Characterization and catalytic activity of V_2O_5/Al_2O_3-TiO_2 for selective oxidation of 4-methylanisole

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Abstract

The vapour phase selective oxidation of 4-methylanisole to *p*-anisaldehyde and *p*-anisic acid was investigated over V_2O_5/Al_2O_3-TiO_2 catalysts containing various amounts of V_2O_5 (2–16 wt.%) in the temperature range 523–723 K under normal atmospheric pressure. The Al_2O_3-TiO_2 (1:1.3 mole ratio) binary oxide support was prepared by a homogenous coprecipitation method using urea as precipitating reagent. The V_2O_5/Al_2O_3-TiO_2 catalysts were prepared by a wet impregnation method from ammonium metavanadate dissolved in oxalic acid solution. The Al_2O_3-TiO_2 support and V_2O_5/Al_2O_3-TiO_2 catalysts were subjected to various calcination temperatures (773–1073 K) to understand the dispersion and thermal stability of catalysts and were characterized by means of X-ray diffraction, FT-infrared, X-ray photoelectron spectroscopy, O_2 chemisorption and BET surface area methods. The physicochemical characterization results reveal that the Al_2O_3-TiO_2 mixed oxide is homogeneous and thermally quite stable retaining titania-anatase phase up to 1073 K. The alumina-titania support also accommodates a monolayer equivalent of V_2O_5 in a highly dispersed state when calcined at 773 K. This observation is supported from XRD, FTIR and O_2 uptake results. The XPS studies reveal that titania, alumina and vanadia are in Ti(IV), Al(III) and V(V) oxidation states irrespective of calcination temperature employed. The O 1s, Ti 2p, Al 2p and V 2p photoelectron peaks of the V_2O_5/Al_2O_3-TiO_2 samples are highly sensitive to the calcination temperature as well as V_2O_5 coverage. The 16 wt.% V_2O_5/Al_2O_3-TiO_2 catalyst exhibits more conversion and more product selectivity to *p*-anisaldehyde when compared to other samples.
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1. Introduction

Heterogeneous catalysts based on supported vanadium oxide have been the subject of numerous investigations due to their wide range of applications. These catalysts are extensively used in several industrially important catalytic processes that include, selective catalytic reduction (SCR) of NO_x [1–3], oxidation of SO_2 to SO_3 [4,5], ammoxidation of aromatic hydrocarbons [6–8], oxidative dehydrogenation of alkanes [9,10] and selective oxidations of *o*-xylene to phthalic anhydride [11], methanol to formaldehyde [12–14] and ethylbenzene to acetophenone [15]. Depending on the nature of reaction to be catalyzed, supports for V_2O_5 have been varied. Most of the investigations reveal that the activity and selectivity of the catalyst is highly sen-

sitive to the nature of the support employed and the amount of vanadium oxide impregnated apart from other preparative variables [16–20]. The physicochemical nature of the support mainly contributes to the metal dispersion and electronic effects, respectively, besides rendering high specific surface area and better thermal stability [21,22]. Thus, the surface structure of vanadium oxide dispersed on various supports namely, TiO_2, Al_2O_3, SiO_2, ZrO_2 and CeO_2 have been studied quite extensively by several analytical techniques such as, O_2 chemisorption [19], Raman spectroscopy [23,24], ESR [25,26], NMR [27,28], EXAFS/XANES [29,30] and other techniques [16,17]. Most of these studies reveal that depending on the concentration of V_2O_5 and the nature of support involved, dispersed vanadium oxide exists as isolated, monomeric (monovanadate) and polymeric (polyvanadate) species [16,17,31].

Particularly, the V_2O_5/TiO_2 catalyst has emerged as an excellent combination among various supported vanadium oxide catalysts because of its high activity and selectivity for selective oxidation of *o*-xylene and SCR of NO_x. In recent years,

the V_2O_5/TiO_2 catalysts have also been employed for oxidation of lactic acid, methanol and other reactions [32,33]. In the case of V_2O_5/TiO_2 catalysts, the dispersed vanadium oxide is very sensitive to the phase of support [16,20]. Among the three structural polymorphs of TiO_2, namely anatase, rutile and brookite, anatase is most preferred phase [16,34–38]. Unfortunately, TiO_2-anatase support possesses major drawbacks like low specific surface area and low thermal stability of the active anatase phase at high temperatures. A loss in activity normally occurs due to sintering and subsequent phase transformation from anatase to thermodynamically stable rutile form. Therefore, several attempts could be found in the literature to obtain titania-based systems combined with another stable oxide to make better catalysts for various applications [39,40].

