

Ammoxidation of 3-picoline over V_2O_5/TiO_2 (anatase) system

I. Relationship between ammoxidation activity and oxidation state of vanadium

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Abstract

A series of titania (anatase)-supported vanadia catalysts ranging in V_2O_5 content from 0.4 to 9.9 mol% was prepared by wet impregnation technique, characterized by BET surface area measurement and X-ray diffraction, and evaluated for ammoxidation of 3-picoline. The average oxidation number of vanadium in the fresh and used catalysts was determined by titrimetric methods. The ammoxidation activity and the average oxidation number were observed to increase with vanadia loading up to 3.4 mol% in the catalyst which corresponds to a monolayer coverage. The phase transformation of anatase to rutile after the reaction was observed at a V_2O_5 loading of 5.9 mol%. The slow decrease of ammoxidation activity beyond 3.4 mol% V_2O_5 was attributed to the coverage of active monomeric VO_x species on the support by bulk vanadia and by other oxides, and also to compound formation with ammonia.

Keywords: 3-Picoline ammoxidation; Average oxidation number; Monolayer coverage

1. Introduction

The heterogeneously catalysed ammoxidation of heteroalkyl aromatics, especially picolines, to the corresponding nitriles has been the subject of many patents [1–3]. The resulting nitriles are important intermediates to produce

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respective acids or amides which are very useful compounds in the pharmaceutical industry. For example, a derivative of 2-pyridine carboxylic acid can be used as a local anaesthetic. Niacin and nicotinamide are important vitamins of B-complex, and a derivative of isonicotinic acid is an important anti-tubercular drug. The advantage of ammoxidation step is that it is possible to obtain the corresponding acid and amide by hydrolysis of nitrile with higher purity and yield than that obtained by direct vapor phase oxidation [4].

Vanadium oxide catalysts on different supports are good catalytic systems for the selective oxidation and ammoxidation of organic compounds [5–10]. According to Bond et al. [11], a particular kind of interaction between V_2O_5 and the support TiO_2 (anatase) leads to the formation of an active and selective monolayer of vanadia spread over the support. Therefore, considerable attention has been focused on the monolayer catalysts during the last few years. V-Ti-O catalysts reported in the literature are prepared by various techniques [12–18]. In the present investigation, V-Ti-O catalysts have been prepared by the conventional wet impregnation technique and the influence of V_2O_5 loading has been studied on the activity of the catalyst for ammoxidation of 3-picoline and on the average oxidation number of vanadium in the used catalysts. The activities of the catalysts have been correlated to the average oxidation numbers of the used catalysts.

2. Experimental

2.1. Catalyst preparation

The requisite amount of AR grade NH_4VO_3 dissolved in aqueous oxalic acid solution was contacted with titania (anatase) support (Ti-oxide make, UK) at room temperature and stirred well for two hours. The solid mass was dried at $110^\circ C$ overnight. The dried sample was then subjected to calcination in air at $300^\circ C$ for 6 h and finally at $450^\circ C$ for 6 h. The calcined sample was pelletized, crushed and sieved to $-18/25$ mesh size. The vanadia loading varied from 0.4 to 10 mol% in the catalyst.

2.2. Adsorption measurements and determination of oxidation states of vanadium

BET surface areas of the catalysts were measured by physical adsorption of nitrogen at 77 K using an all-glass high-vacuum system capable of attaining pressure as low as 10^{-6} torr. XRD measurements were carried out with Philips PW 1140 X-ray diffractometer using Ni-filtered $FeK\alpha$ radiation. The average oxidation number of vanadium in V_2O_5/TiO_2 catalysts has been determined by volumetric titrations [19]. The catalyst was dissolved in 10 ml 18N H_2SO_4 and 5

ml of 48% HF solution and the degree of lower oxidation states were determined manganometrically, i.e. by 0.1N KMnO_4 solution. Assuming that the catalyst sample contains V^{5+} , V^{4+} and V^{3+} , the titration amount of KMnO_4 can be taken as

