Abstract
The present investigation comprises of an attempt to investigate the titania supported chromia catalysts using X-ray diffraction measurements (XRD), evolved gas analysis (EGA), FT infrared spectroscopy (FTIR) and FT-Raman spectroscopic techniques with catalytic evaluation by dehydrogenation of cyclohexane. Evolved Gas Analysis shows a modified decomposition pattern than that of bulk chromia and presence of surface heterogeneity owing to the modified surface anchored chromia species formed as a result of interaction between chromia and titania. Above 773 K, Cr$^{6+}$ is not stable over TiO$_2$ surface and the reduction of the Cr$^{6+}$ to intermediate chemical states take place. XRD investigations illustrate the significance of X-ray source in examining supported chromia catalysts to study the morphological modifications of the active phase when crystalline supports are employed. FT Raman spectra reveals that on calcining the sample at 573 K, for 2 hours, the chromia phase assumes a monomerically anchored molecular state. Longer calcination time (6 hours) at the same temperature, leads to the diffusion of insitu formed Cr$^{3+}$ ions into the anatase lattice. On calcination at 973 K for 6 hours, amorphous chromia phase is no more stable on TiO$_2$ support resulting in agglomeration leading to the germination of microcrystalline $\alpha$–Cr$_2$O$_3$. Evaluation of catalytic performance of above catalysts by dehydrogenation of cyclohexane confirms the fact that diffusion of part of Cr$^{3+}$ species into the bulk of anatase phase occurs under reaction conditions.

Introduction
Supported chromia systems find their applications in polymerisation reactions and many catalysted reactions such as dehydrogenation of alkanes, dehydrocyclisation, catalytic reforming, hydrodesulphurisation and partial oxidation of hydrocarbons [1]. Despite the extensive physico-chemical studies carried out over these systems for the past three decades, the comprehension of the surface structures of chromium oxide species (CrO$_x$) stabilised on various supports and of the true nature of these species in various catalytic processes is still a matter of debate [1-13]. Recently we have made an attempt to investigate the supported chromia systems in our laboratory and are reported elsewhere [14-17].

In the recent years TiO$_2$ supported systems have drawn the attention of many scientists because of the possible strong metal support (SMSI) [16], oxide-oxide (OOI) interactions and also due to their potential applications as environmental catalysts [10]. Its catalytic properties were examined for the selective catalytic reduction of NO$_x$ [10]. Thus it is realised that the activity and the selectivity behaviour of these catalysts towards SCR of NO$_x$ with NH$_3$ are influenced by the morphology (amorphous or crystalline) of the active phase [18]. The morphological property of the active chromia phase is directly controlled by the support matrix on which chromia is coated through anchoring process.

Thus the identification of the morphology of the active phases in supported chromium oxide systems is significant, in gaining a deeper insight into the mechanism by which the substrate is activated. X-ray diffraction analysis plays a significant part in identifying the crystalline phases of both the support and the active component of the supported oxide catalysts. When chromium oxide is supported on another amorphous oxide such as SiO$_2$, ZrO$_2$ of high surface area, the identification of the active phase (if crystalline) using XRD will be relatively easier, as the diffraction pattern of the support display less intense features compared to the active phase.
the contrary, when crystalline supports are employed, the less intense features relating to chromia phases such as pure CrO_3 and Cr_2O_3 are often masked due to the heavy scattering exhibited by the support phase. As a result chromia related phases find less prominence in the XRD patterns. This has been the case with the diffractometric studies carried out on the supported chromia systems having crystalline supports using Co Kα and Cu Kα as X-ray sources for structural investigations. The absence of chromia related phases in the diffraction pattern of the supported chromia systems even at higher loadings can often been misconstrued as chromia phase stabilised in its amorphous form. The possible explanations accessible so far in the literature for the absence of chromia related phases are that they are highly dispersed or amorphous in nature. This suggests the need of an appropriate X-ray source that displays enhanced features of the active chromia phase, while exhibiting alleviated reflections from the crystalline support in order to realise a lucid picture on surface properties of chromia phase.

