The influence of support on ammoxidation of 3-picoline over vanadia catalyst

Shyam Kishore Roy, P. Dutta, L.N. Nandi, S.N. Yadav, T.K. Mondal,
S.C. Ray, Swapan Mitra, P. Samuel*

Central Fuel Research Institute, Dhanbad 828108, India

Abstract

The influence of high content of MoO_3 (32 mol%) in V_2O_5–MoO_3–P_2O_5 catalyst system supported on alumina, silica, HZSM-5 and modified clay was investigated for ammoxidation of 3-picoline. Unsupported VMPO catalyst and supported catalysts were prepared by incipient wet impregnation method keeping the mole ratio of V_2O_5–MoO_3–P_2O_5 (1.00:3.27:0.14) constant. FT-IR spectra and X-ray diffractograms showed interaction among the active oxides and the support. The major phases identified were $Mo_4V_6O_{25}$, $Mo_6V_9O_{40}$ and MoV_2O_8. TG–DTA also showed the exothermic peaks indicating the formation of new compounds above 400 °C. The physico-chemical properties of the catalysts were correlated with their activity and selectivity for ammoxidation of 3-picoline. The unsupported catalyst showed 96.0% selectivity whereas VMPO/HZSM-5 showed the highest selectivity (91.3%) amongst the supported catalysts.
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1. Introduction

Supported vanadium oxide catalysts are good catalyst systems for selective oxidation and ammoxidation [1,2] of organic compounds as well as for selective catalytic reduction (SCR) of NO with ammonia [3]. The catalytic properties of vanadium oxides are highly influenced by the nature of support, type of promoter and the method of preparation. The structure and the composition of the materials used as supports influence the activity and selectivity of the active phase to a marked degree [4–6]. Alumina, silica, titania and zirconia are the most common oxide supports which are generally used in oxidation and ammoxidation processes and have been widely investigated. Molybdenum, chromium and phosphorous are generally incorporated with vanadium oxide because they improve the activity and selectivity of the catalyst due to change in the phase composition of the catalyst [7,8]. The

activity and selectivity of V_2O_5–MoO_3 catalysts vary significantly with MoO_3 content. The maximum selectivity in benzene oxidation for industrial production of maleic anhydride has been reported [9] at around 30 mol% MoO_3. The role of high content of MoO_3 in VMPO catalyst for ammoxidation has not yet been studied. Earlier, we had reported vanadia catalysts with low content of MoO_3 for ammoxidation of alkyl pyridines over alumina support [10,11].

Recently vanadium modified ZSM-5 zeolite has been reported for oxidation and ammoxidation of 3-picoline with 62.6% yield of nicotinonitrile at 88% conversion [12]. It has been observed that oxidation properties of zeolite are confined to dehydroxylated surfaces of decationated zeolites and the oxygen chemisorption occurs on anion and cation lattice vacancies [13]. Modified clay has also been used as support for SCR of NO with NH_3 [14].

This paper deals with physico-chemical studies of V_2O_5–MoO_3–P_2O_5 catalyst system with high content of MoO_3 (32 mol%) supported over alumina, silica, HZSM-5 and modified clay for ammoxidation of 3-picoline to

* Corresponding author.

nicotinonitrile. Nicotinamide and niacin are important pharmaceutical ingredients which can be produced either by multi-step route of oxidation or by single step catalytic hydration of nicotinonitrile [15] obtained in a single step ammoxidation reaction of 3-picoline. We report here for the first time the use of modified clay as support for ammoxidation reaction as well as the effect of higher concentration of MoO_3 in the system.

2. Experimental

2.1. Preparation of catalyst

Materials used: vanadyl oxalate (prepared by refluxing V_2O_5, Loba chemie, G.R.Grade, in water with oxalic acid), ammonium heptamolybdate (AnalaR, BDH), orthophosphoric acid (85%), γ-alumina (SA = 160 m^2/g), silica (SA = 200 m^2/g), ZSM-5 (SiO_2:Al_2O_3 = 400) UCIL, Baroda. HZSM-5 was prepared by ammonium ion exchange. Bentonite clay was modified with group-IV metal salt.

