



Structural Properties and Catalytic Behaviour of CrO_x/TiO₂ Systems

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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, Cr⁶⁺ is not stable over TiO₂ surface and the reduction of the Cr⁶⁺ 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 *in situ* formed Cr³⁺ ions into the anatase lattice. On calcination at 973 K for 6 hours, amorphous chromia phase is no more stable on TiO₂ support resulting in agglomeration leading to the germination of microcrystalline α -Cr₂O₃. Evaluation of catalytic performance of above catalysts by dehydrogenation of cyclohexane confirms the fact that diffusion of part of Cr³⁺ species into the bulk of anatase phase occurs under reaction conditions.

Introduction

Supported chromia systems find their applications in polymerisation reactions and many catalysed 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 TiO₂ 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].

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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 NH₃ 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 SiO₂, ZrO₂ 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. On

the contrary, when crystalline supports are employed, the less intense features relating to chromia phases such as pure CrO₃ and Cr₂O₃ 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 K_α and Cu K_α 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 be 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 K_α 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

cyclohexane 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 TiO₂ (Baker analysed) as support and aqueous CrO₃ 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 (CrO₃).

Chemical analysis

The chemical analysis of Cr⁶⁺ was carried out based on the property that water removes CrO₃ 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 K_α and Co K_α radiations for bulk CrO₃, Cr₂O₃, TiO₂ 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 (CrO_x) 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

