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Influence of V_2O_5 content on ammoxidation of 3-picoline over V_2O_5/AlF_3 catalysts

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Abstract

V_2O_5/AlF_3 catalysts with V_2O_5 loadings ranging from 2 to 15 wt% were prepared by the conventional wet impregnation method, using nonporous $AlF_3 \cdot 3H_2O$ sample as the support for impregnating NH_4VO_3. It was found that the catalysts evolve porous structures upon calcination at 723 K. The influence of V_2O_5 content was studied on ammoxidation of 3-picoline on the reduced catalysts. The catalyst with 15 wt% V_2O_5 exhibited the highest selective ammoxidation acitivity towards nicotinonitrile. The XRD and oxygen chemisorption studies revealed that vanadia is in a highly dispersed state in the catalysts. © 2002 Published by Elsevier Science B.V.

Keywords: Ammoxidation; 3-Picoline; HTOC; V_2O_5/AlF_3 catalysts

1. Introduction

Support plays a decisive role in influencing the dispersion of vanadia and thereby the activity and selectivity of supported vanadia catalysts in a variety of reactions [1–3]. Considerable amount of work has been done on the elucidation of molecular structures of vanadium oxides by the application of LASER Raman, NMR, FTIR, ESR and other spectroscopic techniques [4–8] and on ammoxidation of alkyl aromatic and heteroatomic hydrocarbons over vanadia catalysts dispersed on inorganic oxides such as TiO_2 and Al_2O_3 [2,8–11]. Recently, an excellent overview of the state of the art and future trends in vapor phase oxidation and ammoxidation of substituted methyl aromatics and heteroaromatics is published by Martin and Lucke [12].

In a search for novel nonconventional supports, we have recently found that CeF_3 supported V_2O_5 catalyst exhibited high activity in the ammoxidation of 3-picoline [11]. Literature reveals that aluminum fluoride as such or as a component of other catalysts can be applied to catalyze various organic reactions [13–15]. The most important use of AlF_3 is as a catalyst or as a promoting support for other catalysts for the production of hydrofluorocarbons (HFCs) to be used as substitutes for chloro-fluorocarbons (CFCs), which are ozone-depleting

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44 agents [14–16]. According to Coq et al. [16] AlF_3 is
45 found to be an ideal support for metals like Pd for
46 hydrodechlorination of CCl_2F_2. In the present
47 paper we are reporting the results of a preliminary
48 investigation on the use of AlF_3 as a support for
49 vanadia catalysts in the ammoxidation of 3-pico-
50 line to nicotinonitrile, an intermediate to nicotinic
51 acid which is used as a component of vitamin-B
52 complex [10].

2. Experimental

2.1. Catalyst preparation

55   AlF_3 supported vanadia catalysts were prepared
56 by the wet impregnation [10] of support particles
57 ($AlF_3 \cdot 3H_2O$, Loba Chemie, India) (18–25 BSS
58 mesh) with requisite amount of NH_4VO_3 (Aldrich,
59 USA) dissolved in aqueous oxalic acid solution.
60 The impregnated samples were evaporated to
61 dryness on a water bath, dried at 393 K in an oven
62 for 16 h and then calcined at 723 K for 6 h. Va-
63 nadium contents of the catalysts were estimated
64 using an Atomic Absorption Spectrometer (Per-
65 kin-Elmer, Model: 2380) after decomposing them
66 in aquaregia and making aqueous solutions of
67 desired concentration range.

2.2. X-ray diffraction

69   X-ray diffraction (XRD) patterns of the calc-
70 ined V_2O_5/AlF_3 catalysts were recorded on a
71 Philips PW-1140 X-ray diffractometer using Ni
72 filtered Cu K_α radiation.