$$T_1 = \text{V}^{4+} + 2\text{V}^{3+} \quad (1)$$

The solution thus obtained after titration against KMnO_4 contains all vanadium in the form of V^{5+} species. V^{5+} ions are reduced to V^{4+} by titrating against 0.1N Mohr's Salt solution. The titre value T_2 represents,

$$T_2 = \text{V}^{5+} + \text{V}^{4+} + \text{V}^{3+}. \quad (2)$$

On the other hand, the amount of V^{5+} species which are inherently present in the catalyst can be obtained by titrating the solution containing the sample in H_2SO_4 -HF against Mohr's salt. Thus

$$T_3 = \text{V}^{5+} \quad (3)$$

using Eqs. (1), (2) and (3), one can easily estimate the concentrations of V^{3+} , V^{4+} and V^{5+} . The average oxidation number of vanadium can be obtained by the expression,

$$\text{Av. Oxdn. number of V} = \frac{3\text{V}^{3+} + 4\text{V}^{4+} + 5\text{V}^{5+}}{\text{V}^{3+} + \text{V}^{4+} + \text{V}^{5+}}$$

2.3. Activity measurements

Activities of the catalysts for ammoxidation of 3-picoline were determined in a continuous fixed-bed microcatalytic reactor made of pyrex glass and heated by means of an electric furnace. A schematic diagram of experimental set up is shown in Fig. 1. About 2 g of catalyst particles [$-18 + 25$ BS mesh] were packed in-between two quartz wool plugs in the glass reactor and reduced at

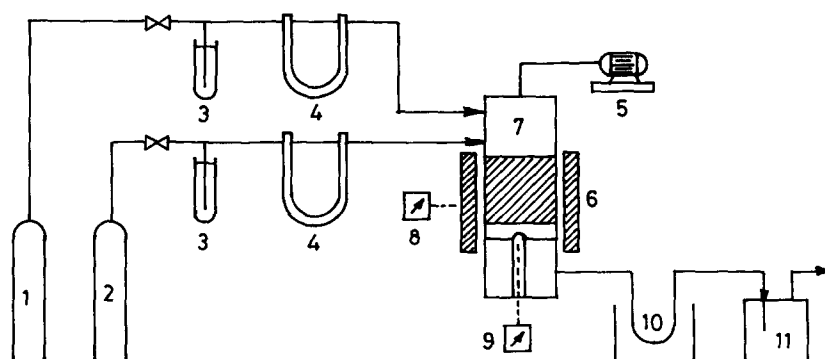


Fig. 1. A schematic diagram of experimental set up for determination of ammoxidation activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ (anatase) catalysts. 1. Air cylinder 2. NH_3 cylinder 3. Bleed-off tube 4. Flowmeter 5. Syringe pump 6. Electrical furnace 7. Reactor 8. Temperature indicator controller (TIC) 9. Temperature indicator (TI) 10. Condenser 11. BaCl_2 solution.

450°C in a stream of hydrogen (60 ml h⁻¹) for 2 h. The catalyst bed was cooled to 330°C in H₂ stream. The H₂ gas stream was replaced by NH₃ + air mixture (mole ratio 5:46) stream from compressed gas cylinders and the catalyst bed temperature raised to 360°C. The feed 3-picoline dissolved in water (mole ratio 1:13) was injected into the reactor at the rate of 2 ml h⁻¹ by means of a high-precision infusion pump, Secura FT (M/s B. Braun, Germany). The feed vapour along with NH₃ + air mixture enters the preheater zone which contains glass beads and is maintained at 250°C before entering the catalyst bed. Two thermocouples were positioned, one at the centre of the catalyst bed to indicate reaction temperature, and the other was attached to the furnace through temperature indicator cum controller to monitor the temperature of the furnace.

The nongaseous products and unreacted 3-picoline were trapped in a condenser at -30°C at the bottom of the reactor. CO and CO₂ formed during the reaction were estimated by ORSAT apparatus and by BaCl₂ method. The amounts of carbon oxides were always found to be negligible. The liquid products collected from the cooled condenser were analysed by a gas chromatograph, (M/s Sigma Instruments, Baroda, India) equipped with a FID and with a 3-m column of 10% OV-17 on chromosorb W. It was observed that the catalysts attained steady state activity after 1 h.