Anisaldehyde (4-methoxybenzaldehyde) is an important chemical intermediate having many potential applications in the preparation of perfumes, pharmaceuticals and agrochemicals. Substituted benzaldeheydes are normally synthesized from the corresponding substituted toluenes in the liquid phase in the presence of Co, Ce and Mn salts in acetic acid medium or by electrochemical methods [41]. However, efficiencies of these routes are not so high and also produce more wasteful products causing environmental problems. There are several advantages for carrying out this reaction in the vapour phase and some attempts were made in this direction [42,43]. The present investigation was undertaken against the aforesaid background. In this study, a series of Al_2O_3-TiO_2 supported V_2O_5 catalysts with various amounts of vanadium oxide were employed for the title reaction under normal atmospheric pressure in the vapour phase. In particular, the structural evolution of V_2O_5/Al_2O_3-TiO_2 under the influence of thermal treatments was examined by using XRD, FTIR, XPS, O_2 chemisorption and BET surface area methods.

2. Experimental

2.1. Catalyst preparation

The Al_2O_3-TiO_2 (1:1.3 mole ratio) support was prepared by a homogeneous coprecipitation method using urea as precipitating reagent [43]. For precipitation with urea, a mixed aqueous solution of $NaAlO_2$ (Loba Chemie, GR grade), $TiCl_4$ (Fluka, AR grade) and urea (Loba Chemie, GR grade) was heated to 368 K with vigorous stirring. The titanium tetrachloride was first digested in cold concentrated HCl and subsequently diluted with deionized water and to which $NaAlO_2$ 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 was gradually occurred and pH of the solution increased. The precipitate was heated for 6 h more to facilitate aging, 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 a closed electrical furnace in air atmosphere.

The V_2O_5/Al_2O_3-TiO_2 catalysts with V_2O_5 loadings ranging from 2 to 16 wt.% were prepared by a wet impregnation method.

For this purpose, the requisite quantity of ammonium metavanadate (Fluka, AR grade) was dissolved in 1 M oxalic acid solution and the support was added to this solution. The excess water was evaporated on a water bath with continuous stirring. The resultant solid was then oven-dried at 383 K for 12 h and calcined at 773 K for 6 h in oxygen atmosphere. The finished catalysts were once again treated at various temperatures, 873, 973 and 1073 K, respectively for 6 h in a closed electric furnace in air atmosphere.

2.2. Catalyst characterization

X-ray powder diffraction analysis was performed on a Philips PW 1051 instrument, using monochromated Fe Kα radiation and standard recording conditions. The XRD phases present in the samples were identified with the help of ASTM Powder Data Files. The FTIR 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 ml min^{-1}). Prior to oxygen uptakes, the 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 absorption isotherms obtained at 643 K. More details of this method was described elsewhere [44]. The BET surface areas of the samples were determined by N_2 physisorption at liquid N_2 temperature (77 K).

XPS spectra were recorded on a VG-ESCA Lab 210 spectrometer working in the constant analyzer energy mode with a pass energy of 50 eV and Mg Kα radiation as the excitation source. Before experiments, the spectrometer was calibrated against E_b(Au 4f$_{7/2}$) = 84.0 eV and E_b(Cu 2p$_{3/2}$) = 932.6 eV. The Ti 2p$_{3/2}$ was taken as internal reference with a binding energy of 458.5 eV [45]. A finely ground oven-dried samples were mounted on the standard sample holder, which can house four samples at a time. The XPS analysis was done at room temperature and pressures typically in the order of 10^{-10} Torr.

2.3. Catalytic activity

The vapour phase conversion of 4-methylanisole to *p*-anisaldehyde and *p*-anisic acid was investigated under normal atmospheric pressure, in a down flow fixed bed differential micro-reactor, at different temperatures. In a typical experiment ca. 0.2–1.0 g of catalyst sample was secured between two plugs of quartz wool inside the glass reactor. Ceramic beads were filled above the catalyst bed to act as preheating zone. The reactor was placed vertically in a tubular furnace connected to temperature-controller-indicator. Catalyst sample was preheated under flowing air at 523 K for 4 h, prior to the reaction. The 4-methylanisole reactant was fed with a motorized syringe pump (Perfusor Secura FT, Germany) into the vaporizer at a rate of 1.5–3.0 ml h^{-1} and dry air was used as O_2 source and passed at a flow rate of 45–60 ml min^{-1}. The liquid products were col-

lected in ice cold freezing traps and were analyzed by a gas chromatograph with SE-30 packed column and flame ionization detector (FID). The main reaction products observed were *p*-anisaldehyde, *p*-anisic acid and some unknown products. The conversion and product selectivity were calculated as per the procedure described elsewhere [43].

