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Dispersion and thermal stability of vanadium oxide catalysts supported on titania–silica mixed oxide [☆]

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The influence of heat treatments on the dispersion and thermal stability of series of titania–silica mixed oxide supported vanadia catalysts has been investigated by X-ray diffraction, infrared, oxygen chemisorption and surface-area measurements. The results of V_2O_5/TiO_2–SiO_2 catalysts calcined at 773 K suggest that vanadia (upto 20 wt%) is in highly dispersed state on the carrier. Thermal treatments at 873 K and above transform vanadia and titania into crystalline phases and then TiO_2 anatase into rutile. In the absence of vanadia the TiO_2–SiO_2 remains unaffected by thermal treatments.

Keywords: Vanadia; titania–silica; dispersion; monolayer; oxygen uptake

1. Introduction

Supported vanadium oxide catalysts are well known for catalyzing a great variety of oxidation and ammoxidation reactions. They are also widely used in the selective catalytic reduction (SCR) of nitrogen oxides with ammonia, where the NO_x is reduced by NH_3 to form N_2 and H_2O [1–3]. The SCR of NO_x with NH_3 is largely employed to reduce pollution from stationary power sources. The increasing problem of air pollution by NO_x has resulted in more stringent emission regulations in many countries and a great increase of interest in the development of effective SCR catalysts. Presently, supported vanadium oxide catalysts are used because of their high activity at low temperatures in the presence of oxygen and their resistance to poisoning by sulfur dioxide which is also present in flue gases [1,2]. Though titania has very often been used as a support material, alumina and to a lesser extent silica, are also used. Titania is used primarily because of the remarkable fit of the crystal patterns in contact at the V_2O_5–TiO_2 (anatase) interface, which is supposed to give rise to an epitaxial growth of vanadia exposing the (010)

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plane at monolayer or slightly less than monolayer coverages [4]. This in turn results in highly dispersed vanadate species individually attached to the support.

Titania is used as a support for vanadia in spite of the fact that it has a low surface area, a poor mechanical strength and presents inferior resistance to sintering compared with other conventional supports such as Al_2O_3 and SiO_2 because silica and alumina were found to exhibit unfavourable properties when used as carriers for vanadia in SCR catalysts [2]. Silica–vanadia interaction is known to be weak, consequently the dispersed vanadium oxide species agglomerate and form relatively large particles [5], whereas alumina supported vanadia catalysts are not resistant enough to poisoning by SO_2 [2]. To avoid these deficiencies some investigators have proposed the application of a TiO_2–SiO_2 mixed oxide support for vanadia [1–3,6,7]. In fact, recent studies revealed that TiO_2–SiO_2 is the optimal support for vanadia based catalysts for NO_x reduction with NH_3 [7] since it combines both the mechanical properties of silica and the chemical properties of active titania. Thus, a partial substitution of SiO_2 for TiO_2 in V_2O_5/TiO_2 catalysts results in a larger surface area, superior sintering resistance, and low cost compared to the TiO_2 support alone. In comparison to the single component supported vanadia systems (V_2O_5/TiO_2, V_2O_5/SiO_2 and V_2O_5/Al_2O_3) [8], the mixed oxide system of V_2O_5/TiO_2–SiO_2 is, however, not fully characterized nor well understood. In the present study effect of thermal treatments (773–1073 K) on TiO_2–SiO_2 support and V_2O_5/TiO_2–SiO_2 catalysts (1–30 wt% V_2O_5) have been investigated by means of XRD, IR, and oxygen chemisorption techniques in order to understand the thermal stability and dispersion of these catalysts.

2. Experimental

2.1. CATALYST PREPARATION

The titania–silica (1 : 1 mol ratio) mixed oxide support was prepared by homogeneous precipitation method from acidified mixed solutions of sodium metasilicate and titanium tetrachloride, using urea as the neutralizer [2,9]. In a typical experiment, an aqueous solution, containing required quantities of Na_2SiO_3 (Loba-Chemie, GR grade), $TiCl_4$ (Fluka AR grade) and $CO(NH_2)_2$ (Loba-Chemie, GR grade) was heated to 95°C with constant stirring until precipitation was complete ($pH > 7$). The coprecipitate thus obtained was filtered off and washed thoroughly with doubly distilled water until no chloride ions could be detected with Ag^+ in the filtrate. The obtained cake was oven dried at 120°C for 16 h and again washed successively with portions of 5% ammonium nitrate (Loba-Chemie, GR grade) solution and then with hot distilled water to remove sodium ions. The pure $Ti(OH)_4$–$Si(OH)_4$ coprecipitate thus obtained was oven dried at 120°C for 16 h and calcined at 773 K for 6 h in an open air furnace.

