SHORT PAPER

J. Chem. Research (S),
2000, 408–410

Ammoxidation of 3-picoline over vanadia-molybdena catalysts supported on γ-Al_2O_3[†]

Komandur V.R. Chary*, Thallada Bhaskar, Mamidanna R.V.S. Murthy, Kothapalli Kalyana Seela and Vattikonda Venkat Rao

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

---

Ammoxidation of 3-picoline to nicotinonitrile was carried out on V_2O_5-MoO_3 catalysts supported on γ-alumina. The results suggest that the addition of MoO_3 improves catalytic properties during ammoxidation.

Nicotinamide, a component of vitamin B, is an important compound for metabolism in human beings and animals and is used as a food additive. It is usually synthesized by the ammoxidation of 3-picoline to nicotinonitrile and further hydrolysis of the nitrile formed.[1–3] Vanadium oxide catalysts either unsupported or supported on oxides such as TiO_2, ZrO_2 and Nb_2O_5 have been employed for the vapour phase ammoxidation of 3-picoline.[1–6] The catalytic properties of vanadium oxide are strongly influenced by the method of preparation, nature of support and type of promoter. It is generally believed that optimal catalytic activity and selectivity is achieved when a monolayer of vanadium oxide is dispersed on supported oxides. Molybdenum is frequently added as a promoter to vanadium based catalysts for a number of selective oxidations[7–10]. In the present investigation we report the influence of MoO_3 on the catalytic properties of V_2O_5/γ-Al_2O_3 for the ammoxidation of 3-picoline. Furthermore, we report reducibility of V_2O_5 supported on γ-Al_2O_3, upon addition of MoO_3 and its consequential effect on the activity and selectivity of the catalysts during ammoxidation of 3-picoline to nicotinonitrile. We also report the characterization of these catalysts by pore size distribution (PSD) and temperature programmed reduction (TPR).

The catalysts have been prepared in two steps. In the first step 10% V_2O_5 (w/w) supported on γ–Al_2O_3 (Harshaw Al-111-E) was prepared by wet impregnation of the alumina support using an aqueous solution containing ammonium metavanadate. After impregnation the sample was dried at 383 K and calcined in air at 773 K for 6 h. In the second step a series of V_2O_5–MoO_3 catalysts with varying MoO_3 content ranging from 1 to 5% (w/w) were prepared by wet impregnation of previously prepared 10% V_2O_5/γ-Al_2O_3 catalysts using stoichiometric amounts of an aqueous solution containing ammonium heptamolybdate. TPR studies were conducted on an Autochem 2910 (Micromeritics, USA) instrument. The reaction was carried out for eight to ten runs and each run was about 6 h. The details of the experimental procedure are given elsewhere.[6] Pore size distribution (PSD) studies were performed on an Auto Pore III (Micromeritics, USA) using the mercury penetration method.

Figure 1 represents incremental intrusion volume vs pore diameter for various V_2O_5/γ-Al_2O_3 and V_2O_5-MoO_3/γ-Al_2O_3 samples. All the samples show bimodal distribution with the majority of pores present in large pore diameter (>1000 Å). It has been observed that the average pore diameter increased marginally with MoO_3 loading. This change might be due to blockage of pores in the range of 100 Å, which can be noticed from the decrease in the intensity of pores in this range. Similarly, the total pore area also decreased with addition of MoO_3. The details of total pore area, total intrusion volume and average pore diameter of V_2O_5-MoO_3/γ-Al_2O_3 catalysts are given in Table 1.