Supported and unsupported catalysts in the weight ratio of V_2O_5:MoO_3:P_2O_5:support (1.00:2.57:0.11:1.91) were prepared in aqueous medium by incipient wet impregnation method. A mixed solution of the required amount of vanadyloxalate and orthophosphoric acid and another solution of ammonium heptamolybdate were separately heated over steam bath and the former was added to the latter followed by addition of support. This was mixed thoroughly and refluxed over steam bath till the mass reduced to about half. The impregnated catalyst was oven dried at 120 °C for 15 h and calcined first at 300 °C for 3 h and then at 450 °C for 15 h. The catalyst was pelleted and sized (−6 + 14 BS mesh).

2.2. Activity studies

Ammoxidation reaction was carried out using a down flow, fixed bed, pyrex glass reactor of 20 mm i.d. The reaction mixture (3-picoline and water) was fed from the top using a syringe pump. Ammonia gas and air were fed through calibrated flow meters. The reaction was carried out in the temperature range 375–475 °C and contact time 0.7–1.5 s. The product was collected at the bottom using ice cold water and was analysed by gas chromatograph with carbowax 20 M column at 160 °C temperature and TCD detector.

2.3. Catalyst characterization

The phase composition of calcined catalysts was determined by XRD recorded in D-8 ADVANCE diffractometer (Bruker AXS, Germany) using Cu Kα radiation at 40 kV and 40 mA in parallel beam geometry. Infrared spectra were recorded in Perkin-Elmer FT-IR-2000 Spectrometer using KBr pellet in the range of 4000–400 cm^{-1}. TG–DTA of the catalyst samples was done using Netzsch Thermal Analyser Model STA 409C. The experiment was conducted in ambient condition under constant heating at 10 °C/min up to 600 °C. Surface area and pore volume of supports and catalysts were determined by surface area Analyser (Micromeritics – ASAP 2010) by nitrogen adsorption at liquid nitrogen temperature (77 K).

Surface acidity of the catalysts was determined by NH_3-TPD (Micromeritics Auto Chem 2910). Catalyst sample (0.1 g) was placed in a pulse reactor and calcined at 500 °C in a flow of helium for 2 h. The temperature of the reactor was brought down to 100 °C. Then a series of 0.5 ml NH_3 gas pulses were continued until no more uptake of NH_3 was observed. The system was flushed with helium for 30 min, then the adsorbed ammonia was desorbed at a programmed heating rate of 10 °C/min. The desorbed ammonia was detected by a thermal conductivity detector.

