J. Chem. Research (S),
1997, 328–329†

CeF_3 as a Novel Support for Preparing Highly Active and Selective Vanadia Catalysts for the Ammoxidation of 3-Picoline†

Kalevaru Venkata Narayana, Sheik Khaja Masthan, Vattikonda Venkat Rao and Panja Kanta Rao

Catalysis & Physical Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India

V_2O_5–CeF_3 catalysts are found to be highly active and selective in the ammoxidation of 3-picoline; the catalytic performance is attributed to the formation of $CeVO_4$ as evidenced by XRD.

Vanadia supported on oxides like TiO_2, SiO_2 and ZrO_2 have been used as catalysts for oxidation, oxidative dehydrogenation and ammoxidation reactions.[1–6] The search for new supports for vanadia is continuing in order to design oxidation and ammoxidation catalysts with improved selectivity. We found that CeF_3 can be used as an effective support to disperse vanadia and the resulting V_2O_5–CeF_3 catalyst showed high activity and selectivity in the industrially important ammoxidation of 3-picoline to nicotinonitrile.

Experimental

V_2O_5–CeF_3 catalysts were prepared by impregnating CeF_3 support (Fluka, Switzerland, BET surface area of 33.9 $m^2\,g^{-1}$) in aqueous oxalic acid containing a requisite amount of NH_4VO_3 (Aldrich, USA). The solution was evaporated to dryness on a water bath and the resulting mass was calcined at 450 °C for 4 h. The experimental procedure for determining the ammoxidation activity of the catalysts for 3-picoline was similar to the one used for V_2O_5–TiO_2 catalysts.[7] The ammoxidation runs were carried out in a fixed bed microcatalytic reactor made of pyrex glass of length 350 mm and an id of 25 mm which was heated in an electrical furnace. About 2 g of catalyst particles (−18 to +25 BS mesh) mixed with glass beads were packed in between two quartz wool plugs and reduced in a stream of hydrogen at 450 °C for 2 h. The temperature of the catalyst bed was measured with a Pt–Rh thermocouple inserted into the thermowell in the middle of the catalyst bed and connected to a temperature indicator controller. The catalyst bed was cooled to an ambient temperature in a H_2 stream. The H_2 gas was replaced by a mixture of NH_3 and air from pressurised gas cylinders and the catalyst bed was raised to reaction temperature. 3-Picoline dissolved in H_2O (1:13) was passed into the catalyst bed by means of an infusion pump (M/S.B.Braun, Perfusor Secura FT). The reaction mixture (3-picoline:H_2O: NH_3:air = 1:13:6:44) was preheated in a preheater zone filled with beads. The non-gaseous products and unreacted 3-picoline were trapped in condensers at below −10 °C. The liquid products collected were analysed by a gas chromatograph equipped with FID with a column of 10% OV-17 on Chromosorb W (3 mm × 3 m).

Table 1 Influence of vanadia loading on BET surface area, activity and selelctivity of various V_2O_5/CeF_3 catalysts in the ammoxidation of 3-picoline. Reaction temperature: 390 °C; Feed Rate: 2 ml/h; Wt. of the catalyst 2 g; Molar Ratio of 3-picoline:H_2O:NH_3:Air = 1:13:6:44; N-S = Nicotinonitrile selectivity; P-S = Pyridine selectivity

Catalyst (% V_2O_5)	BET SA ($m^2\,g^{-1}$)	% Conv.	% Selectivity N-S	P-S	Others
2.0	26.0	57.9	65.4	17.5	17.1
5.0	25.0	61.7	72.2	11.3	16.5
7.5	23.4	67.0	84.0	7.2	8.8
10.0	19.3	74.1	86.8	6.1	7.1
15.0	19.1	89.2	94.1	4.1	1.8

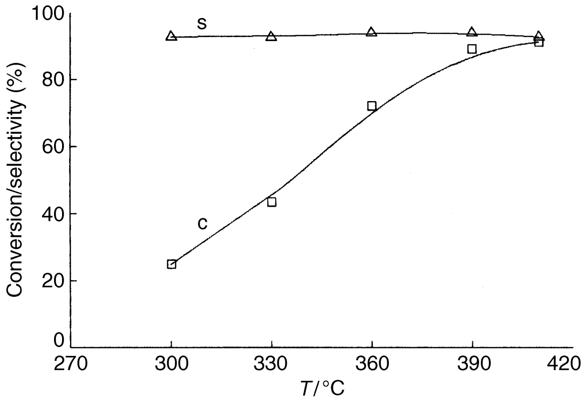

Fig. 1 Effect of temperature on 3-picoline conversion (□) and nicotinonitrile selectivity (Δ) over 15 mass% V_2O_5–CeF_3 catalyst at 2 ml h^{-1} feed rate. Mass of the catalyst = 2 g

Results and Discussion

The BET surface areas of the catalysts determined by N_2 adsorption at 77 K decreased from 26 $m^2\,g^{-1}$ at 2 mass% V_2O_5 to 19 $m^2\,g^{-1}$ at 15 mass% V_2O_5 loading on CeF_3. The vanadia loading on CeF_3 and the reaction temperature have significant effect on the ammoxidation activity of the catalysts. Both the conversion of 3-picoline and the selectivity for nitocinonitrile (Table 1), at 390 °C and at a 3-picoline: H_2O:NH_3:air mole ratio of 1:13:6:44, increase with increase in vanadia loading up to 89.2 and 94.1% respectively. The other reaction product was pyridine, produced as a result of dealkylation. On a 15 mass% V_2O_5–CeF_3 catalyst, while the 3-picoline conversion increases with increase in reaction temperature from 25% at 300 °C to 91.3% at 410 °C, the selectivity to nicotinonitrile remains almost the same (*ca.* 94%) at all the temperatures studied (Fig. 1). These observations indicate the facile nature of the active sites on the 15 mass% V_2O_5–CeF_3 catalyst.