V_2O_5/TiO_2–SiO_2 catalysts, with V_2O_5 content varying from 1 to 30 wt%, were prepared by wet impregnation method, the impregnations being performed with aqueous solutions of ammonium metavanadate (Fluka, AR grade) in oxalic acid solution, oven dried at 120°C for 12 h and subsequently calcined at 773 K for 4 h under a flow of oxygen. The finished catalysts were once again treated at 873, 973 and 1073 K for 6 h in a closed electrical furnace in open air atmosphere. The rate of heating (as well as cooling) was maintained at 10 K/min.

2.2. X-RAY DIFFRACTION AND INFRARED SPECTRA

XRD patterns were obtained on a Philips PW 1051 diffractometer. Ni-filtered Cu K_α radiation was used as the incident X-ray source. XRD phases present in the samples were identified with the help of ASTM Powder Data Files. For comparison purpose, the fraction of rutile in the catalysts was estimated using the following equation:

$$X_R = (1 + 0.794 I_a/I_r)^{-1} ,$$

where I_a and I_r are intensities of (101) and (110) reflections for anatase and rutile, respectively [6]. IR spectra were recorded on a Nicolet 740 FTIR spectrometer using KBr disc technique.

2.3. OXYGEN UPTAKES

A conventional standard static volumetric high vacuum (1×10^{-6} Torr) system, with the facility for reducing the samples in situ by flowing purified hydrogen ($35\ cm^3\ min^{-1}$) was used for oxygen uptake measurements. Catalyst samples (ca. 0.5 g) were reduced for 4 h at 643 K followed by evacuation at the same temperature for 2 h (1×10^{-6} Torr) prior to O_2 uptakes. The amount of oxygen chemisorbed was then determined as the difference between two successive adsorption isotherms obtained at 643 K. Keeping the temperature constant (643 K), the sample was evacuated for 1 h between the first and second adsorptions. Finally, after the chemisorption experiment the BET surface area of the catalyst was determined by N_2 physisorption at 77 K.

3. Results and discussion

XRD patterns of V_2O_5/TiO_2–SiO_2 catalysts together with that of TiO_2–SiO_2 support, calcined at 773 K are presented in fig. 1. In the case of TiO_2–SiO_2 support the diffractogram consists of broad diffraction peaks of TiO_2 anatase (JCPDS Files No. 21-1272), with no evidence of the presence of either rutile (JCPDS Files No. 21-1276) or SiO_2 phase. However, for samples containing 25 and 30% vanadia, in addition to anatase reflections new broad peaks appear at $d = 4.37$, 3.39 and 2.87 Å which are attributed to the presence of crystalline V_2O_5

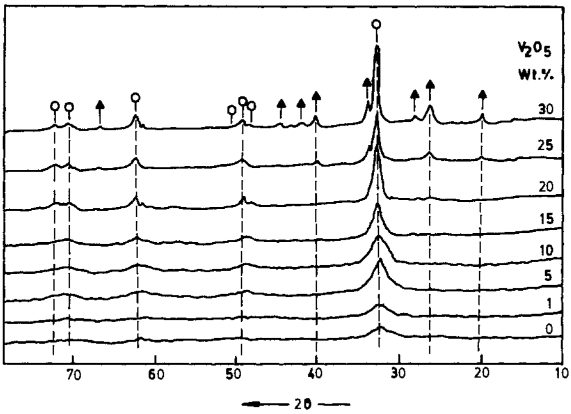

Fig. 1. X-ray powder diffraction patterns of V_2O_5/TiO_2–SiO_2 catalysts calcined at 773 K: (○) TiO_2 (anatase); (▲) V_2O_5.

(JCPDS Files No. 9-387). The absence of V_2O_5 pattern in samples containing less than 25% of vanadia suggests unequivocally that it is in amorphous or highly dispersed state on the surface of the support. The quantity of vanadia required to cover the support surface as a monolayer or monomolecular layer can be estimated from the area occupied per $VO_{2.5}$ unit of bulk V_2O_5 (0.105 nm^2) [5]. The monolayer capacity of the TiO_2–SiO_2 support (BET SA: 238 m^2 g^{-1}) comes out to be 23.8 wt% V_2O_5 using one of the recommended values of 0.10 wt% V_2O_5 per m^2 of the support [8]. XRD results thus show that crystalline V_2O_5 is formed only when the amount of vanadium oxide exceeds the quantity necessary for the monolayer capacity of the support. Another interesting point from fig. 1 is the intensity of the peak corresponding to the diffraction by (101) plane of anatase which sharpens with increase in V_2O_5 content.

