

Vapor phase oxidation of 4-fluorotoluene over vanadia–titania catalyst

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Abstract

The vapor phase oxidation of 4-fluorotoluene has been carried out over vanadia–titania catalysts with moderate conversion and selectivity for 4-fluorobenzaldehyde. Two series of V₂O₅/TiO₂ catalysts with 1–10 mol% vanadia were prepared by sol–gel technique using vanadium and titanium peroxide as vanadia and titania precursors respectively and by impregnation technique using vanadium peroxide on anatase titania support. The samples were characterized by X-ray diffraction, NH₃-TPD, FT-IR and BET surface area measurements. The XRD of the catalysts prepared by impregnation technique showed retention of the anatase titania whereas the catalysts prepared by sol–gel technique showed the formation of rutile titania with minor amount of anatase phase at lower vanadia content (1–3%), which completely transformed into anatase phase at higher vanadia loading. The samples prepared by sol–gel method showed higher acidity and surface area compared to the samples prepared by impregnation. Pyridine adsorption study by FT-IR revealed the presence of Lewis acidity at lower vanadia loading (1–3%) and presence of both Lewis as well as Bronsted acidity at higher vanadia loading. The catalytic activity for oxidation of 4-fluorotoluene increased with vanadia loading in the sol–gel catalysts. The catalysts prepared by impregnation technique were found to be less active. However the selectivity for 4-fluorobenzaldehyde decreased with increase in vanadia content. The influence of vanadia loading, reaction temperature and contact time on the catalytic activity for 4-fluorotoluene oxidation has been investigated. The structure of the catalyst and its catalytic activity has been correlated.

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1. Introduction

The selective oxidation of alkyl aromatics to the corresponding aldehydes or acids over heterogeneous catalysts is an area of intense research due to its well-known advantages over the conventional oxidation using homogeneous catalysts. Various solid acid catalysts have been investigated for the partial oxidation of toluene to benzaldehyde as a model reaction and most of these catalysts are based on vanadia supported either on SiO₂ or TiO₂ [1–3]. Fluorobenzaldehydes are known to be very important intermediates in the preparation of fluorine containing agriculture chem-

icals or pharmaceuticals. Conventionally fluorobenzaldehydes are prepared by a method wherein firstly fluorine is introduced into aromatic ring followed by introducing an aldehyde group by various means such as a method of hydrolyzing a fluorobenzylidene chloride derived from fluorotoluene [4] or a method of oxidizing a fluorochlorobenzyl alcohol [5]. Fluorobenzaldehydes can be prepared by halogen exchange method using chlorobenzaldehyde, potassium fluoride and quaternary compounds as catalysts in an organic solvent [6]. Fluorobenzaldehydes are also prepared by a process, which comprises heating a mixture of fluorobenzene and a strong Lewis acid with dissolved hydrogen chloride in an atmosphere of carbon monoxide at about 45–100 °C and at a total pressure of about 150 psig. The resulting Lewis acid complex of 4-benzaldehyde is broken by quenching the

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reaction mass with a Lewis acid solvating liquid [7]. Industrially 4-fluorobenzaldehyde is prepared on more than 100 tons scale from fluorobenzene by bromination and subsequent reaction with magnesium and DMF [8]. This route is becoming less competitive and alternate routes are under investigation. These processes are multi-step, cumbersome and involve tedious work up procedure as well as pose environmental problems. Hence oxidation of fluorotoluenes to fluorobenzaldehydes using heterogeneous catalysts will be an attractive alternative.