3. Results and discussion

FT-IR spectra of VMPO catalyst system, unsupported and supported over alumina, silica, HZSM-5 and modified clay are shown in Fig. 1. It is evident from all the spectra that most of the bands for all the catalysts are in the range of 400–1500 cm^{-1}. V=O stretching band in pure and crystalline V_2O_5 is generally at 1020 cm^{-1}, the shifting of 1020 cm^{-1} band towards lower frequency is in good agreement with the observation that when MoO_3 is added to V_2O_5 the absorption band weakened and shifted to lower wave number between 974 and 1014 cm^{-1}. The shift from 1020 band to 1014 cm^{-1} is observed only in unsupported catalyst which indicates the presence of V=O stretching frequency. The shifting of 1020 cm^{-1} band towards lower frequency is due to introduction of Mo into the lattice of V_2O_5 resulting in the stretching of metal oxygen bond. The band at 989 cm^{-1} is observed in the catalysts supported on zeolite, alumina and also in unsupported VMPO catalyst. This band has further shifted to 977 cm^{-1} in modified clay and 974 cm^{-1} in silica due to metal oxygen multiple bond which has the frequency similar to that of MoO_3 (995 cm^{-1} band), which suggests that intermediate compounds with doubly bonded oxygen appear as oxygen coordinated to Mo atoms and not to V atoms [16]. The multiple bonds may be due to the formation of $Mo_6V_9O_{40}$ and $Mo_4V_6O_{25}$ and MoV_2O_8 intermediate compounds which is evident from the phases identified by XRD. These bands are more intense in zeolite based catalyst than other supported and unsupported catalysts. The sharp bands are observed at 894 cm^{-1} in alumina 872 cm^{-1} in zeolite, 883 cm^{-1} in silica and 894 cm^{-1} in unsupported catalyst. A small peak is also observed at 817 cm^{-1} in the supported catalyst. The bands in the region of 800–900 cm^{-1} are attributed to the vibration of polymeric chains M−O−M−O in which oxygen atoms are in coordinated polyhedra. The bands which are in the region of 1003–1362 cm^{-1} may be due to the P−O stretching vibration related to phosphate, pyrophosphates and metal phosphates and weak bands between 409 and 733 cm^{-1} present in all the catalysts may be due to the
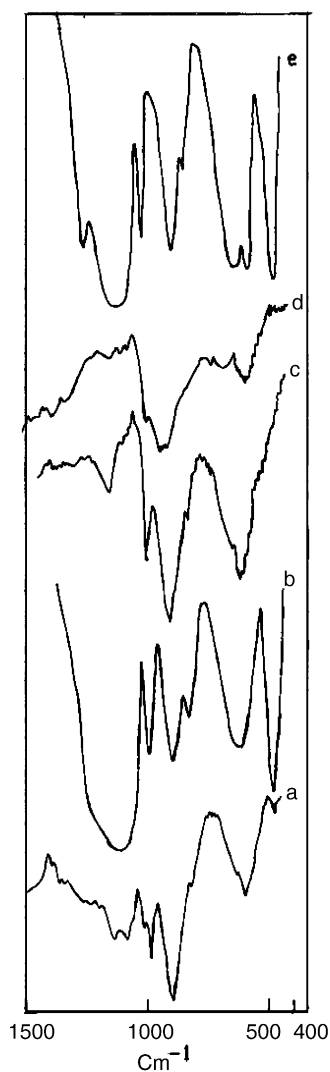
Fig. 1. FT-IR spectra of (a) VMPO, (b) VMPO/SiO$_2$, (c) VMPO/Al$_2$O$_3$, (d) VMPO/modified clay, (e) VMPO/ZSM-5.

Fig. 2. XRD pattern of (a) VMPO, (b) VMPO/SiO$_2$, (c) VMPO/Al$_2$O$_3$, (d$_1$) VMPO/modified clay before reaction, (d$_2$) VMPO/modified clay after reaction, (e) VMPO/ZSM.

presence of V–O and P–O stretching vibration of phosphates of vanadium [17,18].

X-ray powder diffraction patterns of supported and unsupported VMPO catalysts are presented in Fig. 2. The various crystalline phases identified are MoO$_3$, V$_5$O$_{12}$6H$_2$O, MoV$_2$O$_8$, Mo$_4$V$_6$O$_{25}$, Mo$_6$V$_9$O$_{40}$, AlVO$_3$, V(PO$_3$)$_3$, MoO$_{0.03}$ VP$_{1.1}$O$_{4.84}$ with some other minor unidentified phases in varying intensities as well as the broad phases due to support materials. The "*d*" values obtained are in agreement with JCPDS Values of the above phases. The active intermediate phases are MoV$_2$O$_8$, Mo$_4$V$_6$O$_{25}$, Mo$_6$V$_9$O$_{40}$ which are present in all the catalysts. The X-ray diffractogram of VMPO on zeolite support exhibits a number of sharp peaks as compared to alumina/silica/modified clay supported catalysts. This may be due to specific physico-chemical properties of HZSM-5. The introduction of high content of MoO$_3$ (32 mol%) into the lattice of V$_2$O$_5$ forms a solid solution after calcining up to 500 °C, it generates V^{4+} due to promoting effect of hexavalent molybdenum, which
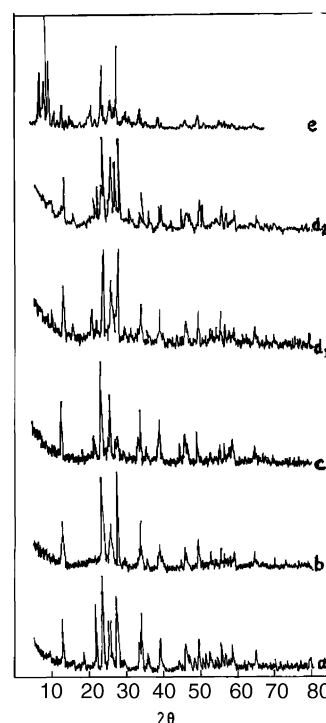
helps in the formation of intermediate phases. This is in good agreement with the observations of Satsuma et al. [9] and Munch and Pierron [19]. It seems that incorporation of low concentration of oxide of phosphorus in the catalyst system also helps in the formation of intermediate phases like phosphates and pyrophosphates of vanadium as is evident from FT-IR and XRD studies. Phosphorus oxide generally increases the selectivity and life of the catalyst.