In order to see the thermal stability samples were heated to higher temperatures. XRD profiles of these catalysts calcined at 873, 973 and 1073 K are presented in figs. 2, 3 and 4 respectively. Upon calcination of V_2O_5/TiO_2–SiO_2 catalysts at 873 K a further improvement in the crystallinity of anatase phase is noted and its intensity also increases with increase in vanadia content. A partial transformation (ca. 5–15%) of anatase into rutile starts from 10% vanadia loading and crystalline V_2O_5 is observed from 20% and above. Further, no substantial changes in the diffractograms of TiO_2–SiO_2 support and 1% V_2O_5/TiO_2–SiO_2 catalyst are observed except a small improvement in the intensity of anatase pattern. At 973 K (fig. 3), XRD patterns of rutile and V_2O_5 become stronger with the intensity increasing with increase in vanadia content. Here again, for the TiO_2–SiO_2 support and 1% V_2O_5/TiO_2–SiO_2 catalyst the broad diffraction pattern due to anatase phase persists. It, however, diminishes in intensity with increase in vanadia loading. At 1073 K (fig. 4) anatase phase disappears totally in the case of catalysts containing 10–30% vanadia. But it remains as broad background peaks in pure TiO_2–SiO_2 sup-

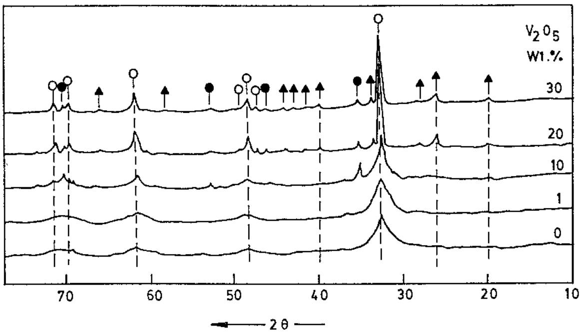

Fig. 2. X-ray powder diffraction patterns of V_2O_5/TiO_2–SiO_2 catalysts calcined at 873 K: (○) TiO_2 (anatase); (●) TiO_2 (rutile); (▲) V_2O_5.

port and 1% V_2O_5/TiO_2–SiO_2 catalyst. Silica, however, remains as amorphous in all the cases. The XRD patterns of TiO_2–SiO_2 support thus indicate that SiO_2 and most of the TiO_2, despite heating to 1073 K, remain in amorphous state. It may, therefore, be inferred that TiO_2–SiO_2 mixed oxide support obtained by homogeneous precipitation method is thermally quite stable in the absence of vanadium oxide on its surface. Even 1 wt% V_2O_5 seems to be insufficient to induce the so-called phase transformation of anatase into rutile which is known to be notoriously affected by crystallite size and presence of impurities [10].

Baiker et al. [3] using alkoxides as precursors for TiO_2–SiO_2 mixed oxide, observed that the XRD patterns of the support containing 1–10 mol% of titania did not have any long range order of the constituents, whereas the samples containing 20 mol% and higher amounts of it show the most prominent reflection of anatase (101) as a broad diffraction peak like the one observed in the present study. However, in their samples with increase of TiO_2 to 50 mol%, diffraction lines due to ana-

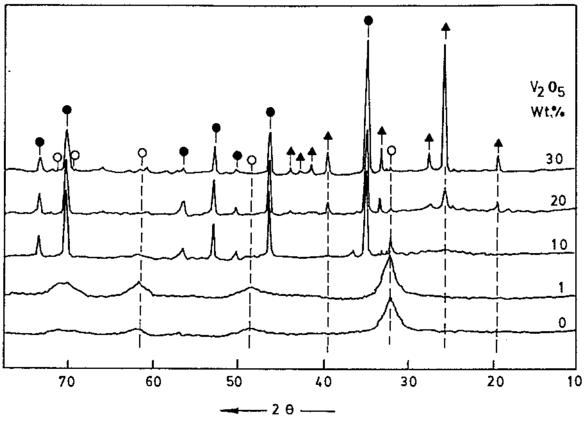

Fig. 3. X-ray diffraction patterns of V_2O_5/TiO_2–SiO_2 catalysts calcined at 973 K: symbols as in fig. 2.