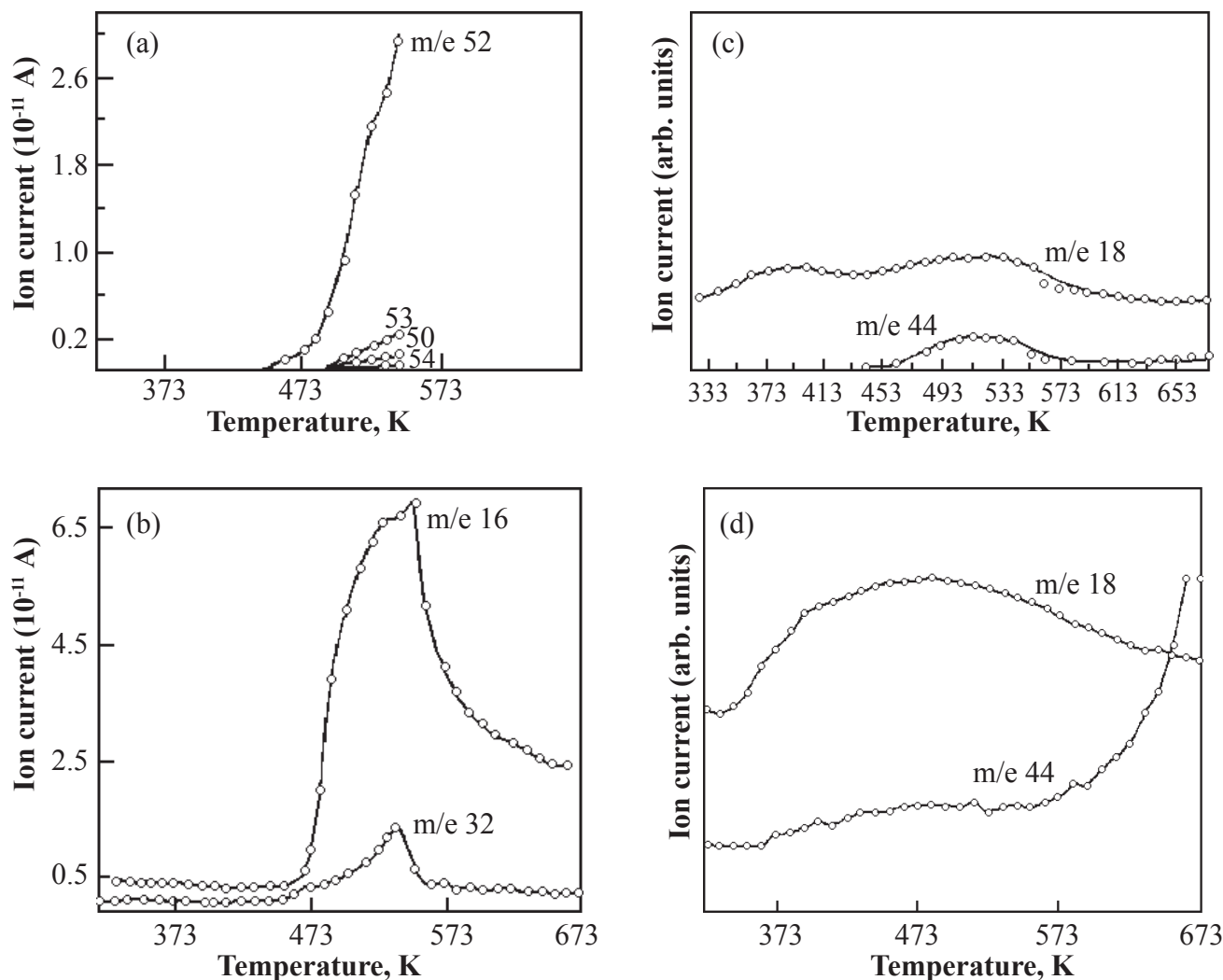


Fig. 1. Evolved gas profiles of (a, b and c) Pure CrO_3 (d) TiO_2 (Baker analysed).

O. Desorption of water had a broad maximum between 413-513 K. Rapid increase in the desorption of CO_2 can be seen above 573 K. As expected, there

is no peak corresponding to m/e 52.

The EGA profiles show that when CrO_3 is supported on TiO_2 the peak at m/e 52 starts appearing

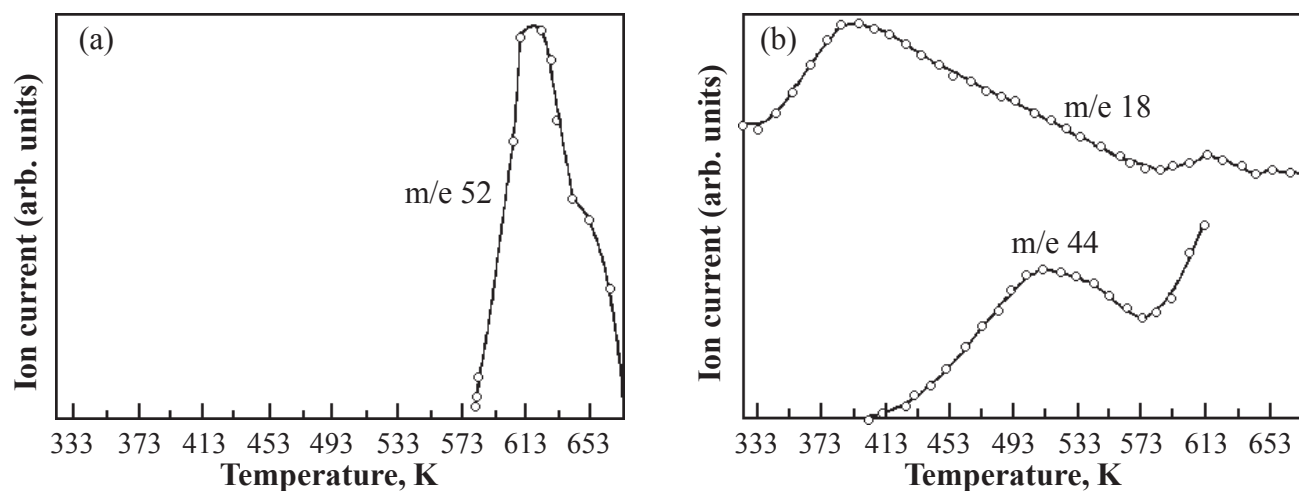
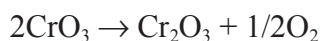


Fig. 2. Evolved gas profiles of commercial CrTi 5 wt.% of chromia.

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 *in situ* formed dehydrated chromia species (CrO_x) do not decompose into O_2 and Cr_2O_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_2O_3 as a result of decomposition:



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 $\text{Cr}^{\text{n+}}_{\text{cus}}-\text{O}^{2-}_{\text{cus}}$ (coordinatively unsaturated) couples, isolated cations and isolated anions [23].

X-ray diffraction

The XRD patterns recorded for pure CrO_3 and Cr_2O_3 and TiO_2 using Co K_α and Cr K_α are shown in Figs. 3 and 4 respectively, in order to compare the intensities of the peaks. The expediency in using Cr K_α for the titania supported chromia catalysts can be justified from the intense diffraction features observed for chromia phase (CrO_3 and Cr_2O_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_α sources. The less prominence of chromia related phases could be ascribed to the low scattering efficiency with respect to Co and Cu K_α sources towards chromia phases. The diffraction patterns obtained with Co K_α 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_α 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_α has been employed for studying supported chromia systems.

