Dispersion and thermal stability of vanadium oxide catalysts supported on titania–alumina binary oxide ✩

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Titania–alumina binary oxide supported vanadia catalysts calcined at different temperatures were studied by X-ray diffraction, infrared, oxygen chemisorption and surface area measurements to establish the effects of vanadia loading and thermal treatments on the structure of the dispersed vanadium oxide species. The results suggest that vanadia when calcined at 773 K is in highly dispersed state on the support surface. This dispersion is mostly retained upto a calcination temperature of 873 K. However, thermal treatments above 873 K transform vanadia and titania into crystalline phases and then TiO_2 anatase into rutile.

Keywords: vanadia; titania–alumina; dispersion; monolayer; oxygen uptake

1. Introduction

Supported vanadium oxide catalysts have been studied quite extensively [1] because of their use in several industrial heterogeneous catalytic processes, such as partial oxidation of *o*-xylene [2,3], ammoxidation of aromatic hydrocarbons [4–6], and selective catalytic reduction (SCR) of nitrogen oxides [7]. The SCR of nitrogen oxides with ammonia is largely employed to reduce atmospheric pollution from stationary power sources and this process has gained tremendous importance recently due to more stringent emission regulations in many countries. Therefore, several efforts are being made on the one hand to develop various kinds of new catalysts to satisfy the needs of practical applications, and, on the other hand, to explore the nature of SCR catalysts and the structure of the active phase of the catalysts by using several modern physico-chemical techniques.

A wide variety of catalysts have been tested for their behaviour in the SCR of NO_x using NH_3 as reductant [7–10]. Most commercially utilized catalyst formulations contain vanadium pentoxide as the active component and titanium dioxide as the support material. However, the titania support presents some disadvantages, such as a lack abrasion resistance, a low specific surface area, and a high price. In addition, the anatase phase in titania catalysts has a poor thermal stability at high temperatures. Because of these reasons, attempts to obtain a titania based support, mixed with highly stable support in order to improve the thermal stability, mechanical strength and high surface area have been the object of some very recent investigations. A few studies

concerning the surface properties of TiO_2–Al_2O_3 and TiO_2–SiO_2 binary oxides and vanadia impregnated catalysts have been reported [11–19]. In the present study an attempt has been made to explore the effect of thermal treatments on the morphology and surface characteristics of TiO_2–Al_2O_3 and V_2O_5/TiO_2–Al_2O_3 catalysts. The primary purpose of this work was to identify changes in the structure of the dispersed vanadia as a function of V_2O_5 loading and calcination temperature. The techniques of X-ray diffraction, FTIR and O_2 chemisorption have been used for this purpose.

2. Experimental

2.1. Catalyst preparation

The TiO_2–Al_2O_3 (1.3 : 1 molar ratio) support was prepared by a homogeneous precipitation method using urea as precipitation reagent [20]. For precipitation with urea, a mixed aqueous solution of $TiCl_4$ (Fluka, AR grade), $NaAlO_2$ (Loba Chemie, GR grade) and urea (Loba Chemie, GR grade) was heated to 368 K with vigorous stirring. Cold titanium tetrachloride was first digested in cold concentrated HCl and subsequently diluted with deionized water and then $NaAlO_2$, dissolved separately in deionized water, was added. In about 6 h of heating, as decomposition of urea progressed to a certain extent, the formation of precipitate gradually occurred and the pH value of the solution increased. The precipitate was heated for six more hours to facilitate ageing, then filtered, washed until free from chloride ions and dried at 383 K for 16 h. In order to remove sodium ions the oven dried precipitates were again washed with ammonium nitrate solution several times and dried once again at 383 K for 16 h and were finally calcined at 773 K for 6 h in an open-air furnace.

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The V_2O_5/TiO_2–Al_2O_3 catalysts with vanadia loadings ranging from 2 to 20 wt% were prepared by a wet impregnation method. To impregnate V_2O_5, the requisite quantity of ammonia metavanadate (Fluka, AR grade) was dissolved in 1 M oxalic acid solution and the support material was added to this solution. Excess water was evaporated on a water bath with continuous stirring. The resultant solid was then dried at 383 K for 12 h and calcined at 773 K for 5 h in flowing oxygen. Thus finished catalysts were again treated at various temperatures, 873, 973 and 1073 K respectively for 6 h in a closed electric furnace in open air atmosphere.