2.3. Surface area, O_2 and NH_3 chemisorption and catalytic activity

75   The surface areas of the catalysts were deter-
76 mined by N_2 adsorption at liquid N_2 temperature
77 using BET method. The details of the experimental
78 procedures for the high temperature oxygen
79 chemisorption (HTOC) for the determination of
80 irreversible oxygen chemisorption carried out at
81 640 K after reducing the catalyst at 640 K and of
82 ammonia chemisorption at room temperature
83 (RTAC) after degassing the catalyst at 423 K for 2

84 h and activity of the catalysts for ammoxidation of
85 3-picoline are given elsewhere [10,17,18]. For the
86 activity studies, typically, about 2 g of catalyst is
87 taken in a micro catalytic reactor placed in an
88 electrically heated furnace. The catalyst sample is
89 then reduced in H_2 flow at 723 K followed by
90 cooling to room temperature where H_2 is replaced
91 with NH_3, and air. The temperature is slowly
92 raised to reaction temperature (633 K) where the
93 liquid feed (mixture of 3-picoline and H_2O;
94 2 ml h^{-1}) along with NH_3 and air are fed and
95 maintained in a mole ratio of 3-pico-
96 line:$H_2O:NH_3:Air = 1:13:6:44$. The dispersions of
97 the catalysts (O_a/V_t), (where V_t is the total num-
98 ber of vanadium atoms) were calculated assuming
99 a stoichiometry of 1:1 (O_a/V_s) between the num-
100 ber of irreversibly chemisorbed oxygen atoms (O_a)
101 and the number of reduced surface vanadium at-
102 oms (V_s) [17,18].

3. Results and discussion

104   The surface areas (S_{BET}), the irreversible O_2 and
105 NH_3 uptakes and vanadium dispersions of the
106 catalysts are listed in Table 1. The commercial
107 $AlF_3 \cdot 3H_2O$ has a surface area of 1.75 m^2 g^{-1} and
108 pore volume of 0.51 cm^3 g^{-1}. The support and the
109 catalysts develop porous structures and surface
110 areas upon calcination at 723 K (Table 1), obvi-
111 ously due to decomposition of $AlF_3 \cdot 3H_2O$ and
112 NH_4VO_3. The surface areas of calcined catalysts
113 decrease with increasing vanadia content due to
114 blocking of pores and deposition of vanadia on
115 pore surface. The amounts of irreversibly ad-
116 sorbed oxygen and ammonia continuously in-
117 crease with increase in V_2O_5 loading. The surface
118 areas of the catalysts determined after the oxygen
119 adsorption measurements are always higher than
120 those of calcined catalysts and tend to become
121 nearly equal (72.8–66.0 m^2 g^{-1}). Increase in sur-
122 face areas of the catalysts may be attributed to
123 opening of small pores on pore walls and spread-
124 ing of vanadia phase during reduction, O_2 ad-
125 sorption and degassing at 640 K [17,18]. The V_2O_5
126 dispersion increases from 0.34 to 0.47 when the
127 V_2O_5 content is increased from 1.96 to 7.60 wt%
128 and declines beyond this V_2O_5 content. The high-

Table 1
BET surface areas, irreversible O_2 and NH_3 uptakes and vanadium dispersions of V_2O_5/AlF_3 catalysts

V_2O_5/AlF_3 catalysts (V_2O_5 wt%)	S_{BET} ($m^2 g^{-1}$)	HTOC[a] ($\mu mol\ g^{-1}$)	RTAC[b] ($\mu mol\ g^{-1}$)	Dispersion[c] (O_a/V_t)	S_{BET}, after HTOC[a] ($m^2\ g^{-1}$)
1.96	61.9	36.4	553.3	0.34	72.8
5.71	54.1	92.9	578.2	0.30	72.1
7.58	46.2	196.5	696.7	0.47	70.3
10.52	38.7	206.7	771.6	0.35	70.1
14.98	27.8	222.4	966.4	0.27	66.0
Pure AlF_3	78.0	–	382.4	–	47.8
Pure V_2O_5	6.0	24.3	62.6	–	25.4

[a] High temperature oxygen chemisorption.

[b] Room temperature ammonia chemisorption.

