

# Characterization and aniline alkylation activity of vanadia and silica-supported vanadia catalysts

S. Narayanan\*, B. Prabhu Prasad

*Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India*

Received 28 June 1994; accepted 5 August 1994

---

## Abstract

Vanadia and silica-supported vanadia have been characterized by XRD, ESR and chemisorption of oxygen at low temperature (COLT) to assess the nature of the vanadia dispersion on the support. Aniline alkylation studies on the effect of temperature and contact time on the conversion and selectivity of the products reveal that supported vanadia is significantly more active than vanadia and SiO<sub>2</sub>. The alkylation reaction proceeds through consecutive formation of secondary, tertiary and C-alkylated anilines. Reaction conditions can be favourably modified to get selectively N-ethylaniline over vanadia–silica. An attempt has been made to correlate dispersion and catalytic activity with the active species.

*Keywords:* Alkylation; Aniline; Silica; Supported catalysts; Vanadia

---

## 1. Introduction

Alkylamines are important intermediates for the pharmaceuticals, drugs, agrochemicals and dye industries. They are usually synthesized in the liquid phase under pressure with corrosive acids as catalysts causing disposal problems. The traditional route also suffers from the disadvantage of high capital cost, reactor corrosion and formation of by-products that cannot be recycled. In order to overcome these problems, we are studying alkylation reactions under vapour phase conditions using solid acids as catalysts. We have shown that both simple and mixed oxides can be conveniently used for phenol alkylation [1–5]. Rice and Kohn [6] have described alkylation of aniline in which a primary arylamine is refluxed

with an excess of a primary aliphatic alcohol in the presence of Raney nickel to yield an N-alkylarylamine. Rusek [7] used multimetallic catalysts for N-alkylation of sterically hindered aniline in the presence of hydrogen. The advantage of vapour phase alkylation of aniline is that the alkylanilines can be selectively synthesized with product recycling options. Alkylation of aniline results in secondary and tertiary amines along with C-alkylated products. The product selectivity depends to some extent on reaction conditions and catalyst characteristics. The present investigation focuses attention on the vapour phase ethylation of aniline over vanadia and supported vanadia catalysts.

Vanadia and supported vanadia are probably the most exhaustively studied systems. ESR spectroscopy has proved to be a powerful method for detecting the presence of the paramagnetic V<sup>4+</sup> species in vanadium based catalysts [8]. Yoshida

---

\*Corresponding author.

et al. [9] concluded from ESR spectra that on  $\gamma$ - $\text{Al}_2\text{O}_3$   $\text{VO}_x$  is present as square pyramidal  $\text{VO}_5$  units while on  $\text{SiO}_2$  it exists as tetrahedral  $\text{VO}_4$  units. At low vanadium content, isolated  $\text{VO}_4$  tetrahedra have been detected and polymeric octahedral  $\text{VO}_6$  species at higher loading. Various disordered paracrystalline  $\text{V}_2\text{O}_5$  phases have been seen when more than a monolayer loading is present. As per the structure of vanadia on silica prepared by impregnation methods, many researchers concluded the presence of microcrystallites of  $\text{V}_2\text{O}_5$  [10–14]. Tanaka et al. [13] claimed from EXAFS analysis that microcrystallites of  $\text{V}_2\text{O}_5$  are formed on  $\text{SiO}_2$  and that the vanadia atoms are atomically dispersed on  $\text{SiO}_2$  when sodium hydroxide is added to the impregnating solution. Inumaru et al. [15] observed from EXAFS that in 5.8 wt.%  $\text{V}_2\text{O}_5/\text{SiO}_2$  prepared by impregnation,  $\text{V}_2\text{O}_5$  is present mainly as crystallites, whereas in  $\text{V}_2\text{O}_5/\text{SiO}_2$  prepared by chemical vapour deposition method, it is present as thin films. Based on their experimental results on supported vanadia catalysts, Nag et al. [16] proposed a model for the surface structure of the dispersed phase of vanadia on silica. It has been envisioned that a monolayer phase containing a small part of isolated  $(\text{VO})^{4-}$  species and a great part of dimeric  $\text{V}^{5+}$  oxide species, both in tetrahedral coordination, is formed at low vanadia loading region, while at loadings beyond the so-called 'monolayer' coverage, the second phase consisting of only  $\text{V}^{5+}$  oxide in square pyramidal or octahedral surroundings (a two dimensional structure akin to that of bulk  $\text{V}_2\text{O}_5$ ) is formed preferentially on the top of the monolayer phase. The physicochemical properties of the support affect the dispersion of vanadia and therefore the catalytic activity. Most of the investigations on vanadia systems are directed towards oxidation [17–19], ammoxidation [20–23] and reduction [24–27] reactions. Species in the monolayer are effective catalysts for oxidation, ammoxidation and selective reduction but how they affect aniline alkylation is still open to discussion. There is evidence for the use of simple oxides such as alumina [28,29], zeolites [30,31],  $\text{AlPO}_4$  [32] as catalysts for aniline alkyl-