2.2. Catalyst characterization

X-ray diffraction analysis was performed on a Philips PW 1051 instrument, using monochromated Fe K_α radiation and standard recording conditions. 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 the intensities of (101) and (110) reflections for anatase and rutile, respectively [16]. Infrared spectra were recorded on a Nicolet 740 FTIR spectrometer, using KBr discs, with a nominal resolution of 4 cm^{-1} and averaging 100 spectra.

Oxygen uptake measurements were conducted on a standard static volumetric high vacuum (1 × 10^{-6} Torr) system having the facility for reducing the samples in situ by flowing purified hydrogen (35 cm^3/min). Prior to oxygen uptakes catalyst samples were reduced for 4 h at 643 K followed by evacuation at the same temperature for 2 h. The amount of O_2 chemisorbed was determined as the difference between two successive adsorption isotherms obtained at 643 K. More details are described elsewhere [21]. After the chemisorption experiment the BET surface area of catalyst sample was determined by N_2 physisorption at 77 K.

3. Results and discussion

The BET surface area of the TiO_2–Al_2O_3 support calcined at 773 K was found to be 159 m^2 g^{-1}. The quantity of vanadia required to cover the support surface as a monomolecular layer can be estimated from the area occupied per $VO_{2.5}$ (10.3 × 10^4 pm^2) unit of the V_2O_5. This theoretical estimation yields a load of 0.145 wt% per m^2 of the support to cover its surface with a compact single lamella of the vanadium pentoxide structure [22]. In reality, the maximum amount of vanadium oxide that can be formed as a two-dimensional monolayer depends not only on the support surface area but also on the con-

centration of reactive surface hydroxyl groups. Therefore, the actual vanadia content that can be needed to cover the support surface as a single monolayer was always less than the theoretical monolayer capacity and ranged between 0.1 and 0.07 wt% per m^2 of support [1,19]. In view of these observations a range of V_2O_5 loadings were selected in the present investigation. Catalyst compositions, BET surface areas and the theoretical surface coverages of various samples are presented in table 1.

The X-ray diffraction profiles of TiO_2–Al_2O_3 support and V_2O_5/TiO_2–Al_2O_3 catalysts of various V_2O_5 contents calcined at 773 K are presented in fig. 1. No XRD lines due to crystalline V_2O_5 phase are present up to the highest loading of 16 wt%. Only broad diffraction lines due to anatase phase are seen in all the spectra. The TiO_2–Al_2O_3 binary oxide support obtained via a homogeneous precipitation method and calcined at 773 K apparently shows the peaks of anatase, however, they are very broad and not well defined indicating a lack of good crystallinity. Further, there is no evidence of the presence of either rutile or alumina phase. The absence of crystalline V_2O_5 pattern is an indication of high dispersion of vanadia on the TiO_2–Al_2O_3 mixed oxide support. The V oxide phase will be present as a two-dimensional monolayer, as can be estimated from the amount of vanadia involved (16 wt% V_2O_5) and the BET surface area of 119 m^{2}g^{-1}, yielding 8.9 Å^2 per V oxide unit. In crystalline V_2O_5, which has a lamellar structure, the calculated surface area per $VO_{2.5}$ unit in the (010) plane is 10.3 Å^2 [23]. This is further supported from FTIR and O_2 uptake data which will be dealt with in the later paragraphs.