In case of fluorobenzaldehyde, the electron withdrawing fluorine at *ortho* or *para* position makes the aldehyde group very reactive and it is likely to get converted to carboxylic group and/or hydroxyl group lowering the selectivity of the fluorotoluene oxidation to fluorobenzaldehyde and reaction goes to carboxylic acid formation. The gas phase selective synthesis of 3-fluorobenzaldehyde from 3-fluorotoluene over bulk iron molybdate oxide in borelite/zeolites host has been investigated by Centi et al. [9,10]. Higher conversion and selectivity was obtained in case of Fe–Mo oxide inside borelite/zeolite matrix, which was correlated to the active site isolation inside the zeolite matrix. In our previous nitration work [11] we found that 4-fluorotoluene is highly susceptible to oxidation rather than nitration as compared to the remaining two isomers. To our knowledge, the oxidation of 4-fluorotoluene over solid catalyst has not been investigated before and prompted us to investigate systematically. Initially vanadia–titania catalyst has been used for this study because of its well known activity for oxidation reactions. It is well accepted that for vanadia/titania systems, structural characteristic, catalytic activity and selectivity depends on method and conditions of preparation, crystallographic titania structures, vanadia loading and calcination temperatures [12]. Generally the vanadia–titania catalyst prepared by sol–gel technique show higher catalytic activity because of high surface area and isolation of catalytically active sites. In our previous study we have followed the sol–gel process for preparation of titania catalyst using titanium peroxides as precursor in sol–gel synthesis, which led to high surface area titanium oxide [13]. The vanadium pentoxide also forms vanadium peroxide when treated with hydrogen peroxide and may be used as potential vanadia source in sol–gel synthesis. Vanadium and titanium peroxide precursor solutions are unstable and form the respective oxides with slow decomposition of the peroxides. When these solutions are mixed together forming a homogeneous solution, it slowly transforms to a transparent viscous gel and leads to a very uniform dispersion of vanadia on high surface area titania support. The present procedure has the advantage over the conventional alkoxide based sol–gel route where a very critical control of the preparation parameters is required to obtain a good homogeneous transparent gel. It also requires very dry solvent to avoid precipitation of hydroxide due to moisture sensitive nature of metal alkoxides. Metal peroxides are comparatively easier to prepare with proper precautions and since they are aqueous solutions, peroxides can be decomposed at lower

temperatures to respective oxides without any carbon contamination. We have used this modified sol–gel procedure for the preparation of the vanadia–titania catalyst for the present investigation. Other catalyst samples were prepared for comparison by impregnation technique using vanadium peroxide and commercial anatase titania as vanadia and titania precursors, respectively.

2. Experimental

2.1. Catalyst preparation

A series of vanadia–titania catalysts with varying vanadia concentration (1–10 mol%) were prepared by sol–gel technique using vanadium peroxide and titanium peroxide as vanadium and titanium precursors respectively. In a typical synthesis of 5 mol% vanadia–titania catalyst, 4.03 g titanium butoxide (Aldrich make) was hydrolyzed with 100 g deionized water. To this, 20 ml aqueous hydrogen peroxide (30%, Qualigen) was added to get a transparent orange sol of titanium peroxo complex. 0.113 g vanadium pentoxide (Loba make, AR grade) was suspended in 25 ml deionized water to which 3 ml 30% aqueous hydrogen peroxide solution was added to get a clear solution. Peroxovanadic acid solution thus formed was added to the titanium peroxo complex solution and a transparent greenish yellow viscous gel was formed, which was dried at ambient temperature, heated in an oven at 110 °C and calcined at 400 °C for 8 h in air. Another series of catalysts was prepared with varying vanadia concentration by impregnation technique using vanadium peroxide and anatase titanium dioxide (Merck). In a typical synthesis of 5 mol% vanadia–titania catalyst, 1.37 g V₂O₅ was suspended in 100 ml deionized water to which 1 ml of 30% aqueous hydrogen peroxide was added to get a transparent orange solution. To this, 9.48 g TiO₂ in the powder form was added and stirred at 70 °C until it is dried and heated in an oven at 110 °C and calcined at 400 °C for 8 h in air.