[c] The ratio of number of irreversible chemisorbed oxygen atoms (O_a) and total number of vanadium atoms (V_t).

est dispersion of 0.47 at 7.6 wt% V_2O_5 does not correspond to a monolayer coverage on AlF_3 surface ($O_a/V_t = 1.0$). HTOC (high temperature oxygen chemisorption) is a versatile method for the measurement of vanadia dispersion meaningfully in supported systems (18). In this method the prereduction of the catalyst and subsequent O_2 chemisorption will be carried out at the same temperature (640 K). Thus, this method ensures surface reduction and estimates CUS whereas in low temperature oxygen chemisorption (LTOC) the reduction at high temperature prior to O_2 chemisorption at 195 K results bulk reduction of the catalyst and leads to inaccurate estimation of vanadia dispersion. results. Saleh and Wachs [19] and Inomata et al. [20] have observed that the formation of overlayers and seggregation of bulk oxides may also occur on the first layers even before the formation of a monolayer. Pure AlF_3 (S_{BET} 78 $m^2\ g^{-1}$) has adsorbed 382.4 $\mu mol\ g^{-1}$ of NH_3 at room temperature and no oxygen uptake at 640 K (Table 1). It is interesting to observe that even though the acidity of V_2O_5 (62.6 μmol g^{-1} NH_3) is lower than that of AlF_3 (382.4 μmol g^{-1} NH_3), the acidities of the supported V_2O_5 catalysts are always higher than that of support. It is a clear indication of strong interaction between V-oxide species and the support.

The XRD patterns of the V_2O_5/AlF_3 catalysts (Fig. 1) are found to contain prominent reflections ($d = 3.53, 1.78, 2.13$ and 1.58 Å, ASTM card No. 9-138) of the support AlF_3 and $AlF_{1.96}OH_{1.04}$ phase ($d = 5.56, 2.13$ Å; ASTM card No. 11-631) the intensity of which is decreasing with V_2O_5

loadings of the catalysts. The XRD patterns of the catalysts with V_2O_5 contents up to 7.6 wt% do not contain any XRD reflections characteristic of any oxides of vanadium. This observation suggests that deposited vanadia is in a highly dispersed state probably in the form of highly active monomeric VO_4 units and two dimensional (V–O–V) structures [4–6,21–23] which seem to be responsible for selective ammoxidation of 3-picoline to nicotinonitrile. At 15 wt% V_2O_5 content the intensities of the XRD reflections of the support

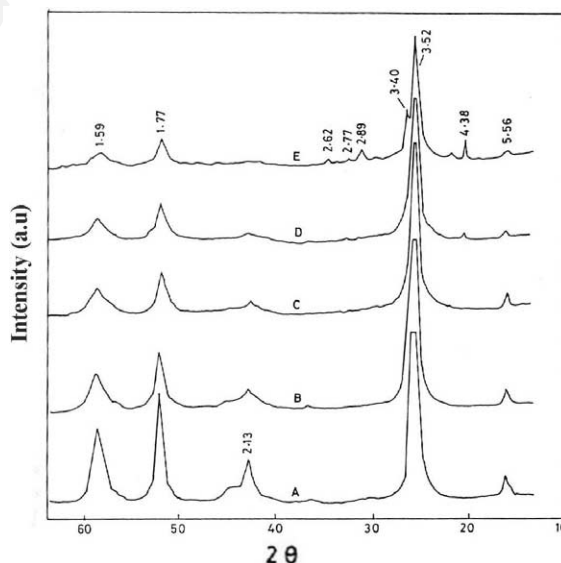Fig. 1. XRD patterns of calcined V_2O_5/AlF_3 catalysts with various V_2O_5 loadings: A – 1.96 wt%, B – 5.71 wt%, C – 7.58 wt%, D – 10.52 wt%, E – 15 wt%.