3. Results and discussion

The X-ray diffraction profiles of Al_2O_3-TiO_2 support calcined at 773 and 1073 K and V_2O_5/Al_2O_3-TiO_2 catalysts of various V_2O_5 contents and calcined at 773 K are presented in Fig. 1. As can be noted from this figure, the Al_2O_3-TiO_2 binary oxide support calcined at 773 K exhibits poor crystallinity. Only broad diffraction peaks due to TiO_2-anatase (JCPDS File No. 21–1272) phase could be seen. There is no evidence for the presence of either TiO_2-rutile (JCPDS File No. 21–1276) or Al_2O_3 phases. Further, despite heating to 1073 K, the XRD patterns indicate that Al_2O_3 is in amorphous state and the titania in anatase form with improved crystallinity. It is known in the literature that transformation of anatase to rutile is thermodynamically feasible beyond 873 K in impurity free TiO_2 samples [46]. Very interestingly, no diffraction lines due to titania-rutile (JCPDS File No. 21–1276) phase are observed even up to the highest calcination temperature of 1073 K in the present study. Therefore, it can be inferred from XRD results that the Al_2O_3-TiO_2 binary oxide support is thermally stable retaining TiO_2-anatase phase up to 1073 K. In the case of V_2O_5/Al_2O_3-TiO_2 samples, no XRD lines pertaining to the crystalline V_2O_5 are present even up to the highest loading of 16 wt.%. Only the broad diffraction lines due to TiO_2-anatase phase are seen. The absence of crystalline V_2O_5 patterns indicate that the deposited vanadium oxide is in a highly dispersed state. The dispersed vanadium oxide on the TiO_2 support is known to lower the activation temperature and accelerate the anatase to rutile phase transformation [47,48]. However, the retention of TiO_2-anatase phase in V_2O_5/Al_2O_3-TiO_2 catalysts is an interesting observation in the present study.
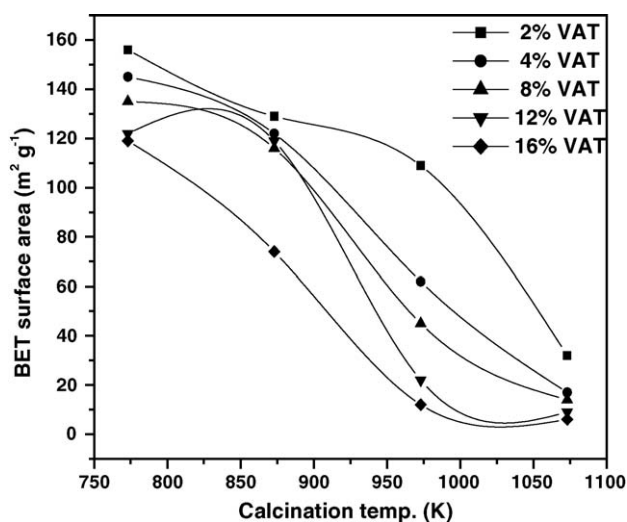

Fig. 2. BET surface area of V_2O_5/Al_2O_3-TiO_2 catalysts calcined at various temperatures.

The BET surface areas of V_2O_5/Al_2O_3-TiO_2 catalysts as a function of calcination temperature are shown in Fig. 2. The BET surface area of the Al_2O_3-TiO_2 support was found to decrease from $159\,m^2\,g^{-1}$ at 773 K to $32\,m^2\,g^{-1}$ at 1073 K due to sintering of the sample at higher calcination temperatures. A progressive decrease in the surface area with increasing calcination temperature is mainly due to sintering of the samples at higher calcination temperatures, which is a normal phenomenon [16,17,49,50]. However, an interesting point to mention here is that despite calcination at 1073 K, the Al_2O_3-TiO_2 binary oxide support retains a reasonable high specific surface area of $32\,m^2\,g^{-1}$. A substantial decrease in the surface area of TiO_2 when subjected to high temperature calcinations is frequently reported [16,46]. With the impregnation of V_2O_5, the active component in the present case, surface area of the support tends to decrease as mentioned elsewhere due to penetration of the dispersed vanadium oxide species into the micropores of the support [16,51]. As expected, the surface area of V_2O_5/Al_2O_3-TiO_2 catalysts decreased with

