

Amoxidation of 3-Picoline to Nicotinonitrile over Highly Dispersed V_2O_5/ZrO_2 Catalysts†

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Vapour phase amoxidation of 3-picoline to nicotinonitrile was carried out on highly dispersed vanadia catalysts supported on zirconia, the results suggest that vanadia/zirconia possesses high activity and selectivity for nicotinonitrile formation.

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 amoxidation of 3-picoline to nicotinonitrile and further hydrolysis of the nitrile formed.^{1–5} Vanadium oxide catalysts either unsupported or supported on anatase TiO_2 , are generally used for this amoxidation.^{2–4} In recent years zirconia has attracted considerable interest because of its potential use as a catalyst support.^{6–16} It has been employed in many industrially important reactions such as hydro-processing,^{8–10} oxidation of alcohols,^{11,12} synthesis of methanol and higher alcohols,^{13–15} and methanation reactions.¹⁶ Here we report the synthesis of nicotinonitrile by the vapour phase amoxidation reaction over highly dispersed vanadia catalysts supported on zirconia. We also report an improved oxygen chemisorption method for determination of the dispersion of vanadia.

Zirconia support was prepared by ammonical hydrolysis of zirconium oxychloride (Fluka) at pH 9, followed by calcination in air at 773 K for 6 h. A series of V_2O_5/ZrO_2 catalysts with vanadia loadings ranging from 1.8 to 10.4 wt.% of V_2O_5 have been prepared by the wet impregnation of ZrO_2 ($84\text{ m}^2\text{ g}^{-1}$) with requisite amounts of aqueous solution containing NH_4VO_3 . The impregnated catalysts were dried at 383 K for 16 h followed by calcination at 773 K for 4 h in air. The vanadium content in the finished catalysts was determined by atomic absorption spectrometry. The dispersion of vanadia was determined by oxygen chemisorption. Prior to adsorption measurements the samples were pre-reduced in a flow of hydrogen (40 ml min^{-1}) at 640 K for 2 h and evacuated at the same temperature for 1 h. Oxygen chemisorption uptakes were determined as the difference between two successive adsorption isotherms measured at 640 K. A down flow fixed-bed reactor operating at atmospheric pressure and made of Pyrex glass was used for catalyst testing during the amoxidation of 3-picoline to nicotinonitrile. About 2 g of catalyst, diluted with an equal amount of quartz grains, were charged into the reactor and supported on a glass-wool bed. Prior to introducing 3-picoline with a syringe pump, the catalyst was pre-reduced at 673 K for 2 h in purified hydrogen flow (40 ml min^{-1}). After reduction, the reactor was fed with 3-picoline, ammonia, and air keeping the mole ratio of 3-picoline– H_2O – NH_3 –air at 1:13:22:44 and contact time 0.6 s. The reaction was carried out at 683 K after optimizing the reaction temperature in the range 598–753 K. The liquid products, mainly nicotinonitrile, were analysed by gas chromatography using an OV-17 column. Traces of carbon oxides were also formed during the reaction.

Fig. 1 shows the dependence of the activity/selectivity on vanadia loading during amoxidation of 3-picoline to

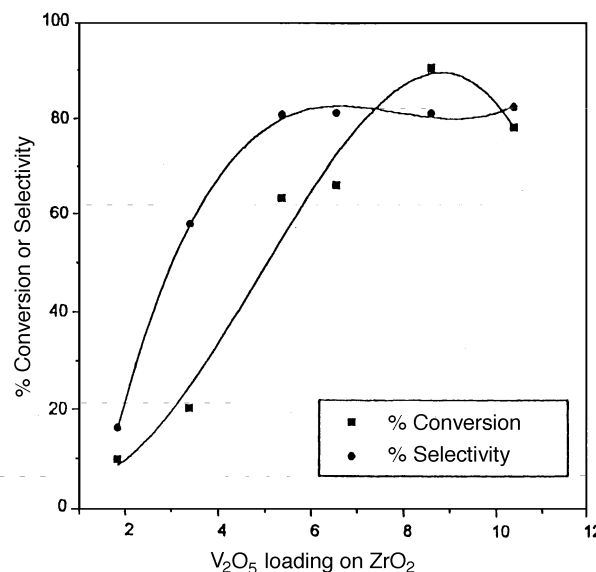


Fig. 1 Amoxidation of 3-picoline to nicotinonitrile over various vanadia–zirconia catalysts

