

Studies on catalytic functionality of V_2O_5/Nb_2O_5 catalysts

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Abstract

A series of V_2O_5/Nb_2O_5 catalysts with V_2O_5 loadings ranging from 2 to 12 wt.% of V_2O_5 were prepared by wet impregnation method. These catalyst samples were characterized by X-ray diffraction (XRD), oxygen chemisorption, electron spin resonance (EPR), temperature-programmed desorption (TPD) of ammonia, and scanning electron microscopy (SEM). The catalytic properties of these catalysts were tested for vapor phase ammoxidation of toluene to benzonitrile and compared with more traditional supports, such as Al_2O_3 , SiO_2 and TiO_2 . Dispersion of vanadia was determined by the static oxygen chemisorption method at 640 K on the samples prerduced at the same temperature. At low vanadia loadings (<6 wt.%) vanadium oxide is found to be present in a highly dispersed state. The X-ray diffraction results suggest the formation of β -(Nb,V) $_2O_5$ phase at higher loadings of V_2O_5 . The EPR spectra obtained under ambient conditions for the catalysts show the presence of V^{4+} ions in a distorted tetrahedral symmetry. SEM results suggest that at low vanadia loadings vanadia is well dispersed and at higher loadings dense clusters are formed. The results of temperature programmed desorption of ammonia indicate that the acidity increases with vanadia loading up to 6 wt.% V_2O_5 and decreases at higher vanadia loadings. The ammoxidation activity also increases with vanadia loading up to 6 wt.%, which corresponds to monolayer coverage and remains constant at higher vanadia loadings. The catalytic properties during ammoxidation of toluene are correlated to the oxygen chemisorption sites and acidic sites.

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1. Introduction

Supported vanadia catalysts have been extensively employed for a variety of commercial applications. For example, vanadium oxide is an important component in the selective oxidation of *o*-xylene to phthalic anhydride [1,2], ammoxidation of alkyl aromatics [3,4] and selective catalytic reduction of NO_x with NH_3 [5]. In addition to these oxidation reactions, supported vanadia catalysts have also been investigated for the oxidative dehydrogenation of alkanes to olefins [6], oxidation of butane to maleic anhydride [7] and selective oxidation of methanol to formaldehyde [8] or methyl formate [9]. The catalytic properties of the active vanadia phase can be greatly influenced by the nature of the supported oxide and the dispersion of the active component. Supported metal oxides are formed when the active

component, usually a transition metal oxide, is dispersed on a high surface area oxide-support to form two-dimensional over layers or surface species. The most commonly used supports are Al_2O_3 , SiO_2 , TiO_2 and ZrO_2 . In recent years, niobium-based materials have been employed as supports in numerous catalytic applications [10–15]. Niobia can be used as a support, as a promoter and as a unique solid acid. In addition to being used as a promoter, niobium oxide (Nb_2O_5) has also been used successfully as a support for preparing supported metal oxide catalysts [16]. Matsuura et al. [17] reported that the catalytic activity during the ammoxidation of isobutane to methacrylonitrile was improved, with Bi–Mo based composites supported on Nb_2O_5 compared to those being supported on γ - Al_2O_3 and SiO_2 . Recent studies on Cr_2O_3/Nb_2O_5 catalysts [18] also show higher yields in oxidative dehydrogenation of propane when compared to Cr_2O_3/Al_2O_3 and Cr_2O_3/TiO_2 catalysts.

Benzonitrile is used as a precursor for resins and coatings as well as an additive in fuels and fibers [19].

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Stobbelaar [19] reported the ammoxidation of toluene over supported metal oxide catalysts and concluded that V/NaY and Mn/NaY catalysts show relatively high benzonitrile yield under optimum conditions. In the present study, the niobia supported vanadium oxide catalysts were successfully tested for the ammoxidation of toluene to benzonitrile and showed much better activity than other supported metal oxide catalysts such as TiO₂, SiO₂ and ZrO₂. The activity results of V₂O₅/Nb₂O₅ catalysts are also comparable to those in the existing reports [20–22]. The characterization of V₂O₅/Nb₂O₅ catalysts was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), oxygen chemisorption, electron spin resonance (EPR) and ammonia temperature-programmed desorption (TPD) methods. The catalytic properties have been evaluated for the vapor phase ammoxidation of toluene.

2. Experimental section

A series of V₂O₅/Nb₂O₅ catalysts with V₂O₅ loadings in the range of 2–12 wt.% were prepared by wet impregnation with an aqueous solution containing ammonium metavanadate (Fluka). Prior to impregnation, the Nb₂O₅ was prepared by calcination of hydrated niobia (supplied by CBMM, Brazil HY-340, surface area 55 m²/g) at 773 K for 4 h. The catalysts were subsequently dried at 383 K for 16 h and calcined in air at 773 K for 5 h. Oxygen chemisorption was measured by a static method using a Pyrex glass system capable of attaining a vacuum of 10⁻⁶ Torr. The details of the experimental set up were given elsewhere [23]. Prior to adsorption measurements the samples were pre-reduced in a flow of hydrogen (40 ml/min) at 640 K for 2 h and evacuated at the same temperature for an hour. Oxygen chemisorption uptakes were determined as the difference of two successive adsorption isotherms measured at 640 K. The surface area of the catalysts was determined by the BET method using nitrogen physisorption at 77 K taking 0.162 nm² as its cross-sectional area.