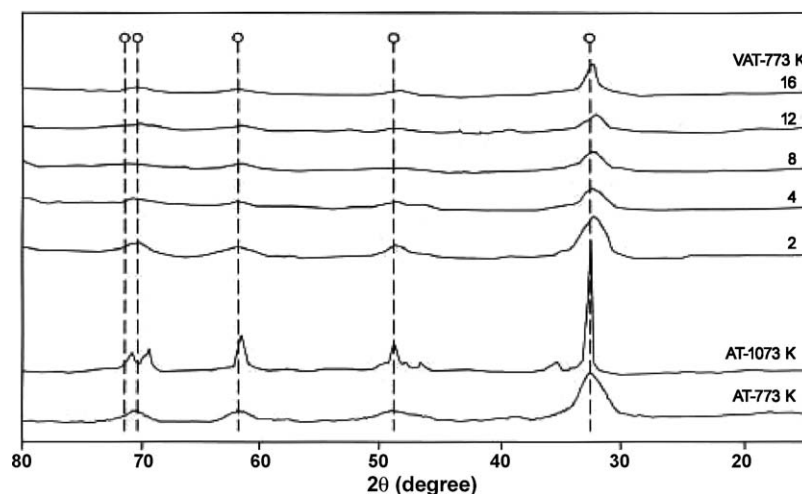Fig. 1. X-ray powder diffraction patterns of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 samples calcined at various temperatures.
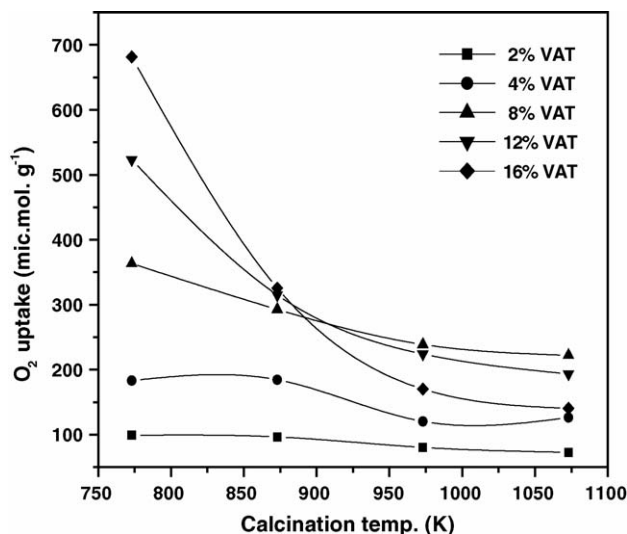
Fig. 3. Oxygen uptakes over various V_2O_5/Al_2O_3-TiO_2 catalysts as a function of calcination temperature.

increase of vanadium oxide loading from 2 to 16 wt.% (Fig. 2). The specific surface area results also reveal that the decrease in the BET surface area is more in the case of vanadia-impregnated samples in comparison to pure support. The noted more decrease is mainly due to a strong interaction between the dispersed vanadium oxide and the support thereby blocking some of the pores of support by the dispersed vanadium oxide [16,51,52].

The numerical values of oxygen uptakes obtained at 643 K on the prereduced V_2O_5/Al_2O_3-TiO_2 catalysts calcined at various temperatures are shown in Fig. 3. The corresponding dispersion defined as the ratio between the uptake and the amount of vanadium oxide deposited (O/V) is shown in Fig. 4 [44]. The pure Al_2O_3-TiO_2 support was also found to chemisorb some small quantities of O_2 under the experimental conditions employed in this study. Therefore, the contribution of the support alone was subtracted from the results before reporting. In general, oxygen
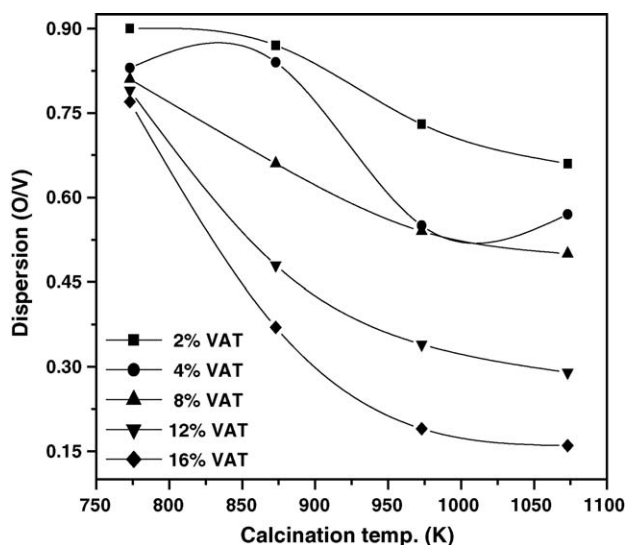

Fig. 4. The V_2O_5 dispersion of various V_2O_5/Al_2O_3-TiO_2 catalysts as function of calcination temperature.