174 AlF$_3$ are drastically reduced and the XRD reflec-
175 tions of V$_2$O$_5$ ($d = 4.36$, 3.40, 2.89, 2.62, 2.77 Å)
176 become prominent indicating that a major part of
177 the support surface is covered by bigger V-oxide
178 structures (polyvanadates) [24] and V$_2$O$_5$ crystal-
179 lites [10]. HTOC results are in line with XRD re-
180 sults.
181   It is clear from Fig. 2 that V$_2$O$_5$ content has a
182 marked influence on ammoxidation activity of the
183 catalysts. The 3-picoline conversion increases at a
184 faster rate from 12.6 to 61.6% when V$_2$O$_5$ content
185 is increased from 1.96 to 7.6 wt%, and at a slower
186 rate from 61.6% to 84.8% when V$_2$O$_5$ content is
187 increased from 7.6 to 15 wt%, in the same manner
188 as the increase in irreversible oxygen chemisorp-
189 tion on the reduced catalysts with V$_2$O$_5$ loading
190 (Table 1). The selectivity towards nicotinonitrile
191 has been enhanced from 83.3% to 93.4% while the
192 selectivity towards pyridine has decreased from
193 8.1% to 3.4% when V$_2$O$_5$ content of the catalysts is
194 increased from 1.96 to 15 wt%. The proportionate
195 increase of 3-picoline conversion with O$_2$ uptakes
196 of V$_2$O$_5$/AlF$_3$ catalysts suggests that oxygen is
197 able to diffuse into the oxide structures, get ad-
198 sorbed and activated on the reduced vanadium
199 sites in the V-oxide structures, which are growing
200 in size with increase in V$_2$O$_5$ content of the cata-
201 lysts. These are coordinatively unsaturated sites
202 (CUS) of vanadium ions, which are formed from
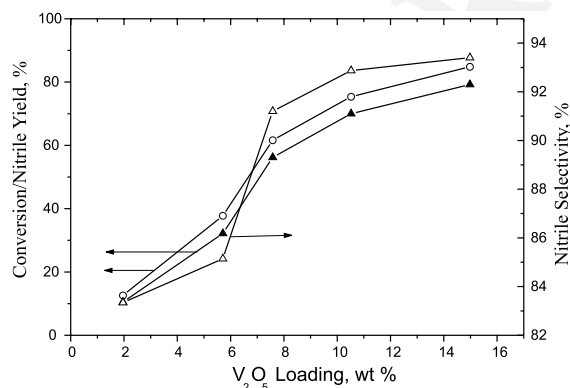203 V^{5+}, after reduction, in the lattice layers of V-oxide

204 structures in the catalysts [25,26]. We reported
205 earlier that the average oxidation state of vana-
206 dium ions during the ammoxidation is lower than
207 +5 and the surface sites of CUS of V-ions in
208 V$_2$O$_5$/TiO$_2$ catalysts can be titrated by oxygen
209 chemisorption experiments [8,10]. The degree of
210 vanadia dispersion on conventional supports is
211 usually very high (close to 1) at low vanadia
212 loadings. At high vanadia loadings, overlayers of
213 vanadia are expected and hence the degree of
214 dispersion will be low. However, from Table 1, it is
215 observed that the degree of dispersion of vanadia
216 is lower even at low loadings. Most probably, the
217 interaction between V-oxide species and AlF$_3$
218 makes these species stabilized towards reduction.
219 Thus the high activity of V$_2$O$_5$/AlF$_3$ catalysts may
220 be due to the combined effect of the number of
221 CUS and the interaction between the active com-
222 ponent and support (see Fig. 3).
223   The rate of conversion of 3-picoline decreases
224 above a V$_2$O$_5$ content of 7.5 wt% due to the for-
225 mation of bigger V-oxide structures (polyvana-
226 dates [26] and free tiny V$_2$O$_5$ crystallites ($d = 4.38$
227 Å) as shown by the XRD patterns of 10.5 wt%
228 V$_2$O$_5$/AlF$_3$ catalyst (Fig. 1)). However, the grad-
229 ual increase in 3-picoline conversion beyond
230 monolayer coverage of V$_2$O$_5$ may be due to the
231 availability of large number of surface sites beyond
232 monolayer loading.
233   When the catalysts are reduced before studying
234 3-picoline ammoxidation, the bulk V-oxides would
235 have been reduced, rendered porous and redi-
236 spersed on AlF$_3$ surface [17,18] and the modified
237 V-oxides are responsible for the activity of the
238 catalysts. This would explain the higher selective
239 ammoxidation activity of 15 wt% V$_2$O$_5$ catalyst.
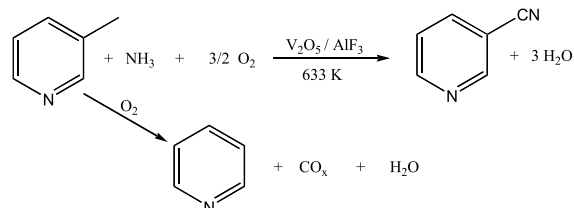240 The amount of carbon oxides is found to be de-

Fig. 2. Influence of V$_2$O$_5$ loading on 3-picoline ammoxidation over V$_2$O$_5$/AlF$_3$ catalysts: ○ – conversion; Δ – nitrile selectivity; ▲ – nitrile yield. Reaction conditions: 3-picoline:H$_2$O:NH$_3$: Air (mole ratio) = 1:13:6:44. Reaction temperature = 633 K.

