A Novel Single Step Synthesis of Nicotinamide by β-Picoline Ammoxidation over MoO_3 and CuO Oxide Catalysts

B. Mahipal Reddy and M. Subrahmanyam

Catalysis Section, Regional Research Laboratory, Hyderabad 500 007, India

Ammonia up-take has been correlated directly, for the first time, with the selective formation of nicotinamide on MoO_3 and CuO; nicotinonitrile on V_2O_5; CO_2 and H_2O on Bi_2O_3 catalysts, with a possible mechanism during ammoxidation of β-picoline.

The vapour phase ammoxidation or oxidative ammonolysis of β-picoline in the presence of a suitable vanadium based catalyst yields nicotinonitrile as the main reaction product.[1—4] However, the mechanism involved in the formation of nicotinonitrile is not clearly understood. Nicotinonitrile is an important intermediate which can be easily hydrolysed to nicotinamide or nicotinic acid both of which are essential for the nutrition of humans and animals.[5] This two-step process is used extensively to produce high yields of nicotinamide or nicotinic acid. In this communication, we report a single step synthesis of nicotinamide observed for the first time, by ammoxidation or oxidative ammonolysis of β-picoline on MoO_3 and CuO catalysts. Possible mechanisms are proposed for the selective formation of nicotinonitrile on V_2O_5 and nicotinamide on MoO_3 or CuO catalysts based on NH_3 uptake data and by using intermediate products as reactants.

The single oxides employed in this study were V_2O_5, MoO_3, CuO, and Bi_2O_3. Ammonia chemisorption was determined on a standard all-glass volumetric high-vacuum system. Samples were evacuated (10^{-6} torr vacuum) for several hours before the chemisorption measurements were taken. Ammonia chemisorption at 25 °C was determined by a double isotherm method developed for a low temperature oxygen chemisorption study.[6] A fixed-bed flow micro-reactor operating under atmospheric pressure was used to determine the activity of the catalysts at 375 °C and products were analysed by gas chromatography. The main reaction products observed were nicotinonitrile, nicotinamide, carbon dioxide, water and traces of pyridine, 3-picolylamine, and 3-pyridinecarbaldehyde.

The ammonia uptake values and ammoxidation or oxidative ammonolysis mode of β-picoline product distribution of the

Table 1. Ammonia chemisorption and β-picoline ammoxidation product distribution (selectivity %) on various catalysts.

Catalyst	Ammonia uptake μ mole g^{-1} cat.	Ammoxidation[a]				Oxidative ammonolysis[b]			
		Nicotinamide	Nicotino-nitrile	3-Picolyl-amine	3-Pyridine-carbaldehyde	Nicotin-amide	Nicotino-nitrile	3-Picolyl-amine	3-Pyridine-carbaldehyde
V_2O_5	27.6	2.5	32.0	Trace	—	2.0	24.0	Trace	—
MoO_3	8.8	56.0	0.1	—	Trace	45.0	0.0	—	Trace
CuO	11.2	58.0	0.1	—	Trace	52.0	0.1	—	Trace
Bi_2O_3	0.1	—	—	—	—	—	—	—	—

[a] Contains gas phase oxygen in the feed. [b] Contains no gas phase oxygen in the feed.

Table 2. Product distribution (selectivity %) of ammoxidation of 3-picolylamine and 3-pyridinecarbaldehyde.

Catalyst	3-Picolylamine				3-Pyridinecarbaldehyde			
	Ammoxidation		Oxidative ammonolysis		Ammoxidation		Oxidative ammonolysis	
	Nicotinamide	Nicotinonitrile	Nicotinamide	Nicotinonitrile	Nicotinamide	Nicotinonitrile	Nicotinamide	Nicotinonitrile
V_2O_5	0.4	61.0	0.2	34.3	52.8	0.0	47.8	0.0
MoO_3	0.7	47.0	0.8	33.7	46.5	0.1	23.5	0.1
CuO	0.9	58.0	0.9	24.8	48.0	0.1	40.7	0.1
Bi_2O_3	—	—	—	—	—	—	—	—

catalysts are presented in Table 1. The product distribution varies interestingly with the nature of metal oxide tested. The product nicotinonitrile was formed over V_2O_5, and total combustion products, CO_2 and H_2O, with Bi_2O_3. Interestingly, nicotinamide is the major product over MoO_3 and CuO catalysts. Baiker and Zollinger[3] have also observed selective formation of nicotinonitrile over a V_2O_5 catalyst. Bismuth oxide is quickly reduced to the metallic state indicating an analogous total oxidation mechanism as observed with propan-2-ol.[7] The product distribution obtained on V_2O_5, MoO_3, and CuO catalysts clearly demonstrates that the reaction proceeds through at least two different distinct routes. The possible mechanisms are presented in Schemes 1 and 2 respectively.