In the present study we endeavour to compare the appropriateness of Co, and Cr Kα as X-ray source, in investigating the titania supported chromia systems for the first time. The decomposition behavior of titania supported chromia catalysts has been studied using evolved gas analysis (EGA) technique with the aim of determining the extent of active phase-support interaction and to follow the desorption pattern of surface species. The extreme sensitivity and resolution of this technique makes it useful to study the nature of evolving species during the decomposition of solid oxides. [12,7]. It is able to trace even the species having ion current as low as 10^-14 A [19]. FT Raman technique is also employed in the present work to study the effect of thermal treatments on the molecular structure and the chemical states of the supported metal oxide phase. Raman Spectra is a powerful technique to study the molecular structure, as each molecular state possesses a unique vibrational spectrum related to its structure [20]. The inherent sensitivity limits of XRD forbid the identification of microcrystalline or amorphous phases whereas Raman scattering is competent enough to be substituted for XRD in tracing even microcrystalline phases of particle size lesser than 40 Å. The present investigation is essentially directed towards further verifying the validity of the structural and thermoanalytical investigations made by catalytic evaluation of the above catalyst by conducting dehydrogenation of cyclehexane as a model reaction.

**Experimental**

**Catalyst preparation**

The catalysts of various chromia loading ranging from 0.4 to 16 wt.% of chromia were prepared by impregnation method using commercial TiO_2 (Baker analysed) as support and aqueous CrO_3 as precursor. The impregnated catalysts were dried at 393 K for 12 hours and calcined in an atmosphere of air at various temperatures. The dried samples will be hereafter referred to as the “fresh” catalysts. The titania supported chromia catalysts prepared will be denoted as CrTi X where X is the loading expressed in weight percent of chromia (CrO_3).

**Chemical analysis**

The chemical analysis of Cr^{6+} was carried out based on the property that water removes CrO_3 from the support [2]. The estimation was carried out spectrophotometrically at λ_{max} of 350 nm; this is reported to be a highly suitable method for determining chromium bound to the support in +6 oxidation state [21]. To complement with the above technique inductively coupled plasma (ICP) analysis was also carried out to determine chromia loading.

**X-ray diffraction (XRD)**

X-ray diffraction measurements were carried out on a Rigaku, miniflex diffractometer in the range 5-90 deg/min (chart speed 20 mm/min) using Cr Kα and Co Kα radiations for bulk CrO_3, Cr_2O_3, TiO_2 and for supported chromia catalyst samples of various loading and at different calcination temperatures.

**Evolved gas analysis (EGA)**

The temperature-programmed study was carried out for fresh catalysts between 323-673 K by monitoring the evolved gases with mass spectrometric analyser (Balzers GAM 442 gas analyser) at a scanning rate of 10 deg/cycle. Prior to recording EGA profiles of the samples the system was baked at 358 K for 4 hours and cooled to room temperature.

**FTIR spectroscopy**

An FTIR spectrum was recorded on Bruker IFS
66V FTIR Spectrometer for sample containing 5 wt.% of chromia loading calcined at 773 K in air using KBr pellets.

**FT Raman spectroscopy**

FT Raman spectral analysis was carried out for TiO2 supported chromia samples using Raman module (Model FRA 106) having YAG laser source attached to the Bruker IFS 66V FTIR Spectrometer, delivering 1-200 mW incident radiation measured at the sample.

**Catalytic studies**

**Reactor system**

Catalytic evaluation was carried out by dehydrogenation of cyclohexane using a glass reactor by charging 3.5 g of catalyst. Dehydrogenation was conducted under vapour phase conditions between 723 and 753 K and at varying flow rates of cyclohexane. Flow rates were administered through infusion pump at 2.5 to 10 mL/hr. The temperature in the reactor was maintained and monitored using a chromel alumel thermocouple connected to temperature controller. Initially the reaction was allowed to progress for 10 min, till the steady state is attained. The reaction was then allowed to continue for 30 min and the product was recovered in a collector placed in an ice-cold waterbath. In order to monitor the evolution of gaseous hydrogen at equal intervals, the outlet of the collector was coupled with the gas burette. Further, the activation of the catalysts after each catalytic run was carried out in an atmosphere of dry oxygen at 773 K for 1.5 hours.