2.2. Catalyst characterization

X-ray diffraction analysis was carried out using XRD 7 Seiffert-FPM with Cu K α radiation. BET surface area and pore volume distribution were measured on a micrometrics ASAP2010 analyzer using N₂ as the adsorbent. Temperature programmed desorption of ammonia (NH₃-TPD) was employed for the determination of the acidity. About 200 mg sample (0.3–0.5 mm diameter fraction) was pretreated under nitrogen (35 ml/min) at 400 °C for 1 h, then cooled to 120 °C, and then exposed to NH₃. The physisorbed ammonia was removed for 1 h at 120 °C. After cooling to 80 °C, the TPD program (10 °C/min, up to 460 °C, keeping 30 min) was started. Desorption of ammonia was continuously monitored by IR spectroscopy (FT-IR system 2000, Perkin-Elmer).

2.3. Pyridine adsorption

Nature and strength of the acidity of the catalyst was determined by pyridine adsorption studies using Shimadzu 8000 series FT-IR using DRIFT assembly. The sample was placed in the DRIFT cell and heated to 400 °C in flow of inert gas (N₂) for 2 h. It was cooled to 100 °C and pyridine was adsorbed on the sample. The physisorbed pyridine was removed by flushing the cell with N₂ for 30 min at 100 °C. The temperature programmed desorption of pyridine was studied at 200, 300 and 400 °C. The spectra were recorded after maintaining the temperature for 30 min. The spectrum of the neat catalyst (before pyridine adsorption) at 100 °C was subtracted from all the spectra.

2.4. Catalytic activity measurements

Catalytic tests were carried out using quartz continuous down flow reactor (4 mm inner diameter) operating at atmospheric pressure, which was loaded with 0.2 g of catalyst in the form of granules (0.5–1.0 mm range). The feed composition was 0.398 ml/min 4-fluorotoluene (vapor phase), 18.9 ml/min air and 32 ml/min argon. A GHSV of 20,000 was used for the regular test at different temperatures. Different tests were performed to optimize GHSV by varying carrier gas flow. For each test the constancy of catalytic performance was monitored for at least 4–5 h. In the absence of the catalyst it was found that 4-fluorotoluene does not react at 400 °C or lower temperature. Before the catalytic tests the catalysts were conditioned at 400 °C for 8 h in the flow of an inert gas. The product mixture was adsorbed in traps containing acetone cooled to –5 °C. The product in the trap was analyzed using a GC (HP 5890 series II, HP-Innowax 30 m Capillary column) equipped with a FID detector whereas the gaseous samples were analyzed after regular time interval using GC–MS (Shimadzu QP 5000, PONA 50 m Capillary column).

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of the samples prepared by sol–gel technique are shown in Fig. 1. Predominantly rutile phase is seen at lower vanadia content (1%) with minor amount of anatase phase, which increases with increasing vanadia content (3–10%). Interestingly no separate vanadia phase is seen in the XRD pattern at all vanadia loadings indicating formation of vanadia–titania solid solution or very high dispersion of vanadia on titania prepared by sol–gel compared to samples prepared by impregnation. The formation of rutile phase at lower vanadia content may be due to formation of very high surface area titanium dioxide by decomposition of titanium peroxide, which lowers the phase transformation temperature of anatase to rutile. The formation of anatase

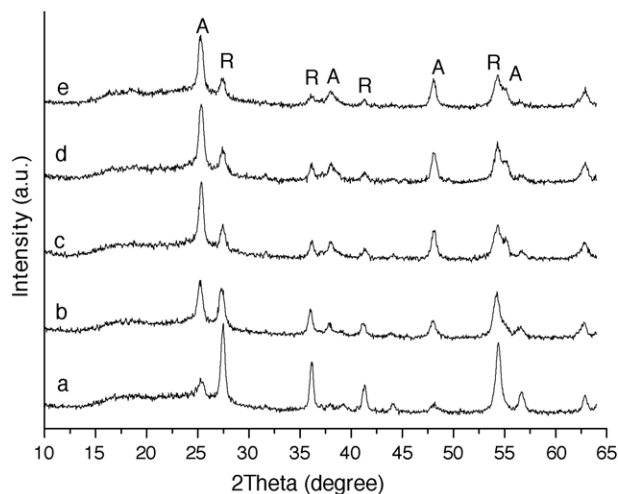


Fig. 1. XRD pattern of (a) 1%, (b) 3%, (c) 5%, (d) 7% and (e) 10% V₂O₅/TiO₂ sol–gel catalysts. R: rutile, A: anatase.

phase at higher vanadia loading may be due to the formation of vanadia–titania solid solution or because of strong interaction of vanadia on high surface area titania support.