3. Results and discussion

Table 1 shows the BET surface areas and the concentrations of V³⁺, V⁴⁺ and V⁵⁺ ions of fresh and used catalysts. In fresh as well as used catalysts, the surface area decreased with V₂O₅ loading as expected due to pore blocking. No significant difference in the surface areas of fresh and used catalysts of the same V₂O₅ loading was observed.

Table 1
BET Surface area, V³⁺, V⁴⁺ and V⁵⁺ concentrations of fresh and used catalysts

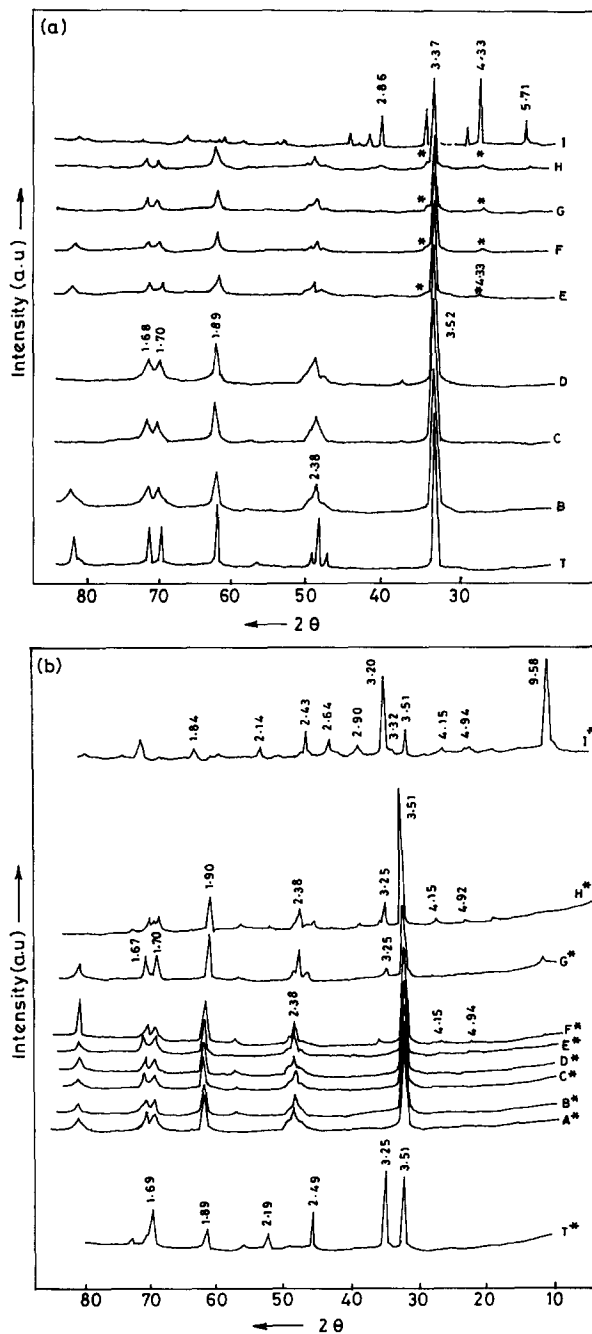
V ₂ O ₅ loading (mol-%)	BET surface area (m ² g ⁻¹)		V ³⁺ (%)		V ⁴⁺ (%)		V ⁵⁺ (%)	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
0	79.3	31.7	—	—	—	—	—	—
0.4	76.0	50.3	10.4	34.0	9.3	28.5	80.3	37.5
1.3	69.8	63.5	5.6	32.0	8.3	26.8	86.1	41.2
2.3	58.5	54.3	1.3	18.9	11.6	17.1	87.1	64.0
3.4	55.1	54.2	3.0	16.2	6.9	3.2	90.1	80.6
4.7	39.8	42.6	4.0	12.4	4.1	3.3	91.9	84.3
5.9	28.3	22.8	4.2	6.8	3.0	11.2	92.8	82.0
7.2	18.6	20.1	3.9	5.6	2.1	11.6	94.0	82.8
9.9	19.4	23.9	3.7	5.0	0.3	8.1	96.0	86.9
100% V ₂ O ₅	2.5	3.5	—	0.6	—	18.8	100.0	80.6