**Product analysis**

The dehydrogenation products were identified using Gas chromatography. The oven temperature of the same was maintained to be at 338 K. The injector and detector temperatures were regulated at 413 K.

**Results and discussion**

**Evolved gas analysis**

The evolved gas analysis pattern of bulk CrO3 has been recorded and the profile is shown in Fig. 1. The analysis of the thermal decomposition behaviour of pure chromia (bulk) shows the peak observed between 473–543 K corresponding to mass 52 and is assigned to chromium ions detected as Cr⁺ due to the decomposition of CrO₃. This observation can be further substantiated by the evolution of isotopic peaks of mass 50, 53, 54 along with 52 the mass of elemental chromium. It is also known that the melting point of bulk chromia is 474 K. Consequently, it begins to decompose into Cr₂O₃ and O₂ at 533 K [22]. The DSC study carried out in our laboratory for bulk CrO₃ shows an exothermic peak at 474 K corresponding to the melting point of CrO₃ and is in accordance with the literature [2]. Additional support for the decomposition of bulk chromia can be found from the evolution of atomic and molecular oxygen species in the same temperature range between 474–543 K (Fig. 1) with the corresponding peaks observed at mass 16 and 32 respectively. These observations further corroborate the presence of Cr⁺ species in the gas phase due to the decomposition of bulk CrO₃. The detection of mass 18 over the entire temperature range, with diffuse peaks at 373 K and 533 K, is due to the moisture present in the system. This indicates that desorption of physisorbed water occurs at 373, as chromia is hygroscopic in nature. Desorption of water can also be attributed to the surface dehydroxylation occurring at higher temperature.

Evolved gas analysis has been made for samples containing 0.4, 1.8 and 5 wt.% of chromia loadings. The EGA profiles of chromia loading 1.8 and 5 wt.% have been found to be identical with respect to the nature of species evolved as a function of temperature. The EGA profile for 2.7 wt.% of chromia content is shown in Fig. 2. The EGA profile for TiO₂ supported chromia catalysts showed the pattern corresponding to m/e at 52, 44 and 18. The peak at m/e 52 is due to thermal desorption of chromium under vacuum and is originating from surface chromia species (CrOₓ) on samples containing 1.8, 2.7 wt.% of chromia loading. Moreover, the peak at m/e 52 appeared at a higher temperatures compared to bulk chromia. Evolution of species corresponding to mass 44 is generally ascribed to the desorption of adsorbed CO₂. The adsorption of CO₂ is from the atmosphere, through several mechanisms leading to different carbonate-like species, as the sample has been dried in air at 393 K for over night. CO₂ desorption occurs in two stages at 513 K and above 573 K respectively. EGA profile for the species at m/e 18 evolving between 373 and 473 K is attributed to water. The pattern shown in Figure 1 for the commercial TiO₂ (Baker analysed) showed the species corresponding to m/e at 44, 18 due to the desorption of CO₂, H₂ and
Desorption of water had a broad maximum between 413-513 K. Rapid increase in the desorption of CO₂ can be seen above 573 K. As expected, there is no peak corresponding to m/e 52.

The EGA profiles show that when CrO₃ is supported on TiO₂ the peak at m/e 52 starts appearing.