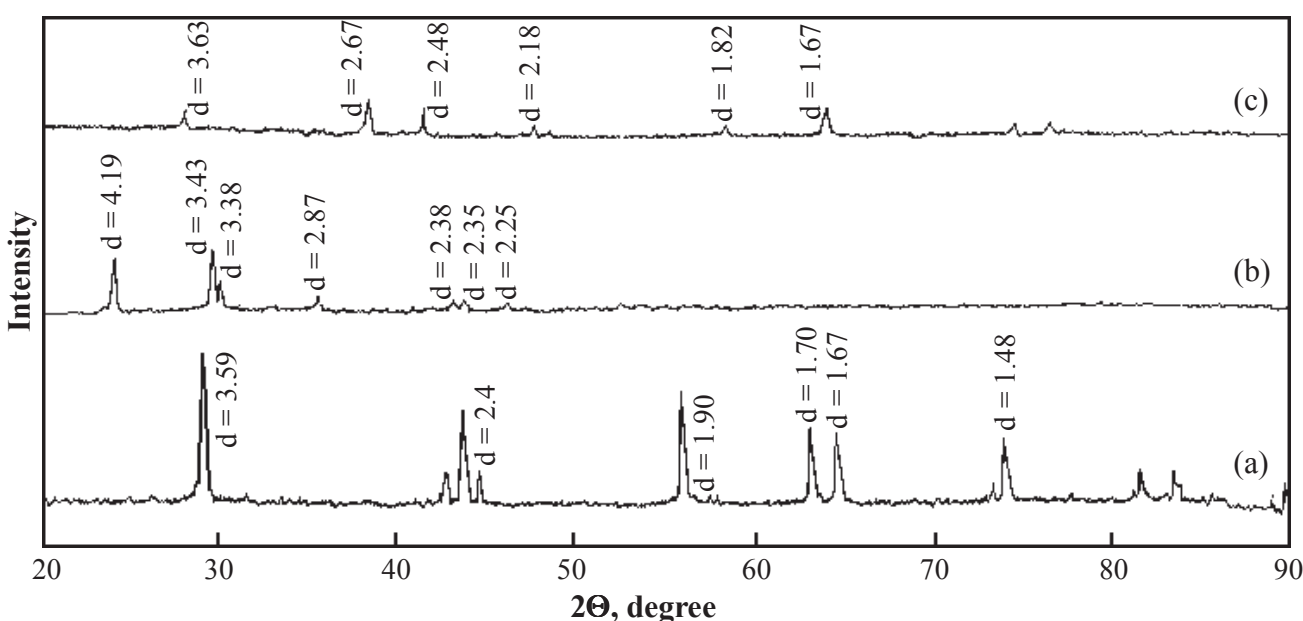


Fig. 3. XRD patterns of: a) Pure TiO_2 ; b) bulk CrO_3 ; c) Cr_2O_3 using Co K_α .