Table 2
Summary of XRD results of fresh and used catalysts; the different crystalline phases of TiO₂ and vanadium oxides along with their relative XRD peak intensities

V ₂ O ₅ loading (mol %)	TiO ₂ (Anatase)		TiO ₂ (Rutile)		V ₂ O ₅		V ₂ O ₄		V ₃ O ₅		NH ₄ VO ₃		NH ₄ V ₄ O ₁₀	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
			3.52, 2.38, 1.99, 1.70	3.25, 2.49, 2.19	4.33, 3.37, 2.86	3.20, 2.43, 2.14	2.64, 2.90, 3.32	4.15, 4.94	9.58, 3.51, 1.84					
0 (TiO ₂)	major	major	—	—	—	—	—	—	—	—	—	—	—	—
0.4	major	major	—	—	—	—	—	—	—	—	—	—	—	—
1.3	major	major	—	—	—	—	—	—	—	—	—	—	—	—
2.3	major	major	—	—	—	—	—	—	—	—	—	—	—	—
3.4	major	major	—	—	—	—	—	—	—	—	—	—	—	—
4.7	major	major	—	—	minor	—	—	—	—	—	—	—	—	—
5.9	major	major	—	minor	minor	—	—	—	—	—	—	—	—	—
7.2	major	major	—	minor	medium	—	—	—	—	—	—	—	—	—
9.9	major	major	—	medium	medium	minor	—	—	—	—	—	—	—	—
100% (V ₂ O ₅)	—	—	—	—	major	minor	major	—	—	medium	—	—	—	medium

The *d* values were calculated from 2 θ values of XRD peaks given in Figs. 2(a) and 2(b). Identification of crystalline phases was made referring to ASTM cards.

The XRD patterns of fresh catalysts are shown in Fig. 2(a). The results are summarised in Table 2. Anatase has been observed as a major crystalline phase of TiO_2 in all the catalysts. Crystallinity due to V_2O_5 starts appearing from 4.7



mol% V_2O_5 loading onwards. Inomata et al. [12] also observed a crystalline anatase phase only in impregnated catalysts with V_2O_5 loading below 5 mol%. Andersson [15] and Andersson and Lundin [20] have observed a crystalline phase due to rutile only in a 10 mol% V_2O_5/TiO_2 catalyst calcined at 1150°C.

The XRD patterns of used V_2O_5/TiO_2 catalysts are shown in Fig. 2(b). It is clear that ammoxidation reaction brings about transformation of pure anatase to rutile (Table 2, Fig. 2a and Fig. 2b) accompanied by drastic reduction in surface area of the starting material (Table 1). The XRD patterns (Fig. 2b) reveal that addition of a small quantity of V_2O_5 (0.4 mol%) prevents the conversion of anatase to rutile when subjected to ammoxidation reaction conditions (Fig. 2b, curve A). However, beyond 4.7 mol% V_2O_5 , formation of rutile and NH_4VO_3 phase is evident, the intensities of XRD peaks of these phases (Fig. 2b) increasing with an increase in V_2O_5 loading. At a loading of 9.9 mol% V_2O_5 , the V_2O_4 phase is detected in addition to the above phases. Pure V_2O_5 has developed V_3O_5 phase and $NH_4V_4O_{10}$ phase due to interaction of NH_3 with vanadia during ammoxidation reaction (Table 2, Fig. 2b). Thus, it is clear from XRD results that the drastic changes that take place in the catalysts during ammoxidation process have a detrimental effect on anatase-to-rutile transformation.

It is evident from the concentrations of vanadium ions in Table 1, estimated by titrimetric methods, that the catalyst with V_2O_5 loading of 0.4 mol% has the highest concentrations of V^{3+} and V^{4+} ions after ammoxidation reaction, and these decrease with an increase in V_2O_5 loading. Also the concentration of V^{5+} ions increases with an increase in V_2O_5 loading with the used catalysts always having lower concentrations of V^{5+} than the fresh catalysts. This means the reducibility of the catalyst increases with a decrease in V_2O_5 content of the catalyst. The reduction in the oxidation number of vanadium during the reaction was also observed by Niwa and Murakami [21]. The average oxidation number of vanadium increases far above 3+ upon increasing the V_2O_5 loading (Fig. 3) and records maximum values of 4.9 ± 0.02 and 4.7 ± 0.05 for fresh and used catalysts, respectively, with V_2O_5 content beyond 3.4 mol%.