X-ray diffractograms were recorded on a Siemens D-5000 diffractometer using graphite filtered Cu K α radiation.

SEM analysis was performed on a Leo VP1530 Field emission scanning electron microscope (FESEM). The sample was mounted using double-sided carbon tapes. The samples were sputter coated with 50 nm of Au–Pd. The images were obtained using the JEOL JSM-6400.

EPR measurements were recorded at room temperature on a Bruker ESP 300 E (X-band) spectrometer ($\nu = 9.473$ GHz) with 100 kHz modulation. The samples in powder form were loaded in quartz tubes (4 mm internal diameter). The magnetic field was scanned from 2200 to 4200 G. A microwave power of 20 mW and modulation amplitude of 2 G was used for each measurement. The numerical double integration of spectra was performed using WINEPR software.

Acidity of the samples was measured by stepwise temperature programmed desorption (STPD) of ammonia using a

pulse chemisorb 2700 unit (Micromeritics). A detailed procedure has been given elsewhere [24]. A powdered sample (ca. 300 mg) was introduced in to the sample tube. It was pretreated in a helium flow (20 ml/min) for 2 h at 723 K. The sample temperature was brought down to 353 K. Using the loop (0.984 cm³) saturated with ammonia, several pulses were flushed through the sample tube. The sample was thus saturated with ammonia (normally it takes 5–6 pulses of 30 s duration each). The saturation of the sample with ammonia is evidenced by the appearance of a constant peak area on the chart and by the constant digital reading. After saturation, the sample is flushed in a helium flow for 30 min to remove any loosely bound ammonia on the sample at 353 K. The temperature of the sample was then raised to 423 K and the ammonia was allowed to desorb at this temperature. The completion of desorption of ammonia at this temperature was verified from digital readings on the instrument as well as by the steady base line on the strip chart recorder. The desorbed ammonia in this temperature region 353–423 K is taken as physisorbed or weakly chemisorbed ammonia corresponding to catalytic sites of weak acidic strength. The sample temperature was then raised to 573 K. The desorbed ammonia is again recorded on the chart as well as on the instrument. The ammonia desorbed in the temperature region from 423 to 573 K is considered to represent the catalytic sites of medium acidic strength. The desorption process is repeated by raising the temperature to 723 K and the ammonia desorbed in this temperature region is considered to represent catalytic sites of strong acid strength. The qualitative distribution of the relative number and the strength of acid sites can thus be evaluated by this method of temperature programmed desorption of ammonia.

The ammoxidation of toluene to benzonitrile reaction was carried out in a fixed-bed down-flow, cylindrical Pyrex reactor with 20 mm internal diameter. About 0.5 g of the catalyst with a 18–25 mesh size diluted with an equal amount of quartz grains of the same dimensions was charged into the reactor and supported on a glass wool bed. In order to minimize the adverse thermal effects, the catalyst was diluted to its same volume with quartz grains of similar particle size. Prior to introducing the reactant toluene with a syringe pump (B-Braun perfusor, Germany) the catalyst was oxidized at 673 K for 2 h in air flow (40 ml/min) and then the reactor was fed with toluene, ammonia and air in the mole ratio of 1:13:26. The zone above the catalyst bed filled, with quartz glass particles heated up to 473 K for adequate vaporization of liquid feed served as the pre-heater. The reaction products benzonitrile and benzene were analyzed by an HP 6890 gas chromatograph equipped with flame ionization detector (FID) using HP-5 capillary column. The carbon oxides were analyzed by HP-5973 GC-MS using carboxisieve column. The activity of pure Nb₂O₅ was also tested and found to be inactive for the ammoxidation of toluene under the present experimental conditions.

3. Results and discussion

The XRD patterns of V_2O_5/Nb_2O_5 catalysts are presented in Fig. 1. It can be seen from the figure that all the samples showed XRD peaks due to low temperature form of TT phase of Nb_2O_5 with an intense peaks at $2\theta = 22.5$ (100%) and 28.5 (90%). However, XRD peaks corresponding to V_2O_5 at $2\theta = 20.2$ can be seen only from 6 wt.% samples in addition to the intense niobia peaks. The intensity of the V_2O_5 at $2\theta = 20.2$ increases with vanadia loading in the catalysts (shown in Fig. 1, ∇). The absence of XRD peaks due to V_2O_5 at lower composition (below 6 wt.%) indicates that vanadium oxide is present in a highly dispersed amorphous state on Nb_2O_5 support surface. A mixed vanadium and niobium oxides such as $\beta-(Nb,V)_2O_5$ (JCPDS card No: 16–132) was formed at moderately high vanadia content and increases with further increase of vanadia content. This $\beta-(Nb,V)_2O_5$ phase can be observed with $d = 3.77$, 3.56 , and 3.40 Å ($2\theta = 23.6$, 25 , and 26.19) for samples containing 10 and 12 wt.% V_2O_5 supported on Nb_2O_5 shown with closed cir-