![Fig. 1. Evolved gas profiles of (a, b and c) Pure CrO₃ (d) TiO₂ (Baker analysed).](image)

![Fig. 2. Evolved gas profiles of commercial CrTi 5 wt.% of chromia.](image)
above 593 K, which is higher than that for bulk chromia. This difference in decomposition behaviour can be explained on the basis of dispersion or anchoring of CrO$_3$ on to the support surface. Upon heating, the physisorbed water molecules on the support and around chromia phase are removed, which is evidenced by the species at m/e 18 evolving around 403 K shown in Fig. 2. The *insitu* formed dehydrated chromia species (CrO$_x$) do not decompose into O$_2$ and Cr$_2$O$_3$ (like bulk CrO$_3$), but are anchored by an esterification reaction with the hydroxyl groups of the inorganic oxide, resulting in the formation of stable surface chromia species (CrO$_x$). Hence, compared to bulk CrO$_3$ higher temperature of calcination is needed to increase the mobility of CrO$_3$ on the support leading to the formation of Cr$_2$O$_3$ as a result of decomposition:

$$2\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + \frac{1}{2}\text{O}_2$$

The interaction of the chromia species (CrO$_x$) with the oxide support surface through esterification reaction is further supported by the shift in Raman band (section Raman spectroscopy) from 963 cm$^{-1}$ to 972 cm$^{-1}$ [1]. Absence of peak in EGA profile at m/e 52 for 0.4 wt.% of chromia loading suggests that at lower loading of chromia the free or loosely bound chromia is absent.

The desorption of CO$_2$ occurring in two stages can be due to the presence of different binding sites. The weakly adsorbed CO$_2$ undergoes desorption around 483 K and the strongly adsorbed above 573 K and thus displaying the surface heterogeneity [23]. The strongly chemisorbed species can essentially be attributed to Cr$^{m+}$–O$^{2-}$ ( coordinatively unsaturated) couples, isolated cations and isolated anions [23].

### X-ray diffraction

The XRD patterns recorded for pure CrO$_3$ and Cr$_2$O$_3$, and TiO$_2$ using Co K$_{\alpha}$ and Cr K$_{\alpha}$ are shown in Figs. 3 and 4 respectively, in order to compare the intensities of the peaks. The expediency in using Cr K$_{\alpha}$ for the titania supported chromia catalysts can be justified from the intense diffraction features observed for chromia phase (CrO$_3$ and Cr$_2$O$_3$) with the broad and diminished features of titania (TiO$_2$) phase. This removes the obstruction in locating the diffraction patterns of less intense chromia related phases, as is normally perceived with Cu and Co K$_{\alpha}$ sources. The less prominence of chromia related phases could be ascribed to the low scattering efficiency with respect to Co and Cu K$_{\alpha}$ sources towards chromia phases. The diffraction patterns obtained with Co K$_{\alpha}$ for CrCe catalysts showed the evolution of chromia related phases only around 16 wt.%. This would possibly lead to the wrong end of the stick resulting in incorrect deductions on the monolayer coverage. Thus the above facts suggest that Cr K$_{\alpha}$ would be a better substitute for studying the supported chromia catalysts containing catalytic amount of chromia coated on the support. It is the first instance in the literature that Cr K$_{\alpha}$ has been employed for studying supported chromia systems.

![XRD patterns](image-url)
The effect of calcination has also been studied for CrTi 5 (comm.) CrTi 8 (comm.) at 573 K and under the reaction conditions (773 K). The XRD pattern (using Cr K$_\alpha$) corresponding to CrTi 8 as a function of calcination temperature is shown in Fig. 5. It is observed that chromia phase could not be traced even with the chromia loading of 8 wt.% under the above-mentioned calcination temperatures.

From the above observations it can generally be concluded that TiO$_2$ supported chromia systems exhibit enhanced ability of stabilising the amorphous chromia phase even at chromia loading of 8 wt.% on TiO$_2$ (comm.) support [10]. Although it seems reasonable to conclude from the above results that titania supported samples have more morphological control over the active chromia phase in relation to ceria supported samples, the above conclusion is realised to be only partly true. In order to obtain a comprehensive picture of the morphological properties of the anchored chromia species (CrO$_x$), further evaluation of the samples by Raman spectroscopy has been carried out as it is capable of tracing even X-ray amorphous.