The plot between V_2O_5 loading and conversion and selectivity (Fig. 4) shows that conversion of 3-picoline increases steadily up to 3.4 mol% V_2O_5 and remains almost constant above this loading. The catalyst maintains almost 100% selectivity for nicotinonitrile up to 3.4 mol% V_2O_5 which corresponds to a monolayer coverage of anatase surface by vanadia. Similarity between the plots,

Fig. 2. a) X-ray diffractograms of fresh V_2O_5/TiO_2 (anatase) catalysts. T. 100% TiO_2 (anatase). B. 1.3 mol % V_2O_5 ; C. 2.3 mol % V_2O_5 ; D. 3.4 mol % V_2O_5 ; E. 4.7 mol % V_2O_5 ; F. 5.9 mol % V_2O_5 ; G. 7.2 mol % V_2O_5 ; H. 9.9 mol % V_2O_5 ; I. 100% V_2O_5 . b) X-ray diffractograms of used V_2O_5/TiO_2 catalysts. T* 100% TiO_2 . A*. 0.4, mol % V_2O_5 ; B*. 1.3 mol % V_2O_5 ; C*. 2.3 mol % V_2O_5 ; D*. 3.4 mol % V_2O_5 ; E*. 4.7 mol % V_2O_5 ; F*. 5.9 mol % V_2O_5 ; G*. 7.2 mol % V_2O_5 ; H*. 9.9 mol % V_2O_5 ; I*. 100% V_2O_5 . (* represents used catalysts).

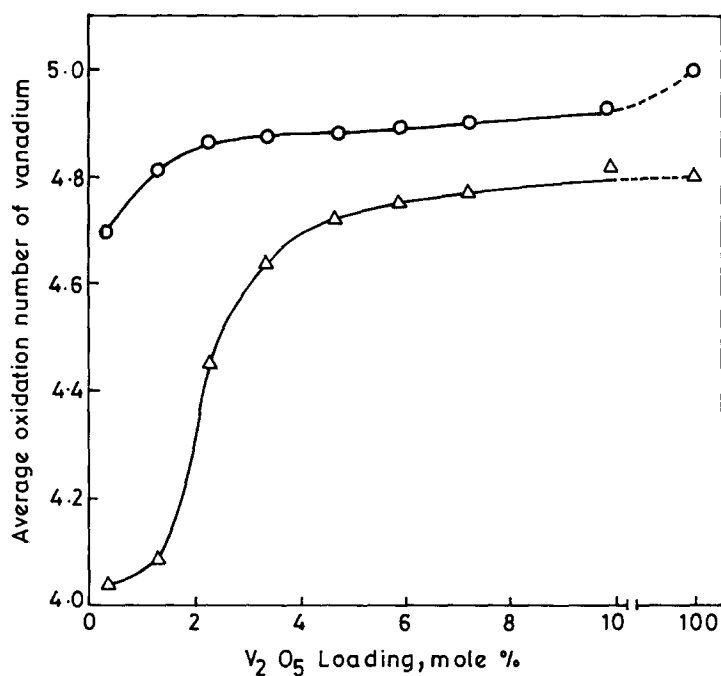


Fig. 3. Effect of vanadia loading on the average oxidation number of vanadium over V₂O₅/TiO₂ catalysts fresh catalysts (○); used catalysts (△).