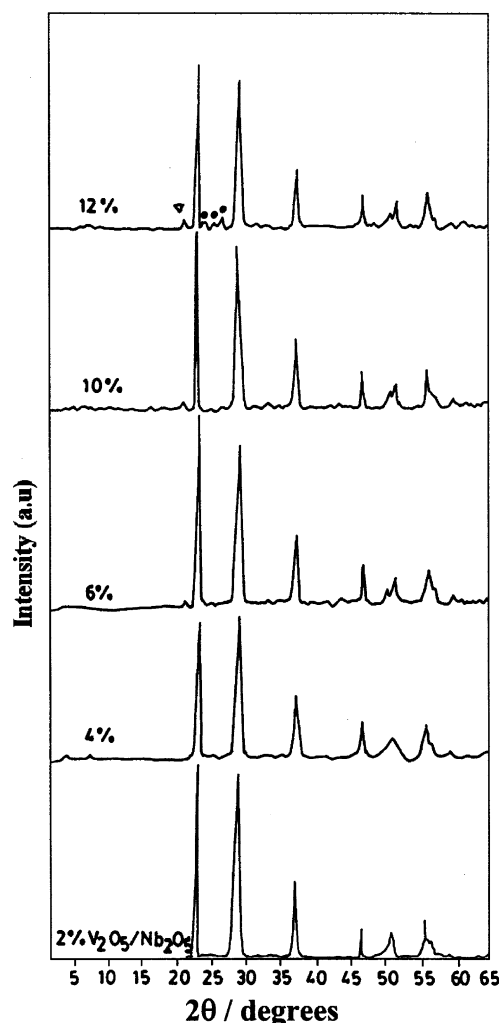


Fig. 1. X-ray diffraction patterns of V_2O_5/Nb_2O_5 catalysts [26]. (●) Peaks due to $\beta-(Nb,V)_2O_5$ phase; (∇) peaks due to V_2O_5 .

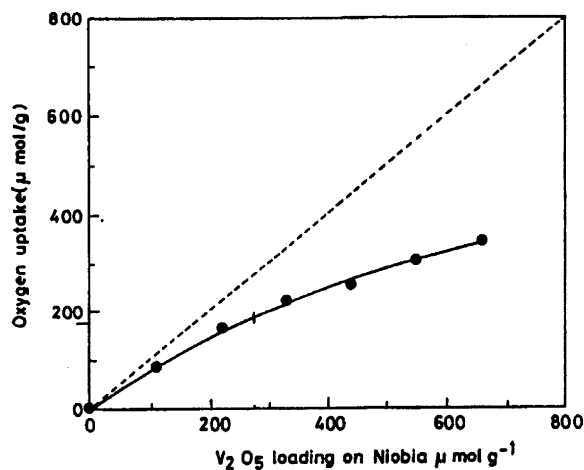


Fig. 2. Oxygen uptake plotted as a function of vanadia loading on Nb_2O_5 [26] ($T_{ads} = T_{red} = 640$ K).

cles in Fig. 1. We have also discussed these XRD results in our recent studies [25,26]. Watling et al. [12] observed a $\beta-(Nb,V)_2O_5$ phase at 7 mol% of vanadia in their studies.

Fig. 2 shows the oxygen uptake at 640 K for various V_2O_5/Nb_2O_5 catalysts plotted as a function of V_2O_5 content. For low vanadia loadings, a limiting stoichiometry of one adsorbed oxygen atom per vanadium atom is obtained. This stoichiometry is used to calculate dispersions ranging from 76 to 51% for supported V_2O_5 samples of 2–12% weight loading. These data are produced in Table 1. Pure Nb_2O_5 was also reduced under identical conditions and its oxygen uptake was corrected for all the supported catalysts. Dispersion is defined as the fraction of total oxygen atoms to total vanadium atoms in the sample. Dispersion depends not only on the support but also on the preparation method. Wachs et al. [27] prepared various supported vanadium oxide catalysts including V_2O_5/Nb_2O_5 catalysts by the incipient-wetness impregnation method using vanadium isopropoxide as the precursor in methanol solution. This method suggests that vanadia is highly dispersed on niobia support. However, in the present study we have prepared the catalysts by standard wet impregnation method using ammonium meta vanadate as the precursor. The oxygen uptakes are found to increase with vanadia content but in a non-linear fashion implying that the dispersion decreases steadily with increase of vanadia content. The dispersion values at higher loadings did not change much with an increase of vanadia loading which might be due to the formation of $\beta-(Nb,V)_2O_5$ phase as evidenced from XRD results. Wadsley and Andersson [28] suggested that, in this phase, vanadium replaces the niobium present in isolated tetrahedral sites at the junction of blocks of NbO_6 octahedra. Thus, the number of surface vanadium species decreases when $\beta-(Nb,V)_2O_5$ is present in the catalysts. According to Smits et al. [13], the activities of oxidative dehydrogenation of propane was much less for samples containing $\beta-(Nb,V)_2O_5$ phase.