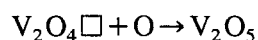
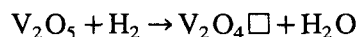
ation. We have earlier reported [33–35] on the acidity dependence of aniline alkylation activity of oxides and supported vanadia. This work reports on the dispersion properties of vanadia on silica support along with the vapour phase aniline alkylation activity.

## 2. Experimental

Vanadia was prepared by the calcination of ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) in air at 773 K for 6 h. Silica support was of commercial origin (AKZO Chemie Si2-5P). Silica tablets were crushed and particles of 400–500  $\mu\text{m}$  were used in the catalyst preparation. Different loadings of vanadia on silica (5 to 25 wt.% of  $\text{V}_2\text{O}_5$ ) were obtained by wet impregnation of the support with the appropriate concentration of ammonium metavanadate in aqueous oxalic acid, allowing the materials to dry at room temperature and again overnight at 393 K and finally calcining at 773 K in air for 6 h. 5 wt.%  $\text{V}_2\text{O}_5/\text{SiO}_2$  was pale yellow in colour and the intensity of yellowishness increased with vanadia loading.

The BET surface area of the samples was measured using nitrogen as adsorbate at 77 K in a constant volume static adsorption system. Chemisorption of oxygen at low temperature (COLT) on reduced vanadia samples was carried out following the method of Parekh and Weller [36] to calculate the dispersion. Supported vanadia was reduced in flowing hydrogen at 673 K for 6 h. Before oxygen chemisorption, the sample was degassed at 673 K for 2 h and at the temperature of oxygen chemisorption (77 K) for another hour. After the first adsorption isotherm which includes both physisorption and chemisorption the sample was degassed for an hour at adsorption temperature. This was followed by a second adsorption which accounts for the physical adsorption of oxygen. From the difference in the two parallel isotherms, the chemisorbed oxygen was determined and used for the calculation of dispersion on the assumption that  $\text{V}_2\text{O}_5$  is reduced to  $\text{V}_2\text{O}_4$  during reduction at 673 K for 4 h in hydrogen; thus one

oxygen atom corresponds to two vanadium atoms.



It cannot be excluded that under the experimental conditions also some bulk reduction takes place. The reduction might also lead to  $\text{V}_2\text{O}_3$  species and to possible aggregation of  $\text{V}_2\text{O}_5$ .

XRD patterns of powdered-calcined samples were taken using a Philips PW-1051, X-ray diffractometer with Ni filtered  $\text{CuK}_\alpha$  radiation. ESR spectra were taken at room temperature with a Bruker ER 200D SRC X-band spectrometer at microwave frequency of 9.76 GHz and modulation frequency of 100 KHz. Before taking the spectrum the powdered sample at known weight (ca. 200 mg) was dried overnight at 393 K in an impurity-free ESR tube.

Ca. 0.5 g of catalyst of particle size 400–500  $\mu\text{m}$  was loaded in a vertical glass flow reactor (2 cm, o.d. and 20 cm long). Ceramic beads packed above the catalyst bed act as a pre-heater. The catalyst sample was activated in nitrogen flow at 773 K for 3 h. Vapour phase alkylation of aniline was carried out at atmospheric pressure by injecting from the top a calibrated volume of aniline–ethanol mixtures with a motorised syringe. An aniline to ethanol mole ratio of 1 : 10 was chosen after preliminary experiments, which showed the conversion of aniline at this ratio to be maximal. Feed rate of aniline was varied between  $\text{WHSV} = 0.8\text{--}6.4 \text{ h}^{-1}$  on ethanol-free basis. Nitrogen was used as a carrier gas. The reaction was carried out in the temperature region 523–673 K. The liquid products were collected in a trap and analysed by a Chemito 3865 gas chromatograph with an 8 ft. ss column of 1/8 in. o.d. packed with 10% Apiezon L treated with 2% KOH on chromosorb AW (80/100). The products contained mainly *N*-ethylaniline (NEA) along with *N,N'*-diethylaniline (NN'DEA) and traces of C-alkylated products (others).