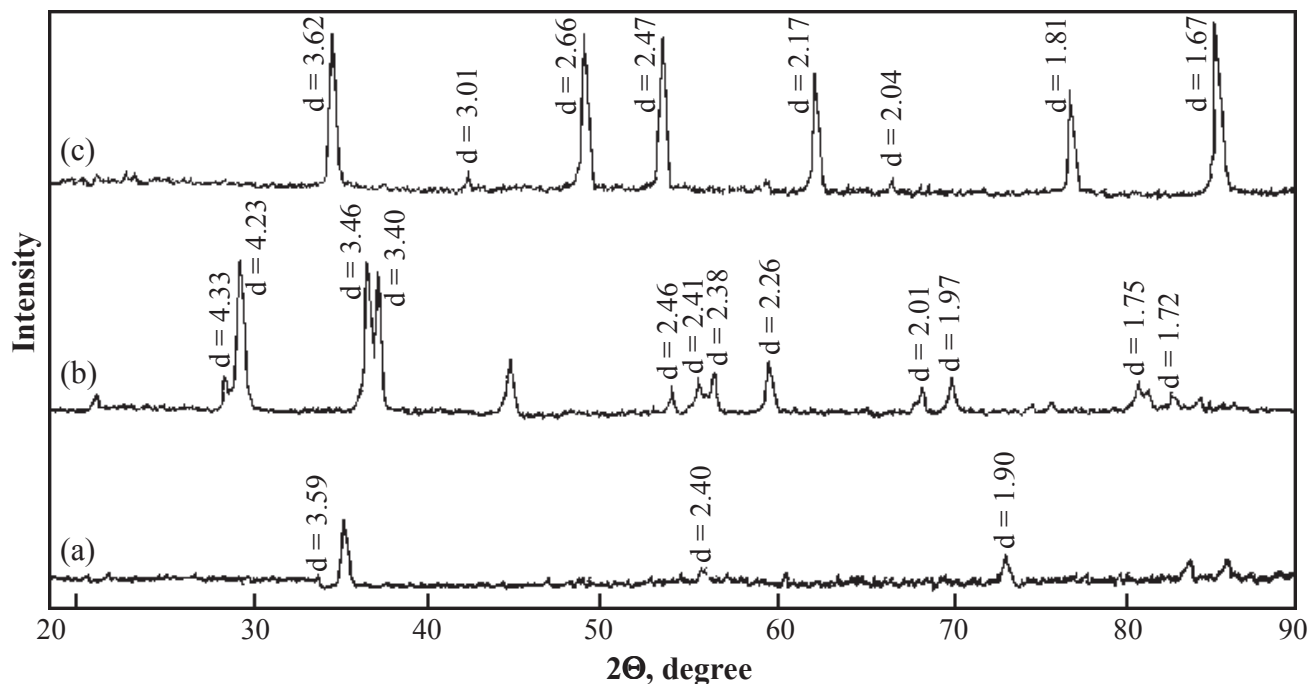


Fig. 4. XRD patterns of a) Pure TiO_2 b) bulk CrO_3 c) Cr_2O_3 using $\text{Cr K}\alpha$,

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 $\text{Cr K}\alpha$) 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 shoul-

der around 980 cm^{-1} in FTIR is due to the stretching mode of $\text{Cr}^{\text{V}}=\text{O}$ 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 $\text{Cr}=\text{O}$ stretching vibrations of several coordinatively saturated chromia species (CrO_x) on the surface of the titania support [18]. Bands between $1300\text{--}1600\text{ cm}^{-1}$ 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 $3400\text{ and }3500\text{ cm}^{-1}$ [25]. These observations corroborate the results from EG analysis for the presence of adsorbed CO_2 and H_2O moieties on the surface.

Raman spectroscopy

The advantage of Raman spectroscopic study is that chromia precursor (CrO_3) displays intense Raman bands between $800\text{--}1100\text{ cm}^{-1}$ 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