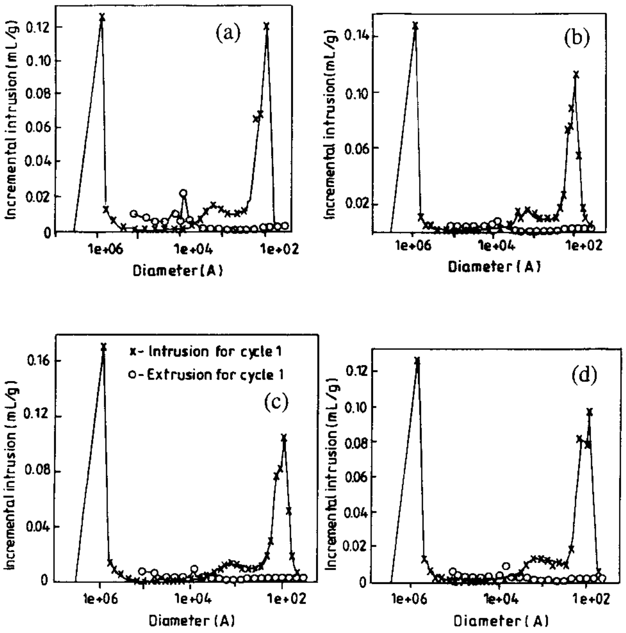

Fig. 1 Pore size distribution studies of V_2O_5/γ-Al_2O_3 and V_2O_5–MoO_3/γ-Al_2O_3 catalysts: (a) 10% V_2O_5/γ-Al_2O_3; (b) 1.0 % MoO_3–V_2O_5/γ-Al_2O_3; (c) 3.0% MoO_3-V_2O_5/γ-Al_2O_3; and (d) 5 % MoO_3–V_2O_5/γ-Al_2O_3

Temperature programmed reduction (TPR) profiles of various V_2O_5/γ-Al_2O_3 and MoO_3-V_2O_5/γ-Al_2O_3 samples are shown in Figure 2. The dependence of T_{max} values on the MoO_3 content is given in Table 2. TPR of V_2O_5/Al_2O_3 show a single peak with T_{max} at 838 K, which is attributed to reduction of V^{4+}. Our TPR results are in agreement with the results of Koranne *et al.*[11] wherein, they found a single major reduction peak above 773 K in the TPR of V_2O_5/Al_2O_3. The results of TPR of various MoO_3–V_2O_5–γ–Al_2O_3 catalysts show a systematic change in the reduction of vanadia with the increase of molybdena loading. The TPR profiles for all samples have shown two prominent maxima (T_{max}) and their position are listed in Table 2. The low temperature peak in the region of 796–799 K is due to reduction of V^{5+} to V^{4+}. The T_{max} did not change with increase of molybdenum oxide and it is lower than V_2O_5/Al_2O_3 (Table. 2). However, the T_{max} values of the first major peak in all V_2O_5–MoO_3/Al_2O_3 samples are found to be lower than V_2O_5/Al_2O_3. In the TPR of V_2O_5–MoO_3/Al_2O_3 the second major peak appeared above 1003 K due to reduction of MoO_3. The T_{max} values for the second peak were found to increase with MoO_3 loading. TPR

---

* To receive any correspondence.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Results of pore size distribution (PSD), temperature programmed reduction (TPR) profiles for the $V_2O_5/\gamma\text{-}Al_2O_3$ and $V_2O_5\text{-}MoO_3/\gamma\text{-}Al_2O_3$ catalysts

No.	Wt% of MoO_3 on $V_2O_5/\gamma\text{-}Al_2O_3$	Total intrusion volume (ml/g)	Total pore area (m^2/g)	Average pore diameter Å	T_{max} (K) I Peak	T_{max} (K) II Peak
1	0	0.7911	196.277	161	838	1004
2	1	0.8105	190.342	170	796	1113
3	2	—	—	—	799	1144
4	3	0.8162	184.861	177	803	1153
5	4	—	—	—	792	1211
6	5	0.7661	179.318	171	799	1212