### 3. Results and discussion

#### 3.1. Characterization

In Fig. 1, X-ray diffraction patterns of vanadia and silica supported vanadia are shown along with that of the silica support. Silica is amorphous to X-ray diffraction. Vanadia shows peaks characteristic of its crystallinity. Supported vanadia catalysts on the other hand with vanadia content of 5–25% show no characteristic peaks of vanadia. This suggests that vanadia is either amorphous

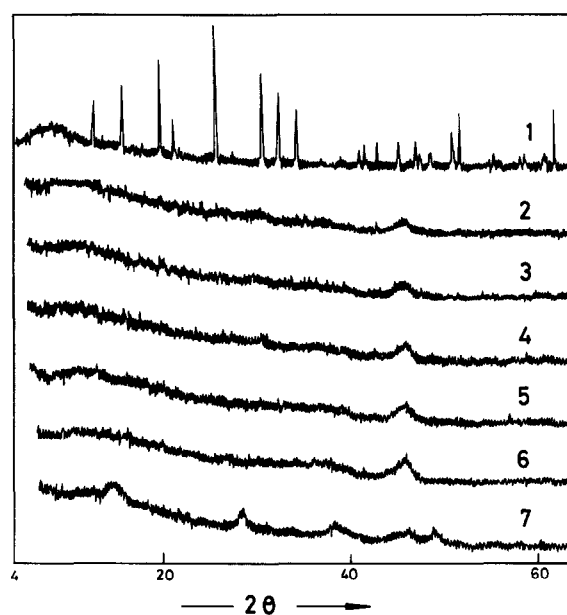


Fig. 1. XRD patterns of vanadia, silica and silica supported vanadia catalysts. 1:  $\text{V}_2\text{O}_5$ ; 2: 25%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 3: 20%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 4: 15%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 5: 10%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 6: 5%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 7:  $\text{SiO}_2$ .

Table 1  
Surface area and oxygen adsorption data on catalysts

Catalyst	Surface area $\text{m}^2 \text{g}^{-1}$ catalyst	Oxygen uptake $\mu\text{mol g}^{-1}$ catalyst	Vanadia dispersion (%)
$\text{SiO}_2$	190	–	–
$\text{V}_2\text{O}_5$	30	–	–
5% $\text{V}_2\text{O}_5/\text{SiO}_2$	185	35	25
10% $\text{V}_2\text{O}_5/\text{SiO}_2$	185	79	29
15% $\text{V}_2\text{O}_5/\text{SiO}_2$	183	52	13
20% $\text{V}_2\text{O}_5/\text{SiO}_2$	145	59	11

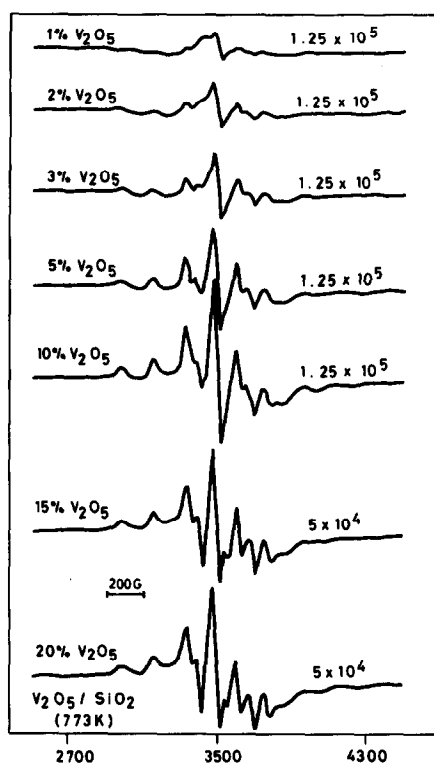


Fig. 2. ESR spectra of  $V_2O_5$ , and silica supported vanadia catalysts.

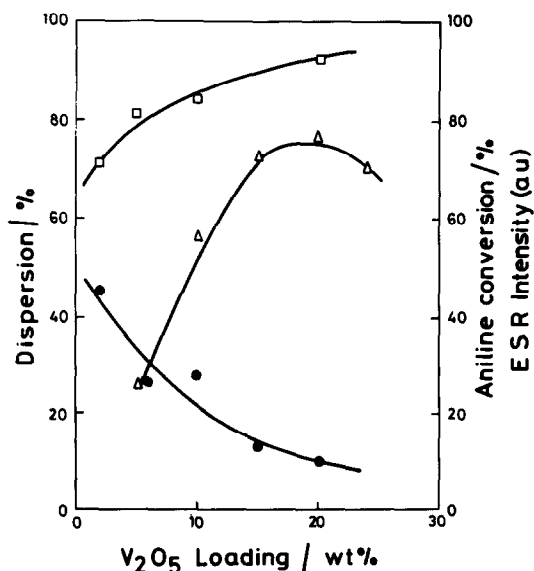


Fig. 3. Variation of vanadia dispersion, ESR intensity and aniline conversion at 673 K with vanadia loading on silica: (●) dispersion; (Δ) ESR intensity; (□) aniline conversion.

when supported on silica or that the particle size is below the detection limits of the X-ray technique.