The X-ray diffraction patterns of various vanadia–titania catalysts prepared by impregnation method showed peaks of TiO₂ with an intense peak at $2\theta = 25.28$ corresponding to the diffraction by planes of (1 0 1) of anatase TiO₂. However XRD peaks corresponding to V₂O₅ at $2\theta = 20.26$ can be found only in the case of samples with vanadia loading ≥ 5 mol%. The intensity of V₂O₅ peaks increases with increase in the vanadium loading in the catalysts. The absence of XRD peaks due to V₂O₅ at lower vanadia content (<5%) indicates that vanadium oxide is present in highly dispersed amorphous state on TiO₂. However the possibility cannot be ruled out for the presence of vanadia crystallites having size less than 5 nm, which is beyond the detection capacity of the powder X-ray diffraction technique. XRD peaks corresponding to rutile TiO₂ were not observed in all the calcined samples suggesting that the anatase to rutile phase transition of TiO₂ did not occur at any stage of preparation. From these results it is clear that the samples prepared by peroxide base sol–gel synthesis leads to the formation of vanadia–titania catalysts with different structural characteristics than that of samples prepared by impregnation technique. The XRD results of impregnated catalyst are in good agreement with that reported by Chary et al. [14]. According to the literature, the transformation of anatase to rutile is an efficient process for TiO₂ samples calcined above 700 °C [15]. Balikdjian et al. [16] and recently Rodella et al. [15] have studied the thermal behavior of V/Ti systems with different vanadia loadings obtained by sol–gel technique under acid conditions and found that with increasing vanadia content the phase transition temperature of anatase to rutile increases. Titania without vanadia prepared by sol–gel technique under acid conditions show predominant rutile phase at 450 °C and as the vanadia content was increased, this phase transition temperature increased and with 6% vanadia loading

Table 1

V ₂ O ₅ content (mol%)	Sol-gel catalyst		Impregnation catalyst	
	Surface area (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	Surface area (m ² g ⁻¹)	PV (cm ³ g ⁻¹)
1	56.77	0.295	8.49	0.045
3	90.27	0.316	11.09	0.087
5	93.44	0.249	8.68	0.071
7	94.80	0.303	7.59	0.050
10	102.41	0.218	7.19	0.052

the complete transformation of anatase to rutile occurred at 600 °C.

3.2. BET surface area

The BET surface area and pore volumes of all the catalysts are given in Table 1. Initially there is an increase in the surface area from 56.77 to 90.27 m² g⁻¹ when vanadia loading is increased from 1 to 3% and then there is small increase in the surface area when vanadia loading is gradually increased to 10%. When vanadium peroxide is added to titanium peroxide solution it forms a homogeneous greenish transparent gel up to 5% vanadia loading. When the vanadia content is further increased to 7% then the gel characteristic changes and a non-homogeneous opaque gel with agglomerated flocculates is formed. The flocculates swell in the non homogeneous gel upon drying in air under ambient conditions leads to the formation of vanadia xerogel on titania support, which gives rise to increase in surface area [17]. Similarly pore volumes for the catalysts prepared by sol-gel technique are large (0.218–0.316 cm³ g⁻¹) as compared to the catalysts prepared by impregnation technique (0.045–0.087 cm³ g⁻¹). The vanadium and titanium peroxides decompose to corresponding metal oxides with the evolution of oxygen, which makes the product more porous with high surface area.