**FTIR spectroscopy**

The FTIR spectra obtained for titania samples containing chromia loading of 5 wt.% calcined at 773 K for 6 hours is shown in Fig. 6. The pattern showing a broad band at 1021 cm$^{-1}$ with the shoulder around 980 cm$^{-1}$ in FTIR is due to the stretching mode of Cr$^v$=O species on the surface indicating the stabilisation of intermediate chemical states of chromium [24]. Further the absence of band at 907 cm$^{-1}$ indicates that Cr$^{6+}$ is not stabilised over TiO$_2$ phase at higher temperature [24]. It would have got partly converted into its lower chemical states. Absorption below 990 cm$^{-1}$ arises from Cr=O stretching vibrations of several coordinatively saturated chromia species (CrO$_x$) on the surface of the titania support [18]. Bands between 1300-1600 cm$^{-1}$ region is owing to the adsorption of CO$_2$ on the surface as carbonate like species revealing the presence of residual CO$_2$ even at such a higher temperatures. The presence of water molecules adsorbed on the surface of supported chromium oxide can be deduced from the OH stretching modes corresponding to the broad band between 3400 and 3500 cm$^{-1}$ [25]. These observations corroborate the results from EG analysis for the presence of adsorbed CO$_2$ and H$_2$O moieties on the surface.

**Raman spectroscopy**

The advantage of Raman spectroscopic study is that chromia precursor (CrO$_3$) displays intense Raman bands between 800-1100 cm$^{-1}$ region and the support phase (TiO$_2$) shows strong Raman features due to anatase phase below 700 cm$^{-1}$. The Raman bands and the corresponding assignments for CrO$_3$
solid are shown in Fig. 7.

The FT Raman spectra recorded for CrTi 5 at various calcination temperatures are shown in Fig. 8 and the assignment of the bands are listed in Table 1. Sample A showed broad bands around 904 cm$^{-1}$ and 972 cm$^{-1}$ corresponding to symmetric stretching mode of (CrO$_3$) and that of (CrO$_2$) in polymeric chromium oxide on the surface. The bands exhibited by sample B at 893 cm$^{-1}$ and at 1037 cm$^{-1}$ are due to symmetric stretching mode of (CrO$_3$) on monomeric chromium oxide over TiO$_2$ phase. Strong Raman features of TiO$_2$ anatase phase alone are observed for sample C calcined for longer duration. The treatment at high temperatures (sample D) revealed emergence of a shoulder at 550 cm$^{-1}$ (owing to the chemical state of Cr$^{3+}$ in perfect octahedral coordination) over the surface indicating the formation of $\alpha$-Cr$_2$O$_3$.

The FT Raman spectra revealed the molecular structure of chromia species (CrO$_x$) on support phase at various calcination temperatures. The symmetric stretching modes of (CrO$_3$) and (CrO$_2$) observed at 904 cm$^{-1}$ and 972 cm$^{-1}$ as less intense, broad and diffused bands between 800-1100 cm$^{-1}$, manifests the presence of polymeric chromium oxide on the sup-
The appearance of the band at 972 cm$^{-1}$ (963 cm$^{-1}$ for isolated chromia species in aqueous chromium oxides) is due to the interaction of the chromia species (CrO$_x$) with the oxide support surface. The interaction between oxygen from CrO$_4^{2-}$ ion and the support surface will decrease the negative charge on the chromate ion thus resulting in shifting of Raman bands to higher frequencies with respect to the chromate ion in aqueous solution. The band at 904 cm$^{-1}$ corresponds to the surface chromia species (CrO$_x$) that are interacting with the surface hydroxyl of the support. The presence of (CrO$_2$) stre-
ching mode at 972 cm⁻¹ indicates the presence of trimeric or tetrameric species over the support [1].

For sample B the broad and diffuse bands centered at 893 cm⁻¹ and 1037 cm⁻¹ point to the presence of monomeric species indicating that under this condition, TiO₂ support phase can stabilise the chromium oxide species (CrOₓ) as Cr⁶⁺ in tetrahedral coordination. The bands at 893 cm⁻¹ and 1037 cm⁻¹ are due to splitting of the band at 887 cm⁻¹ owing to dehyd-ration [1].

