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Characterization of Surface Chromia Species on CrO_x/TiO_2 Catalysts

P. Wilson[1] and R.P. Viswanath[2*]

[1]Blechner Center for Industrial Catalysis and process Development, Department of Chemical Engineering, Ben-Gurion University of the Negev, Beersheva, Israel

[2]Department of Chemistry, Indian Institute of Technology (Madras), Chennai – 600 036, India

Abstract

Titania supported chromia catalysts have been employed for selective catalytic reduction (SCR) process because of their higher activity and selectivity. The catalytic activity of the titania supported chromia system is owing to the stabilization of the anchored chromia species having multiple chemical and molecular states on the surface**.** In the present work an attempt has been made to prepare titania supported chromia catalysts, from $TiCl_4$ and CrO_3 as precursors for the support and active phase respectively. Characterization of the catalysts have been made using FTIR spectroscopy and thermo analytical techniques such as thermogravimetric analysis (TGA), evolved gas analysis (EGA) and temperature programmed reduction (TPR). The EGA, TGA and FTIR results indicate that the surface hydroxyl groups of TiO_2 (gel) has an influence on the chemical state of the chromium. Due to the surface anchoring, Cr^{+5} species have been detected on the surface of the fresh catalyst which decomposes to lower valence state on calcination. EGA results indicate that Cr^{+3} species having higher degree of coordinatively unsaturated centers is stabilized by gel titania as support. EG analysis and FTIR studies illustrate the coverage of the surface with similar type of sites at 10 wt.% chromia loading. TPR studies demonstrate the presence different kinds of surface chromia species with respect to chromia content.

Introduction

Supported chromia catalysts are widely used in industrial catalysis for dehydrogenation, polymerization and oxidation reactions owing to their ability of various supports to stabilize different chemical states on the surface [1]. In the recent years TiO_2 supported systems have drawn the attention of many workers because of the possible oxide-oxide interaction [2] and also due to their potential applications as environmental catalysts [3,4]. The catalytic activity for dehydrogenation of isobutene over CrO_x/TiO_2 has been found to be relatively more active per unit surface area of the catalyst [5,6]. The knowledge of the surface characteristics of the supported chromia system is essential in order to comprehend the dynamics of their catalytic behaviour towards various industrially significant catalytic reactions. In the present study we have made an effort to characterise the surface properties of the laboratory synthesized titania (TiO_2 *gel*) supported chromia catalysts as a function of calcination temperature and chromia loading using spectroscopic and thermoanalytical techniques.

Experimental

Catalyst preparation

The titania gel was prepared by the hydrolysis of titanium tetrachloride ($TiCl_4$). The required volume of $TiCl_4$ (E.Merck, GR) was dissolved in distilled water in the ratio of 1:4 in an atmosphere of nitrogen. To this excess of aqueous ammonia was added dropwise with constant stirring to maintain a pH at 7. A white gel was formed which was then filtered and washed repeatedly with distilled water to remove final traces of chloride ion. The gel was dried at 383 K and finally calcined at 773 K for 24 h to form crystalline titania of pure *anatase* form. This gel used as the support over which CrO_3 was coated by impregnation method. The impregnated catalysts were dried at 393 K for 12 h and calcined at 573 K for 2 h. The oven dried samples are referred as *fresh*. The different loadings of chromia are designated as CrTi X,

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*corresponding author. E-mail: rpv@iitm.ac.in where ‘X’ refers to the amount of weight % of CrO_3 loaded. Details of chemical analysis are reported elsewhere [7].

Characterization of catalysts

Experimental details and the instruments used for FTIR, EGA and TPR studies are reported elsewhere [8].