TG–DTA graph of VMPO catalyst supported on HZSM-5 and modified clay is shown in Fig. 3. In addition to the endothermic peaks due to loss of water, exothermic peaks are observed between 280–440 and 440–500 °C in zeolite supported catalyst. This probably indicates that initially decomposition of the precursor salts takes place and then resulting oxides interact to form new compounds. For the catalyst supported on modified clay, exothermic peak between 165 and 320 °C also shows the decomposition of the salts after that weak exothermic peaks are observed indicating the weak interaction. However, the catalyst is stable up to 600 °C.

The concept that the lattice oxygen of reducible metal oxides would serve as a more versatile and functional oxidizing agent than molecular oxygen [20] play the crucial factor in selecting the ammoxidation catalyst because the reaction is governed by both oxidation and reduction process. To have an insight into the promotive action of MoO$_3$ on V$_2$O$_5$, FT-IR spectra of different catalyst samples are shown in Fig. 1. It is evident that 1020 cm^{-1} characteristic band of V$_2$O$_5$ is shifted to lower frequencies by adding MoO$_3$, this may be explained as that the promotive action
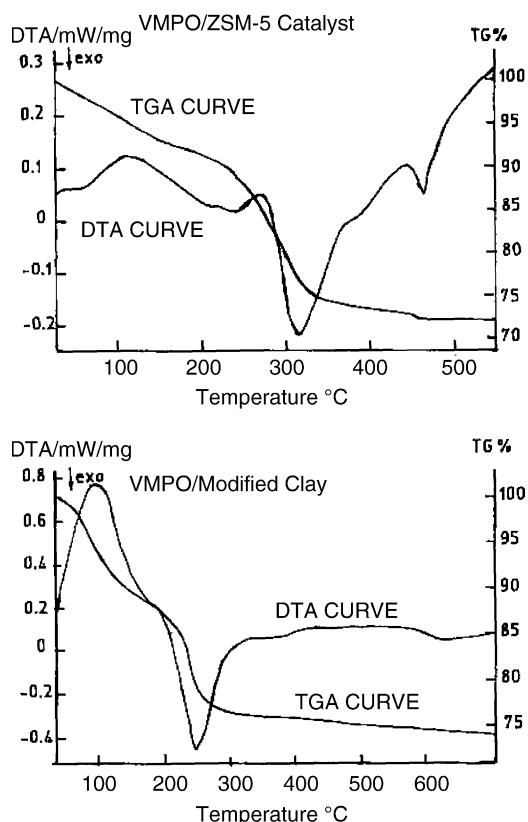
Fig. 3. TG/DTA curves of VMPO/modified clay and VMPO/ZSM-5 catalysts.

action of the metal oxide forming intermediate compounds showing better activity and selectivity for ammoxidation of 3-picoline.

Surface acidity of the supports, supported and unsupported catalysts has been determined by NH_3-TPD, which are presented in Table 1. It is evident that surface acidity is decreased after loading VMPO on the supports. VMPO catalyst has very low surface acidity (0.007 mmol/g) giving highest yield of nicotinonitrile and conversion of 3-picoline. It is observed that supported catalysts have higher surface acidity than VMPO. It may be inferred that due to higher acidity, ammonia may neutralize the acid sites during ammoxidation reaction thereby lowering the active centers responsible for the reaction. This in turn results in decreasing the yield and conversion using supported VMPO catalysts. However, regarding the role of MoO_3 in the catalyst system it is reported [9] that acid sites do not seem to be responsible for improvement of catalytic activity because the type, strength and surface concentration of acid sites are not varied by addition of MoO_3.

