Dispersion and reactivity of vanadium oxide catalysts supported on niobia

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Vanadium oxide catalysts supported on niobia are found to be highly active for ammoxidation of 3-picoline and it is found that the catalytic properties are directly related to the dispersion of vanadia.

Recently, there has been growing interest in the study of niobium-based materials as catalysts in various catalytic transformations.[1–7] Niobium(v) oxide can be used as a support, as a promoter and also as a unique solid acid. There are several advantages of using niobium(v) oxide as a catalyst support for vanadium oxide catalysts. These include the fact that (i) niobium is in the same group of the Periodic table as vanadium and is expected to have similar properties. (ii) Niobium(v) oxide is much more difficult to reduce than vanadium (easy reduction often causes low selectivity in oxidation reaction). (iii) Addition of niobium(v) oxide to a mixture of molybdenum and vanadium oxide improves the activity and selectivity during oxidation, ammoxidation and oxidative dehydrogenation reactions.[6,7]

Nicotinamide is an important chemical compound for the metabolism of 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.[8–11] Vanadium oxide catalysts, either unsupported or supported, are generally used for this ammoxidation process. We report here, for the first time, the use of V_2O_5 catalysts supported on niobium(v) oxide for ammoxidation of 3-picoline to nicotinonitrile. The purpose of this work is to determine the degree of dispersion of vanadium oxide supported on niobium(v) oxide and to understand the relation between activity of the catalysts and oxygen chemisorption sites.

Niobium(v) oxide was prepared by calcination of niobium pentoxide hydrate (Niobia HY-340 AD/1227, CBMM, Brazil) in air at 773 K for 4 h. A series of V_2O_5 catalysts with V_2O_5 loadings in the range 2–12 wt% supported on Nb_2O_5 (surface area 55 $m^2\ g^{-1}$) were prepared by impregnation with an aqueous solution containing ammonium metavanadate (Fluka). The catalysts were subsequently dried at 383 K for 16 h and calcined in air at 773 K for 5 h. Oxygen chemisorption was measured by a static method using a Pyrex glass system capable of supporting a vacuum of 10^{-6} Torr. Details of experimental set up have been given elsewhere.[14] Prior to chemisorption measurements, *ca.* 0.250 g of the sample was pre-reduced in a flow of hydrogen (40 ml min^{-1}) at 640 K for 2 h and the catalyst cell was evacuated at the same temperature for 1 h. Oxygen chemisorption uptakes were determined as the difference of 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 testing the catalysts during ammoxidation of 3-picoline to nicotinonitrile. About 2 g of catalyst diluted with an equal amount of quartz grains was charged into the reactor and was supported on a glass wool bed. Prior to introducing the reactant 3-picoline with a syringe pump, the catalyst was reduced at 673 K for 2 h in purified hydrogen flow (40 ml min^{-1}). After prereduction the reactor was fed with 3-picoline, ammonia and air, keeping mole ratio of 3-picoline : H_2O : NH_3 : air at 1 : 13 : 22 : 44 and contact time at 0.6 s. The reaction was carried out at various temperatures ranging from 573 to 683 K. The liquid products obtained (mainly nicotinonitrile) were analysed by gas chromatograph using an OV-17 column. Traces of carbon oxides were also formed during the reaction.

The oxygen chemisorption capacities of various V_2O_5/Nb_2O_5 catalysts are presented along with other information in Table 1. Pure Nb_2O_5 was also reduced under identical conditions and its oxygen uptake was taken into account for the supported catalysts. The results show that oxygen chemisorption capacities are found to increase with increase of vanadia content on niobia (Table 1). However, the dispersion of vanadia (O/V) is found to decrease steadily with increase of vanadia content (Table 1). Dispersion of vanadium oxide is defined as the fraction of total O atoms (determined from oxygen chemisorption) to total V atoms in the sample. The results of oxygen chemisorption results are further supported by powder X-ray diffraction results shown in Fig. 1, wherein a mixed vanadium–niobium oxide such as β-$(Nb, V)_2O_5$ (JCPDS card No: 16-132) was formed at moderately high vanadia content and increases with further increase of vanadia content. This β-$(Nb, V)_2O_5$ phase can be observed with d = 3.77, 3.56 and 3.40 Å for samples containing 10 and 12% V_2O_5 supported on Nb_2O_5 [Fig. 1(d) and (e)]. A decrease in dispersion of vanadia at higher loadings might be due to formation of β-$(Nb, V)_2O_5$.