Electron spin resonance spectroscopy has been widely used for characterizing supported vanadia catalysts to

Table 1

Results of oxygen uptake, dispersion, oxygen atom site density and surface areas of various V₂O₅/Nb₂O₅ catalysts

V ₂ O ₅ loading on Nb ₂ O ₅ (% (w/w))	Surface area (m ² /g)	O ₂ uptake ^a (μmol/g)	Surface area ^b (m ² /g) reduced	Oxygen atom site density (×10 ¹⁸ m ⁻²)	Dispersion ^c O/V
2.0	50.2	83.1	57.0	1.76	0.76
4.0	48.7	161.2	49.1	3.96	0.73
6.0	46.7	217.9	49.1	5.35	0.66
8.0	44.1	249.6	45.7	6.58	0.57
10.0	43.6	300.9	45.2	8.03	0.54
12.0	46.2	340.6	46.2	8.88	0.51

^a T (reduction) = T (adsorption) = 640 K.^b BET surface area determined after oxygen chemisorption.^c Dispersion = fraction of vanadium atoms at the surface assuming $O_{\text{ads}}/V_{\text{surf}} = 1$.

determine the possible coordination environment, i.e., symmetry of vanadium and the effect of support on vanadyl bond strength. The V⁴⁺ species in V₂O₅/Nb₂O₅ catalysts exhibit clear eight line hyperfine splitting due to interaction between electron spin ($S = +1/2$) and nuclear spin ($I = +7/2$). The unpaired electron associated with V⁴⁺ (3d¹) interacts with the nuclear magnetic moment of ⁵¹V ($I = 7/2$) to give rise to eight parallel and eight perpendicular components in the EPR spectrum. The EPR spectra of V₂O₅/Nb₂O₅ catalysts recorded at ambient temperature are shown in Fig. 3, and the Hamiltonian parameters such as g_{\parallel} , A_{\parallel} , g_{\perp} , and A_{\perp} , are given in Table 2. Table 2 also lists the double integrated areas from the EPR spectra for all samples. This area is proportional to the concentration of vanadium ions in the samples. An examination of EPR spectra of the samples suggests the spectra are well resolved up to 6 wt.% V₂O₅/Nb₂O₅ catalysts. The intensity of the EPR signals increases gradually (see Table 2) as the vanadia loading increases up to 10 wt.% and then decreases for 12 wt.%. This might be due to the formation of crystallites of V₂O₅ and β-(Nb,V)₂O₅ phase as evidenced by XRD results resulting in spin–spin coupling and also due to changes in the crystal structure of niobia. The well-resolved EPR spectra at lower loadings might be due to the presence of the highly dispersed vanadia phase as determined by the oxygen chemisorption, XRD and SEM results of the present study.

Temperature programmed desorption (TPD) of probe molecules like ammonia or pyridine is a well-known method for the determination of acidity of solid catalysts as well as acid strength because it is an easy and reproducible. Ammonia is used frequently as a probe molecule because of

its small molecular size, stability and strong basic strength ($pK_a = 9.2$) [29]. The total acidity measurements of V₂O₅/Nb₂O₅ samples have been carried out by step-wise temperature programmed desorption (STPD) of NH₃. The acid strength distribution is classified depending on the desorption temperature of NH₃. Desorption temperature region

Table 2

Spin Hamiltonian parameters of V⁴⁺ in V₂O₅/Nb₂O₅ Catalysts

V ₂ O ₅ on Nb ₂ O ₅ (wt.%)	g_{\parallel}	A_{\parallel} (G)	g_{\perp}	A_{\perp} (G)	Double integrated area (×10 ⁷)
2	1.9706	194	1.9875	75	3.78
4	1.9692	197	1.9865	73	6.79
6	1.9690	194	1.9859	71	7.71
10	1.9680	193	1.9871	72	9.76
12	1.9712	190	1.9903	74	5.32

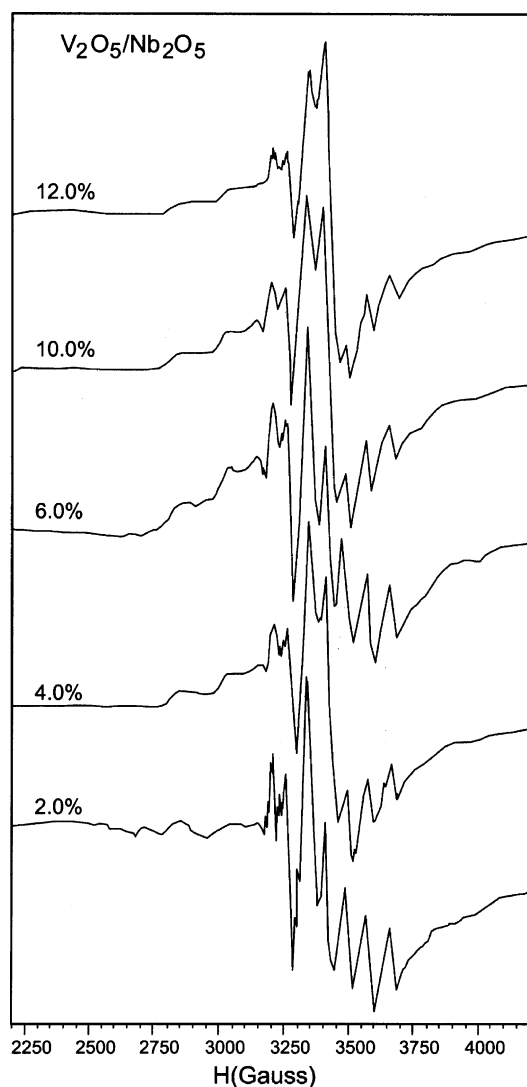
Fig. 3. Electron spin resonance spectra of V₂O₅/Nb₂O₅ catalysts.