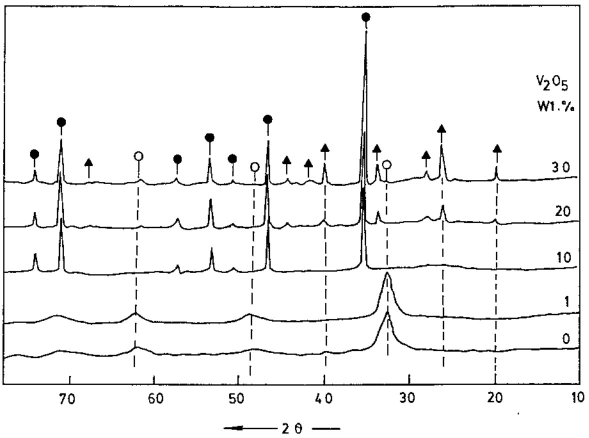

Fig. 4. X-ray diffraction patterns of V_2O_5/TiO_2–SiO_2 catalysts calcined at 1073 K: symbols as in fig. 2.

tase phase became sharp. The broad diffraction peaks indicate that part of titania is present as small crystalline particles in the amorphous titania–silica matrix. The amount of crystalline form appears to depend on the quantity of titania present in TiO_2–SiO_2 mixed oxide and on the method of preparation. The present XRD results further confirm that the interaction of V_2O_5 with TiO_2 is stronger than that of V_2O_5 or TiO_2 with SiO_2 [11]. As mentioned earlier the XRD patterns of the TiO_2–SiO_2 supported vanadia catalyst exhibit reflections of V_2O_5 along with the two modifications of TiO_2, whereas for a high surface area silica support neither TiO_2 nor V_2O_5 are in crystalline state [12]. This indicates that the mutual interaction between V_2O_5 and TiO_2 weakens the interaction of vanadia and titania with the silica surface resulting in the formation of their crystalline phases. Additionally, anatase transformation into rutile is in agreement with the earlier study of Bond et al. [13]. This anatase to rutile phase transformation is known to be activated by the remarkable fit of the crystallographic patterns in contact at the V_2O_5–TiO_2 (anatase) interface [4,9,13]. Therefore, it can be concluded that titania cannot undergo polymorphic transformation when it is well dispersed on silica surface.

FTIR spectra of TiO_2–SiO_2 and V_2O_5/TiO_2–SiO_2 catalysts calcined at 773 K are shown in fig. 5. The IR spectrum of pure vanadia gives sharp bands at 1020 and 825 cm^{-1} which are due to the V=O stretching and V–O–V deformation modes of vanadium oxide respectively. X-ray analysis indicated that crystalline V_2O_5 is present only when the amount of vanadia exceeds the amount necessary for the monolayer capacity of the support. In agreement with this argument IR spectra of 25–30% V_2O_5 catalysts reveal a new band at 1020 cm^{-1}. This is the characteristic more intense stretching mode of V=O bonds in crystalline V_2O_5. As noted above, for lower vanadia contents, crystalline V_2O_5 is not found in XRD patterns. IR spectra also do not indicate its presence. Thus, vanadia content of upto monolayer capacity is stabilized by the interaction with the support surface and is present in a

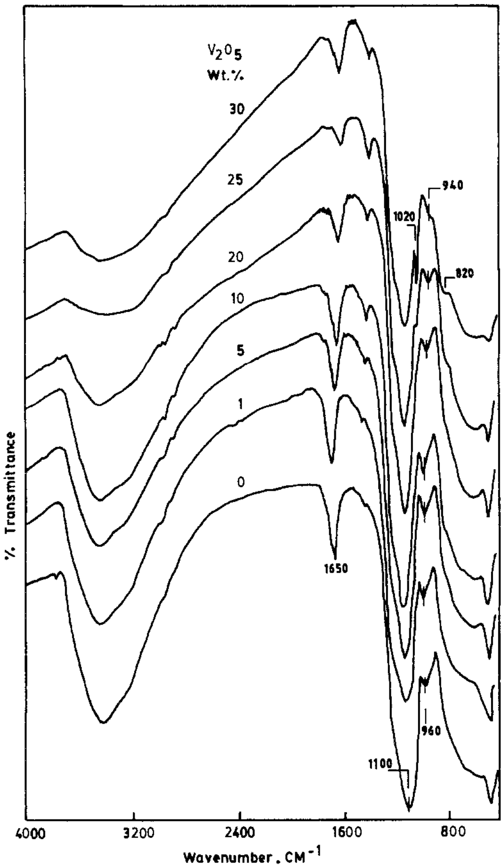

Fig. 5. FTIR spectra of V_2O_5/TiO_2–SiO_2 catalysts calcined at 773 K.