uptakes increased with increase in vanadia loading from 2 to 16 wt.% at a given calcination temperature and decreased with increase of calcination temperature (Fig. 3). However, the numerical values of O_2 uptakes change appreciably and are maximum in case of catalysts calcined at 773 K and minimum at 1073 K. A large difference, except on 2 wt.% sample, in the oxygen uptakes is noted between 873 and 973 K treated samples. Such difference is not observed above and below the temperature range 873–973 K. It can therefore be inferred that calcination of V_2O_5/Al_2O_3-TiO_2 catalysts at 973 K (melting point of V_2O_5 is 963 K) and above apparently results in the formation of more crystalline vanadia (not detectable by XRD), which leaches out from the micropores of the support material where it was initially in a highly dispersed state.

The FTIR spectra of V_2O_5/Al_2O_3-TiO_2 samples calcined at various temperatures were recorded in the range of 400–1800 cm^{-1}, where those bands due to $\nu_{V=O}$ are expected to be observed. Normally, the IR spectrum of unsupported crystalline V_2O_5 shows sharp absorption bands at 1020 and 820 cm^{-1} due to V=O stretching and V−O−V deformation modes, respectively [16]. 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/Al_2O_3-TiO_2 catalysts calcined at 773 K indicated that the vanadium oxide is in highly dispersed state. A gradual shift of the band at 935–970 cm^{-1} was noted with increase in vanadia content. Absorption bands observed in the region 1000–940 cm^{-1} could be attributed to the surface vanadate species, which have been frequently reported for amorphous two-dimensional monolayers of V_2O_5 on TiO_2 support [16,48]. There was no evidence for the formation of crystalline V_2O_5 even in the case of 16 wt.% V_2O_5 loaded sample. With increase in calcination temperature from 773 to 1073 K, a gradual change from amorphous to crystalline anatase phase was observed in line with XRD results. No absorption bands due to crystalline V_2O_5 were seen at 1020 and 840 cm^{-1} indicating that the dispersed vanadia is not transforming into crystalline V_2O_5. However, an improved sharp band in the region 650–850 cm^{-1} was seen, suggesting that titania has been transformed into the crystalline anatase phase.