Table 3
NH₃ TPD results of various V₂O₅/Nb₂O₅ catalysts

V ₂ O ₅ on Nb ₂ O ₅ (wt.%)	Acidity (μmol/g) NH ₃			
	Physisorbed (A)	Weak (B)	Medium (C)	Strong (D)
0	100	36	232	–
2	76	49	85	–
4	95	47	127	–
6	89	62	134	–
10	80	67	120	–
12	93	76	103	–

Desorption temperature: A = 353–423 K, B = 423–523 K, C = 523–623 K, D = 623–723 K.

for physisorbed = 353–423 K, weak = 423–523 K, medium = 523–623 K and strong = 623–723 K. The TPD results of various V₂O₅/Nb₂O₅ catalysts are given in Table 3. The TPD results indicate that the acid sites in the temperature region 523–623 K are due to moderate acidic sites. The acidity of the pure support Nb₂O₅ decreases with the addition of vanadium oxide. It could be due to masking of acidic sites of niobia support by highly dispersed vanadium oxide phase on the surface of the support. The acidity decreases drastically in 2 wt.% V₂O₅/Nb₂O₅ and increases marginally with vanadia loading up to monolayer loading (6 wt.%) is due to increase in active vanadia sites. The decrease in

acidity above monolayer loadings may be due to the formation of the β-(Nb,V)₂O₅ phase., the conversions in the ammoxidation of toluene also increases up to this loading and levels off at higher vanadia loadings. This indicates that the moderate acidic sites are responsible for activity during the ammoxidation of toluene. The acidity generation is caused by an excess of a negative or positive charge in a model structure of binary oxide related to the coordination number of a positive element and a negative element. Infrared spectroscopic studies of pyridine adsorbed on solid surfaces have made it possible to distinguish between Bronsted and Lewis acid sites [30,31]. Miyata et al. [31] reported that concentration of Bronsted acidic sites increases with increasing content of vanadium oxide on V₂O₅/TiO₂ catalysts, suggesting that vanadia acts as the Bronsted acid sites. Representative electron micrographs of V₂O₅/Nb₂O₅ catalysts are shown in Fig. 4. This figure shows that vanadia is well dispersed at lower loadings and the crystallinity increases with loading. Dense type clusters were observed at higher loadings. The SEM results are thus in agreement with the results of XRD, oxygen chemisorption and other techniques.

The ammoxidation results of toluene on various V₂O₅/Nb₂O₅ catalysts at 640 K are shown in Fig. 5. The conversion increases with increase in V₂O₅ loading up to 6 wt.% V₂O₅ and beyond this loading the activity did not

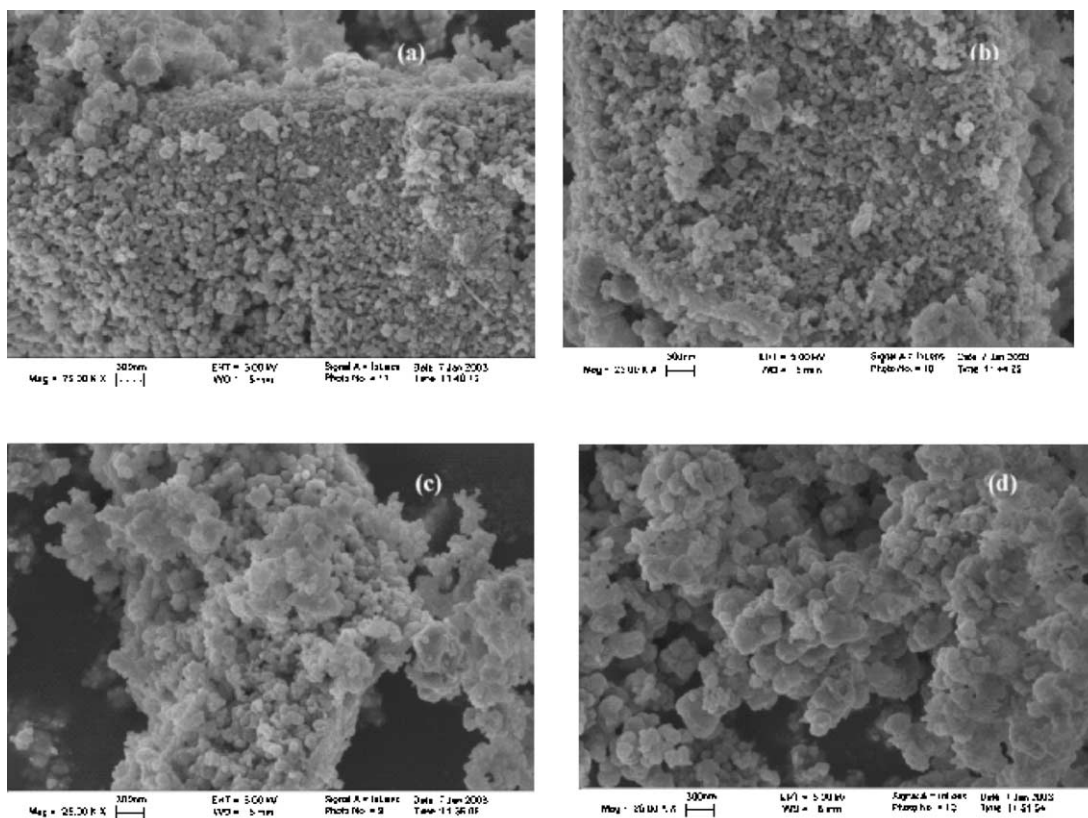


Fig. 4. Scanning electron micrographs of various V₂O₅/Nb₂O₅ catalysts: (a) 2% V₂O₅/Nb₂O₅, (b) 6% V₂O₅/Nb₂O₅, (c) 10% V₂O₅/Nb₂O₅ and (d) 12% V₂O₅/Nb₂O₅.