3.3. Pyridine adsorption studies

Pyridine adsorption studies using FT-IR (Fig. 2) showed the presence of Lewis acidity (peak at 1445 cm⁻¹) for all the samples and presence of Bronsted acidity (peak at 1540 cm⁻¹) for 5–10% vanadia loading. The Lewis acidity is found to increase initially from 1 to 3% and then slowly decrease up to 10% vanadia loading. The initial increase in the Lewis acidity is due to the transformation of titania rutile phase to anatase. Titania is reported to contain only Lewis acidity in anatase as well as rutile phase, however the number of Lewis sites are more in case of anatase as compared to rutile phase [18]. The decrease in the Lewis acidity from 3 to 10% loading may be due to the formation of vanadia clusters on titania support. When vanadia content is increased from 5 to 10%, the multilayer vanadia species are formed generating Bronsted acidity due to the terminal hydroxyl groups on surface vanadium oxide. Similar observation has been made

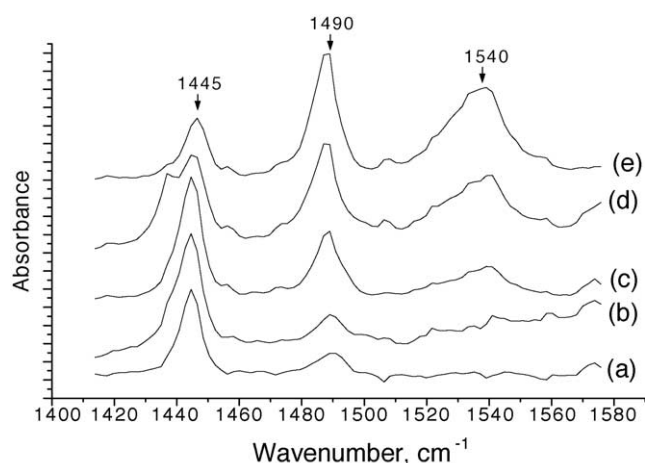


Fig. 2. Pyridine adsorption spectra of (a) 1%, (b) 3%, (c) 5%, (d) 7% and (e) 10% V₂O₅/TiO₂ (sol-gel).

by Akbas et al. [19] for the vanadia–titania catalysts prepared by grafting technique.

3.4. Temperature-programmed desorption (TPD)

Temperature-programmed desorption of ammonia (NH₃-TPD) for different combinations of V/Ti sol-gel catalysts (Fig. 3) shows that the overall acidity is higher in case catalysts with low vanadium content. From the spectra it also

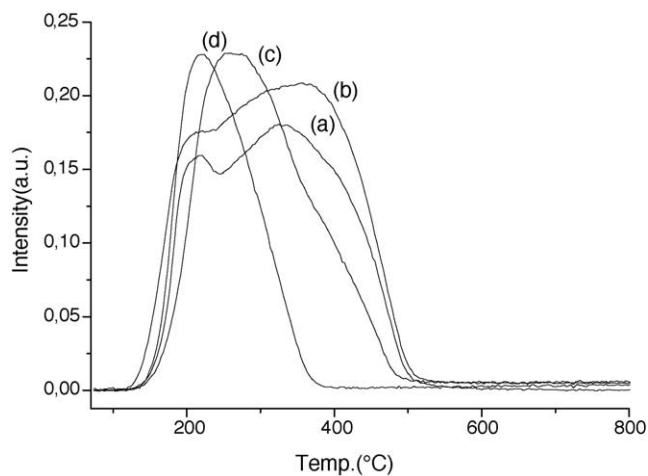


Fig. 3. NH₃-TPD of (a) 1%, (b) 3%, (c) 7% and (d) 10% V₂O₅/TiO₂ sol-gel catalysts.