Results and Discussion

FTIR spectra of fresh (gel) samples of CrTi 1, CrTi 5 and CrTi 10 are given in Fig. 1. The intensity of the band at 1631 cm^{-1} and 3400 - 3600 cm^{-1} decreases with increase in chromia content. The diffused peak at 3400 - 3600 cm^{-1} is due to the surface hydroxyl and at higher chromium content (10%) due to anchoring of the chromia species through the surface hydroxyl one finds a decrease in its intensity. Similarly the peak at 1600 cm^{-1} is due to non dissociative adsorption of water on titania which is also drastically affected by the surface esterification process (surface anchoring). Similar observations have been made by Martin *et al* [9]. The intense twin features observed at 1382 cm^{-1} and 1404 cm^{-1} are attributed to the adsorption of CO_2 in various modes and it becomes a single intense peak at 10% chromia content, showing that the surface is completely covered with similar type of sites uniformly throughout.

Figure 2 shows the effect of calcinations on the surface chromia species. The bands at 1004 to 1034 cm^{-1} (Fig 2 a) indicate the dehydration of the surface due to chromia anchoring and the stabilization of mono-oxo chromyl species having the oxidation state of chromium close to +5 [10-12]. On calcination at 573 K in air, the chromia related bands disappear (Fig 2 b) indicating the growth of lower valence states of chromium [13]. This may be due to the instability of chromia (Cr^{+6}) phase and indicating a weaker interaction of surface hydroxyl of the support phase.

Evolved gas analysis (EGA) profile of the TiO_2 (gel) for the species of atomic oxygen (m/e = 16) are shown in Fig. 3. It can be seen that the peak temperature for the evolution of oxygen decreases (from ~625 to ~570 K) with increase in chromia loading. This suggests that the removal of oxygen becomes relatively facile resulting in enhanced surface dehydroxylation. This implies that probably the active anchored Cr^{+3} species having higher degree of coordinatively unsaturated centers is stabilized by gel titania. This observation supports the results from FTIR.

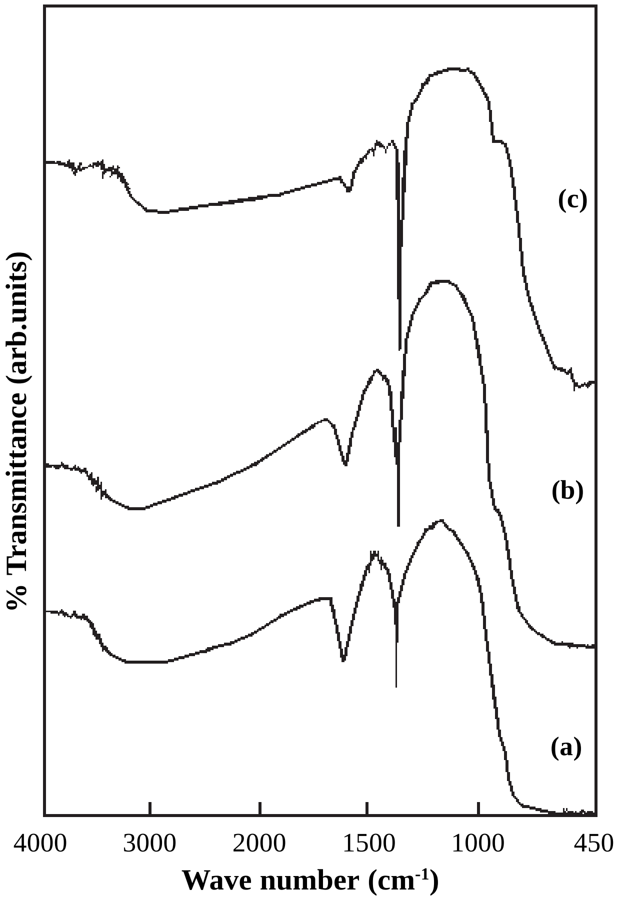

Fig. 1. FTIR spectra of fresh CrTi (gel) catalyst: (a) CrTi 1; (b) CrTi 5; (c) CrTi 10.