In order to see the thermal stability of TiO_2–Al_2O_3 support as well as V_2O_5/TiO_2–Al_2O_3 catalysts the calcined samples were again subjected to various high temperature treatments. XRD profiles of these samples calcined at 873, 973 and 1073 K are shown in figs. 2, 3 and 4 respectively. Upon calcination of the samples at 873 K (fig. 2) an improvement in the crystallinity of the anatase phase is noted and its intensity also increased with increase in vanadia content. The peak at 3.51 Å corresponding to diffraction by planes (101) of anatase was the most intense, while the other lines, namely the triplet at 2.40 Å due to diffraction by planes (103), (004), and (112), as well as the doublet at 1.71 Å due to diffraction by planes of (105) and (211), are seen only in the case of samples containing 12 and 16 wt% V_2O_5. Further, a partial transformation of anatase into rutile was noted from 12 wt% and above loadings. In addition, the XRD lines due to crystalline V_2O_5 phase are also seen in the spectra. On further raising the calcination temperature to 973 K (fig. 3), the XRD lines due to rutile become stronger with their intensity increasing with increase in vanadia content. A total transformation of anatase into rutile was noted from 8% and above loadings of V_2O_5. Up to this loading level the lines due to ana-

Table 1
O_2 uptake on V_2O_5/TiO_2–Al_2O_3 catalysts calcined at different tempatatures

Sample [a]	SA $(m^2\,g^{-1})$	Surface density [b] (V atoms/nm^2)	O_2 $(\mu mol\,g^{-1})$	Dispersion [c]
T = 773 K				
2% V_2O_5/TiO_2–Al_2O_3	156	0.85	98.9	0.90
4% V_2O_5/TiO_2–Al_2O_3	145	1.83	183.2	0.83
8% V_2O_5/TiO_2–Al_2O_3	135	3.92	356.3	0.81
12% V_2O_5/TiO_2–Al_2O_3	122	6.51	523.2	0.79
16% V_2O_5/TiO_2–Al_2O_3	119	8.90	681.6	0.77
T = 873 K				
2% V_2O_5/TiO_2–Al_2O_3	129	1.03	96.3	0.87
4% V_2O_5/TiO_2–Al_2O_3	122	2.17	184.4	0.84
8% V_2O_5/TiO_2–Al_2O_3	116	4.57	292.7	0.66
12% V_2O_5/TiO_2–Al_2O_3	119	6.68	314.9	0.48
16% V_2O_5/TiO_2–Al_2O_3	74	14.32	325.5	0.37
T = 973 K				
2% V_2O_5/TiO_2–Al_2O_3	109	1.21	80.2	0.73
4% V_2O_5/TiO_2–Al_2O_3	62	4.27	120.2	0.55
8% V_2O_5/TiO_2–Al_2O_3	45	11.77	238.8	0.54
12% V_2O_5/TiO_2–Al_2O_3	22	36.13	224.1	0.34
16% V_2O_5/TiO_2–Al_2O_3	12	88.31	170.1	0.19
T = 1073 K				
2% V_2O_5/TiO_2–Al_2O_3	32	4.14	72.6	0.66
4% V_2O_5/TiO_2–Al_2O_3	17	15.58	126.2	0.57
8% V_2O_5/TiO_2–Al_2O_3	14	37.85	222.1	0.50
12% V_2O_5/TiO_2–Al_2O_3	9	88.31	193.4	0.29
16% V_2O_5/TiO_2–Al_2O_3	6	176.61	140.4	0.16

[a] V_2O_5 content in wt%.

[b] Theoretical surface coverage. In crystalline V_2O_5 the (010) face contains 9.7 V atoms per nm^2, corresponding to 0.103 nm^2 per $VO_{2.5}$ unit [23].