form not detectable as bulk V_2O_5. However, different species of vanadium oxide can be traced in the monolayer region. For example, Nakagawa et al. [14] reported a shift of V=O bond stretching frequency from 1020 (bulk V_2O_5) to 980 cm^{-1} in the IR spectra of the vanadium oxide monolayer species supported on TiO_2. According to these authors, the vanadium oxide on the support surface is present as an amorphous V_2O_5 at low vanadium contents and amorphous and crystalline V_2O_5 at higher loadings. Other studies using IR technique have also corroborated with these findings [8].

Silica, in the absence of titania, shows a strong absorption at 1100 cm^{-1}, which is due to Si–O, and another band at 974 cm^{-1} due to the O–H bending vibration of the silanol group [14,15]. However, in the presence of TiO_2 the bending vibration band shifts to lower frequency and becomes broader with increasing TiO_2 content. This shift of the bending band of the silanol groups to a lower frequency is caused by the interaction between TiO_2 and SiO_2 [15]. It is known that in the absence of any adsorbed moisture the FTIR spectra of silica give a band at 3740 cm^{-1} due to

Si–OH stretching vibration [14]. The absorption intensity in this –OH stretching vibration region is found to decrease with increase in vanadia content on the support, the intensity for the 30% catalyst being 1/10 the intensity for the support alone. Therefore, the possibility of interaction of some of the vanadia with the SiO_2 in TiO_2–SiO_2 support cannot be ruled out. The peak observed at 1610–1640 cm^{-1} (fig. 5) can be related to the ammonia formed during preparation, which remains adsorbed on the catalyst surface even after evacuation [14]. The FTIR spectra of the V_2O_5/TiO_2–SiO_2 catalysts calcined at higher temperatures also gave similar information which is in agreement with the results obtained from XRD study.

Oxygen uptakes at 643 K on the prereduced V_2O_5/TiO_2–ZrO_2 catalysts, calcined at different temperatures, as a function of vanadia loading are shown in fig. 6. The pure TiO_2–SiO_2 support was found to chemisorb some small amount of O_2 under the experimental conditions employed in this study. Therefore, the contribution of the pure support alone was subtracted from the results. Oxygen uptake (fig. 6) increases with increase in V_2O_5 loading irrespective of the calcination temperature. However, the numerical values of O_2 uptakes vary appreciably and are maximum in the case of catalysts calcined at 773 K and minimum at 1073 K. A large difference in the O_2 uptakes is noted between 873 and 973 K treated samples and such difference is found neither between 773 and 873 K nor between 973 and 1073 K treated ones. It can therefore be inferred that calcination of V_2O_5/TiO_2–SiO_2 catalysts at 973 K (the melting point of V_2O_5 is 963 K) and above apparently results in the formation of more crystalline V_2O_5, which perhaps leaches out from the micropores of the support material where it was initially in a highly dispersed state. A substantial loss in the specific surface of the catalysts depending on the calcination temperature and vanadia content is also noted (table 1). Thus, calcination

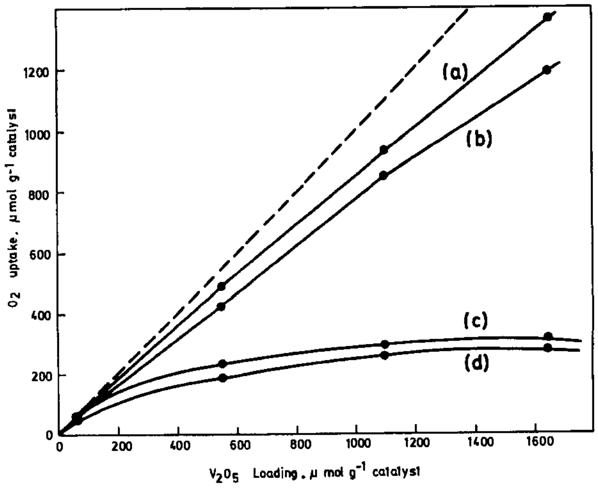

Fig. 6. Oxygen uptake at 643 K plotted as a function of V_2O_5 content of the catalysts calcined at different temperatures: (a), 773 K; (b) 873 K; (c) 973 K; (d) 1073 K.