In Table 1, the surface area and the oxygen adsorption results of the catalysts are given. Surface area of vanadia is  $30 \text{ m}^2 \text{ g}^{-1}$  and that of silica is  $190 \text{ m}^2 \text{ g}^{-1}$ . Addition of vanadia by the impregnation method does not change the surface area of the catalysts significantly up to 15 wt.% of vanadia. However, 20 wt.% vanadia-silica catalyst shows a decrease in the surface area of about  $45 \text{ m}^2 \text{ g}^{-1}$ . The fact that the surface area is not affected when the vanadia content is 5–15% suggests that the vanadia is dispersed as small particles on the support surface. The decrease in surface area at 20% vanadia loading may be due to the formation of crystalline vanadia phases. However, X-ray diffraction information does not support any crystalline phase on the catalysts containing 5–25 wt.% of vanadia. As mentioned earlier, the crystallites might be smaller than 4–5 nm even in 25 wt.% vanadia catalysts.

Chemisorption of oxygen per gram of catalyst measured at low temperature (77 K) is also given in Table 1. The oxygen uptake per gram of catalyst increases with vanadia content and goes through a maximum at 10 wt.% vanadia. Beyond 10 wt.% of vanadia probably there is a saturation of the surface with vanadia and the oxygen uptake per gram of catalyst decreases. The dispersion of vanadia calculated from oxygen uptake supports this observation. For example, 10% vanadia shows a maximum dispersion of 29%.

The ESR spectra of pure vanadia and silica supported vanadia samples show interesting results and seem to support the dispersion of  $V_2O_5/SiO_2$  (Fig. 2). All the spectra are taken under identical conditions at room temperature ( $\nu = 9.76 \text{ GHz}$ , modulation = 100 KHz, gain =  $5 \times 10^4$  and time constant =  $1 \times 1500 \text{ s}$ ). Unsupported vanadia does not show any ESR signal. However, silica-supported vanadia samples show well resolved ESR signals with distinct hyperfine splitting (hfs) due to  $^{51}\text{V} (I = 7/2)$ . The signal intensity and hfs increase from 5 wt.% and both reach a maximum around 15–20 wt.% of  $V_2O_5$  beyond which it tends

to diffuse gradually. The ESR signal becomes more asymmetric beyond 10 wt.% of vanadia loading. Fig. 3 clearly shows the decrease in dispersion of vanadia with loading. ESR signal intensity (arbitrary units) measured as the peak to peak height of the most intense signal in the hfs, however, increases with vanadia content on silica reaching a maximum around 15 wt.%. The presence of hfs is an indirect evidence for the high dispersion of vanadia as paramagnetic  $V^{4+}$  ions on the silica support. This also suggests that even though silica is a relatively non-interacting support compared with  $\gamma\text{-Al}_2\text{O}_3$  or  $\text{TiO}_2$  (anatase) it can still hold the  $V^{4+}$  ions onto the surface without allowing them to agglomerate giving rise to dipolar broadening. The formation of a V–O–Si bond during calcination though weak and reversible has been proposed by several workers [37,38]. Unsupported vanadia when scanned at high sensitivity (gain =  $2 \times 10^5$ , time constant =  $10^2 \times 10^1$  s) shows a singlet ESR signal and this may be attributed to  $V^{4+}$  in vanadia as dense clusters. Dipolar bonding leads to a singlet ESR spectrum when the paramagnetic species remain in close proximity with each other on a surface [39].