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

tase phase still persist with their intensity improving with increase in vanadia content. At 1073 K calcination (fig. 4), the anatase phase disappears totally in the case of catalysts containing 8–16% vanadia. The TiO_2 remains predominantly as anatase phase in pure TiO_2–Al_2O_3 and 2% V_2O_5/TiO_2–Al_2O_3 catalyst. However, the lines due to alumina are not seen in all the cases. Thus XRD patterns of the TiO_2–Al_2O_3 support indicate that Al_2O_3 and most of TiO_2, despite heating to 1073 K, remain in amorphous state. Therefore, it may be inferred that the TiO_2–Al_2O_3 binary oxide support obtained by a homogeneous precipitation method is thermally stable
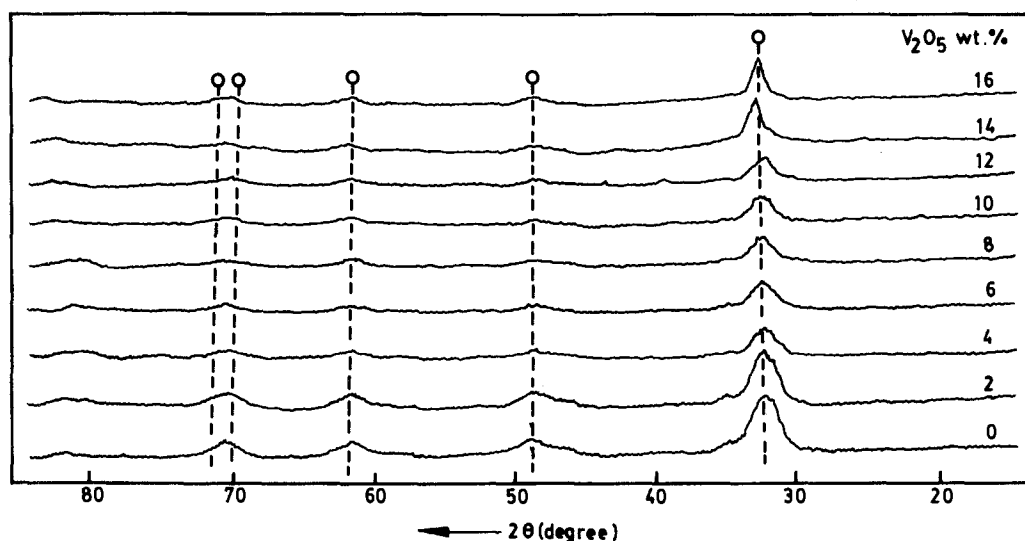

Fig. 1. X-ray diffraction patterns of V_2O_5/TiO_2–Al_2O_3 catalysts calcined at 773 K; (Q) Characteristic lines due to TiO_2 anatase phase.
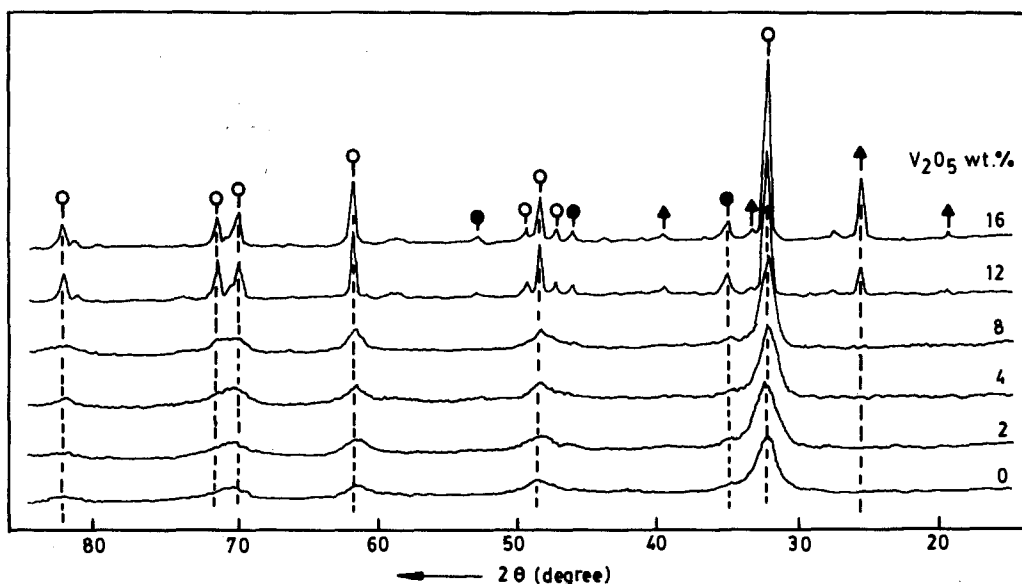
Fig. 2. X-ray diffraction patterns of V_2O_5/TiO_2–Al_2O_3 catalysts calcined at 873 K; (◯) lines due to anatase phase; (●) lines due to rutile phase; (▲) due to V_2O_5.

in the absence of vanadium oxide on its surface. Even small contents of V_2O_5 seem to be insufficient to induce the so-called phase transformation of anatase into rutile, which is known to be affected by crystalline size and presence of impurities [24].