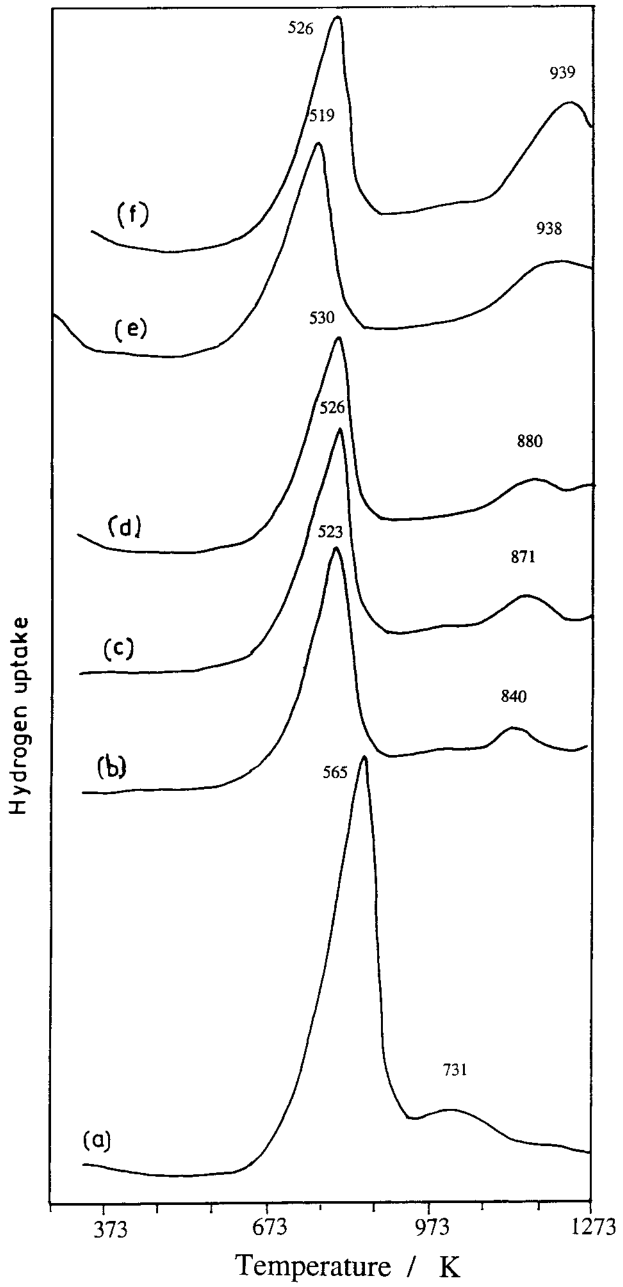

Fig. 2 Temperature programmed reduction (TPR) profiles of vanadia-molybdena catalysts; (a) 10% $V_2O_5/\gamma\text{-}Al_2O_3$; (b) 1 % $MoO_3\text{-}V_2O_5/\gamma\text{-}Al_2O_3$; (c) 2 % $MoO_3\text{-}V_2O_5/\gamma\text{-}Al_2O_3$; (d) 3 % $MoO_3\text{-}V_2O_5/\gamma\text{-}Al_2O_3$; (e) 4 % $MoO_3\text{-}V_2O_5/\gamma\text{-}Al_2O_3$; and (f) 5 % $MoO_3\text{-}V_2O_5/\gamma\text{-}Al_2O_3$

results of molybdenum promoted samples are in agreement with the recent H_2–TPR work of Casagrande *et al.*[12]

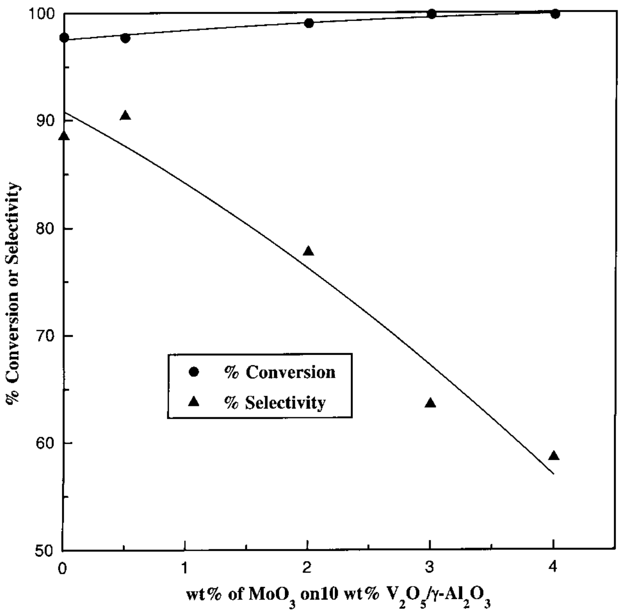

Fig. 3 Ammoxidation of 3-picoline over vanadia-molybdena catalysts (reaction temperature 633 K).