According to Smits *et al.*,[6] the activity for oxidative dehydrogenation of propane was much reduced for samples containing the β-$(Nb, V)_2O_5$ phase. Wadsley and Andersson[13] also suggested that, in this phase the vanadium is replaced by the niobium present in isolated tetrahedral sites at the junction of blocks of NbO_6 octahedra. Thus the number of surface vanadium species are found to decrease when β-$(Nb, V)_2O_5$ is present in the catalyst.

The conversion and selectivity during ammoxidation of 3-picoline are reported in Table 1. The results show that conversion of 3-picoline increases up to 6% of V_2O_5 and did not

Table 1 Results of oxygen uptake, dispersion, oxygen atom site density, surface area and ammoxidation of 3-picoline for various V_2O_5/Nb_2O_5 catalysts

Sample	Wt% of V_2O_5 on Nb_2O_5	Surface area/ $m^2\ g^{-1}$	Oxygen uptake[a]/ $\mu mol\ g^{-1}$	Surface area[b] $m^2\ g^{-1}$	Oxygen atom site density/$10^{18}\ m^{-2}$	Dispersion[c] (O/Mo)	Ammoxidation of 3-picoline[d] % Conversion	Ammoxidation of 3-picoline[d] % Selectivity
1	2	50.2	83.1	57.0	1.76	0.76	73.80	97.60
2	4	48.7	161.2	49.0	3.96	0.73	80.20	95.70
3	6	46.7	217.9	49.1	5.35	0.66	90.30	98.05
4	8	44.1	249.6	45.7	6.58	0.57	88.60	96.60
5	10	43.6	300.9	45.2	8.03	0.54	85.70	97.20
6	12	44.2	340.6	46.2	8.88	0.51	82.85	95.30

[a] $T_{Reduction} = T_{Adsorption} = 640$ K. [b] BET surface area determined after oxygen chemisorption. [c] Dispersion = fraction of vanadium atoms at the surface assuming $O_{ads}/V_{surf} = 1$. [d] Reaction temperature = 683 K.

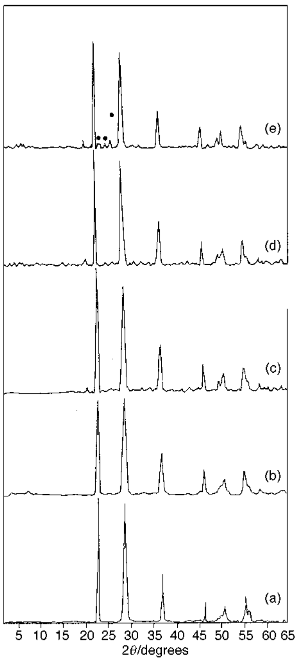

Fig. 1 X-Ray diffraction of V_2O_5/Nb_2O_5 catalysts: (a) 2%, (b) 4%, (c) 6%, (d) 10%, (e) 12% V_2O_5/Nb_2O_5. (●) Indicates XRD peaks arising from β-(Nb, V)$_2$O$_5$.

change appreciably at higher loadings. However, the selectivity of nicotinonitrile was found to be independent of vanadia loading in the catalyst. Watling *et al.*[7] also observed a similar trend in the activity for oxidative dehydrogenation (ODH) of propane over V_2O_5/Nb_2O_5 catalysts. They noticed that the rate of propane ODH first increases linearly with vanadia loading up to 6% and then remains constant at higher vanadia loadings. It is worth noting here that this vanadia loading corresponds closely to a theoretical monolayer capacity of V_2O_5 supported on a niobia having a specific surface area of 55 $m^2\ g^{-1}$. This indicates that indeed a monolayer of vanadium oxide is formed at this concentration of V_2O_5 on niobium oxide.