In the supported oxide catalyst, the oxide exists generally in the form of a layer or molecular dispersion and is maximally influenced by the support [21,22]. Oxide layers also appear to be quite thermally stable. Ease of formation and thermal stability of monolayers has been related to the ratio of the charge on the support cation to the sum of the cation and oxide ion radii [23]. The stabilization of the monolayer species on the surface of the support as a result of interaction can be viewed either in terms of minimization of surface free energy or in terms of the formation of new chemical compounds.

Ammoxidation reaction of 3-picoline was carried out in the temperature range of 375–475 °C using 8–12 g of catalyst. The performance of all the supported and unsupported catalysts is given in Table 2. It is evident that unsupported VMPO catalyst is highly active and selective (96.0% yield with 98.0% conversion). Amongst the supported catalysts VMPO supported on zeolite and modified clay gave higher yield of nicotinonitrile (81.3% and 80.5%) with higher conversion of 3-picoline as compared to alumina and silica supported catalysts (71.1% and 72.8%). Fig. 4 shows the effect of reaction temperature on conversion of 3-picoline and selectivity to nicotinonitrile with different supported and unsupported catalysts. Both the conversion and selectivity

of MoO_3 on V_2O_5 is due to weakening of V=O stretching bond by doping of MoO_3. This may be caused by increase of V^{4+} resulted from the substitution of V^{5+} with Mo^{6+} and the high concentration of Mo with V_2O_5 in the catalyst system leading to the formation of intermediate phases like $Mo_4V_6O_{25}$, $Mo_6V_9O_{40}$ and MoV_2O_8 in the catalyst. This has also been observed by Munch and Pierron [19]. Surface area, pore volume and surface acidity data of supports and catalysts are presented in Table 1. Surface area and pore volume of supported VMPO catalysts decrease drastically due to high concentration of metal oxide on the support. However, zeolite supported catalyst has the highest surface area (116.8 m^2/g) and pore volume (0.08 cm^3/g) due to microporous structure of zeolite. This may help for better inter-

Table 1
Physico-chemical properties of supports/catalysts

Supports/catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)	Surface acidity (mmol/g_{cat})
Alumina	160.00	0.7438	0.432
Silica	200.00	–	–
HZSM-5 (SiO_2/Al_2O_3 = 400)	400.00	0.11	0.462
Modified clay	183.8	–	0.506
VMPO	–	–	0.007
VMPO/SiO_2	14.60	0.0471	0.219
VMPO/HZSM-5	116.8	0.0797	0.116
VMPO/modified clay	5.2	0.0269	0.151

Table 2
Ammoxidation of 3-picoline to nicotinonitrile over different catalysts

Catalysts	Conversion of 3-picoline (wt.%)	Yield (wt.%)		
		Pyridine	Nicotinonitrile	Others
VMPO	98.0	2.0	96.0	0.0
VMPO/Al$_2$O$_3$	75.2	4.1	71.1	0.0
VMPO/SiO$_2$	79.6	2.2	72.8	4.6
VMPO/HZSM-5	87.7	1.9	81.3	4.5
VMPO/modified clay	87.6	7.1	80.5	0.0

Reaction temperature 425 °C, contact time 1.1–1.3 s, mole ratio of 3-picoline:NH$_3$:air = 1:9.7:18, 3-picolone:water = 1:3 (vol.%).
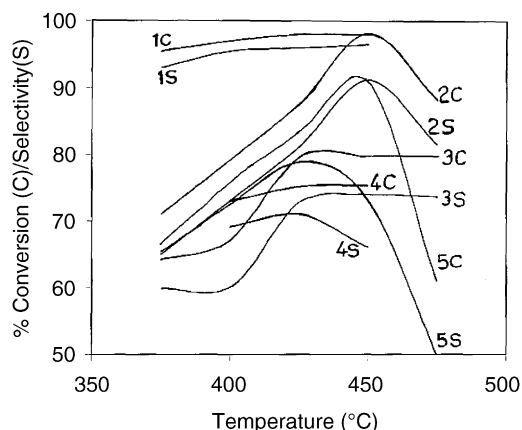