Figure 3 shows the dependence of activity and selectivity on the molybdena loading during the ammoxidation of 3-picoline to nicotinonitrile at 633 K by various $V_2O_5\text{–}MoO_3/Al_2O_3$ catalysts. The conversion of 3-picoline is found to increase marginally with addition of of molybdena compared to the 10wt% $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst. However, the selectivity to nicotinonitrile was found to decrease with increase of molybdena loading on $V_2O_5/\gamma\text{-}Al_2O_3$. Pure $\gamma\text{-}Al_2O_3$ was found to be inactive for nicotinonitrile formation under the experimental conditions of reaction employed for various $V_2O_5\text{–}MoO_3/\gamma\text{-}Al_2O_3$ catalysts. The results are specific for the mole ratio of 3-picoline:H_2O:NH_3:air at 1:13:22:44 at 633 K.[6] Andersson *et al.*[1–3] studied the acid–base properties of V–Ti–O catalysts in the ammoxidation of 3-picoline, which corresponds to a relatively small amount of acidic sites. A catalyst which is selective in the formation of nicotinonitrile requires a high concentration of both acidic-basic sites. The conditions in the ammoxidation of 3-picoline are both reductive and oxidative; *i.e.* the hydrocarbons consume oxygen from the catalyst, which is then reoxidized. It can be expected that under steady state conditions, the catalyst will contact a certain amount of lower oxides formed by reduction of the originally charged catalyst.

The addition of molybdena to the $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst is found to increase the reducibility of vanadia supported on alumina. Thus, molybdena addition to V_2O_5 increases the catalytic activity during ammoxidation of 3-picoline to nicotinonitrile. However, it favours the decrease of selectivity to nicotinonitrile with MoO_3 loading. The low selectivity during ammoxidation of $V_2O_5\text{–}MoO_3/\gamma\text{-}Al_2O_3$ catalysts is attributed to the inhibition of interaction between V_2O_5 and the $\gamma\text{-}Al_2O_3$ surface. The pore size distribution studies reveal that the total pore area is decreasing due to blocking of pores by MoO_3 in $V_2O_5/\gamma\text{-}Al_2O_3$.

We thank Dr K.V. Raghavan, Director, IICT for encouragement. TB Thanks CSIR, New Delhi for the award of Research Associate. KKS and MRVSM thanks DIICT for a project trainee position.

Received 5 May 2000; accepted 27 July 2000
Paper 00/313

References

1 A. Andersson and S.T. Lundin, *J. Catal*., 1979, **58**, 383.
2 A. Andersson and S.T. Lundin, *J. Catal*., 1980, **65**, 9.
3 A. Andersson, J.O.Bovin and P. Walter, *J. Catal*., 1980, **98**, 204.
4 K.V.R.Chary, G. Kishan and T. Bhaskar, *J.Chem.Soc., Chem. Commun*., 1999, 1399.
5 K.V.R.Chary, G. Kishan, K.V.Narayana and T. Bhaskar, *J. Chem Res (S)*, 1998, 314.
6 K.V.R.Chary, G. Kishan, T. Bhaskar and Ch. Sivaraj, *J. Phys.Chem*., 1998, **102**, 6792
7 M. Najbar, *J. Chem. Soc., Faraday Trans*., 1986, **82**, 1673.
8 Z.X. Liu, Y.Q. LI, S.X. Qi, K. Xie, N.J. Wu and Q.X. Bao, *Appl. Catal*., 1989, **56**, 207.
9 A. Dejoz, J.M. Lopez Nieto, F. Marquez, M.I. Vazquez, *App. Catal A*, 1989, **180**, 83.
10 A. Satsuma, A. Hattori, K. Mizutani, A. Furuta, A. Miyamoto, T. Hattori and Y. Murakami, *J. Phys. Chem*., 1989, **93**, 1484.
11 M.M. Koranne, J.G. Goodwin, Jr., G. Marcelin, *J. Catal*., 1994, **148**, 369.
12 L. Casagrande, L. Lietti, I. Nova, P. Forzatti and A. Baiker, *Appl. Catal. B*., 1999, **22**, 63.