

Oxidation and ammoxidation of 4-picoline over vanadium-silico-aluminophosphate catalysts[†]

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Vanadium-silico-aluminophosphate (VSAPO), vanadium-aluminophosphate (VAPO) and silico-aluminophosphate (SAPO) catalysts have been synthesized using tetrapropylammonium bromide as a template. The resulting catalytic materials are as-synthesized crystalline molecular sieves or composite catalysts of molecular sieves. The XRD, IR and ESR studies of these catalysts have been studied. The oxidation and ammoxidation of 4-picoline over vanadium-silico-aluminophosphate (VSAPO) and vanadium-aluminophosphate (VAPO) catalysts lead to corresponding 60-95% yields of aldehydes and nitriles. We report crystalline and amorphous modified V-silico-aluminophosphates as a new class of oxidation and ammoxidation catalytic materials.

Recently zeolite molecular sieves are being used in the synthesis of speciality and fine chemicals¹⁻¹². The oxidation reactions have been carried out preferentially and successfully over vanadium- and titanium-silicates¹³⁻¹⁵. We have reported⁹ a clean one step ammoxidation of ethanol to acetonitrile over silico-aluminophosphate catalyst (SAPO-40 type) with high yield (98%) and selectivity. Silico-aluminophosphate (SAPO) molecular sieve is a mild and selective oxidation and ammoxidation catalyst. The ammoxidation of toluene and picolines over SAPO resulted into the corresponding nitriles with low yields (<40%) and high selectivity¹⁶. Thus the attempts have been made to lower the exothermicity and to reduce the high-boiling products in the reaction, using the shape-selectivity. The resulting nitriles in the ammoxidation of picolines are important intermediates in the synthesis of several pharmaceuticals and agrochemicals¹⁷. In presently known processes, the ammoxidation of picolines has been carried out over non-uniform porous V₂O₅ or α -VOPO₄ supported over various supports like Al₂O₃, SiO₂-Al₂O₃, Cr₂O₃, TiO₂, etc¹⁸⁻²⁷. In this paper, we are reporting for the first time, the oxidation and ammoxidation of 4-picoline over SAPO molecular sieves and vanadium silicoaluminophosphate (VSAPO) catalysts. The VSAPO, VAPO catalysts are either vanadium impregnated

or incorporated VAPO amorphous sieves or composite catalysts with SAPO molecular sieves as a matrix component.

Materials and Methods

The crystalline VSAPO, VAPO and SAPO catalytic materials were hydrothermally synthesized using aluminium sulphate, phosphoric acid, sodium silicate, vanadium pentoxide, with or without sodium chloride and tetrapropylammonium bromide as a template at 200°C for 24-80 h at 20 atm autogeneous pressure. All chemicals are LR or AR grade.

X-ray diffraction patterns were taken using Philips instrument with FeK α ($\lambda = 1.9359\text{\AA}$) radiation from $2\theta = 4$ to 70. FT-infra-red spectra were recorded using KBr pellet on Nicolet 740 model (USA). Electron-spin resonance spectra were recorded using BRUKER ER-200D-SRC instrument. The reaction was carried out using a down-flow, fixed-bed, pyrex reactor of 20 mm internal diameter. The reaction was carried out in the temperature range of 300-420°C; 0.25 to 1 h⁻¹ weight hourly space velocity (WHSV) and the amount of catalyst was 4 g. The reaction mixture was fed from top using a syringe pump (Sage Instruments, USA). The product was cooled using ice-cooled water and collected at the bottom. The required number of ice-cooled traps were used to collect the total amount of products. The products were analyzed by SE-30 (5%) and chromo-

Table 1—Chemical composition of the catalysts^a

Catalyst	Atom. wt%				Nature of catalyst	NH ₃ ^b at 20°C	<i>n</i> -BA ^c at 25°C
	Al	V	P	Si			
VSAPO (TPA-A)	15.3	11.7	7.4	10.0	Composite	5.3 × 10 ¹⁹	3 × 10 ¹⁹
VAPO (B)	32.5	8.52	10.96	—	Composite	2.7 × 10 ¹⁹	1.9 × 10 ¹⁹
VAPO (C)	17.41	2.4	10.96	—	Amorphous	3.1 × 10 ¹⁹	1.4 × 10 ¹⁹
VAPO (D)	31.6	3.16	5.82	—	Amorphous	2.9 × 10 ¹⁹	1.8 × 10 ¹⁹

(a) After removal of template (tetrapropylamine), as used in the reaction.