Table 1
Influence of calcination temperature on the surface area ($m^2 g^{-1}$) and dispersion of V_2O_5/TiO_2–SiO_2 catalysts

V_2O_5 content (wt%) [a]	773 K		873 K		973 K		1073 K	
	SA [b]	D [c]	SA	D	SA	D	SA	D
0	238	–	227	–	189	–	172	–
1	237	0.98	200	0.98	197	0.76	141	0.75
10	193	0.88	133	0.76	25	0.41	19	0.34
20	125	0.83	41	0.77	12	0.26	5	0.23
30	71	0.82	41	0.72	7	0.19	2	0.17

[a] The balance is TiO_2–SiO_2.

[b] By N_2 physisorption at 77 K and after O_2 uptake measurements on the reduced catalysts.

[c] Dispersion = fraction of vanadium atoms at the surface, assuming $O_{ads}/V_{surf} = 1$.

of the vanadia containing catalysts brings about a decrease of the specific surface area in all the samples studied, being proportional to the temperature of calcination. With increase in the V_2O_5 loading a sharp decrease in the surface areas can also be noted. This is primarily because, vanadia blocks the pores of the support. When the uptake of oxygen is plotted against V_2O_5 loading, it is observed that at very low loadings the slope approaches unity (fig. 6). This indicates a limiting stoichiometry of $O_2/V_2O_5 = 1$. Using this stoichiometry, Oyama et al. [16] defined dispersion as the ratio of molecular oxygen uptake to V_2O_5 content. Table 1 lists the dispersions derived from O_2 uptake measurements. The apparent dispersion decreases with increase in vanadia loading. It is a general phenomenon observed in any supported catalyst system [16]. Increasing the calcination temperature also results in a tremendous decrease in the dispersion of V_2O_5, especially in the case of catalysts calcined at 1073 K. However, for the samples calcined at 773 K dispersion remains high at all the loadings. Another interesting point from table 1 is that V_2O_5 dispersion is reasonably high even at 873 K.

One of the best ways of characterizing a supported catalyst is by determining dispersion and effective surface area of the catalytically active component. The dispersion of metal catalysts is normally determined by the selective chemisorption of H_2 and to some extent CO at appropriate conditions. The quest for similar method for metal oxide systems lead to the development of simple low temperature oxygen chemisorption (LTOC) methods by Parekh and Weller [17] for supported molybdena catalysts, and Nag et al. [18] and Fierro et al. [19] for supported vanadia systems. The LTOC method [18] was proved to yield valuable information such as active vanadia area, oxygen atom site density and apparent dispersion etc. and was extensively utilized by the authors to characterize vanadium oxide catalysts supported on various carriers [20]. In a recent study Oyama et al. [16] have emphasized the significance of temperature of reduction as well as uptake and showed that at around 640 K sample reduction followed by O_2 uptake would yield more valid information in the case of V_2O_5/SiO_2 catalysts. In the present study preliminary observations on V_2O_5/TiO_2–SiO_2 catalysts reveal that this simple technique can be used for other systems also. Further work is under active progress to fully standardize this technique.

4. Conclusions

The following conclusions can be drawn from this study: (1) TiO_2–SiO_2 mixed oxide support prepared by homogeneous precipitation method exhibits reasonably high specific surface area and good thermal stability upto a calcination temperature of 1073 K. (2) The vanadia, upto 20 wt% in V_2O_5/TiO_2–SiO_2 catalysts calcined at 773 K, is in a highly dispersed state on the carrier as an amorphous phase. Above this loading crystalline V_2O_5 phase co-exists. (3) Calcination at 873 K and above result in the crystallization of V_2O_5 and TiO_2 with simultaneous transformation of TiO_2 anatase into rutile phase. This crystallization of TiO_2 to anatase and subsequent transformation of anatase into rutile is predominant in the catalysts containing more than 1 wt% V_2O_5. Without and with $\leqslant 1$ wt% of vanadia, the TiO_2–SiO_2 support is thermally quite stable even upto 1073 K. (4) The technique of oxygen uptake can be utilized for the quick determination of the dispersion of vanadium oxide on TiO_2–SiO_2 support.

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