X-Ray diffractograms of the catalysts (Fig. 2), taken on a Phillips PW 1140 X-ray diffractometer, provide information on the species present in the V_2O_5–CeF_3 catalysts. At 7.5 mass% V_2O_5 content very weak peaks of $CeVO_4$ appear and the intensity of these peaks increases with an increase in the V_2O_5 content of the catalysts. The presence of traces of free V_2O_5 is indicated by very weak XRD peaks with *d*-values of 4.38 and 3.4 Å in the X-ray diffractogram of the catalyst with the highest vanadia loading (15 mass%).

These findings suggest that the active sites on V_2O_5–CeF_3 that catalyse the ammoxidation of 3-picoline may not only be the V^{4+} ions in the V-oxide structures that can be visualised in the V_2O_5–TiO_2 catalysts,[7] but are perhaps V^{4+} ions associated with $CeVO_4$ formed from CeF_3 and V_2O_5 when calcined at 450 °C. CeF_3 is a strong Lewis acid catalyst. The ammoxidation activity and selectivity appears to be related to the acid–base and redox properties of the catalysts. Formation of

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

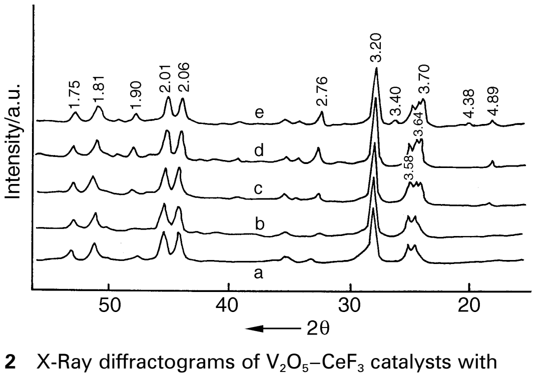

Fig. 2 X-Ray diffractograms of V_2O_5–CeF_3 catalysts with different V_2O_5 loadings. (*a*) 2.0 mass%; (*b*) 5.0 mass%; (*c*) 7.5 mass%; (*d*) 10.0 mass%; (*e*) 15.0 mass%. XRD peaks with *d*-values 3.20, 2.01, 2.06, 3.64 Å (ASTM Card No. 8-45) belong to the CeF_3 phase; XRD peaks with *d*-values 3.70, 2.76, 1.90 and 4.89 Å (ASTM Card No. 12-757) belong to the $CeVO_4$ phase. XRD peaks with *d*-values 4.38 and 3.4 Å (ASTM Card No. 9-387) belong to the V_2O_5 phase

this compound appears to be essential for obtaining catalysts with high activity and nicotinonitrile selectivity. At lower V_2O_5 loadings where $CeVO_4$ formation was low (Fig. 2), more pyridine was formed due to dealkylation (Table 1) over the acidic surface of the support, CeF_3.

This study has shown that CeF_3 is an effective and novel support for V_2O_5. 15 mass% V_2O_5 catalyst is a highly active and selective catalyst for the ammoxidation of 3-picoline to nicotinonitrile with a conversion of 91.3% and a selectivity of 94% at 410 °C. This compares well with the performance of V_2O_5–TiO_2 catalysts.[7]

The results of this investigation on the V_2O_5–CeF_3 system are expected to help in the development of a new class of efficient catalysts for ammoxidation reactions.

K. V. N. thanks the CSIR, New Delhi, for the award of a Senior Research Fellowship.

Received, 13th May 1997; Accepted, 15th May 1997
Paper E/7/03328A

References

1 G. Deo, I. E. Wachs and J. Haber, *Crit. Rev. Surf. Chem.*, 1994, **4**, 141.
2 G. Busca and L. Marchetti, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1003.
3 C. R. Dias, M. F. Portela and G. C. Bond, *J. Catal.*, 1995, **157**, 344.
4 E. A. Mamedov and V. C. Corberon, *Appl. Catal.*, 1995, **127**, 1.
5 A. Andersson and S. L. T. Lundin, *J. Catal.*, 1980, **65**, 9.
6 B. Jonson, B. Rebenstorf, R. Larsson and S. L. T. Andersson, *J. Chem. Soc., Faraday Trans.*, 1988, **84**, 1897.
7 K. V. Narayana, A. Venugopal, K. S. Rama Rao, V. Venkat Rao, S. Khaja Masthan and P. Kanta Rao, *Appl. Catal.*, 1997, **150**, 269.