant in offering thermal stability to the chromate species anchored on to the support. Though initially at 773 K the hydroxyl content of TiO<sub>2</sub> (comm.) is comparable with CeO<sub>2</sub> (comm.), the hydroxyl density drops off suddenly in the beginning and decrease steadily with the increase in calcination temperature.

It is to be remembered that apart from the hydroxyl density and strength of hydroxyl groups, the nature of hydroxyl groups (acidic or basic) of the support also play a substantial role in anchoring. Ceria, being a basic oxide, and chromia being acidic in nature, the interaction between the active phase and the support

can very well be considered as an acid–base reaction [32]. Thus the degree of interaction in ceria-supported system is significantly enhanced. This renders ceria an enhanced ability to stabilise the chromia phase in its higher chemical state. The above fact is also established from scattering and spectroscopic studies reported elsewhere [22,28].

#### 4.3. Temperature programmed reduction

TPR study carried out in the present investigation is aimed at exploring the redox behaviour of the anchored chromia phase. TPR has been proved to be a technique of its own merits [33]. It has also been applied in the study of supported chromia catalysts [11–13]. TPR studies on ceria-supported chromia catalysts have not been made so far.

In the present work only a broad and diffuse reduction pattern (Fig 5(a)) with negligible consumption of hydrogen was observed around 723 K corresponding to  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>. However, it is reported by Zaki et al. [11] that neither  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> nor surface chromates attached to  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> were reducible at temperature below 1023 K. On the other hand, Curry-Hyde et al. [7] have observed the main peak at 523 K, a shoulder around 453 K and a weak one at 633 K. Recently, Grzybowska et al. [34] have noticed a similar reduction pattern consisting of temperature maxima at 463, 623 and 723 K, respectively. The basic assumption made in the reduction process is that Cr<sup>6+</sup> gets reduced to Cr<sup>3+</sup> and chromium species having valence state lower than +3 is not regarded as being formed, since calcination of all the samples were carried out in air containing moisture to some extent. It is a known fact that presence of water can oxidise Cr<sup>2+</sup> to Cr<sup>3+</sup> [35,36].

The TPR profiles of ceria-supported samples show the reduction pattern consisting of two well separated temperature maxima. Similar observations of two reduction maxima have already been reported by Niiyama et al. [37] and Jagannathan et al. [38] for alumina-supported chromia catalysts. There are also reports showing the presence of a single reduction peak for alumina-supported chromia samples [11,34].

TPR studies carried out in the present investigation agree well with the results obtained by Parlitz et al. [35]. They have also observed two peaks, one around 640 K (Peak A) and the other around 725 K (Peak B). Thus keeping all the observations in mind the

following explanation is considered reasonable. The sample of lower chromia content (CrCe 2) contains a major amount of chromate species (surface anchored chromate species) which are strongly bound to the support as a result of interaction between chromia and the support phase leading to the high temperature peak maximum (Peak B). The interaction resulting in the formation of Cr–O–X (X = support) bond is capable of modifying the redox properties of the surface chromate species. On the contrary, with the increase in chromia content, the pH at PZC (point zero charge) decreases resulting in the formation of polychromate species. Contact of these species with the moisture (calcination in air) leads to partial hydrolysis of the surface compounds followed by some aggregation of Cr<sup>6+</sup> species; these were more easily reduced than the isolated ones and caused the emergence of Peak A at lower temperature. Thus it can be stated that thermally stable chromate species (Peak B) are reoxidisable, whereas thermally unstable species (bulk like aggregates) are not reoxidisable after reduction or thermal decomposition. Since only a small amount of the sample (0.175 g) is being taken, the kinetic effect for the temperature shift may be ruled out.

The lower temperature maximum (Peak A) can be assigned to the formation of polychromates and the one at higher temperature side (Peak B) are due to surface anchored chromia species. The fact that the temperature maximum corresponding to Peak A shifts towards higher temperature with the consequent enhancement in hydrogen consumption, on increasing the chromia content (from 2 to 8 wt.%) suggests the corresponding increase in amount of the aggregates of Cr<sup>6+</sup> species. Analysis of Peak B indicates the relative enhancement in hydrogen consumption till 5 wt.% and further diminution for 8 wt.%. This observation clearly illustrates the formation of the badly dispersed chromia phase beyond the monolayer coverage. Analogous deduction has been made from NIR–DRS study [22] by monitoring the bands corresponding to free hydroxyl groups with the increase in chromia content and also from FTIR investigation by monitoring the band due to CO<sub>2</sub> adsorption [28]. Further EGA results of the present investigation also corroborates the above fact that CrCe 8 sample showed the evolution of species of mass 52 indicating the manifestation of bulk like behaviour.