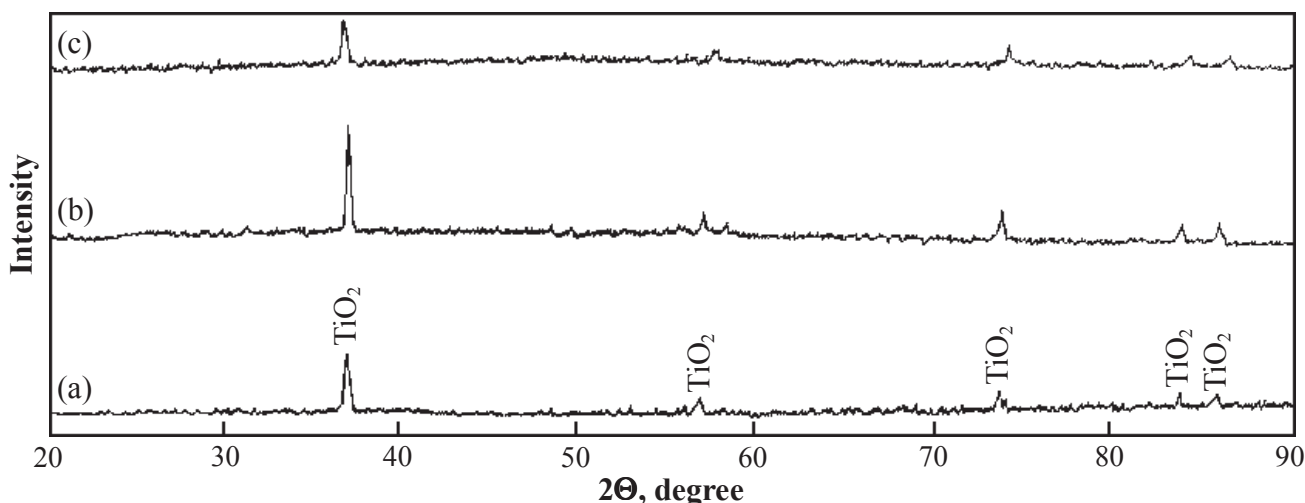


Fig. 5. XRD pattern of CrTi 8 as a function of calcination temperature: a) fresh; b) calcined at 773 K, 2h (air); c) calcined at 973 K, 2 hours (air).

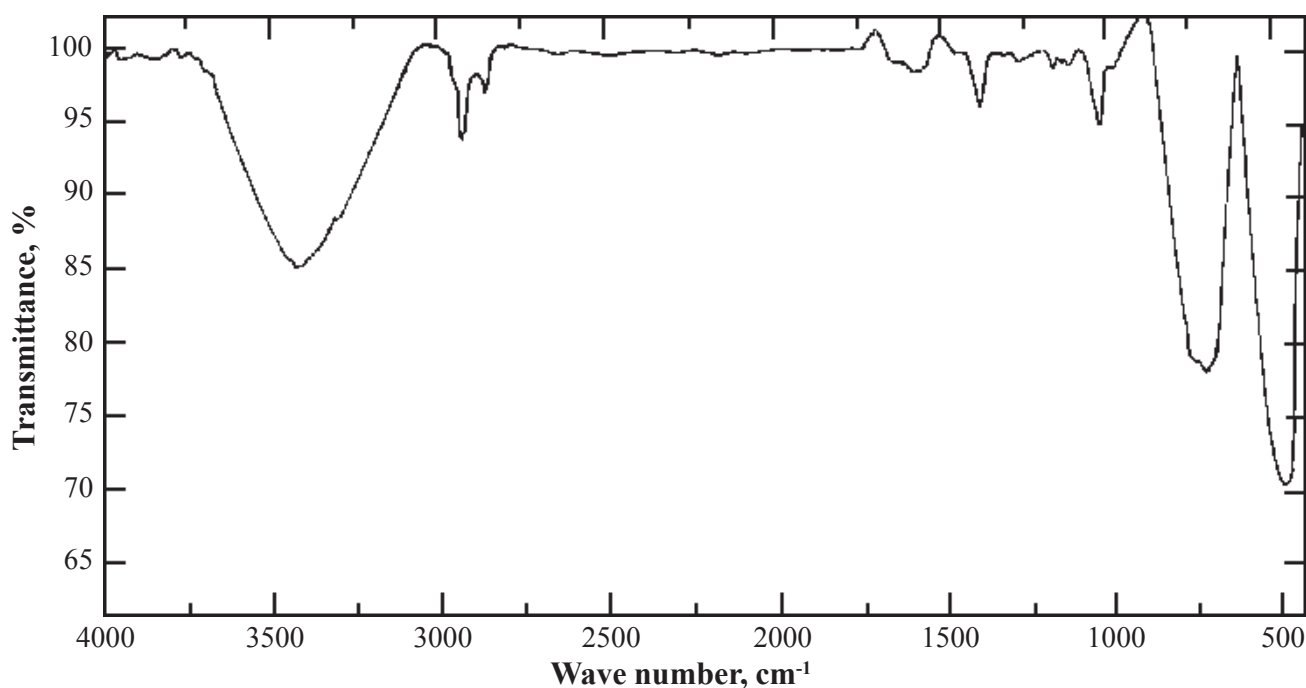


Fig. 6. FTIR spectrum of CrTi 5 calcined in air at 773 K for 2 hrs.

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 cal-

culated 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 $\alpha\text{-Cr}_2\text{O}_3$.