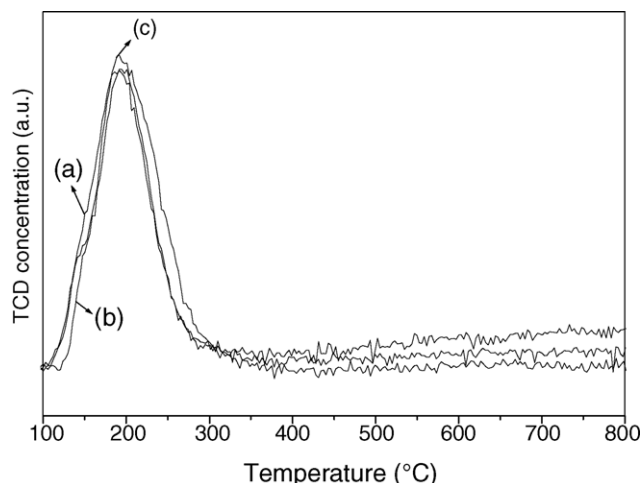


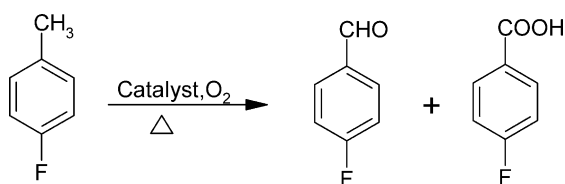
Fig. 4. NH_3 -TPD of (a) 1%, (b) 5% and (c) 10% $\text{V}_2\text{O}_5/\text{TiO}_2$ impregnation catalysts.

seems that the major acidity is attributed to TiO_2 for samples with low vanadia content (1–3%). The desorption of ammonia in two different temperature ranges indicates the presence of two types of acid sites with different strengths and can be correlated with XRD pattern which shows two phase titania samples. At low vanadia content (1%) the rutile phase is predominant with very high dispersion of vanadium either in substitutional position or on the surface leading to the higher acid strength. With increase in vanadia content the formation of bulk vanadia on anatase titania phase is observed which shows lower acidity. The catalysts prepared by impregnation technique using anatase titania did not show any measurable effect of vanadia content on the NH_3 -TPD spectra (Fig. 4) and the results match with the samples prepared by sol–gel with higher vanadia content.

3.5. Catalytic activity

The catalytic oxidation of 4-fluorotoluene to 4-fluorobenzaldehyde and further oxidation to benzoic acid is represented in Scheme 1.

Fig. 5 displays the catalytic behavior of 1 and 3% $\text{V}_2\text{O}_5/\text{TiO}_2$ prepared by sol–gel technique for oxidation of 4-fluorotoluene. As V_2O_5 content is slightly increased from 1 to 3 mol%, a drastic change in the conversion and selectivity has been observed. In case of 1% $\text{V}_2\text{O}_5/\text{TiO}_2$ very high selectivity (60–80%) for 4-fluorobenzaldehyde (4-FBZ) is obtained at lower conversion (1–8%) in the temperature range of 300–375 °C. In case of 3% $\text{V}_2\text{O}_5/\text{TiO}_2$, though the



Scheme 1.

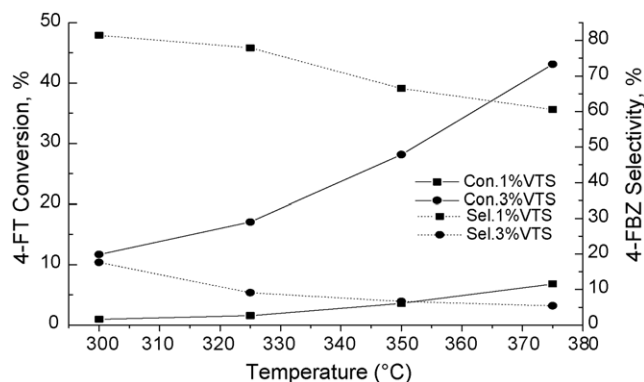


Fig. 5. Influence of temperature on conversion and selectivity. Reaction conditions: catalyst 1 and 3% $\text{V}_2\text{O}_5/\text{TiO}_2$ (sol–gel), catalyst amount 200 mg, mole ratio (FT: O_2) = 1:10, GHSV: 20,000 h^{-1} , TOS 4 h; 4-FT: 4-fluorotoluene, 4-FBZ: 4-fluorobenzaldehyde, VTS: vanadia–titania by sol–gel.

conversion increased up to 12–43% the selectivity dropped down drastically to 5–18%. This drastic fall in 4-FBZ selectivity may be due to higher conversion to fluorobenzaldehyde, which further gets converted to fluorobenzoic acid (4-FBA). At high temperature, corrosion of reactor and products trap has been observed which indicates the formation of HF by decomposition of fluorotoluene. At higher temperature (>350 °C), formation of CO and CO_2 was observed.