(b) Number of ammonia molecules sorbed at 20°C.

(c) Number of *n*BA (*n*-butylamine) molecules sorbed at 25°C.

Table 2—Spin Hamiltonian parameters of vanadium in VSAPO and VAPO catalysts

Catalyst	g_{\parallel}	g_{\perp}	$A_{\parallel}(G)$	$A_{\perp}(G)$	ΔH
V-SAPO (A)	2.0221	2.044	197	55	90
VAPO (B)	2.0046	2.038	175	58	89
VAPO (C)		2.1644		—	1150
VAPO (D)	2.0174	2.0560	167	55	142
V-SAPO (A) calcined		1.9785		—	350
VAPO (D) calcined	2.296	2.223	350	235	665

Table 3(a)—Ammoxidation of 4-picoline: Variation of catalysts

Reaction temp. = 420°C; WHSV = 0.5 h⁻¹; atmospheric pressure; flow rate of air = 60 cc per min; wt. of the catalyst = 4 g; picoline: H₂O = 1:3 volume; picoline: NH₃ = 1:16 molar

Catalysts	Time on stream (h)	Conversion of 4-picoline (wt%)	Yield (wt.%) ^b	
			4-Cyanopyridine	Pyridine
V-SAPO (A)	3	100.0	91.1	6.4
VAPO (B)	1	65.4	49.7	1.8
VAPO (B) ^a	4	46.9	35.6	4.3
SAPO (TPA) ^c	2	41.7	39.9	0.2
VAPO (C)	1	67.2	59.3	0.5
VAPO (D)	4	66.9	60.1	—
SAPO (TBA) ^c	1	45.2	44.0	1.2
VSAPO (TBA, 1% V) ^c	1	41.9	37.4	4.5
SAPO-37	3	20.1	18.0	—
SAPO-11	3	21.7	6.0	—
SAPO-5	2	45.4	38.3	0.2
Sb ₂ O ₃ -VSAPO-A	3	48.6	43.2	5.4

(a) Picoline: H₂O = 1:1; (b) based on 4-picoline; (c) TPA, TBA templates removed.