To investigate thermal stability, samples of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 (16 wt.% V_2O_5) calcined at various temperatures have been investigated by XPS technique. The photoelectron peaks of O 1s, Ti 2p, Al 2p and V 2p obtained for 773 and 1073 K calcined samples are presented in Figs. 5–8, respectively. The corresponding electron binding energies (E_b) for O 1s, Ti 2p, Al 2p and V 2p core levels are presented in Table 1. All these figures and Table 1 clearly indicate that XPS bands depend on the calcination temperature and coverage of vanadium oxide on the mixed oxide carrier, in agreement with earlier reports [53–55]. As presented in Fig. 5, the O 1s peak is, in general, broad and complicated due to non-equivalence of surface oxygen ions. It is due to the overlapping contribution of oxygen from alumina and titania in the case of Al_2O_3-TiO_2 support and from alumina, titania and vanadia in the case of V_2O_5/Al_2O_3-TiO_2 catalyst. In the case of Al_2O_3-TiO_2, two oxygen peaks are observed at both calcination temperatures. The intense peak at lower binding energy ($E_b = 530.0$–530.4 eV) can be attributed to the oxide ions
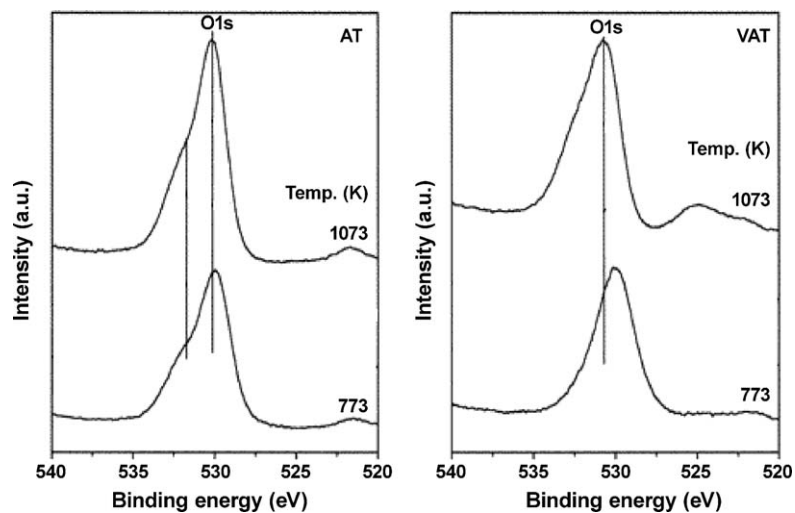
Fig. 5. The O 1s XPS spectra of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 samples calcined at 773 and 1073 K.
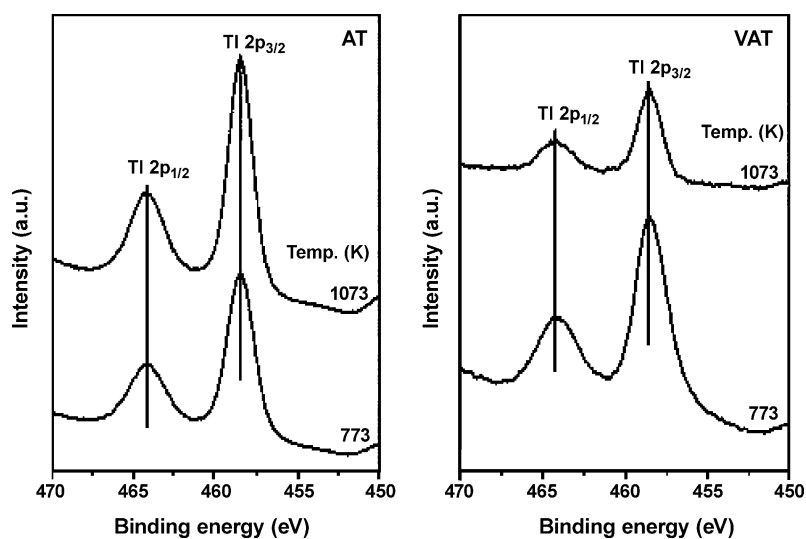
Fig. 6. The Ti 2p XPS spectra of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 samples calcined at 773 and 1073 K.
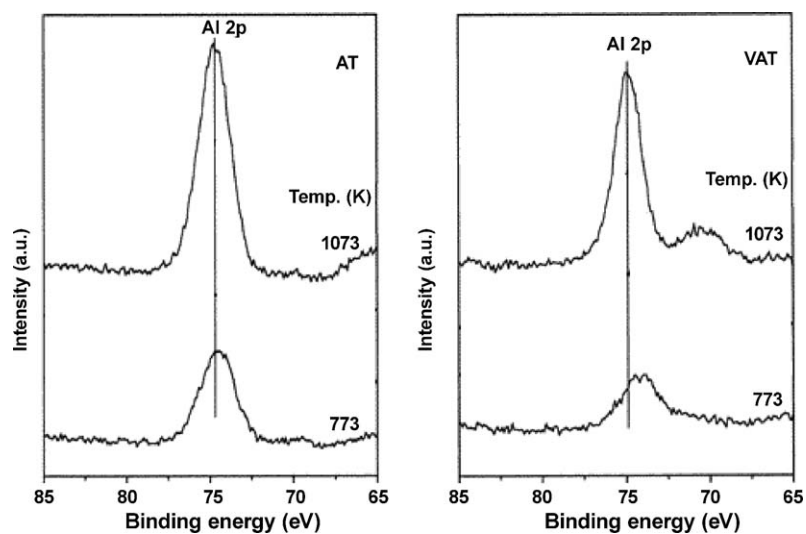
Fig. 7. The Al 2p XPS spectra of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 samples calcined at 773 and 1073 K.
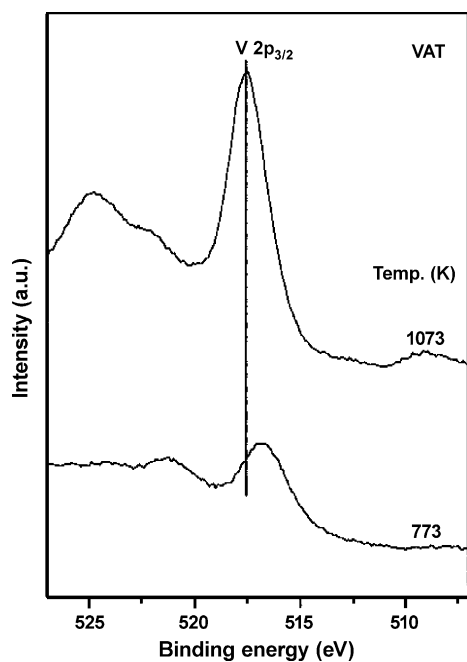
Fig. 8. The V 2p XPS spectra of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 samples calcined at 773 and 1073 K.

bound to Ti (i.e., TiO_2) and the other at higher binding energy ($E_b = 531.1$–531.4 eV) belongs to aluminum oxide ions, in line with literature reports and judging from the electronegativity of the elements involved [45]. The binding energy of the most intense O 1s peak of pure support is almost constant at all calcination temperatures. However, O 1s peak of vanadia-impregnated samples show a clear increase in the binding energy, which can be attributed to the segregation of vanadium oxide on the support surface with increasing calcination temperature.