The influence of vanadia content on the catalytic activity is shown in Figs. 6 and 7 for catalysts prepared by impregnation and sol–gel techniques, respectively. Catalysts prepared by impregnation technique (Fig. 6) showed very low conversion (about 10%) and did not show any regular trend in conversion and selectivity with increasing vanadia content. The lower activity may be due to low surface area and non-uniform distribution of vanadia on anatase titania. The cata-

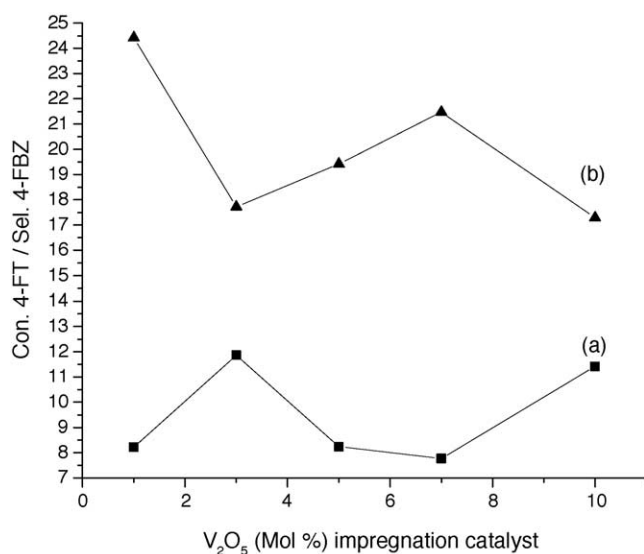


Fig. 6. Influence of vanadia loading in impregnation catalysts on (a) conversion and (b) selectivity. Reaction conditions: catalyst amount 200 mg, temperature 300 °C, mole ratio (FT: O_2) = 1:10, GHSV 20,000 h^{-1} , TOS 4 h.

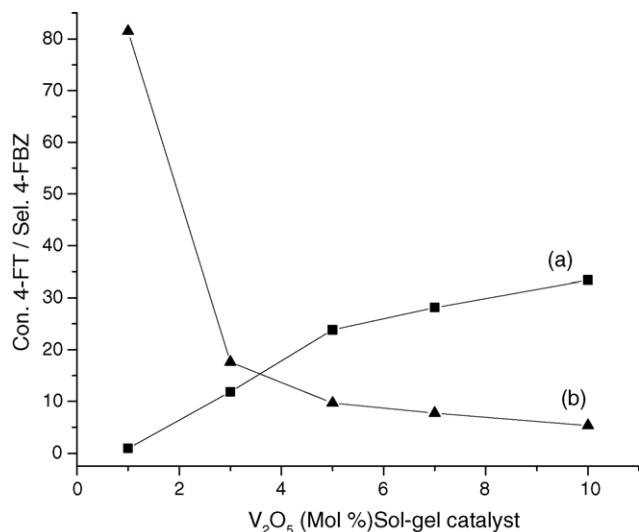


Fig. 7. Influence of V₂O₅ loading in sol-gel catalysts on (a) conversion and (b) selectivity. Reaction conditions: catalyst amount 200 mg, temperature 300 °C, mole ratio (FT:O₂) = 1:10, GHSV 20,000 h⁻¹, TOS 4 h.

lysts prepared by sol-gel technique (Fig. 7) showed continuous increase in conversion and decrease in selectivity with increase in vanadia content. The decrease in the selectivity was due to the consecutive oxidation of 4-fluorobenzaldehyde to 4-fluorobenzoic acid, which is a solid and was deposited at the outlet of the reactor as white crystalline solid (like glass wool) which was analyzed by gas chromatograph after dissolving in a solvent. The deposition of 4-fluorobenzoic acid at the outlet of the reactor increased the pressure drop due to which the reaction could not be continued.