Thermogravimetric analysis has also been used to compute the hydroxyl density and the thermal stability of the hydroxyl groups of the supports employed using equations 1 and 2 [14] as the hydroxyl chemistry of the supports is said to extend a significant consequence

$$\sigma\ (\text{OH content}) = \left\{ \frac{\left[\frac{WL_0 - W L_T}{100} \right]}{17} \right\} \times 1000 \text{ m Moles OH/g} \tag{1}$$

where, WL_o = % weight loss at 1573 K and WL_T = % weight loss at a given temperature.

$$\sigma'\ (\text{OH population}) = \left[\frac{\sigma \times 6.02 \times 10^{20}}{S_{BET} \times 10^{18}}\right] \text{mMoles OH's/nm}^2 \qquad (2)$$

on the distribution of the chromium species [15]. Table 1 shows the change in the hydroxyl population, calculated as per equation 2, as a function of temperature. There is a drastic reduction in the hydroxyl density of TiO_2 (gel) leading to the state of least hydroxyl populated support among all the supports studied.

Table 1
Change in hydroxyl population of the supports as a function of temperature

Temperature, K	Hydroxyl Population, (10^{11}/nm^2)			
	CeO_2 (Comm)	CeO_2 (CAN)	TiO_2 (Comm)	TiO_2 (Gel)
773	1.79	11.10	1.32	0.44
873	1.66	7.29	0.96	0.23
973	1.66	6.05	0.85	0.18
1073	1.45	4.70	0.82	0.16
1173	1.20	2.83	0.80	0.14
1273	0.37	1.11	0.75	0.07
1373	0.25	0.17	0.63	0.04
1473	0.14	0.10	0.23	0.01

In Table 2 results of temperature programmed reduction of CrTi (gel) are reported. Two peaks at 615 and 725 K for CrTi 5 indicate the presence of two different types of surface chromia species. On the other hand as the chromium loading is increased one observes only the presence of lower temperature peak around 615 K. The emergence of lower temperature peak is attributed to the reduction of free chromia and that of higher temperature is due to the anchored chromia [16]. Thus, it may be concluded that the anchored chromia species are stabilized at lower loading and agglomeration of chromia species results on increasing the chromium content (10 wt.%).

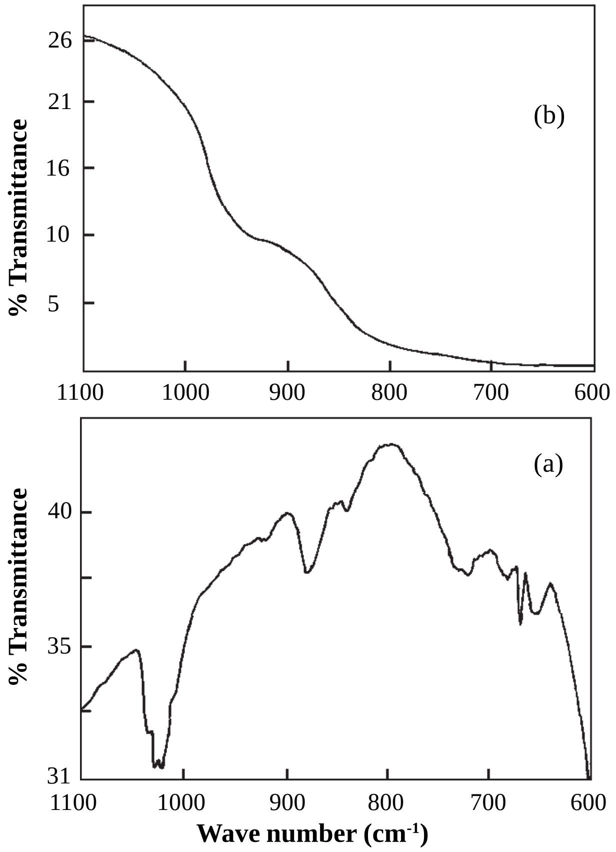

Fig. 2. FTIR spectra of CrTi 5 catalyst: (a) fresh; (b) calcined at 573 K, 2 h in air.