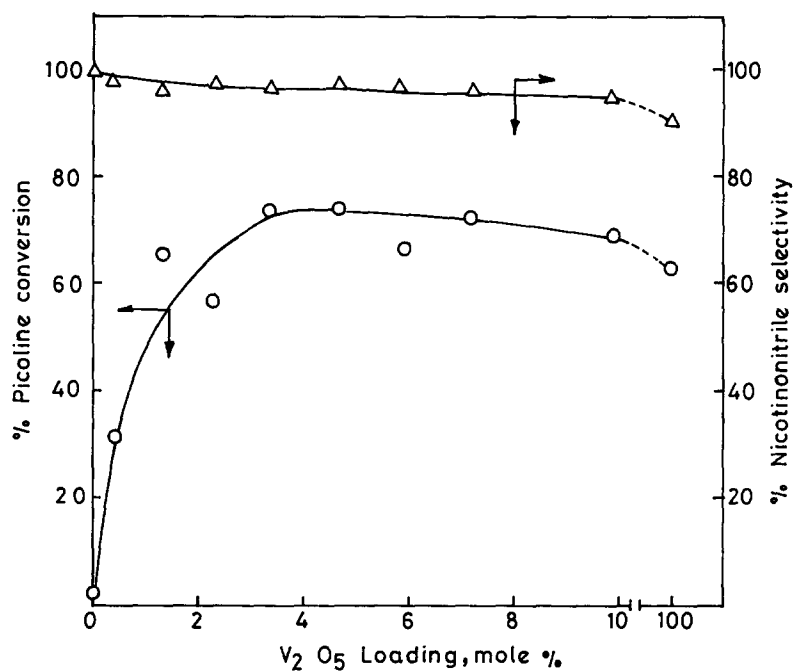


Fig. 4. Effect of vanadia loading on 3-picoline conversion (○) and nicotinonitrile selectivity (△) at 360°C.

conversion versus V_2O_5 loading (Fig. 4) and average oxidation number of vanadium versus V_2O_5 loading (Fig. 3) suggests that a catalyst with 3.4 mol% V_2O_5 /anatase with an average oxidation number of slightly less than 5 is the most suitable catalyst for ammoxidation of 3-picoline. Incidentally, such a catalyst retains anatase phase during reaction. The slight decrease of ammoxidation activity of the catalyst (conversion and selectivity) with V_2O_5 loading beyond 3.4 mol% can be attributed to the phase transformation of TiO_2 , to the formation of bigger crystallinities of V_2O_5 and other oxides and to compound formation of V_2O_5 with ammonia as evidenced from XRD results. The increase in the conversion of 3-picoline and the near 100% selectivity of the product in premonolayer region up to 3.4 mol% V_2O_5 should be attributed to the facile nature of adsorption, and reaction between the reactants on the monomeric VO_x species formed as a result of interaction of vanadia with anatase surface.

Similar catalytic behaviour as in ammoxidation of 3-picoline was also observed by Gasior et al. [22] in the oxidation of *O*-xylene. In the premonolayer region an initial increase in the activity of V_2O_5 /anatase catalysts was observed followed by a high constant activity up to a V_2O_5 loading of 20 mol%. Superior catalytic behaviour in *O*-xylene oxidation was also observed by Dias et al. [23,24] to be associated with a VO_x monolayer on anatase surface. Deo and Wachs [25] have related the high methanol oxidation activity of monolayer catalysts to the participation of oxygen in vanadium-oxygen-support (V-O-S) bonds on the surface of the catalyst in the reaction.

Wachs et al. [6,27], Saleh and Wachs [26] have also observed V_2O_5 crystallites in the post monolayer catalysts. According to Inomata et al. [12] the surface of TiO_2 is covered by increasing number of layers of V_2O_5 lamelle with increasing V_2O_5 loading, with exposure of the (010) plane of V_2O_5 increasing so that about 90% of the vanadia surface is constituted by the (010) crystal plane at 10 mol% V_2O_5 . However, small amounts of crystalline V_2O_5 showing low effective surface area and far lower catalytic activity than VO_x units, do not appear to significantly affect catalyst performance of V_2O_5 /anatase catalysts. According to Vejux and Courtine [28], the high oxidation activity of anatase-supported V_2O_5 catalysts is attributed to the remarkable crystallographic fit between the (010) plane of V_2O_5 and the (010) and (001) planes of anatase.

4. Conclusions

The present investigation reveals that an optimum loading of vanadia on titania support yields selective ammoxidation of 3-picoline to nicotinonitrile which is an important reaction in pharmaceutical industry.