Table 4

Activity results of various supported vanadium oxide catalysts in the ammoxidation of toluene to benzonitrile under low conversion conditions

Catalyst (6 wt.%)	O ₂ uptake ($\mu\text{mol/g}$)	% Conversion	% Selectivity	Turnover frequency (TOF, $\times 10^{-3} \text{ s}^{-1}$)
V ₂ O ₅ /Nb ₂ O ₅	218	10	94	6.0
V ₂ O ₅ /ZrO ₂	214	16	90	9.8
V ₂ O ₅ /TiO ₂ (anatase)	268	20	95	9.7
V ₂ O ₅ /Al ₂ O ₃	198	3	87	2.0
V ₂ O ₅ /SiO ₂	209	1	85	0.6

Reaction temperature: 640 K. Toluene, ammonia and air mole ratio is 1:1:4. Catalyst weight: 100 mg.

Table 5

Activity results of various supported vanadium oxide catalysts in the ammoxidation of toluene to benzonitrile under high conversion conditions

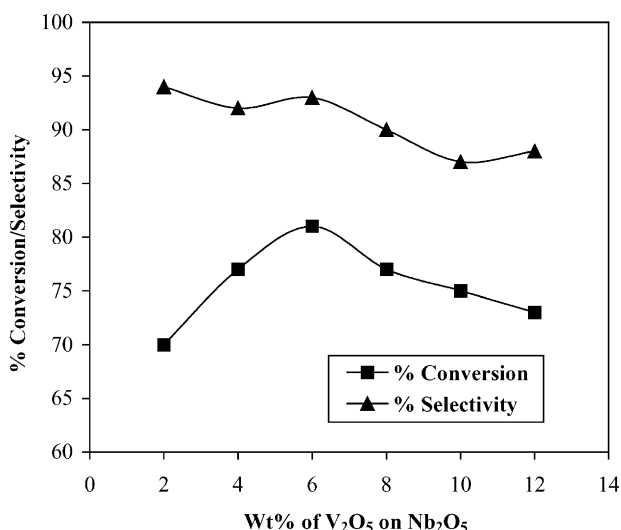
Catalyst (6 wt.%)	O ₂ uptake ($\mu\text{mol/g}$)	% Conversion	% Selectivity	Turnover frequency (TOF, $\times 10^{-2} \text{ s}^{-1}$)
V ₂ O ₅ /Nb ₂ O ₅	218	81	93	0.97
V ₂ O ₅ /ZrO ₂	214	73	87	0.89
V ₂ O ₅ /TiO ₂ (anatase)	268	67	91	0.65
V ₂ O ₅ /Al ₂ O ₃	198	30	84	0.39
V ₂ O ₅ /SiO ₂	209	16	80	0.20

Reaction temperature: 640 K. Toluene, ammonia and air mole ratio is 1:13:26. Catalyst weight: 500 mg.

change much due to the formation of the β -(Nb,V)₂O₅ phase and V₂O₅ crystallites on the surface of Nb₂O₅ support. However, the selectivity to benzonitrile formation was independent of vanadia content in the catalyst. Watling et al. [12] also observed similar activity results for oxidative dehydrogenation of propane. In their study, the rate of reaction increases linearly with vanadia loading up to 6 wt.% and then remains constant. This indicates that a monolayer loading of vanadia on niobia is reached at this composition. This loading corresponds close to the theoretical monolayer capacity of vanadia supported on a niobia employed in the present study. Pure niobia did not show catalytic activity under similar experimental conditions. Niobia possess isotropic morphologies and the active surface sites relatively

homogeneously dispersed over their surfaces are the surface acidic sites. The bifunctional bulk V₂O₅ is found to exhibit a much higher specific acidic catalytic activity [32]. The bulk properties of the vanadium metal oxides are essentially transferred to the analogous supported vanadium metal oxides, where the active group vanadium metal oxides are present as a two-dimensional monolayer on various oxides supports (e.g., Al₂O₃, TiO₂, ZrO₂ and Nb₂O₅). Recent TPR work by Martin et al. [33] and Chary et al. [34] indicates that niobia reduction occurs at 1270 K and above temperature, which is much higher than the vanadia reduction temperature (640 K). Thus, the redox sites are inactive present on niobia surface under the present ammoxidation reaction conditions. Tables 4 and 5 show the catalytic activity of various vanadia-supported catalysts under high and low conversion conditions respectively. The turn over frequencies of V₂O₅/Nb₂O₅ catalysts are comparable to, or better than, other supported metal oxide catalysts that used more traditional supports, such as Al₂O₃, SiO₂, ZrO₂ and TiO₂. Silica and alumina supported vanadia catalysts are almost inactive under low conversion conditions. The vanadium oxide catalysts supported on Nb₂O₅ are more active under high conversion conditions than TiO₂. At high conversions mass transfer limitations may be more dominant over TiO₂ than Nb₂O₅ leading to a decrease in conversion.