### 3.2. Catalysis

#### 3.2.1. Effect of temperature

Vapour phase alkylation of aniline was carried out at atmospheric pressure over vanadia, silica and supported vanadia catalysts at different temperatures and contact times. In all the experiments, the mole ratio of aniline to ethanol is maintained at 1 : 10.  $\text{N}_2$  is used as a carrier gas  $7 \text{ l h}^{-1}$ . In Fig. 4, the effect of temperature on aniline conversion at a constant feed rate of  $9 \times 10^{-3} \text{ mol h}^{-1}$  of aniline, free of ethanol (WHSV =  $1.6 \text{ h}^{-1}$ ) is shown. The Figure shows that the conversion increases with the temperature on all catalysts reaching a maximum around 673 K. Vanadia and silica show more or less the same activity and the maximum is around 35%. At low temperature especially between 523–573 K, aniline conversion is less than 10% both on pure oxides and on supported vanadia oxides. The striking difference in

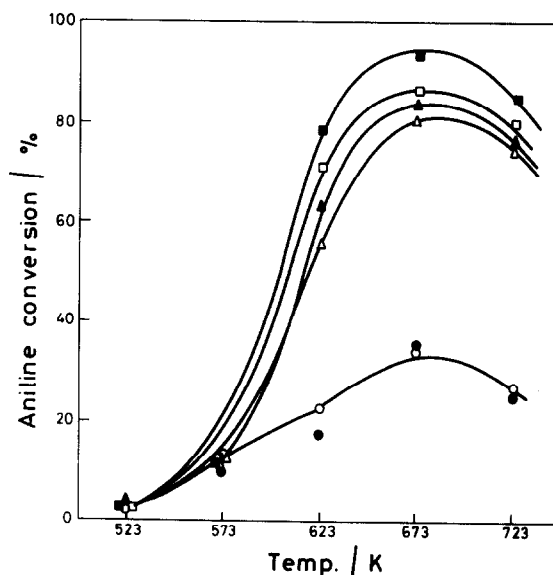


Fig. 4. Effect of temperature aniline conversion. Pressure, 1 bar; WHSV,  $1.6 \text{ h}^{-1}$ : (●)  $\text{SiO}_2$ ; (○)  $\text{V}_2\text{O}_5$ ; (△) 5%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; (▲) 10%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; (□) 15%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; (■) 20%  $\text{V}_2\text{O}_5/\text{SiO}_2$ .

conversion takes place on supported vanadia catalysts. With increase in vanadia content there is an increase in aniline conversion at high temperatures, although it is not very significant. The main product is *N*-ethylaniline. At high temperatures, other products such as *N,N'*-diethylaniline and *C*-alkylated anilines are also formed. The relative product selectivity over oxides and supported vanadium oxides for aniline conversion in the temperature region 523–723 K is shown in Fig. 5. With an increase in temperature, the main product *N*-ethylaniline decreases on all the unsupported and supported oxides. The other products *N,N'*-diethylaniline and *C*-alkylated anilines increase with temperature.

#### 3.2.2. Effect of feed rate

The effect of contact time on aniline conversion is studied at 673 K and 1 bar by varying the feed rate of aniline–ethanol mixture of 1 : 10 mole ratio (Fig. 6). Aniline conversion with respect to contact time on pure vanadia is compared with silica-supported vanadia catalysts. With decrease in contact time aniline conversion decreases on vanadia as well as on supported vanadia catalysts. The decrease in conversion with decrease in contact

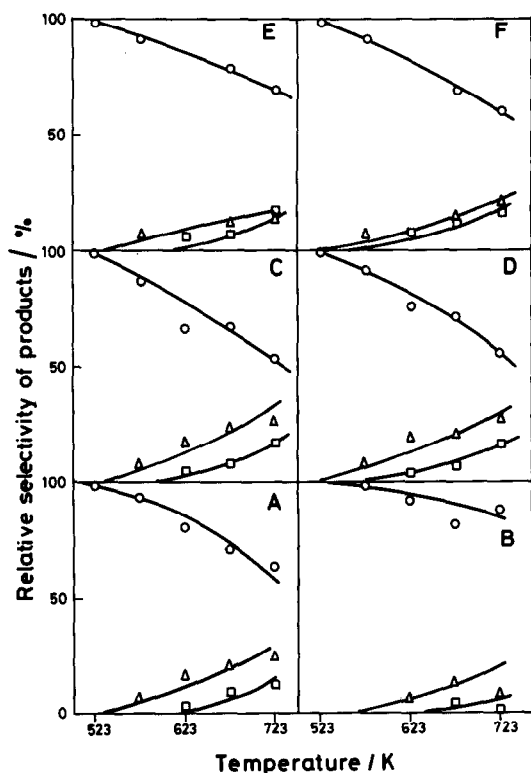


Fig. 5. Effect of temperature on product selectivity. Pressure, 1 bar; WHSV,  $1.6 \text{ h}^{-1}$ : (O) NEA; ( $\Delta$ ) NN'DEA; ( $\square$ ) others; (A)  $\text{V}_2\text{O}_5$ ; (B)  $\text{SiO}_2$ ; (C) 5%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; (D) 10%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; (E) 15%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; (F) 20%  $\text{V}_2\text{O}_5/\text{SiO}_2$ .