nicotinonitrile at 683 K. The conversion of 3-picoline as well as the selectivity for nicotinonitrile increased with increasing vanadia loading in the catalyst. Beyond 5.34% V_2O_5 on ZrO_2 the selectivity for nicotinonitrile was found to be independent of vanadia content in the catalyst. Pure zirconia was inactive for amoxidation under the experimental conditions. The active species for amoxidation of 3-picoline could be the formation of a VO_2 phase, by reduction of the catalysts with hydrogen. The ESR spectra of hydrogen reduced catalysts further support the presence of V^{4+} on zirconia.¹⁷ The spectra at low vanadia loadings are well resolved with hyperfine splitting (hfs) due to ^{51}V ($I = 7/2$). The signal intensity decreases with increasing vanadia content in the catalyst. Spin Hamiltonian parameters $g_{||} = 1.933$, $g_{\perp} = 1.991$, $A_{||} = 187\text{ G}$, $A_{\perp} = 70\text{ G}$ indicate the presence of V^{4+} on zirconia. Andersson and co-workers^{5,18,19} proposed that the active and selective phase in vanadium oxide catalysts for amoxidation is a non-stoichiometric VO_2 or V_6O_{13} phase with an excess of oxygen ions and this phase is formed during the pre-reduction of the catalysts by hydrogen.

In order to optimize the reaction conditions such as temperature the reactivity of 5.34% V_2O_5 – ZrO_2 was studied in the range 598–753 K. The effect of reaction temperature on the catalytic behaviour during amoxidation is shown in Fig. 2. The conversion of 3-picoline increases with increasing temperature up to 683 K and levels off at higher temperatures. However, the selectivity first remains constant up to 683 K and then monotonically decreases with increasing temperature. Thus a reaction temperature of 683 K was selected to screen all other compositions of V_2O_5 – ZrO_2 catalysts for amoxidation.

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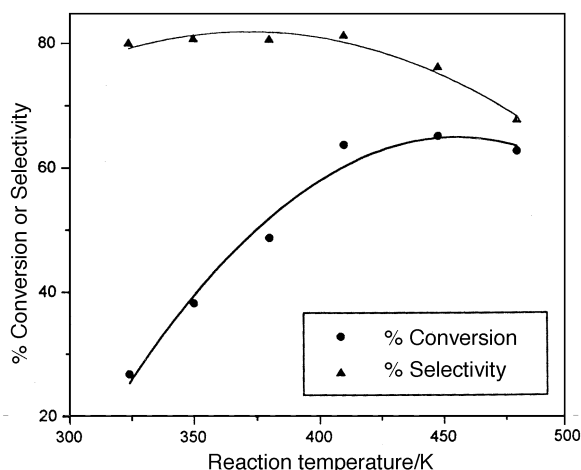


Fig. 2 Dependence of reaction temperature on the conversion or selectivity for 5.34% $V_2O_5-ZrO_2$ catalyst