Fig. 6 represents the binding energies of Ti 2p photoelectron peaks at 458.5 and 464.4 eV corresponding to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ lines, respectively, which agree well with the values reported in the literature [45,53,56]. The Ti $2p_{3/2}$ binding energy values were constant for all samples indicating that the Ti exists in 4+ oxidation state. Interestingly, the intensity of Ti 2p core level spectra increased with increasing calcination temperature

Table 1
Electron binding energy (eV) values of Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 catalysts calcined at various temperatures

Calcination temperature (K)	Binding energy (eV)			
	O 1s	Ti $2p_{3/2}$	Al 2p	V $2p_{3/2}$
Al_2O_3-TiO_2				
773	530.0	458.5	74.5	–
873	530.1	458.5	74.6	–
973	530.1	458.5	74.6	–
1073	530.2	458.5	74.7	–
V_2O_5/Al_2O_3-TiO_2				
773	530.0	458.5	74.2	516.8
873	530.3	458.5	74.5	517.2
973	530.6	458.5	74.6	517.3
1073	530.7	458.5	74.8	517.5

in the case of Al_2O_3-TiO_2 samples due to better crystallization in line with XRD measurements. A decrease in the intensity with increase in calcination temperature is noted in the case of V_2O_5/Al_2O_3-TiO_2 indicating the coverage of dispersed vanadium oxide and its segregation. The Al 2p core level spectra of the Al_2O_3-TiO_2 and V_2O_5/Al_2O_3-TiO_2 samples calcined at 773 and 1073 K are shown in Fig. 7. As presented in Table 1, the core level binding energy of Al 2p increased with increasing calcination temperature. The change in binding energy is slightly more in the case of V_2O_5/Al_2O_3-TiO_2 samples. The increase in the binding energy can be attributed to the disappearance of surface hydroxyl groups of the alumina support. On thermal treatment water is normally evolved from two neighboring hydroxide ions, which leave the coordination sphere of an aluminium ion incomplete. Hence, there is a removal of negative charge density from the alumina center, due to dehydroxylation, which has been reflected in the binding energy values. Dehydroxylation is more in the case of the vanadia-doped samples, which may be due to the formation of V−O−Al bonds during calcination by exchange of surface hydroxyl groups between the active component and the support. Sharp rise in the intensity of the Al 2p core level peaks with increase in calcination temperature has been observed for both cases. This observation may be due to surface enrichment of alumina particles.

The V $2p_{3/2}$ photoelectron peaks of the V_2O_5/Al_2O_3-TiO_2 sample calcined at 773 and 1073 K are shown in Fig. 8. The binding energy of V $2p_{3/2}$ is 516.8 eV for 773 K calcined sample. As the calcination temperature increases from 773 to 1073 K, a gradual increase in the binding energy from 516.8 to 517.5 eV is observed (Table 1). As reported earlier, the binding energy of V $2p_{3/2}$ for V_2O_5 (V^{5+} oxidation state) ranges from 516.4 to 517.4 eV and for V_2O_4 (V^{4+} oxidation state) in the range of 515.4–515.7 eV [16,57]. This shift in the binding energy with increasing calcination temperature may be due to the transformation of dispersed vanadium oxide into microcrystalline V_2O_5. It is an established fact in the literature that the vanadium oxide when present at very low concentration forms isolated vanadium oxide (VO_x) species; at higher concentrations, but still below the theoretical monolayer capacity, a two-dimensional surface phase is known to develop. A disordered or a paracrystalline V_2O_5 phase exists at concentrations above the monolayer point [16]. As described earlier, the vanadium oxide is in a highly dispersed state on the amorphous carrier in the sample calcined at 773 K. As the calcination temperature increases, the crystallization of titania occurs, thereby decreasing the proportion of amorphous material, and the V^{5+} is stabilized on the support surface. Thus, the XPS results corroborate well with the XRD and FTIR measurements.