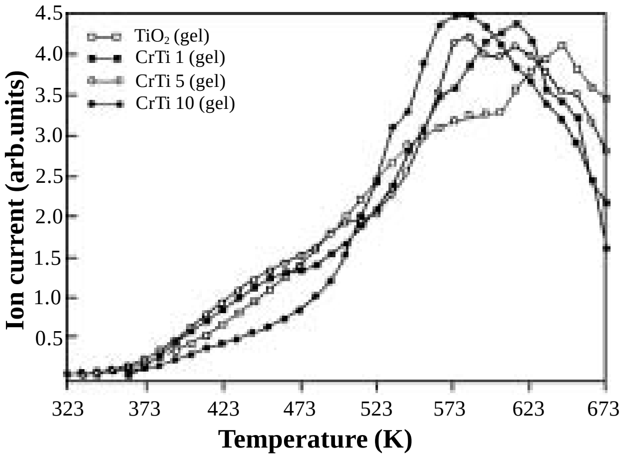

Fig.3. Oxygen evolution from the surface, as function of temperature, for different catalysts

Conclusions

Table 2

Temperature programmed reduction results of CrTi (gel)

Sample	Peak A		Peak B	
	Temperature maximum, (K)	H_2 consumption mmoles/g	Temperature maximum, (K)	H_2 consumption mmoles/g
CrTi 5	615	0.345	724	0.085
CrTi 10	611	0.220	–––	–––

The following are some of the conclusions derived from the above results of TiO_2 (gel) supported chromia system:

1. The support surface is uniformly covered with similar type of sites as chromium loading is increased
2. stabilisation of monooxochromyl species having the oxidation state of chromium near + 5 has been detected.
3. At higher temperatures, there is a drastic reduction in the hydroxyl density of TiO_2 (gel) support leading to the state of least hydroxyl-populated support among all the supports studied in the present investigation. The lesser stability of the hydroxyl groups and consequent weaker interaction between active and support phases does not stabilize the higher valent chromia species with increase in temperature.
4. Active anchored Cr^{+3} species having higher degree of coordinatively unsaturated centers is stabilized by gel titania with the increase in temperature.
5. Stabilisation of 2 kinds of chromia species have been revealed from TPR studies.

Thus lower chromia loading stabilizes the anchored chromia species where as at 10 wt.% of chromia content formation of bulk chromia phase is indicated.

References

1. F. Hardcastle and I.E. Wachs., J. Mol. Catal., 46 (1988) 173
2. J. Engweiler, J. Nickl, A. Baiker, K. Kohler, C.W. Schlapfer, and A.von Zelewsky, J. Catal., 145 (1994) 141.
3. L.S. Cheng, R.T. Yang and N. Chen, J. Catal., 164 (1996) 70
4. H. Schneider, M. Maciejewski, K. Kohler, A. Wokaun and A. Baiker, J. Catal., 157 (1995) 312
5. S. Udomsak and Anthony R. G. Ind. Eng. Chem. Res., 35 (1996) 47.
6. R. Grabowski, B. Grybowska, J. Stoczynski and K. Wcisto Appl. Catal. A 144 (1996) 335.
7. R.P. Viswanath and P. Wilson Appl. Catal. A: General 201 (2000) 23.
8. P. Wilson, P. Madhusudhan Rao and R.P. Viswanath, Thermochim. Acta (In press)
9. C. Martin, I. Martin, V. Rives, L. Palmisano and M. Schiavello J. Catal. 134 (1992) 434.
10. G. Ghiotti, A. Chiorino and F. Boccuzzi Surf. Sci., 251/252 (1991) 1100.
11. M. A.Vuurman, I. E. Wachs, D. J. Stufkens, and A. Oskam, J. Mol. Catal., 80 (1993), 209
12. U. Scharf, H. Schneider, A. Baiker and A. Wokaun J. Catal., 145 (1994) 464.
13. Zecchina, S. Coluccia, L. Cerruti and E. Borello J. Phys. Chem., 75 (1971) 2774.
14. N.E. Fouad and H. Knozinger, Z. Phys. Chem., 171 (1991) 75.
15. H.J. Lugo, and J.H. Lunsford J. Catal., 91 (1985)155
16. B. Parlitz, W. Hanke, R. Fricke, M. Richter, U. Roost and G. Ohlmann, J. Catal., 94 (1985) 24.

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