An improved method of oxygen chemisorption suggested by Oyama *et al.*²⁰ has been employed for determination of the dispersion of vanadia supported on zirconia. The results of oxygen uptake measured at 640 K and other information such as oxygen atom site density, dispersion, *etc.*, derived therefrom are given in Table 1. At low vanadia loadings the dispersion of vanadia (O/V) is very high and nearly equal to the stoichiometry of one oxygen atom per vanadium atom. X-Ray diffraction shows the presence of a crystalline vanadia phase only at high vanadia loadings in addition to the lines due to the monoclinic and tetragonal phases of zirconia.¹⁷ The decrease in the dispersion with increasing vanadia loading might be due to the presence of a crystalline vanadia phase at higher loadings. For the same composition of V_2O_5 , the dispersion of vanadia supported on zirconia was found to be much higher than that of vanadia supported on $\gamma-Al_2O_3$.²¹ For example, the dispersion of vanadia for a catalyst having 3.38 wt.% V_2O_5 supported on zirconia was 76% (Table 1). However, for the same V_2O_5 content supported on $\gamma-Al_2O_3$ the dispersion was 63%.²¹ The oxygen atom site density values reported in Table 1 were less than the average number density of $V=O$ groups on the low index planes of V_2O_5 ($5.0 \times 10^{18} m^{-2}$)²⁰ and this suggests that the oxygen chemisorption method described here samples the surface but not the bulk.

The reduction behaviour of supported vanadia systems has been of interest in recent years.²⁰⁻²² Oyama *et al.*²⁰ showed that, to achieve complete reduction of the vanadia surface without reducing the bulk, the reduction must be carried out at 640 K. Nag and Massoth²² found using a gravimetric method that reduction with hydrogen at 773 K for 6 h resulted in 70% reduction of silica-supported V_2O_5 to V_2O_3 . However, reduction of $V_2O_5-Al_2O_3$ samples at

Table 1 Oxygen uptake, dispersion, oxygen atom site density and surface area of various $V_2O_5-ZrO_2$ catalysts

Catalyst composition/ wt.% V_2O_5 on ZrO_2	Surface area/ $m^2 g^{-1}$	O_2 Uptake ^a / $\mu mol g^{-1}$	Oxygen atom site density/ $10^{18} m^{-2}$	Dispersion (O/V) ^b
1.83	84	96.4	1.38	0.96
3.38	84	141.1	2.02	0.76
5.34	79	210.5	3.21	0.72
6.53	78	256.6	3.96	0.71
8.59	77	316.0	4.94	0.67
10.38	73	356.2	5.88	0.62

^a $T_{reduction} = T_{adsorption} = 640 K$. ^bDispersion = fraction of vanadium atoms at the surface assuming $O_{ads}/V_{surf} = 1$.

Table 2 Results of ammoxidation of 3-picoline to nicotinonitrile over supported vanadium oxide catalysts

Catalyst	% Conversion	% Selectivity
5.34% $V_2O_5-ZrO_2$	64	81
6% $V_2O_5-TiO_2$	97	92
7% $V_2O_5-Al_2O_3$	55	86

773 K led to the formation of V^{4+} . Thus the formation of V^{3+} depends on the nature of the support employed and also the pre-reduction temperature. In the present investigation oxygen chemisorption was carried out on the samples pre-reduced at low reduction temperatures (640 K) to ensure only surface reduction of vanadia supported on zirconia.

The reactivity of the present $V_2O_5-ZrO_2$ catalysts is compared with those of $V_2O_5-TiO_2$ (anatase) and $V_2O_5-Al_2O_3$ catalysts during ammoxidation of 3-picoline in Table 2. The results show that the $V_2O_5-ZrO_2$ catalysts are more active than $V_2O_5-Al_2O_3$ and less active than $V_2O_5-TiO_2$ (anatase).¹⁸ The high activity of vanadia catalysts supported on zirconia is attributed to the higher acidity of the latter and also its stronger interaction with vanadium oxide. However, we did not find a direct correlation between the oxygen chemisorption capacity of the $V_2O_5-ZrO_2$ catalysts and activity. Thus zirconia-supported vanadia catalysts were highly active and selective for the conversion of 3-picoline into nicotinonitrile, and oxygen chemisorption at 640 K ($T_{reduction} = T_{adsorption} = 640 K$) is found to be a facile method to measure the dispersion of vanadia supported on zirconia.

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