The activity and selectivity for the conversion of 4-methylanisole to p-anisaldehyde and p-anisic acid on various V_2O_5/Al_2O_3-TiO_2 catalysts calcined at 773 K were investigated between 523 and 723 K at normal atmospheric pressure. The activity and selectivity trends on various catalysts followed the same pattern with reaction temperature and contact time. In general, an increase in the conversion with an increase of temperature was observed. Additional side products with traces of CO and CO_2 were also occasionally noted at higher reaction tem-

Table 2
Activity and selectivity of various V_2O_5/Al_2O_3-TiO_2 catalysts for the conversion of 4-methylanisole to p-anisaldehyde and p-anisic acid after 3 h of reaction at 673 K and normal atmospheric pressure

Catalysts	Conversion of 4-methylanisole (%)	Selectivity (%)	
		p-Anisaldehyde	p-Anisic acid
Al_2O_3-TiO_2	2	0	11
2% V_2O_5/Al_2O_3-TiO_2	23	12	83
4% V_2O_5/Al_2O_3-TiO_2	28	14	81
8% V_2O_5/Al_2O_3-TiO_2	38	18	77
12% V_2O_5/Al_2O_3-TiO_2	44	20	75
16% V_2O_5/Al_2O_3-TiO_2	49	26	69

peratures. The activity was slightly high in the first few minutes and dropped (about 1%) to a level where it remained constant up to the 12 h duration studied. There was no substantial change in the conversion and product selectivity during the 12 h time-on-stream. In order to make better comparison, the activity and selectivity results obtained at 673 K after 3 h of reaction and at a fixed optimum contact time are shown in Table 2. The pure Al_2O_3-TiO_2 did not show any appreciable conversion and product selectivity under the experimental conditions used in this study. The activity and anisaldehyde selectivity of V_2O_5/Al_2O_3-TiO_2 catalyst was found to increase with increase of vanadium oxide loading. The present Al_2O_3-TiO_2 supported catalysts provide more anisic acid with good conversion of 4-methylanisole under the experimental conditions used in this investigation in comparison to Ga_2O_3-TiO_2, MgO and CaO-MgO basic oxide supported catalysts reported earlier [42,43]. In general, two reactants take part in the oxidation reactions, i.e. oxygen and the hydrocarbon molecule to be oxidized. Thus, the reaction may proceed both by electrophilic as well as nucleophilic oxidation processes. In the former case, reaction proceeds by the activation of dioxygen to different moieties like, O_2^*, O_2^- and O^-, while in the latter case it starts by the activation of the hydrocarbon molecule and nucleophilic addition of O^{2-} [58]. The hydrocarbon molecule can react with oxygen following many different reaction pathways. Thus, the reaction can proceed through a complex network, which composed of many parallel and consecutive elementary steps, in which different electrophilic and nucleophilic oxygen species may be involved. Although, it is very difficult to point out the exact mechanism of the reaction, however, it gives an impression that the oxidation of 4-methylanisole to p-anisaldehyde and p-anisic acid may proceed via nucleophilic addition of O^{2-} species from the surface of the catalyst [58].

Furthermore, the CO_2 as a side product formed in the reaction can decrease the activity of these catalysts; this is because CO_2, being acidic in nature, attacks the catalyst surface sites. In fact, a small drop in the activity was noted in the first few minutes of the reaction. The effect of catalyst inhibition by CO_2 results in the formation of weakly bound basic carbonates. The carbonate decomposition temperature is, therefore, an important factor in determining the selectivity of these catalysts. In the case of more basic oxides, the intensity of the catalytic oxide–carbon dioxide interaction is likely to be stronger and the resultant carbonate will

be more stable. Thus, the product selectivity entirely depends on the acid-base characteristic of the catalyst surface. The high acidic nature of the V_2O_5/Al_2O_3-TiO_2 catalysts clearly reflected in higher selectivity towards anisic acid formation.

4. Conclusions

The following conclusions can be drawn from the present study: (1) The Al_2O_3-TiO_2 mixed oxide support calcined at 773 K is in amorphous state and also accommodates a monolayer equivalent of V_2O_5 in a highly dispersed state. (2) The specific surface area and dispersion of vanadium oxide decrease with increase in vanadia content as well as calcination temperature. (3) The XRD, FTIR and O_2 uptake results revealed that the catalysts with 16 wt.% or less vanadia consisted of a surface vanadate phase dispersed on the carrier. (4) The XPS studies revealed the presence of titania, alumina and vanadia in their highest oxidation states, Ti(IV), Al(III) and V(V), respectively at the surface of the materials. The O 1s, Ti 2p, Al 2p and V 2p photoelectron peaks are sensitive to the calcination temperature as well as V_2O_5 coverage on the mixed oxide carrier. (5) The 16 wt.% V_2O_5/Al_2O_3-TiO_2 catalyst exhibited more conversion and more p-anisaldehyde product selectivity among various catalysts investigated.

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