A Direct Correlation between Ammoxidation of β-Picoline to Nicotinonitrile and Low Temperature Oxygen Chemisorption on V_2O_5/α-Al_2O_3 Catalysts

B. Narasimha Reddy, B. Mahipal Reddy, and M. Subrahmanyam

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

The amount of O_2 chemisorbed at $-78\,°C$ on reduced V_2O_5 derived from three different precursors over α-Al_2O_3 has been correlated, with the selectivity for nicotinonitrile formation in β-picoline ammoxidation.

Supported vanadia catalysts are widely used in the chemical industry for the ammoxidation and partial oxidation of aromatic hydrocarbons. Nicotinonitrile, an important intermediate, produced from β-picoline ammoxidation can be transformed easily by catalytic hydration to nicotinamide and nicotinic acid, essential for the nutrition of humans and animals.[1] The low temperature oxygen chemisorption (L.T.O.C.) technique has been widely employed for the study of supported molybdenum catalysts with an aim to establish direct correlation, if any, between the amount of oxygen chemisorbed and the activity or selectivity of these catalysts for hydrogenation and hydrodesulphurisation reactions.[2,3] Similar studies on V_2O_5/α-Al_2O_3 catalysts for oxidation or ammoxidation reactions have not been reported so far. In this communication, we report the direct correlation between low temperature oxygen uptake capacity of a series of α-Al_2O_3 supported vanadia catalysts, obtained *via* three different precursors, and their selectivity for the ammoxidation of β-picoline to nicotinonitrile.

The α-Al_2O_3 supported vanadia catalysts, V loading ranging from 0.5 to 6.5 wt.%, were prepared by the standard wet-impregnation technique with aqueous solutions of ammonium metavanadate (AMV), vanadium oxalate (VOX), and non-aqueous vanadium(III) acetylacetonate (VAA). The impregnated samples were dried at 120 °C for 12 h and calcined at 500 °C for 6 h in dry air. Vanadium contents were determined by the X-ray fluorescence technique. A standard volumetric high-vacuum system, with the option of reducing the samples *in situ* by flowing hydrogen, was used for the L.T.O.C. experiments. The details have been described elsewhere.[4] A fixed-bed flow microreactor fitted with the usual feeding and controlling facilities and operating under normal atmospheric pressure was used to determine the

activities of the catalysts at 375 °C and the products were analysed by gas chromatography.

The selectivity for nicotinonitrile formation has been plotted as a function of oxygen uptake in Figure 1.[5] The results for the three catalysts lie along three different correlation lines. Figure 1 demonstrates that the selectivity for nicotinonitrile formation is directly proportional to the amount of oxygen chemisorbed at $-78\,°C$ irrespective of the source. V_2O_5 obtained *via* decomposition of the VAA salt appears to be superior to those of VOX and AMV origin. % Dispersion as a function of vanadium loading is presented in Figure 2. The dispersion, which is directly proportional to the reducibility of the supported V-oxide, shows a parabolic decrease with V-content. This behaviour is attributed to the formation of a highly-dispersed V oxide monolayer due to carrier–catalyst interaction in the lower loading region, and the formation of bulky crystallites of V_2O_5 at higher loadings.[6] The reducibility of the V oxide units decreases with an increase in their crystallite size. The dispersion trends observed in Figure 2 are clearly reflected in Figure 1 for nicotinonitrile production.

Previously it has been observed that oxygen, when chemisorbed at $-78\,°C$ on the reduced vanadia catalysts, dissociatively and selectively chemisorbs at the co-ordinatively unsaturated V-sites which are generated upon reduction in hydrogen.[4] The strong correlation shown in Figure 1 indicates that these co-ordinately unsaturated sites are possible locations for the selective ammoxidation of β-picoline to nicotinonitrile. According to the Mars and Van Krevelen[7] mechanism of sequential reduction and re-oxidation of the catalyst surface under steady state condition in oxidation reactions, the
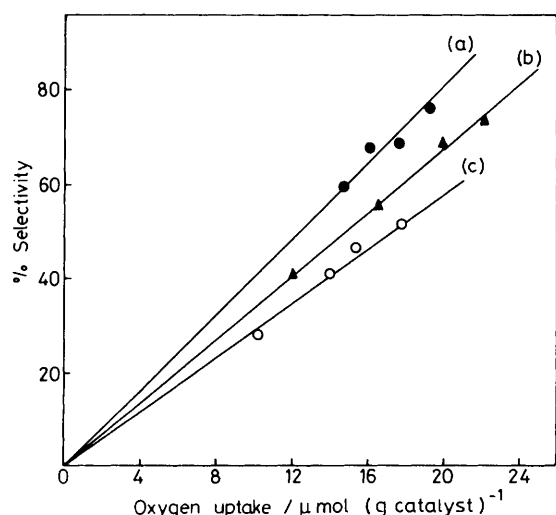

Figure 1. Selectivity for nicotinonitrile as a function of oxygen uptake at $-78\,°C$ on V_2O_5/α-Al_2O_3 catalysts derived from various sources: (a) VAA; (b) VOX; (c) AMV.
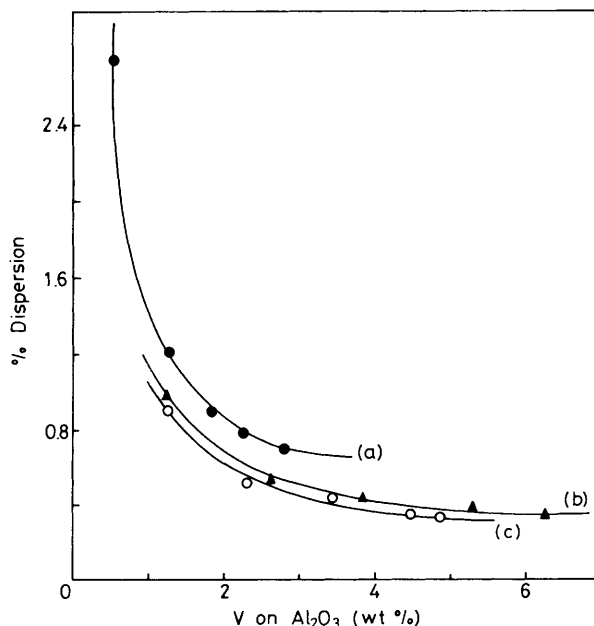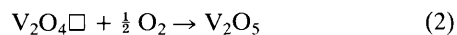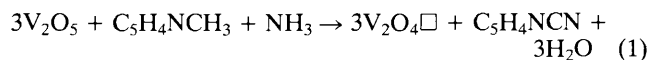

Figure 2. Dispersion plotted as a function of catalyst composition. % Dispersion is defined as: 100 (number of O atoms chemisorbed)/(total number of V atoms).

present ammoxidation sequence can be represented in terms of co-ordinatively unsaturated sites as in equations (1) and (2).

$$3V_2O_5 + C_5H_4NCH_3 + NH_3 \rightarrow 3V_2O_4\square + C_5H_4NCN + 3H_2O \quad (1)$$

$$V_2O_4\square + \tfrac{1}{2}O_2 \rightarrow V_2O_5 \quad (2)$$

From this study it can be concluded that VAA is the best precursor for the preparation of highly dispersed V-oxide catalysts on an α-Al_2O_3 support. L.T.O.C. is a convenient method for rapidly assessing the selectivity of V_2O_5/α-Al_2O_3 catalysts for the ammoxidation of β-picoline to nicotinonitrile.

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