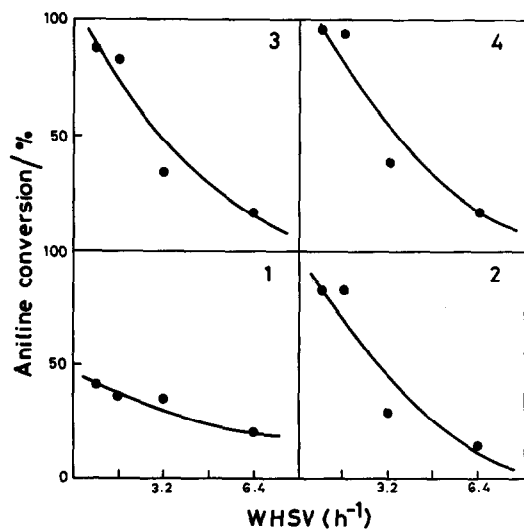


Fig. 6. Feed rate effect on aniline conversion at 673 K and 1 bar: 1:  $\text{V}_2\text{O}_5$ ; 2: 5%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 3: 10%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 4: 20%  $\text{V}_2\text{O}_5/\text{SiO}_2$ .

time is more dramatic on supported vanadia than on vanadia alone. On pure vanadia the conversion (40%) is much less compared to supported vanadia (90%) even at high contact time ( $\text{WHSV} = 0.8 \text{ h}^{-1}$ ). The low conversion is maintained between 40–20% in the WHSV region of 0.8–6.4  $\text{h}^{-1}$  on vanadia. However, on supported vanadia the conversion falls from 90% ( $\text{WHSV} = 0.8 \text{ h}^{-1}$ ) to 15% ( $\text{WHSV} = 6.4 \text{ h}^{-1}$ ) at high feed rate. The observations on the product selectivity with respect to contact time reveal (Fig. 7) that the selectivity for *N*-ethylaniline increases with feed rate (high contact time favouring secondary product formation) and remains steady at high feed rates. Especially at high feed rates there is not much difference between vanadia and supported vanadia in the selectivity for *N*-ethylaniline.

From the characterization studies of supported vanadia catalysts discussed in this paper, it may be concluded that vanadium may be present as a finely dispersed phase up to 15–20 wt.% beyond which vanadium clusters are formed reducing the ESR intensity. This is also shown from oxygen adsorption data, showing decrease in dispersion with vanadia loading. However, aniline alkylation (conversion) shows an increase for a small addi-

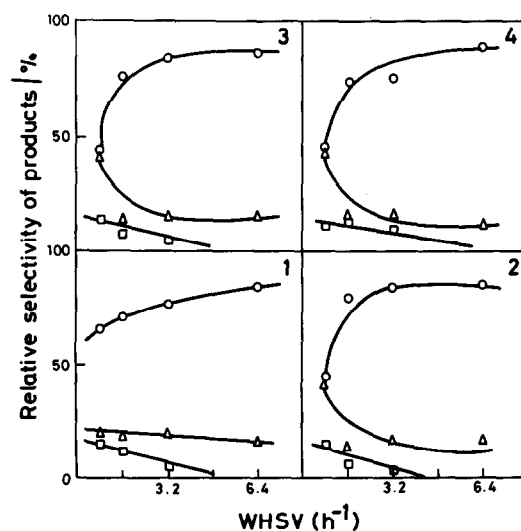


Fig. 7. Feed rate effect on product selectivity at 673 K and 1 bar: (O) NEA; ( $\Delta$ ) NN'DEA; ( $\square$ ) others; 1:  $\text{V}_2\text{O}_5$ ; 2: 5%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 3: 10%  $\text{V}_2\text{O}_5/\text{SiO}_2$ ; 4: 20%  $\text{V}_2\text{O}_5/\text{SiO}_2$ .