A close look into the figs. 1,2,3 and 4 reveals that the heating temperature and concentration of V_2O_5 are both equally important for the phase transformation phe-

nomenon of anatase into rutile. The dispersed vanadia on the TiO_2–Al_2O_3 support surface appears to lower the activation temperature of the anatase-to-rutile phase transformation, which is normally expected to be 973 K and above impurity free TiO_2 samples [25,26]. It is well known that at elevated temperatures the supported vanadia phase initiates the anatase-into-rutile transformation. During this transformation some of the V_2O_5 is
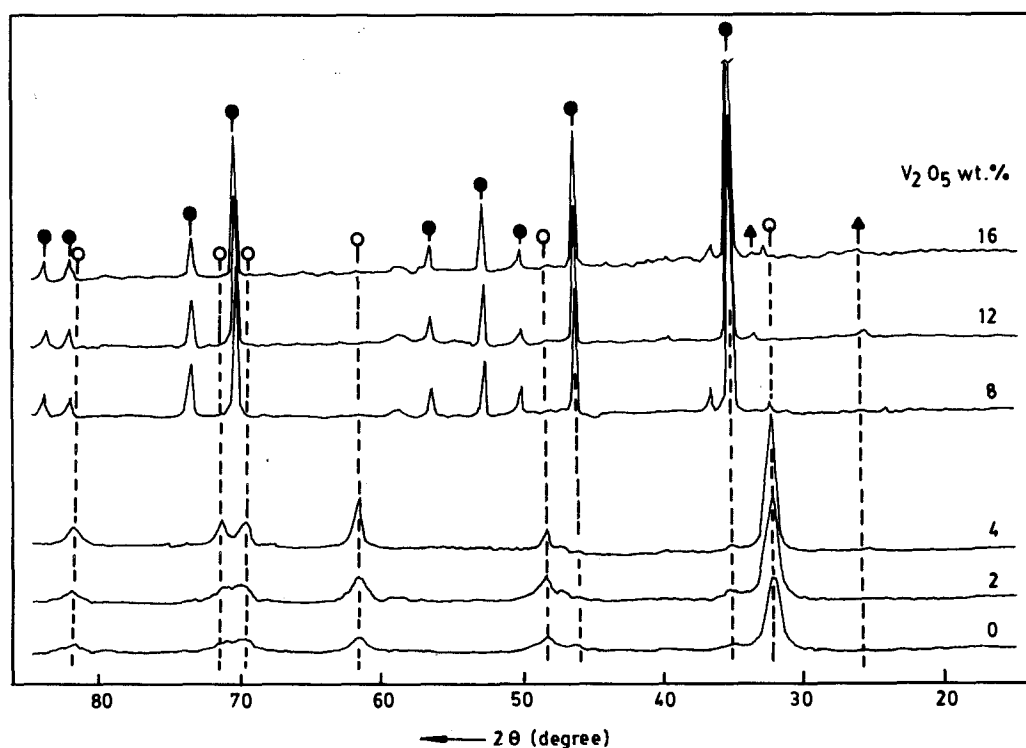