The results of catalytic performance during ammoxidation can be explained by assuming that the active sites are due to vanadium ions at the surface, and the activity and selectivity of this site depends on the number of neighbouring vanadium and niobium ions. According to Smits *et al.*[14] the neighboring vanadium ions provide additional activity, while neighboring niobium ions improve the selectivity. The optimal activity and selectivity is shown a site having both vanadium and niobium as neighbors (V–O–V*–O–Nb).[14] At low vanadium loadings, the possibility of vanadium sites having a vanadium ion as a neighbour are low and thus the catalyst will be selective (Fig. 1) but not very active. The high activity for 6% V_2O_5/Nb_2O_5 catalyst might be due to presence of both vanadium and niobium as neighbors (monolayer loading). At higher loadings of V_2O_5 the activity remains constant due to formation of the new phase *i.e.* β-(Nb, V)$_2$O$_5$. This can be explained based on the assumption that not all the vanadium present in these catalysts contributes to the formation of mixed oxide phase.

To find the relation between the ammoxidation activity of 3-picoline and the dispersion of vanadia, a plot of $1/X$ *versus* the number of surface V_2O_5 moles is shown in Fig. 2, where X is the rate of picoline molecules converted per second per surface V_2O_5. A linear relationship passing through the origin was obtained, which clearly demonstrates that 3-picoline conversion is directly related to oxygen chemisorption measured at 640 K. As reported elsewhere, in connection with vanadium oxide catalysts supported on alumina[12] and on silica,[15] oxygen is chemisorbed at low temperatures selectively on coordinatively unsaturated sites (CUS), generated upon reduction, having a particular coordination environment. These sites are located on a highly dispersed vanadia phase, which is formed only at low vanadia loadings and remains as a ‘patchy monolayer’ on the support surface. At higher vanadia loadings, a second phase forms, in addition to the existing monolayer, and this post monolayer phase does not appreciably chemisorb oxygen. In light of the above, the correlation observed here, indicates that the catalytic functionality of the dispersed vanadium oxide phase supported on niobium(v) oxide is responsible for the ammoxidation of 3-picoline to nicotinonitrile is located on a patchy monolayer phase and that this functionality can be titrated by the oxygen chemisorption method described in this work.

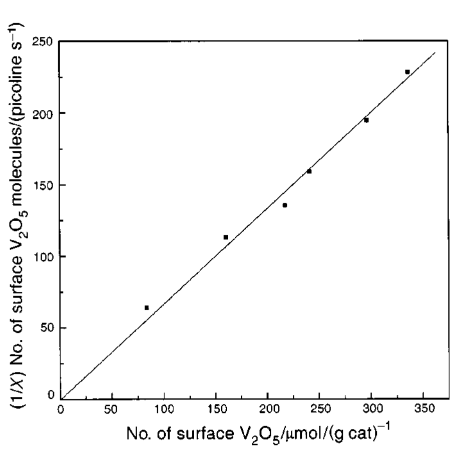

Fig. 2 Relationship between concentration of surface V_2O_5 and the rate of 3-picoline conversion.

Thus at low vanadia loadings the active vanadia phase is present in a highly dispersed state. However, at higher vanadia loadings, a mixed oxide containing β-(Nb, V)$_2$O$_5$ is formed. V_2O_5/Nb_2O_5 catalysts were highly active and selective for the conversion of 3-picoline to nicotinonitrile. The oxygen uptake is found to be directly related to the activity of the catalysts during 3-picoline ammoxidation to nicotinonitrile.

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