Table 2  
Comparison of relative selectivity of products at low conversion<sup>a</sup> level

Catalyst	Conversion (%)	Relative selectivity (%)		
		NEA	NN'DEA	Others
SiO <sub>2</sub>	9	100	–	–
V <sub>2</sub> O <sub>5</sub>	13	94	6	–
5% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	11	87	13	–
10% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	12	91	9	–
15% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	13	92	8	–
20% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	13	92	8	–

<sup>a</sup>T = 573 K, pressure = 1 bar and WHSV = 1.6 h<sup>-1</sup>.

tion of vanadium and reaches a rather steady value at high loading of vanadia. There seems to be no direct relationship between dispersion and conversion (Fig. 3). The absence of V<sub>2</sub>O<sub>5</sub> patterns in X-ray diffraction of supported vanadia catalysts leads us to believe that the vanadium crystallites, if present, must be below the detection limits of X-ray diffraction even at 25 wt.% of vanadia loading. Well-dispersed vanadium oxides represented as VO<sub>x</sub> may be formed on the surface of a supporting oxide by the impregnation method. This dispersed phase is particularly stable on TiO<sub>2</sub> and on Al<sub>2</sub>O<sub>3</sub> but are not readily formed on SiO<sub>2</sub> where aggregation to V<sub>2</sub>O<sub>5</sub> occurs [8].

The vapour phase aniline alkylation studies over vanadia and supported vanadia reveal that pure vanadia and silica alkylate aniline to give *N*-ethylaniline with 80% selectivity at a conversion level of 30–35%. Vanadia, when supported on silica (5–20 wt.%), dramatically increases the conversion to 80–90% (WHSV 1.6 h<sup>-1</sup>, pressure 1 bar and at 673 K), but the selectivity for *N*-ethylaniline remains the same as in the case of pure oxides. The studies on the feed rate effect indicate that low contact time and low temperature favour *N*-ethylaniline selectivity. Comparison of relative products selectivity of aniline alkylation reactions at low and high conversions levels are represented in Tables 2 and 3. At low conversion (9–13%) NEA is the major product and *N,N'*DEA selectivity is only between 8–13% with no other product. At high conversions (33–35% in the case of vanadium and 81–93% in case of supported oxides)

Table 3  
Comparison of relative selectivity of products at high conversion<sup>a</sup> level

Catalyst	Conversion (%)	Relative selectivity (%)		
		NEA	NN'DEA	Others
SiO <sub>2</sub>	35	81	14	5
V <sub>2</sub> O <sub>5</sub>	33	71	20	9
5% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	81	69	25	6
10% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	83	72	21	7
15% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	86	79	13	8
20% V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	93	70	16	14

<sup>a</sup>T = 673 K, pressure = 1 bar, WHSV = 1.6 h<sup>-1</sup>.

apart from NEA, and *NN'*DEA, other products are also formed. NEA selectivity is less than that at low conversion and the selectivity of *N,N'*DEA and others have increased at the cost of NEA. Aniline alkylation under vapour phase condition over solid oxides may proceed in a consecutive mechanistic pathway, namely, the first product secondary aniline (NEA) is formed and is further alkylated to tertiary anilines (*NN'*DEA) which is transformed by intramolecular conversion to *C*-alkylated aniline and toluidines.

#### 4. Conclusion

In conclusion, it may be said that silica supported vanadia catalysts may be judiciously used for selective synthesis of alkylanilines, especially for *N*-ethylaniline. It may also be added that an effort to correlate dispersion phenomena of vanadia with aniline alkylation is not conclusive even though vanadia when supported is catalytically more active than bulk vanadia. Whether the vanadium species responsible for this activity is microcrystalline vanadia or molecular vanadia has yet to be clarified. The types of interacting species involved between the vanadia and support that could be responsible for the high activity must still be identified with respect to the industrially important aniline alkylation reaction.