Fig. 3. X-ray diffraction patterns of V_2O_5/TiO_2–Al_2O_3 catalysts calcined at 973 K; symbols as in fig. 2.
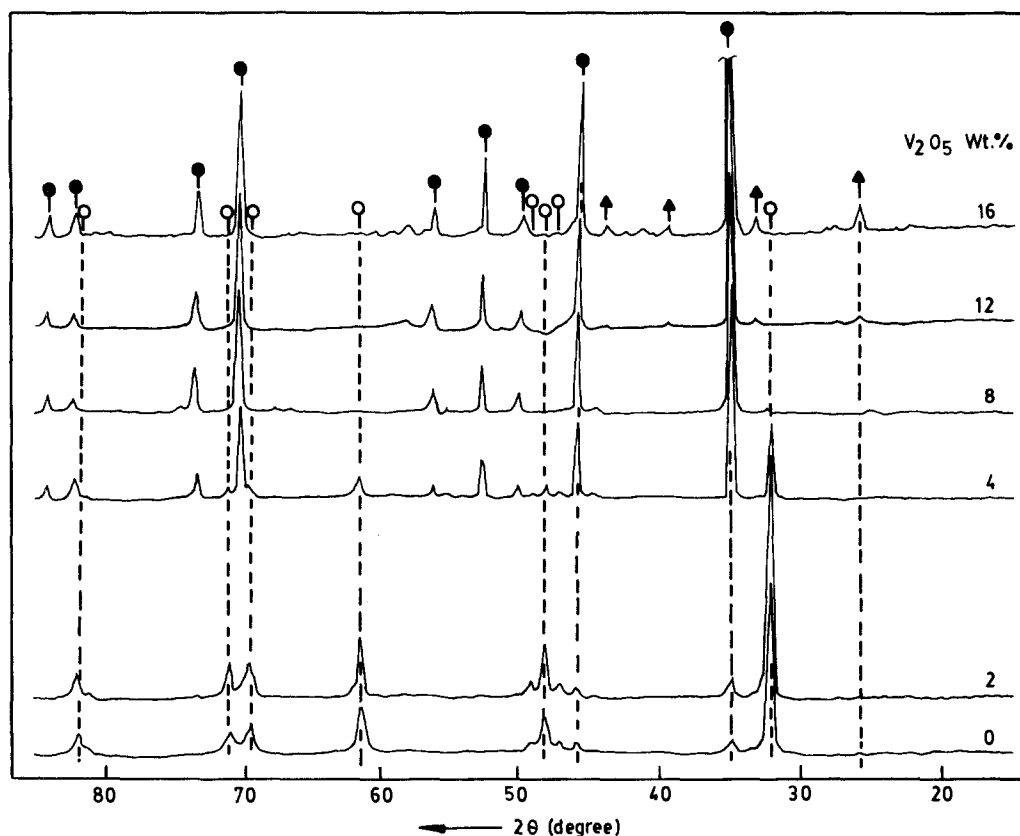
Fig. 4. X-ray diffraction patterns of V_2O_5/TiO_2-Al_2O_3 catalysts calcined at 1073 K; symbols as in fig. 2.

normally reduced and gets incorporated into the rutile structure as $V_xTi_{(1-x)}O_2$ (rutile solid solution) [23,25–27].

Infrared spectroscopy has been widely used to ascertain the nature of the vanadium oxide phases existing on several supports [1]. The FTIR spectra of V_2O_5/TiO_2-Al_2O_3 catalysts calcined at 773 K are shown in fig. 5 in the range 400–1600 cm^{-1}, where those bands due the $\nu_{v=o}$ mode are expected to be recorded. The spectrum of V_2O_5 shows sharp absorption bands at 1020 cm^{-1} and another at 824 cm^{-1}. These agree with the literature [26], which assigns the former to V=O stretching and the latter to the deformation of V–O–V bridges . Anatase and rutile phases of titania exhibit strong absorption bands in the region of 850–650 and 800–650 cm^{-1}, respectively. The FTIR spectra of V_2O_5/TiO_2-Al_2O_3 catalysts indicate that the vanadium oxide is in a highly dispersed state. The spectra show essentially only one band at 935 cm^{-1} for 2% catalyst and at 970 cm^{-1} for 16% catalyst. A gradual shift from 935 to 970 cm^{-1} is noted with gradual increase in vanadia content. Peaks in the 1000–940 cm^{-1} region can be attributed to surface vanadate species as has been previously reported for amorphous two-dimensional monolayers on V_2O_5/TiO_2 catalysts [26,28]. Thus for the catalysts containing 16% or less V_2O_5, no evidence for the crystalline V=O is seen and all vanadia is present as a two-dimensional monolayer on the support surface. Further, the FTIR results are in per-

fect agreement with the results of XRD analysis. However, in the case of samples calcined at 873 K and above temperatures the formation of crystalline V_2O_5 phase was observed from both XRD and IR measurements.