In order to find out the strength of the active V₂O₅ site, a plot between 1/TOF and V₂O₅ loading (Fig. 6) was drawn, where turn over frequency is equal to the rate of toluene molecules converted per second per surface V₂O₅. The TOF has been calculated by considering the dispersion of V₂O₅ obtained from oxygen chemisorption at 640 K. The linear relationship gives an intercept of value 35, which is a measure of intrinsic activity of the V₂O₅ site, i.e., 35 molecules of V₂O₅ on niobia surface are required to convert one molecule of toluene passing per second. Thus, the turnover number

Fig. 5. Ammoxidation of toluene to benzonitrile over various V₂O₅/Nb₂O₅ catalysts.

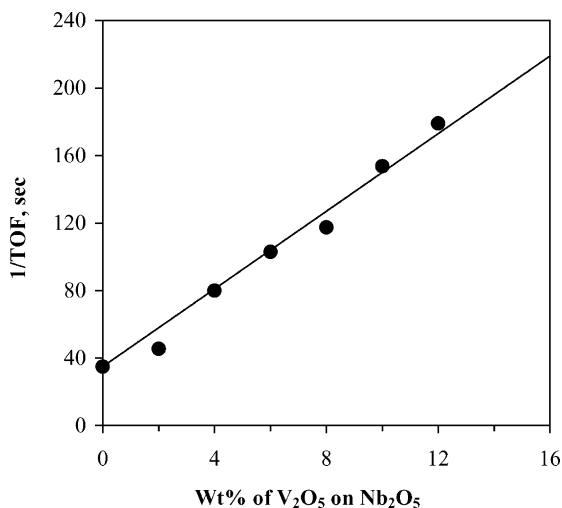


Fig. 6. Effect of vanadia loading on the rate of toluene conversion.

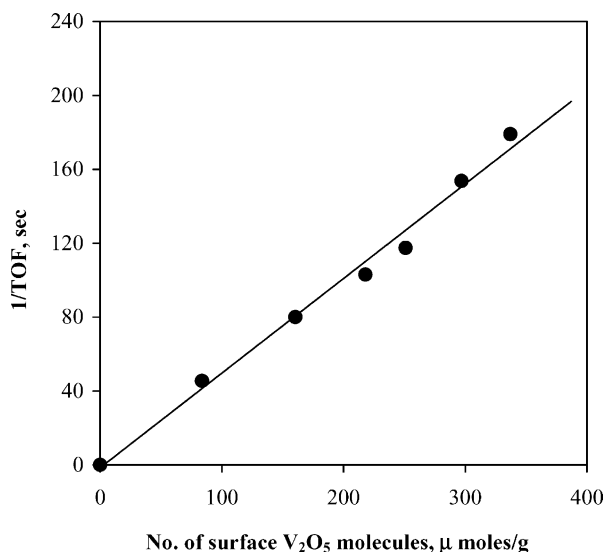


Fig. 7. Relation between number of surface V₂O₅ molecules and rate of toluene conversion.

(number of toluene molecules converted per second per site) is 0.028 S^{-1} . To find the relation between the ammoxidation activity of toluene and the dispersion of vanadia, a plot of $1/\text{TOF}$ versus the number of surface V₂O₅ molecules is shown in Fig. 7. A linear relationship passing through the origin was obtained, which clearly demonstrates that toluene conversion is directly related to oxygen chemisorption measured at 640 K. As reported elsewhere, in connection with vanadium oxide catalysts supported on alumina [35] and on silica [36], oxygen is chemisorbed at 640 K selectively on coordinatively unsaturated sites (CUS), generated upon reduction, having a particular coordination environment. These sites are located on a highly dispersed vanadia phase, which is formed only at low vanadia loadings and remains as a ‘patchy monolayer’ on the support surface. At higher vanadia loadings, a second phase forms, in addition to the

existing monolayer, and this post monolayer phase does not appreciably chemisorb oxygen. In perspective of the above background, the correlation observed here, indicates that the catalytic functionality of the dispersed vanadium oxide phase supported on niobium(V) oxide is responsible for the ammoxidation of toluene to benzonitrile is located on a patchy monolayer phase and that this functionality can be tritiated by the oxygen chemisorption method described in this work.

4. Conclusions

The V₂O₅/Nb₂O₅ catalysts are representative supported metal oxide catalysts for the ammoxidation of toluene to benzonitrile. Various loadings of vanadium oxide on niobia were prepared and characterized by XRD, BET surface area, oxygen chemisorption, NH₃ TPD, EPR and SEM. The catalytic activity of niobia supported vanadia catalysts is comparable to other supported vanadia catalysts. The TOF of the monolayer vanadium oxide species on Nb₂O₅ was comparable to the values obtained on TiO₂ and ZrO₂. The NH₃ TPD results showed that the acidity increases with vanadia loading up to 6 wt.% V₂O₅ and decreased at higher vanadia loadings. The activity of the catalysts was also found to increase with loading up to 6 wt.% V₂O₅ loading and levels off at higher vanadia loadings. Oxygen chemisorption results reveal that vanadium oxide is well dispersed on the Nb₂O₅ support at lower loadings and the dispersion decreases with increase in vanadia loadings. The SEM and EPR results further support these findings. The catalytic activity during toluene ammoxidation can be correlated to the dispersion of vanadia measured by oxygen chemisorption and acidic sites measured by stepwise NH₃ TPD method.