## References

- [1] S. Narayanan, V. Venkat Rao and V. Durga Kumari, *J. Mol. Catal.*, 52 (1989) L29.
- [2] V. Venkat Rao, V. Durga Kumari and S. Narayanan, *Appl. Catal.*, 49 (1989) 165.
- [3] V. Venkat Rao, K.V.R. Chary, V. Durga Kumari and S. Narayanan, *Appl. Catal.*, 61 (1990) 89.
- [4] V. Durga Kumari, G. Sreekanth and S. Narayanan, *Res. Chem. Intermed.*, 14 (1990) 223.
- [5] V. Durga Kumari and S. Narayanan, *J. Mol. Catal.*, 65 (1991) 385.
- [6] R.C. Rice and E.J. Kohn, *J. Am. Chem. Soc.*, 77 (1955) 4052.
- [7] M. Rusek, *Proc. 9th Int. Conf. Catal.*, Calgary, Canada, 3 (1988) 118.
- [8] G.C. Bond and S.F. Tahir, *Appl. Catal.*, 71 (1991) 1.
- [9] S. Yoshida, T. Iguchi, S. Ishida and K. Tarama, *Bull. Chem. Soc. Jpn.*, 45 (1972) 376.
- [10] S.T. Oyama, G.T. Went, K.B. Lewis, A.T. Bell and G.A. Somarjai, *J. Phys. Chem.*, 93 (1989) 6786.
- [11] F. Roozeboom, M.C.M. Hazeleger, J.A. Moulijn, J. Medema, V.H.J. de Beer and P.J. Gellings, *J. Phys. Chem.*, 84 (1980) 2783.
- [12] Y. Murakami, M. Ionomata, K. Mori, T. Ui, K. Suzuki, A. Miyamoto and Y. Hattori in G. Poncelet, P. Grange and P.A. Jacobs (Eds.), *Preparation of Catalysts III*, Proc. 3rd Int. Symp., Elsevier, Amsterdam, 1983, p. 531.
- [13] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans.*, 184 (1988) 2987.
- [14] T. Tanaka, Y. Nishimura, S. Kawasaki, T. Funabiki and S. Yoshida, *J. Chem. Soc., Chem. Commun.*, (1987) 506.
- [15] K. Inumaru, T. Okuhara, M. Misono, N. Matsubayashi, H. Shimada and A. Nishijima, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 1807.
- [16] N.K. Nag, K.V.R. CHary, B. Rama Rao and V.S. Subrahmanyam, *Appl. Catal.*, 31 (1987) 73.
- [17] G.F. Cullis and D.J. Hucknall, in *Catalysis*, Vol. 5, The Royal Society of Chemistry, London, 1982, p. 273.
- [18] G.C. Bond and K. Bruckman, *Faraday Discuss. Chem. Soc.*, 72 (1981) 237.
- [19] F. Roozeboom, P. Cordingly and P.J. Gellings, *J. Catal.*, 68 (1981) 464.
- [20] A. Anderson, *J. Catal.*, 76 (1982) 144.
- [21] A. Anderson and S.T. Lundin, *J. Catal.*, 65 (1980) 9.
- [22] P. Cavalli, F. Cavani, I. Maneti and F. Trifiro, *Ind. Eng. Chem. Res.*, 26 (1987) 639.
- [23] R. Prasad and A.K. Kar, *Chem. Age India*, 26 (1975) 375.
- [24] H. Bosch and F. Janssen, *Catal. Today*, 2 (1988) 369.
- [25] A. Baiker, P. Dollenmeier, M. Glinski, A. Reller and V.K. Sharma, *J. Catal.*, 111 (1988) 273.
- [26] W.C. Wongard and K. Bobe, *Ind. Eng. Chem. Prod. Res. Dev.*, 23 (1984) 564.
- [27] M. Sanati and A. Anderson, *J. Mol. Catal.*, 59 (1990) 233.
- [28] A.G. Hill, J.H. Shipp and A.J. Hill, *Ind. Eng. Chem.*, 43 (1951) 1579.
- [29] L.K. Doraiswamy, G.R. Venkatakrishnan and S.P. Mukerjee, *Chem. Eng.*, 88 (1981) 78.
- [30] O.V. Kikhtyanim, K.G. Ione, L.V. Malysheva and A.V. Toktarev, in T. Inui, S. Namba and T. Tstsumi (Eds.), *Chemistry of Micro Crystals*, Proc. Int. Symp. Chemistry of Micro Porous Crystals, Tokyo, Elsevier, Amsterdam, 1991, p. 319.
- [31] P.Y. Chen, M.C. Chen, H.Y. Chen, N.S. Chang and T.K. Chuang, in Y. Murakami, A. Lizima and W.C. Ward (Eds.), *Proc. 7th Int. Zeolite Conf.*, Tokyo, Elsevier, Amsterdam, 1986, p. 739.
- [32] S. Prasad and B.S. Rao, *J. Mol. Catal.*, 62 (1990) L17.
- [33] S. Narayanan, B. Prabhu Prasad and V. Vishwanathan, *React. Kinet. Catal. Lett.*, 48 (1992) 497.
- [34] S. Narayanan, B. Prabhu Prasad and V. Vishwanathan, *React. Kinet. Catal. Lett.*, 48 (1992) 561.
- [35] S. Narayanan and B. Prabhu Prasad, *J. Chem. Soc., Chem. Commun.*, (1992) 1204.
- [36] B.S. Parekh and S.W. Weller, *J. Catal.*, 47 (1977) 100.
- [37] A. Wokaun, M. Schraml and A. Baiker, *J. Catal.*, 116 (1989) 595.
- [38] B. Taouk, M. Guelton, J. Grimblot and J.P. Bonnelle, *J. Phys. Chem.*, 92 (1988) 6700.
- [39] H. Takahashi, M. Shiotani, H. Kobayashi and J. Shoma, *J. Catal.*, 14 (1969) 134.