The fact that sample C, does not show any chromium related bands corresponding to chromate like species (Cr₆⁺) and the absence of any shoulders at 550 cm⁻¹ on calcining for 6 hours at 573 K can be collectively attributed to the migration of Cr³⁺ in to the anatase lattice and also the possible stabilisation of amorphous Cr₂O₃. This indicates that the interaction of chromia with the TiO₂ support prevents the formation of crystalline Cr₂O₃ even at this longer calcination period. XRD results agree well with the above observations substantiating the absence of growth of crystalline Cr₂O₃ till 8 wt.% of chromia loading (Fig. 5). This being the case the question as to what would have happened to the state of chromia is still to be answered. Considering the ionic radii of Cr³⁺ (r = 0.755 Å) and Ti⁴⁺ in anatase (r = 0.745 Å) supports the view that the structure of anatase is permeable for entry by Cr³⁺ ions although it appears to be more difficult in comparison with the corresponding rutile powder [25-28]. Thus it is clear that apart from stabilisation of amorphous chromia phase leading to absence of chromia patterns, it is also possible that diffusion of Cr ions into the bulk can result in the absence of chromia related signatures in XRD and Raman spectroscopy with longer calcination time. If this deduction is true it should reflect in the catalytic performance of the catalysts, as anchored Cr³⁺ species are responsible for catalytic activity. Studying the effect of longer calcination time is significant in comprehending the behaviour of the catalyst under reaction conditions, which involve longer duration of high temperature exposure after number of catalytic cycles. Thus the validity of present supposition in the present study is further verified through catalytic evaluation of the catalysts.

The above study also verifies that XRD was unable to detect the chromia phase in sample B due to the inherent sensitivity limit to trace the presence of X-ray amorphous phase (< 40 Å) as well as due to diffusin of Cr³⁺ ions in to anatase lattice with longer calcination time. This observation illustrates the point, as to why in the previous literature reports chromia phase could not be traced using diffractometric studies.

The Raman spectra recorded for sample D comprises of the bands due to the support phase and a shoulder at 550 cm⁻¹ related to Cr⁵⁺ in octahedral coordination [1]. This suggests that X-ray amorphous phase is no more stable on TiO₂ phase at this temperature and the agglomeration has commenced leading to the germination of microcrystalline α-Cr₂O₃. XRD patterns do not display the evolution of peaks corresponding to α-Cr₂O₃ at 973 K (Fig. 5) as the inherent sensitivity limit of this technique does not permit the diffraction of crystallites of particle size below 40 Å. The point to be considered here is that even at this high calcination temperature the bulk behaviour is not completely manifested by the chromia phase and only microcrystalline chromia phase is observed over the support phase by Raman spectroscopy.

**Catalytic evaluation of Titania supported chromia systems**

Catalytic examination of TiO₂ supported chromia sample (CrTi 5) has been carried out using dehydrogenation of cyclohexane as a model reaction in order to comprehend the structure in the light of its catalytic performance. The study of catalytic activity for dehydrogenation of cyclohexane has also been
undertaken for bulk Cr$_2$O$_3$, TiO$_2$ (comm.) and CrTi 5 and the results are presented in Table 2. The reaction carried out with pure Cr$_2$O$_3$ showed a maximum conversion of about 22% at the maximum of reaction temperatures studied, with selectivity only towards cyclohexene. The maximum conversion of cyclohexane on TiO$_2$ (comm.) has been found to be 10%.

It can be seen from Table 2 that the catalytic activity (cyclohexane conversion) on both titania and titania supported chromia have little dependence on the temperature or flow rate. The conversion rates are always < 10% but the selectivity towards benzene is slightly higher for supported catalyst. The systems under investigation have negligible catalytic activity at < 723 K. Based on these observations it can be safely concluded that the catalyst surface is saturated (equilibrated) with the substrate and hence one does not observe dependence of catalytic activity on either temperature or flow rate.