Moreover, the emergence of a diffuse reduction pattern for CrCe 8 around 823 K indicates that probably Cr–Ce compound would have been formed. Further support can be deduced from the XRD patterns for CrCe 8 (comm.) calcined at 573, 973 and 1173 K, respectively, reported else where [28]. Thus from the present knowledge, formation of solid solution between Cr–Ce can be proposed. Further, it can be stated that Cr–Ce compound formation is facilitated at high chromia content; probably above the monolayer coverage.

The TPR results of the CrTi 2 (comm.) and CrTi 5 (comm.) (Fig. 6) show that the higher temperature peak maximum was almost negligible at 733 K thus advocating the predominant prevalence of bulk like “aggregates” rather than anchored chromate species. Furthermore, the shifting of Peak A (591 K) to lower temperature (585 K) with the increase in chromia content from 2 to 5 wt.% indicates the formation of polymeric species. The spectroscopic studies reported elsewhere [31] supports the above point that Cr<sup>6+</sup> species are not stable at higher temperatures on titania-supported samples. However, the possibility of diffusion of Cr<sup>3+</sup> ions into anatase lattice cannot be excluded and has also been substantiated using FT Raman spectroscopy [31]. Moreover, the catalytic evaluation of titania-supported catalysts carried out in our laboratory [28] does not exhibit the enhanced conversion due to the formation anchored chromate species, on depositing chromia over titania. This further confirms that the formation of anchored chromates on titania-supported chromia catalysts is relatively declined in comparison with ceria-supported samples. In addition, the factor  $\alpha$  calculated using TG measurements corroborates the above fact that the chemical reactivity at the interface is higher in ceria-supported samples than their titania counterpart. TPR investigations carried out on CrO<sub>x</sub>/TiO<sub>2</sub> system by Engweiler et al. [39] and Fountzoula et al. [40] corresponds to the pattern of two reduction maxima; the lower temperature maximum (Peak A) to be around 575 and 633 K and the higher temperature maximum around 680 and 733 K, respectively. The divergence in the reports on TPR peak maxima observed by different authors is due to the difference in the sample compositions and in the experimental conditions as well [35].

## 5. Conclusions

From the above investigation the following conclusions can be drawn:

1. EG analysis of fresh sample in general shows that at higher chromia content the bulk like behaviour is manifested. On the other hand for calcined samples bulk like behaviour is not observed. This indicates the formation of anchored chromia species. The desorption of CO<sub>2</sub> in multistages indicate in general that the surface is heterogeneous with respect coordinative environments. EGA reveals that CO<sub>2</sub> gets adsorbed on to coordinatively unsaturated chromium sites.
2. TG analysis under isothermal conditions suggests that the interaction is greater in ceria-supported catalytic systems. Though both ceria (comm.) and titania (comm.) as supports have comparable hydroxyl density, the chemical reactivity at the interface is significantly pronounced on the ceria-supported system due to the basic nature of the hydroxyl groups. It is observed from TG studies that the nature, population and strength of the hydroxyl groups are the determining factors for the effective interaction between active chromia phase and the support phase under severe operating conditions.
3. TPR of CrCe catalysts show the stabilisation of two kinds of species on the support; the first type (Peak B) being thermally stable chromate species which are reoxidisable, and the second type (Peak A) is thermally unstable species (bulk like aggregates) which are not reoxidisable after reduction or thermal decomposition. TPR data suggests the formation of solid solution between chromia and ceria for CrCe 8. Further, it can be stated that Cr–Ce compound formation is facilitated at high chromia content; probably above the monolayer coverage.
4. TPR of CrTi (comm.) catalysts advocates the predominant prevalence of bulk like aggregates rather than anchored chromate species. Further, with the increase in chromia content the formation of polymeric species have been observed. The formation of anchored chromates on titania (comm.) supported chromia catalysts is relatively less in comparison with ceria (comm.) supported samples. Thus the knowledge of the chemical stability of these species

would be helpful in accomplishing the true picture of activation process of these systems in the catalytic studies.

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