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-

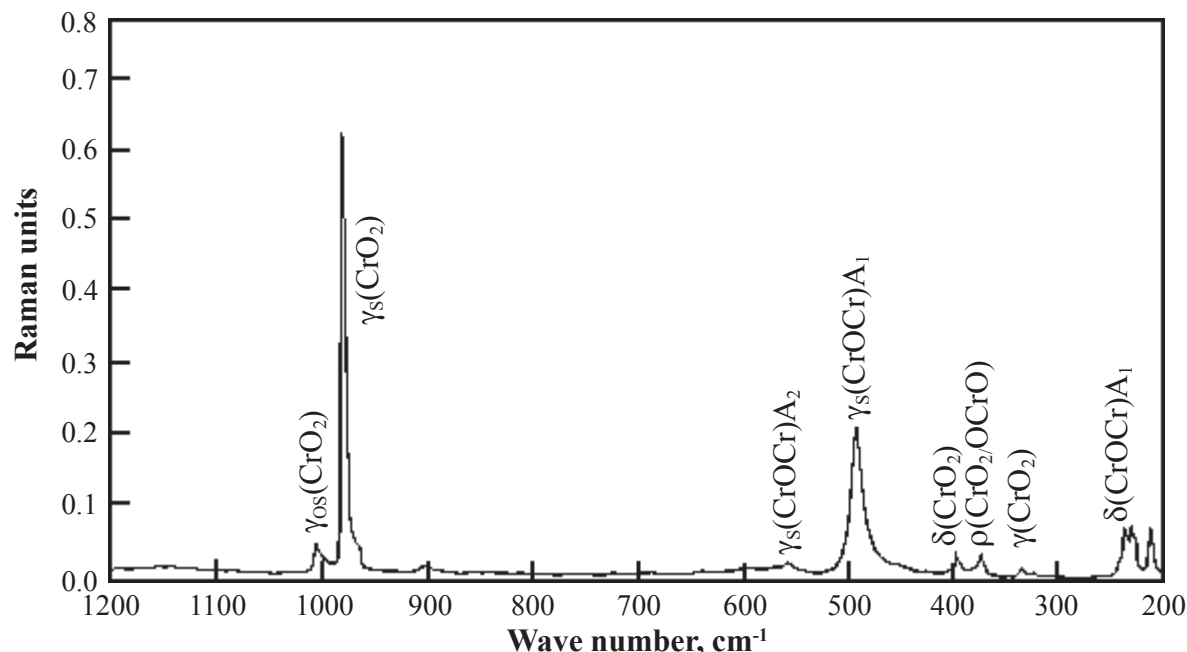


Fig. 7. FT Raman spectrum of pure CrO_3 solid (Dried).