The conversion levels of cyclohexane on CrTi 5 (comm.) sample are shown in Table 2. The conversion observed in the case of pure titania and CrTi 5 has been found to be of the same order (< 10%) irrespective of the flow rates and reaction temperatures, whereas a relative increase in the selectivity towards benzene formation at 753 K with both the flow rates under study has been observed. Thus the enhanced benzene selectivity and reduced side products formation propose that the catalytic activity of the titania supported chromia catalysts is neither due to the support nor due to Cr$_2$O$_3$. On the other hand the modified behaviour can be ascribed to the presence of surface anchored chromia species stabilised as a result of interaction with the support. These results also suggest the formation of relatively diminished side products probably owing to minimised thermal cracking reactions ascribed to the supported chromia phase than with the pure titania as support. The results of the reactions carried out with titania supported chromia sample presented in Table 2 exhibit a comparable conversion level (5-10%) and to some extent the similar selectivity pattern to that of pure titania support. In addition, the bulk chromia (unsupported) as catalyst show a conversion of about 22%, which is far greater than the titania supported chromia sample. These observations collectively indicate the fact that the catalytic activity is neither contributed by surface Cr$^{3+}$ species nor by bulk Cr$^{3+}$ species, rather the only contribution is from the titania surface. The decrease in the conversion can thus be understood in the light of Raman spectroscopic and XRD examination carried out in the present work that owing to the diffusion of a part of Cr$^{3+}$ species into the bulk of anatase phase with longer duration of calcination.

| Sample          | Flow rate | Reaction temperature, K | Cyclohexane conversion, (%) | Product Selectivity (%) |
|-----------------|-----------|-------------------------|-----------------------------|-------------------------|
|                 |           |                         |                             | Cyclohexene  | Benzene  |
| Cr$_2$O$_3$     | 2.5       | 723                     | 19                          | 84          | -        |
|                 | 2.5       | 753                     | 22                          | 66          | -        |
|                 | 5.0       | 723                     | -                           | -           | -        |
|                 | 5.0       | 753                     | 6                           | 33          | -        |
| TiO$_2$ (Comm.) | 2.5       | 723                     | 7.5                         | 37.0        | 20.5     |
|                 | 2.5       | 753                     | 9.0                         | 22.5        | 21.5     |
|                 | 5.0       | 723                     | 4.0                         | 43.5        | -        |
|                 | 5.0       | 753                     | 6.0                         | 28.5        | 26.0     |
| CrTi 5 (Comm.)  | 2.5       | 723                     | 6.0                         | 47.0        | -        |
|                 | 2.5       | 753                     | 10.5                        | 14.5        | 59.5     |
|                 | 5.0       | 723                     | 3.0                         | 34.0        | 28.0     |
|                 | 5.0       | 753                     | 7.0                         | 15.0        | 53.0     |

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Thus it is clear that the catalytic deactivation in titania supported chromia systems is not only due to the germination of $\alpha$–Cr$_2$O$_3$, but also due to the bulk diffusion of chromium ions. However, one cannot exclude the presence of anchored chromia species on titania supported catalysts resulting in the modification of selectivity patterns, (Table 2) though the activity remains comparable to that of pure support. The above result suggests that stabilisation of amorphous chromia over titania support is meaningful only under lower temperature above which deactivation readily takes place. Hence lower temperature activity measurements performed on these systems would be meaningful in characterising them [17].

Conclusions

From the foregoing the following inferences can be arrived at:

- Chromia phase is anchored on TiO$_2$ support with the formation of surface anchored chromia species which behaves different from the bulk chromia. The surface thus modified shows heterogeneity with respect to coordinative unsaturation.
- It is observed that employing Cr K$_{\alpha}$ as X-ray source would be indispensable to perceive the chromia phase when crystallline support is employed.
- Titania surface is not able to stabilize Cr$^{6+}$ above 773 K, and the reduction of the same to lower oxidation state takes place.
- At 573 K, the chromia phase assumes a monomerically anchored molecular state and for the sample calcined at 973 K amorphous chromia phase is no more stable on TiO$_2$ phase resulting in agglomeration leading to the germination of microcrystalline $\alpha$–Cr$_2$O$_3$.
- XRD could not detect the stabilisation of amorphous chromia phase under low temperature calcination of the samples, due to the inherent sensitivity limit and at longer calcination times due to diffusion of Cr$^{3+}$ ions into anatase lattice.
- Structural and catalytic evaluation of titania supported chromia system suggests that catalytic deactivation of is not only due to the germination of $\alpha$–Cr$_2$O$_3$, but also due to the bulk diffusion of chromium ions in to anatase lattice.