Oxygen uptakes at 643 K on the prereduced V_2O_5/TiO_2-Al_2O_3 catalysts calcined at different temperatures are shown in table 1. The pure TiO_2-Al_2O_3 support was also found to chemisorb some small amount of O_2 under the experimental conditions employed in this study. Therefore, the contribution of the support alone was subtracted from the results. In general, oxygen uptake increased with increase in vanadia 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, except on the 2% sample, in the oxygen uptakes is noted between 873 and 973 K treated samples and such difference is not found 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-Al_2O_3 catalysts at 973 K (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 considerable loss in the specific surface areas of the catalysts depending on the calcination temperature and V_2O_5 content is also observed. Calcination of the V_2O_5/TiO_2-Al_2O_3
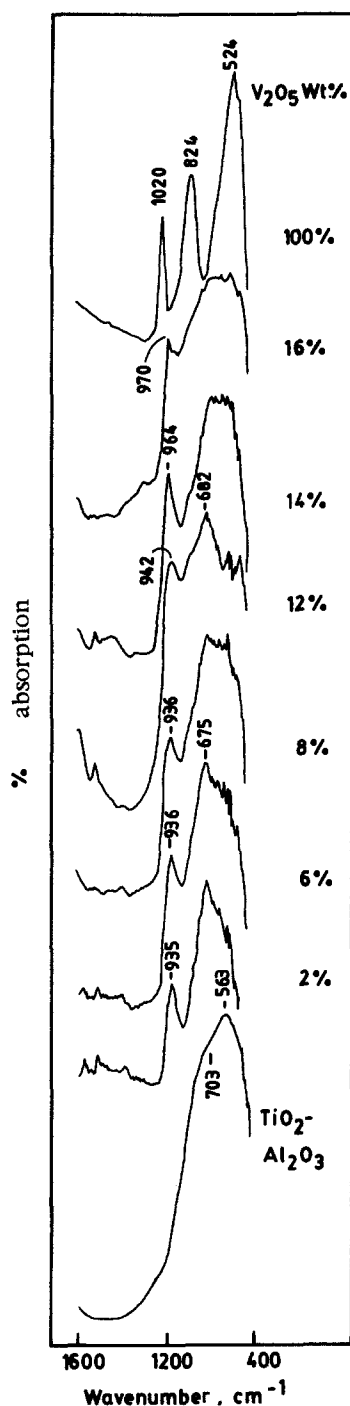
Fig. 5. FTIR spectra of V_2O_5/TiO_2–Al_2O_3 catalysts calcined at 773 K.

catalysts at various temperatures brings about a decrease of its specific surface area in all the samples studied which is proportional to the temperature of calcination. With increase in vanadia loading a sharp decrease in the specific surface areas can also be noted. This is probably due to the blocking of pores of the support by the dispersed vanadia [29]. Table 1 also lists the dispersions derived from O_2 uptake measurements. Dispersion is defined as the ratio of molecular oxygen uptake to V_2O_5 content [30]. The apparent dispersion

decreases with increase in vanadia loading. This is a general phenomenon observed on any supported catalyst system [19,21,30]. Increasing the calcination temperature also results in a tremendous decrease in the dispersion of vanadia, especially in the case of catalysts calcined at 1073 K. As described earlier, some of the vanadia is normally reduced and forms, with the titania support, a solid solution when calcined at elevated temperatures [23,25–27]. However, for the samples calcined at 773 K the V oxide dispersion remains high at all the loadings. Another interesting point to note from table 1 is that V_2O_5 dispersion is reasonably high even at 873 K calcination temperature. Thus, the O_2 uptake results are in line with XRD and FTIR observations.

4. Conclusions

V_2O_5 supported on TiO_2–Al_2O_3 mixed oxide and calcined at 773 K was found to be in a highly dispersed state on the carrier. Characterization of the catalysts with XRD, FTIR and O_2 chemisorption showed that the catalysts with 16% or less vanadia consisted of a surface amorphous vanadate phase dispersed on the carrier. When these catalysts were subjected to thermal treatments from 773 to 1073 K a gradual transformation of anatase into rutile was noted. This transformation phenomenon was highly dependent on the concentration of vanadia and is accompanied by a loss in the specific surface area of the catalysts. However, at very small concentration of V_2O_5, ca. 1–4%, the TiO_2–Al_2O_3 mixed oxide support appears to be quite thermally stable.

Acknowledgement

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