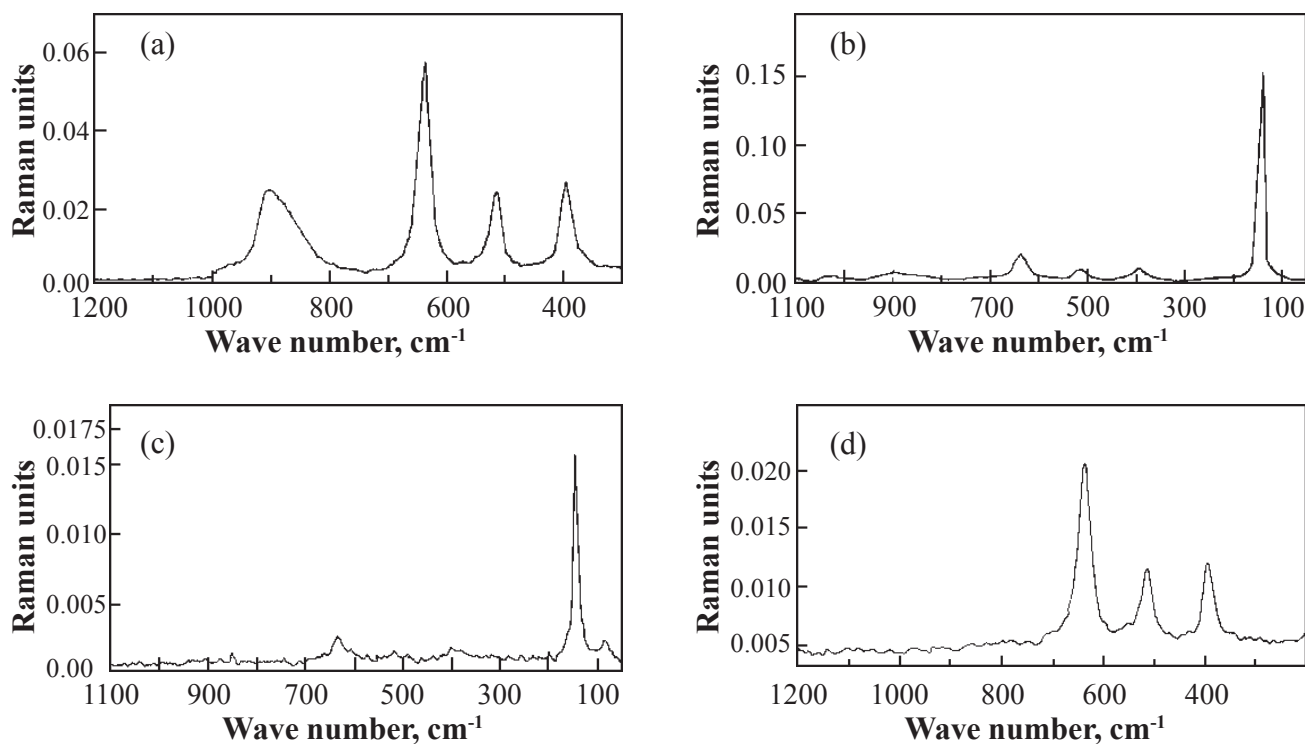


Fig. 8. FT Raman spectra of CrTi 5 at various calcination temperatures:
a) 473 K, 2 hours; b) at 573 K, 2 hours; c) at 573 K, 6 hours; d) at 973 K, 6 hours.

port at this temperature. 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) stret-

Table 1
Raman band assignments for CrTi 5 (comm.)

Code	Calcination conditions (in air)	Band positions	Assignments
A	473 K, 2 hrs	904, 972 cm^{-1} and anatase bands	Trimeric and tetrameric species
B	573 K, 2 hrs	893, 1037 cm^{-1} and anatase bands	Anchored monomeric species
C	573 K, 6 hrs	Only anatase bands	Diffusion of Cr^{3+} species into anatase lattice
D	973 K, 6 hrs	550 cm^{-1} and intense anatase bands	Microcrystalline Cr_2O_3 phase

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, TiO_2 support phase can stabilise the chromium oxide species (CrO_x) as Cr^{6+} 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 dehydration [1].

The fact that sample C, does not show any chromium related bands corresponding to chromate like species (Cr^{6+}) 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 Cr^{3+} in to the anatase lattice and also the possible stabilisation of amorphous Cr_2O_3 . This indicates that the interaction of chromia with the TiO_2 support prevents the formation of crystalline Cr_2O_3 even at this longer calcination period. XRD results agree well with the above observations substantiating the absence of growth of crystalline Cr_2O_3 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 Cr^{3+} ($r = 0.755 \text{ \AA}$) and Ti^{4+} in anatase ($r = 0.745 \text{ \AA}$) supports the view that the structure of anatase is permeable for entry by Cr^{3+} 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 Cr^{3+} 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 ($< 40 \text{ \AA}$) as well as due to diffusion of Cr^{3+} 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 Cr^{3+} in octahedral coordination [1]. This suggests that X-ray amorphous phase is no more stable on TiO_2 phase at this temperature and the agglomeration has commenced leading to the germination of microcrystalline $\alpha\text{-Cr}_2\text{O}_3$. XRD patterns do not display the evolution of peaks corresponding to $\alpha\text{-Cr}_2\text{O}_3$ 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 \AA . 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 TiO_2 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_2O_3 , TiO_2 (comm.) and CrTi 5 and the results are presented in Table 2. The reaction carried out with pure Cr_2O_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_2O_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.

Table 2
Dehydrogenation of cyclohexane with Cr_2O_3 , TiO_2 and CrTi 5 catalysts

Sample	Flow rate	Reaction temperature, K	Cyclohexane conversion, (%)	Product Selectivity (%)	
				Cyclohexene	Benzene
Cr_2O_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

Thus it is clear that the catalytic deactivation in titania supported chromia systems is not only due to the germination of α -Cr₂O₃, 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 TiO₂ 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_α as X-ray source would be indispensable to perceive the chromia phase when crystalline support is employed.
- Titania surface is not able to stabilize Cr⁶⁺ 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 TiO₂ phase resulting in agglomeration leading to the germination of microcrystalline α -Cr₂O₃.
- 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 Cr³⁺ 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 α -Cr₂O₃, but also due to the bulk diffusion of chromium ions in to anatase lattice.

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