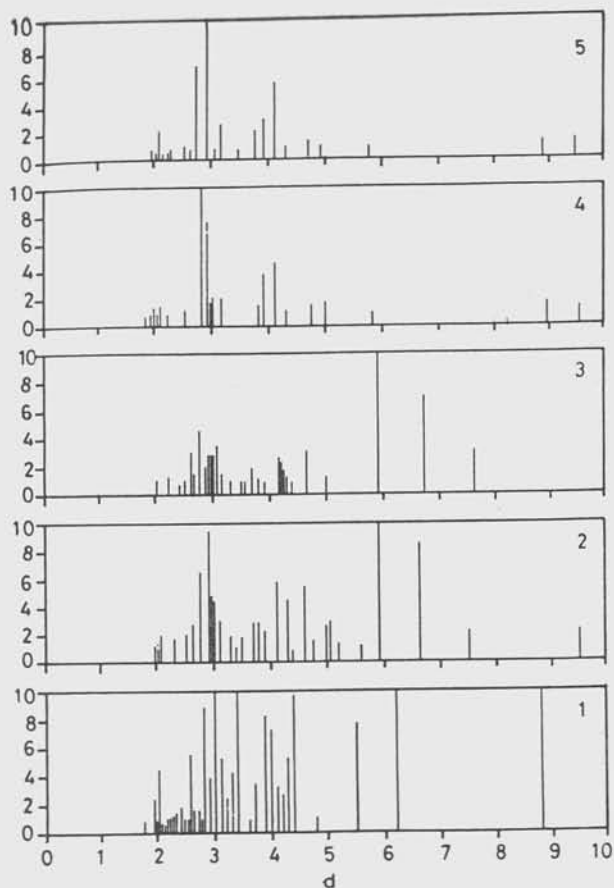


Fig. 1—X-ray diffraction patterns of as-synthesized (1) Silico-aluminophosphate (SAPO-TPA), (2) VAPO (TPA-D), (3) VAPO (TPA-C), (4) VAPO (TPA-B) and (5) VSAPO (TPA-A)

sorb (101) columns. The analysis was confirmed by mass spectra, gc-mass. The mass balance is >95%.

Results and Discussion

Characterization of the catalysts

The chemical composition of the catalysts is given in Table 1 and the X-ray diffraction patterns are given in Fig. 1. The silico-aluminophosphate (SAPO-TPA) is a crystalline, microporous molecular sieve of SAPO-40 type with some differences in XRD patterns, notably the absence of XRD peaks below $2\theta = 10$. The VAPO (TPA-C) and VAPO (TPA-D) are also typical and novel molecular sieves with some impregnated vanadium oxide. The XRD, IR and sorption studies¹⁶ indicate that VSAPO (TPA-A) and VAPO (TPA-B) are composite catalysts.

The infra-red spectra are given in Fig. 2. The ratios of areas of peaks at 1408 and 1128 cm^{-1} for VSAPO (A) and VAPO (D) are 0.3115 and

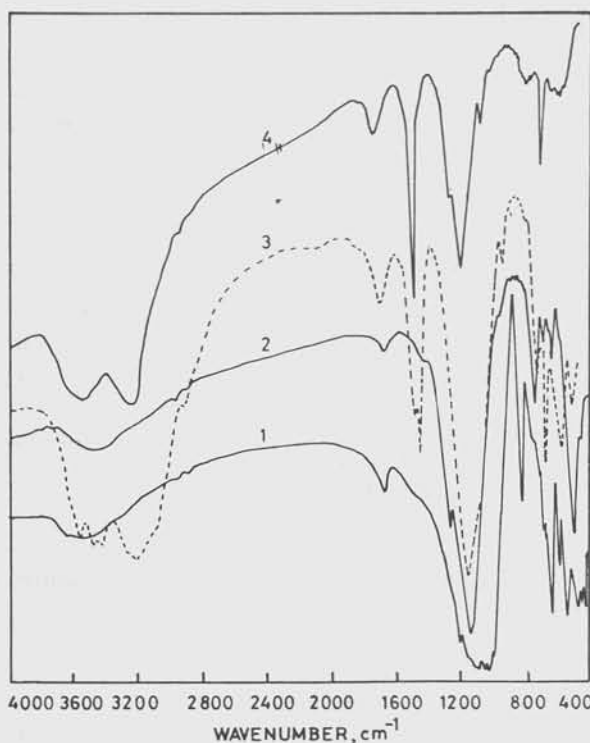


Fig. 2—IR spectra of (1) SAPO (TPA), (2) VAPO (TPA-D) calcined, (3) VAPO (TPA-C), and (4) VSAPO (TPA-A)

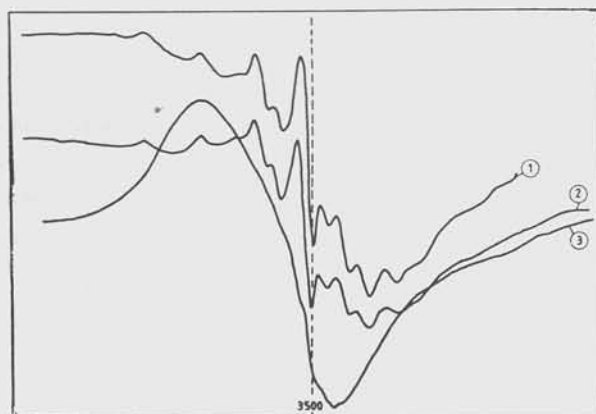


Fig. 3—ESR spectra of as-synthesized (1) VSAPO (TPA-A), (2) VAPO (TPA-B) and (3) VAPO (TPA-C)

0.2148 which are proportional to the amount of vanadium in the catalyst. The IR peak at 1408 cm^{-1} indicates²⁸ the interaction between vanadium and :N of template (TPA).