As reported by Suvorov,[8] in both conventional ammoxidation or oxidative ammonolysis, nitriles can be formed *via* both amines (Scheme 1) and aldehydes (Scheme 2) as intermediates. All the reactions in Scheme 1 and 2 proceed as a chain reaction without the necessity of intermediate desorption or adsorption processes before the final end product is obtained. However, from our results it appears that the V_2O_5 catalyst produces nicotinonitrile as the major end product as in Scheme 1. The formation of nicotinamide on MoO_3 and CuO catalysts suggests that the reaction definitely follows the steps in Scheme 2, but desorption occurs at the intermediate amide formation step itself.

To substantiate the proposed schemes, the intermediate products 3-picolylamine and 3-pyridinecarbaldehyde were fed individually over the oxides under identical conditions of β-picoline ammoxidation. The product distribution is shown in Table 2. As can be seen, 3-picolylamine selectively produces nicotinonitrile whereas, 3-pyridinecarbaldehyde gives nicotinamide irrespective of the oxides used. These results emphasize the fact that the formation of nicotinonitrile is only through 3-picolylamine, and nicotinamide is *via* 3-pyridinecarbaldehyde. In addition to this, the trace amounts of 3-picolylamine on V_2O_5 and 3-pyridinecarbaldehyde over MoO_3 and CuO clearly indicates that nicotinonitrile is formed selectively over V_2O_5 only *via* 3-picolylamine and nicotinamide on MoO_3 and CuO definitely through 3-pyridinecarbaldehyde as per the steps in Schemes 1 and 2 respectively. The higher NH_3 uptake values (Table 1) on V_2O_5 catalyst also

$$PyCH_3 + NH_3 + (O) \rightarrow PyCH_2NH_2 + H_2O$$
$$PyCH_2NH_2 + (O) \rightarrow PyCHNH + H_2O$$
$$PyCHNH + (O) \rightarrow PyCN + H_2O$$

Scheme 1

$$PyCH_3 + 2(O) \rightarrow PyCHO + H_2O$$
$$PyCHO + NH_3 + (O) \rightarrow PyCONH_2 + H_2O$$
$$PyCONH_2 \rightarrow PyCN + H_2O$$

Scheme 2

clearly show that a substantial amount of nicotinonitrile is formed according to the mechanism proposed in Scheme 1, since the important ammonia incorporation is involved in the first step of the mechanism. The lower uptake values of NH_3 on MoO_3 and CuO are also in accordance with its participation only in the second step of the overall reaction mechanism as in Scheme 2. On the other hand, it is interesting that the absence of uptake of NH_3 on Bi_2O_3 results with no end product that contains any nitrogen.

Thus, MoO_3 and CuO oxides have the beneficial effect of avoiding the nicotinonitrile hydrolysis step in the large scale production of nicotinamide if other conditions like deactivation, conversion and selectivities are being controlled.

Received, 24th November 1987; Com. 1710

References

1 A. Anderson, R. Wallenberg, S. T. Lundin, and J. O. Bovin, in 'Proc. 8th Int. Congr. Catal,' Verlag Chemie, Weinheim, 1984, vol. 5, p. 381.
2 R. Prasad and A. K. Kar, *Ind. Eng. Chem., Process Des. Dev.*, 1976, **15**, 170.
3 A. Baiker and P. Zollinger, *Appl. Catal.*, 1984, **10**, 231.
4 B. N. Reddy, B. M. Reddy, and M. Subrahmanyam, *J. Chem. Soc., Chem. Commun.*, 1988, 33.
5 A. Nenz and M. Pieroni, *Hydrocarbon Process.*, 1968, **47**, 139.
6 B. M. Reddy, K. V. R. Chary, V. S. Subrahmanyam, and N. K. Nag, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1655.
7 C. Daniel, M. Subrahmanyam, and J. C. Kuriacose, *Indian J. Chem.*, 1975, **13**, 419.
8 B. V. Suvorov, *Int. Chem. Eng.*, 1968, **8**, 588.