The catalysts exhibit increasing conversion of 3-picoline up to 3.4 mol% V_2O_5 loading with close to 100% selectivity of nicotinonitrile. Above 3.4 mol% V_2O_5 loading, both the conversion and selectivity were observed to decrease

slightly. Anatase-to-rutile transformation was observed at a V_2O_5 loading of 5.9 mol% during the reaction. These ammoxidation results are found to be in good agreement with the results of oxidation of *O*-xylene in the literature suggesting that the same type of coordinatively unsaturated sites (CUS) on vanadium are responsible for oxidation and ammoxidation reactions.

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References

- [1] Eur. Pat. Appl., 80,43,119 (April 1, 1980).
- [2] Ger. Offen. Appl., 3,128,956 (1981).
- [3] Jap. Pat. Appl., 74,28,597 (March 14, 1974).
- [4] Ger. Pat., 1940320 (1972).
- [5] G.C. Bond and P. Konig, *J. Catal.*, 77 (1982) 309.
- [6] I.E. Wachs, R.Y. Saleh, S.S. Chan and C.C. Chersich, *Appl. Catal.*, 15 (1985) 339.
- [7] F. Cavani, E. Foresti, F. Trifiro and G. Busca, *J. Catal.*, 106 (1987) 251.
- [8] P. Cavali, F. Cavani, I. Manenti and F. Trifiro, *Catal. Today*, 1 (1987) 245.
- [9] B. Jonson, B. Rebenstorf, R. Larsson and S.L.T. Andersson, *J. Chem. Soc. Faraday Trans. I*, 84 (1988) 3547.
- [10] M. Sanati and A. Anderson, *J. Mol. Catal.*, 59 (1990) 233.
- [11] G.C. Bond, J.P. Zurita, P.J. Gellings, H. Bosch, J.G. van Ommen and B.J. Kip, *Appl. Catal.*, 22 (1986) 361.
- [12] M. Inomata, K. Mori, A. Miyamoto, T. Ui and Y. Murakami, *J. Phys. Chem.*, 87 (1983) 754.
- [13] F. Roozeboom, M.C. Mittelmeijer-Hazeleger, J.A. Moulijn, J. Medema, V.H.J. de Beer and P.J. Gellings, *J. Phys. Chem.*, 84 (1980) 2783.
- [14] G. Busca, G. Centi, L. Marchetti and F. Trifiro, *Langmuir*, 2 (1986) 568.
- [15] A. Andersson, *J. Catal.*, 76 (1982) 144.
- [16] A. Andersson, S.L.T. Andersson in *Solid State Chemistry in Catalysis*, R.L. Graselli and J.F. Brazdil (Eds.), ACS Sym. Series., 279 (1983) 121.
- [17] G. Busca, L. Marchetti, G. Centi and F. Trifiro, *J. Chem. Soc., Faraday Trans I*, 81 (1985) 1003.
- [18] G.C. Bond and K. Bruckman, *Faraday Discuss. Chem. Soc.*, 72 (1981) 141, 235.
- [19] M. Nakamura, K. Kawai and Y. Fujiwara, *J. Catal.*, 34 (1974) 345.
- [20] A. Andersson and S.T. Lundin, *J. Catal.*, 65 (1980) 9.
- [21] M. Niwa and Y. Murakami, *J. Catal.*, 76 (1982) 9.
- [22] M. Gasior, I. Gasior and B. Grzybowska, *Appl. Catal.*, 10 (1984) 87.
- [23] C.R. Dias, M.F. Portela and G.C. Bond, *J. Catal.*, 157 (1995) 344.
- [24] C.R. Dias, M.F. Portela and G.C. Bond, *J. Catal.*, 157 (1995) 353.
- [25] G. Deo and I.E. Wachs, *Critical Reviews in Surface Science*, 4 (1994) 141.
- [26] R.Y. Saleh and I.E. Wachs, *Appl. Catal.*, 31 (1987) 87.
- [27] I.E. Wachs, R.Y. Saleh, S.S. Chan and C.C. Chersich, *CHEMTECH*, (1985) 756.
- [28] A. Vejux and P. Courtine, *J. Solid State Chem.*, 23 (1978) 93.