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References

- [1] A.I. Anastasev, Chem. Eng. Process. 1 (2003) 89.
- [2] T. Mongkhonsi, L. Kershenbaum, Appl. Catal. A: Gen. 170 (1998) 33.
- [3] M. Sanati, A. Anderson, J. Mol. Catal. 59 (1990) 233.

- [4] Ch. Praveen Kumar, K. Rajender Reddy, V. Venkat Rao, K.V.R. Chary, *Green Chem.* 4 (2002) 513.
- [5] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, D. Forzatti, F. Bregani, *J. Catal.* 187 (1999) 419.
- [6] G. Garcia Cortez, M.A. Banares, *J. Catal.* 209 (2002) 197.
- [7] R. Shimizu, T. Fuchikami, *Catal. Today* 71 (2001) 137.
- [8] J.M. Miller, L.J. Lakshmi, *Appl. Catal. A: Gen.* 190 (2000) 197.
- [9] P. Forzatti, E. Tronconi, G. Busca, P. Tittarelli, *Catal. Today* 1 (1987) 209.
- [10] K. Tanabe, *Catal. Today* 8 (1990) 1.
- [11] R.H.H. Smits, K. Seshan, H. Leemreize, J.R.H. Ross, *Catal. Today* 99 (1995) 9169.
- [12] T.C. Watling, G. Deo, K. Seshan, I.E. Wachs, J.A. Lercher, *Catal. Today* 28 (1996) 139.
- [13] R.H.H. Smits, K. Seshan, J.R.H. Ross, L.C.A. Van den Oetelaar, J.H.J.M. Helwegen, M.R. Anantharaman, H.H. Brongersma, *J. Catal.* 157 (1995) 584.
- [14] K. Tanabe, *Catal. Today* 77 (2003) 65.
- [15] N. Ballarini, F. Cavani, C. Cortelli, C. Guinchi, P. Nobili, F. Trifiro, R. Catani, U. Cornaro, *Catal. Today* 78 (2003) 353.
- [16] J.M. Jehng, A.M. Turek, I.E. Wachs, *Appl. Catal. A* 83 (1992) 179.
- [17] I. Matsuura, H. Oda, K. Hoshida, *Catal. Today* 16 (1993) 547.
- [18] M. Cherian, M. Someswara Rao, G. Deo, *Catal. Today* 78 (2003) 397.
- [19] P.J. Stobbelaar, Ph.D. Thesis, University of Eindhoven, 2000.
- [20] R.H.H. Smits, K. Seshan, H. Leemreize, J.R.H. Ross, *Catal. Today* 16 (1993) 513.
- [21] M. Sanati, A. Andersson, L.R. Wallenberg, B. Robenstorf, *Appl. Catal. A: Gen.* 106 (1993) 51.
- [22] Y. Murakami, M. Niwa, T. Hattori, S. Osawa, I. Igushi, H. Ando, *J. Catal.* 49 (1977) 83.
- [23] K.V.R. Chary, G. Kishan, *J. Phys. Chem.* 99 (1995) 14424.
- [24] S. Narayanan, K. Deshpande, *Appl. Catal. A: Gen.* 135 (1996) 125.
- [25] K.V.R. Chary, G. Kishan, Ch. Praveen Kumar, G. Vidya Sagar, J.W. Niemantsverdriet, *Appl. Catal. A: Gen.* 245 (2003) 303.
- [26] K.V.R. Chary, G. Kishan, T. Bhaskar, *JCS Chem. Commun.* (1999) 1399.
- [27] I.E. Wachs, J.M. Jehng, G. Deo, B.M. Weckhusen, V.V. Guliants, J.B. Benziger, S. Sundaresan, *J. Catal.* 170 (1997) 75.
- [28] A.D. Wadsley, S. Andersson, in: J.D. Dunitz, J.A. Ibers (Eds.), *Perspectives in Structural Chemistry*, vol. 3, Wiley, New York, 1970, p. 19.
- [29] A. Satsuma, Y. Kamiya, Y. Westi, T. Hattori, *Appl. Catal. A: Gen.* 194 (2000) 253.
- [30] J.R. Sohn, S.G. Cho, Y. Pae II, S. Hayashi, *J. Catal.* 159 (1996) 170.
- [31] H. Miyata, K. Fujii, T. Ono, *J. Chem. Soc., Faraday Trans. I* 84 (9) (1988) 3121.
- [32] I.E. Wachs, Y. Chen, J.M. Jehng, L.E. Briand, T. Tanaka, *Catal. Today* 78 (2003) 13.
- [33] C. Martin, D. Klissurski, J. Rocha, V. Rives, *Phys. Chem. Chem. Phys.* 2 (2000) 1543.
- [34] K.V. R Chary, T. Bhaskar, G. Kishan, K. Rajender Reddy, *J. Phys. Chem.* 105 (2001) 4392.
- [35] N.K. Nag, K.V.R. Chary, B.M. Reddy, B.R. Rao, V.S. Subrahmanyam, *Appl. Catal.* 9 (1984) 225.
- [36] N.K. Nag, K.V.R. Chary, B.R. Rao, V.S. Subrahmanyam, *Appl. Catal.* 31 (1987) 87.