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References

1. F.D. Hardcasle and I.E. Wachs, J. Mol. Catal 46, (1988) 173.
2. J. P. Hogan, J. Polymer Sci. A-1, 8, (1970) 2637.
3. O. Glemser, U. Hauschild and F. Trupel, Z. anorg. allg. Chem. 277, (1954) 113.
4. M. A. Mosesman, J. Am. Chem. Soc., 76, (1954) 295.
5. C.S. Kim and S.I. Woo, J. Mol. Catal., 73, (1992) 249.
6. W. Hill and G. Ohlmann, React. Kinet. Catal. Lett., 38(2), (1989) 289.
7. V.J. Ruddick, P.W. Dyer, G. Bell, V.C. Gibson and J.P.S. Badyal, J.Phys.Chem. 100 (1996) 11062.
8. M. Del Arco, J. Catal. 113, (1988) 120.
9. K. Kohler, M. Maciejewski, H. Schneider and A. Baiker, J. Catal., 157, (1995) 301.
10. J. Engweiler, J. Nickl, A. Baiker, K. Kohler, C.W. Schlaper and A. Von Zelewsky, J. Catal., 145 (1994) 141.
11. B.M. Weckhuysen, I.E. Wachs and R.A. Schoonheydt, Chem. Rev., 96 (1996) 3327.
12. F. Cavani, M. Koutyrev, F. Trifiro, A. Bartolini, D. Ghisletti, R. Iezzi, A. Santucci and G. D. Pietro, J.Catal., 158 (1996) 236.
13. G. Ghiotti, A. Chiorino and F. Boccuzzi, Surf. Sci., 251/252 (1991) 1100.
14. R.P. Viswanath, P. Wilson, P. Madhusudhan Rao and A. Mahajabeen, Recent trends in catalysis,V. Murugesan, B. Arabindoo and M. Panalichamy (Eds), Narosa Publications, India, 1999, p 142.
15. R.P. Viswanath and P. Wilson Appl., Catal A: General 201 (2000) 23.
16. Wilson, P., and R.P. Viswanath (2002) Eurasian ChemTech Journal 4, 201 (2002).
17. Wilson, P., P. Madhusudhan Rao and R.P. Viswanath (2001) Thermochimica Acta 399 (2003) 109.
18. M. Schraml Marth, A. Wokaun, H.E. Curry-Hyde and A. Baiker, J. Catal., 133 (1992) 415.
19. J. Rouquerol, Thermochim. Acta., 300, (1997)
247.
20. M.A. Vuurman and I.E. Wachs, J. Phys. Chem., 96 (12), (1992) 5008.
21. S. Haukka, Analyst, 116 (1991) 1055.
22. M.A. Mosesman, J. Am. Chem. Soc. (1954) 76, 295.
23. Zacchina, C. Morterra, G. Ghiotti and E. Borello, J. Phys. Chem., 73, (1969) 1292.
24. U. Scharf, H. Schneider, A. Baiker and A. Wokaun, J. Catal. 145, (1994) 464.
25. P. Ratnasamy and J. Leonard., J. Phys. Chem., 76 (13), (1972) 1838.
26. A. Amorelli, J.C. Evans, C.C. Rowlands and T.A. Egerton, J. Chem. Soc., Faraday Trans. I, 83 (12), (1987) 3541.
27. M.I. Martin, V. Rives, L. Palmisano and M. Schiavello, J. Catal. 134, (1992) 434.
28. A. M. Venezia, L. Palmisano, M. Schiavello, M.I. Martin and V. Rives J. Catal 147 (1994) 115.

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