Fig. 4. Effect of reaction temperature on ammoxidation of 3-picoline with different catalysts (1). VPMO (2). VPMO/ZSM-5 (3).VPMO/SiO$_2$ (4). VPMO/Al$_2$O$_3$ (5). VPMO/modified clay.

increase on increasing the reaction temperature up to 450 °C and then decreases. The maximum yield obtained with zeolite supported catalyst was 91.3% at 450 °C and 80.5% with supported on modified clay at 425 °C. Supported catalysts showed low conversion and yield at lower temperature unlike unsupported catalyst. The increase of selectivity of the product at higher temperature with supported catalyst indicates that the formation of active phases as intermediate compounds occur during the reaction at higher temperature. The formation of active phases is due to segregation in V$_2$O$_5$–MoO$_3$ system in the course of oxidation during the reaction [7]. The interaction of the active oxide components with zeolite and modified clay seems to be stronger than that of alumina and silica due to more active sites which may be the reason for better activity and selectivity of these catalysts for ammoxidation of 3-picoline.

Thus, it may be concluded that the increase in the activity of the catalyst may be attributed to the combined effect of physico-chemical properties of the support and qualitative as well as quantitative change of the surface due to interaction among the active oxides of the catalysts, resulting in compound formation between V and Mo oxides. Although, unsupported catalyst gave higher yield of nicotinon-

itrile (96.0%), the selectivity of the supported catalyst is also sufficiently high >90% and further more, the supported catalyst is stable with the added features.

Acknowledgements

References

[1] A. Beilenski, J. Haber, Catal. Rev. Sci. Eng. 19 (1979) 1.
[2] A. Anderson, J.O. Bovin, P. Walter, J. Catal. 98 (1986) 204.
[3] I.E. Wachs, G. Deo, B.M. Weckhuysen, A. Andrein, M.A. Vuurman, M. de Boer, M.D. Amiridis, J. Catal. 161 (1996) 211.
[4] M. Akimoto, E. Echigoya, J. Catal. 29 (1973) 191.
[5] D. Vanhove, M. Blanchard, J. Catal. 37 (1976) 6.
[6] K.V.R. Chari, C.P. Kumar, K.R. Reddy, T. Bhaskar, T. Rajiah, Catal. Commun. 3 (2002) 7.
[7] A. Beilenski, T. Camra, M. Nazbar, J. Catal. 57 (1979) 326.
[8] M. Ai, Bull. Chem. Soc. Jpn. 44 (1971) 761.
[9] A. Satsuma, A. Hattori, K. Mizuatani, A. Faruta, A. Miyamoto, T. Hattori, Y. Murakami, J. Phys. Chem. 93 (1989) 1484.
[10] S.K. Roy, Ph.D. Thesis, Indian School of Mines, Dhanbad, India, 1984.
[11] Indian Patent Nos. 1106051972 and 1380521972.
[12] R. Ramachandra Rao, S.J. Kulkarni, M. Subramanyam, A.V. Rama Rao, Zeolites 16 (1996) 254.
[13] R.P. Porter, W.K. Hall, J. Catal. 5 (1968) 366.
[14] L.S. Cheng, R.T. Yang, N. Chen, J. Catal. 164 (1996) 70.
[15] S.K. Roy, S.C. Ray, P.K. Roy, J. Indian Chem. Soc. 57 (1980) 195.
[16] F.Y. Robb, W.S. Glausinger, P. Courtine, J. Solid State Chem. 30 (1979) 171.
[17] B. Manohar, B.M. Reddy, J. Chem. Technol. Biotechnol. 71 (1998) 141.
[18] G. Genti, C. Galassi, I. Manenti, A. Riva, F. Trifiro, Stud. Surf. Sci. Catal. 16 (1983) 543.
[19] R. Munch, E. Pierron, J. Catal. 3 (1964) 406.
[20] W.K. Lewis, Ind. Eng. Chem. 41 (1949) 1227.
[21] I.E. Wachs, R.Y. Saleh, S.S. Chan, C.C. Chersich, Appl. Catal. 15 (1985) 339.
[22] G.C. Bond, S. Flamerz, Appl. Catal. 33 (1987) 219.
[23] F. Roozeboom, T. Fransen, P. Mars, P.J. Gellings, Z. Anorg, Allg. Chem. 449 (1979) 25.