Fig. 3. Reaction pathways on supported V$_2$O$_5$ in the ammox-idation of 3-picoline.

Table 2
Product distribution data in the ammoxidation of 3-picoline

S. No.	V_2O_5 loading on AlF$_3$ (wt%)	3-Picoline conversion (%)	Yield (mol%)			
			3-Cyano nitrile	Pyridine	CO	CO$_2$
1	1.96	12.58	83.34	8.06	2.38	6.22
2	7.60	61.61	91.20	4.82	1.21	2.77
3	15.00	84.80	93.40	3.39	1.61	1.60

Reaction conditions: 3-picoline:H$_2$O:NH$_3$:Air = 1:13:6:44; temperature = 633 K.

creasing with increase in vanadia loading (Table 2) and these are ∼3.0% on 15 wt% V_2O_5 catalyst. Recent work on ammoxidation of 3-picoline on V_2O_5/TiO$_2$ catalysts has shown that at a monolayer coverage, monomeric VO$_x$(VO$_4$) units and – V–O–V– structures might be responsible for high nicotonitrile selectivity [8,10]. The 15 wt% catalyst has exhibited very stable ammoxidation activity with producing low amounts of carbon oxides indicating that V-oxide structures generated on AlF$_3$ support are highly stable and facile and do not oxidize 3-picoline, nicotinonitrile and ammonia at 633 K. Large quantity of water used in the reactant feed (3-picoline:H$_2$O mole ratio = 1:13) does not seem to have any deleterious effect on the V-oxides of the catalysts. Wachs and coworkers [5] have observed by LASER Raman spectroscopy that the hydrolysis of the surface V-oxides does not occur to a significant extent at elevated temperatures (>503 K) and the surface vanadia species are stable on the oxide supports in the presence of water vapour. Water molecules tend to complete the oxygen environment up to the octahedral state of vanadium only at low temperatures [25].

It is worthwhile to note that the performance of 15 wt% V_2O_5/AlF$_3$ catalyst (93.4% selectivity at 84.8% conversion; yield = 79.2%) appears to be much superior to that of 7.5 wt% V_2O_5/TiO$_2$ monolayer catalyst (95% selectivity at 73% conversion; yield = 69.4%) [8]. The fact that the cracking products i.e, formation of pyridine and carbon oxides are minimum on V_2O_5/AlF$_3$ catalysts reveal the absence of strong acid sites. Because of interaction between V_2O_5 and AlF$_3$ the total acidity of V_2O_5/AlF$_3$ catalysts are higher than that of V_2O_5 and AlF$_3$, most of these acid sites in supported catalysts are with weak and moderate strength.

The product distribution data is shown in Table 2. This data clearly indicates the absence of ring cleavage. Only small amount of pyridine and carbon oxides are obtained. These products can be formed either due to thermal reaction or due to the presence of low amounts of strong acid sites in the catalysts. The linear tendency between NH$_3$ uptake and the nicotinonitrile selectivity supports the presence moderate acid sites in large quantity. The catalysts were tested continuously for a period of 24 h in the ammoxidation reaction and no significant loss in the activity was observed.

4. Conclusions

Thus the present work has shown that the acidic materials like AlF$_3$ can be employed as supports for preparing highly active and selective catalysts for the ammoxidation of 3-picoline to yield nicotinonitrile by depositing higher amount of vanadia (∼15 wt%) on them. The morphological structure of AlF$_3$ seems to favour high degree of interaction between vanadia and AlF$_3$ species after reducing the catalysts at high temperatures (∼723 K).

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