Fig. 8 displays the influence of GHSV on 4-fluorotoluene conversion and 4-fluorobenzaldehyde selectivity using 3% V₂O₅/TiO₂ sol-gel catalyst. As expected fluorotoluene conversion is decreased at higher GHSV due to lower contact time while the selectivity for 4-fluorobenzaldehyde increased continuously with increasing GHSV. The GHSV could not

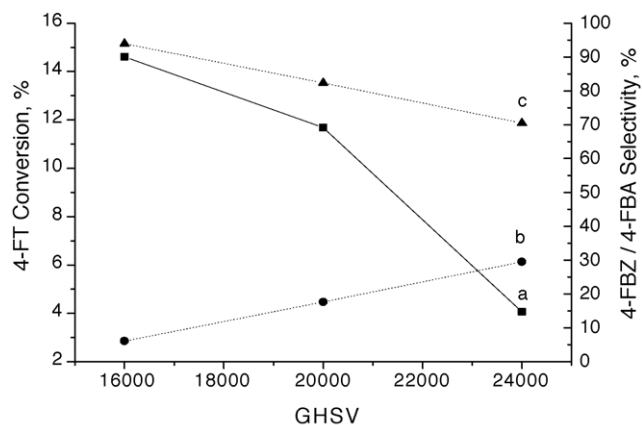


Fig. 8. Influence of GHSV on (a) conversion and selectivity for (b) 4-FBZ and (c) 4-FBA. Reaction conditions: catalyst 3% V₂O₅/TiO₂ (sol-gel), catalyst amount 200 mg, temperature 300 °C, mole ratio (FT:O₂) = 1:10, TOS 4 h.

be increased beyond 24,000 because of the limitations in the experimental set up. Fig. 8 shows decrease in benzoic acid formation with increase in GHSV from 16,000 and 24,000 due to decrease in rate of consecutive reaction, increasing the selectivity for 4-fluorobenzaldehyde.

In the oxidation of straight chain hydrocarbons or of alkyl aromatics the activation of a C–H bond is considered to be first and often rate determining step, which is followed by the step of incorporation of oxygen into the activated organic molecular species. This approach is rather simplified as both, abstraction of hydrogen and addition of oxygen, can take place in a concerted step though the source of oxygen which is incorporating into the organic molecule is still a matter of debate. Both lattice and chemisorbed oxygen have been claimed as a source of oxygen in the literature [20]. Since in the absence of oxygen flow no oxidation was observed even in the presence of catalyst indicating that the oxidation products can be formed with participation of chemisorbed oxygen. In many oxidation reactions, surface oxide ion has been proposed as a site capable of abstracting a hydrogen atom in the form of a proton with the formation of the surface OH group and in this case activity should depend on the nucleophilicity (basicity) of the catalyst oxygen.

4. Conclusion

The vanadia-titania catalysts prepared by sol-gel process showed higher catalytic activity for the oxidation of 4-fluorotoluene to 4-fluorobenzaldehyde compared to the catalysts prepared by impregnation technique. In case of catalysts prepared by sol-gel technique with lower vanadia loadings show predominantly rutile phase whereas catalysts with higher vanadia loadings show anatase phase with vanadium either at substitutional position or highly dispersed on high surface area titania support. Catalysts with lower vanadia loading showed only Lewis acidity with high acid strength whereas at higher loadings Lewis as well as Bronsted acidity is observed. The higher catalytic activity of vanadia-titania catalysts prepared by sol-gel technique may be due to the higher dispersion of vanadia on titania support and its higher Lewis acidity. By using higher GHSV it may be possible to increase the selectivity for benzaldehyde by suppressing the further oxidation to fluorobenzoic acid.

Acknowledgement

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