The ESR spectra are depicted in Figs 3 and 4. The ESR spectra showed hyperfine splitting and the presence of V^{4+} oxidation state in the catalyst samples. The ESR parameters of VSAPO and VAPOs will be discussed elsewhere¹⁶. The g_{\parallel} and g_{\perp} values of VSAPO (A) and VAPO (D) are typically 2.044 (g_{\perp}), 2.0221 (g_{\parallel}) and 2.056 (g_{\perp}),

Table 3(b)—Ammonoxidation of 4-picoline over thermally stable VSAPO and SAPO molecular sieves

Reaction temp. = 400°C; WHSV = 0.5 h⁻¹; atmospheric pressure

Catalyst	Catalyst stability	Time on stream (h)	Conversion of 4-picoline (wt%)	Yield (wt%)	
				4-Cyanopyridine	Others ^a
VSAPO-37	C.T.S	1+2	76.0	48.1	27.9
VSAPO-5 (type)	C.T.S	4	27.9	20.1	7.8
SAPO-37	C.T.S	3	23.2	18.1	5.1
SAPO-11 (type)	C.T.S	4	35.4	21.4	14.0

Yield based on 4-picoline; (a) pyridine is the major product. (b) C.T.S = Crystalline and thermally stable.

Table 4—Ammonoxidation of 4-picoline over VSAPO (A) at different temperatures

WHSV = 0.5 h⁻¹; picoline: H₂O = 1.5 (vol.); picoline: NH₃ = 1:16 molar; atmospheric pressure

Temp.	Time on stream (h)	Conversion of 4-picoline (wt%)	Yield (wt%) ^a	
			4-Cyanopyridine	Pyridine
300	1	20.9	20.6	—
350	1	49.2	30.9	10.0
380	4	70.4	68.0	0.8
400	1	89.8	78.1	1.8
420	2	89.7	81.4	3.4

(a) based on 4-picoline.

2.0174 (g_{||}) respectively²⁹. The g values indicate the presence of V–O bonding. The broad singlet in ESR (Figs 3 & 4) is due to the dipole-dipole interaction in V–O–V linkages with ~5.1 Å distance between vanadium ions³⁰. The ESR parameters are given in Table 2. If the amount of vanadium in SAPO is lower than 3 wt% then the structure and chemical state of V is not changed drastically after calcination or removal of template. After heating at 420°C for 4 h, the as-synthesized catalysts in Table 3(a) lost the 80–90% crystallinity, and microcrystallinity (presence of small unit cells) may be present. The catalysts in Table 3(b) are thermally stable and crystalline.

Ammonoxidation of 4-picoline

The ammonoxidation of 4-picoline over various catalysts has been given in Table 3(a & b). The reaction of 4-picoline, ammonia, water and air was carried out at 420°C, with 0.5 h⁻¹ W.H.S.V. (4 g catalyst) and picoline: water ratio = 1:3. The

yields of 4-cyanopyridine over VSAPO (A), VSAPO (D) and SAPO (TPA) were 91.1, 60.1 and 39.9 wt per cent respectively. The effect of reaction temperature (300–420°C) in the ammonoxidation of 4-picoline over VSAPO (A) at 0.5 h⁻¹ W.H.S.V. is depicted in Table 4. With the increase in reaction temperature upto 420–430°C, the yield of 4-cyanopyridine increases.

The ammonoxidation of 4-picoline was studied by varying weight hourly space velocities from 0.25 to 2 h⁻¹ at 420°C and under identical conditions and results are given in Table 5. The highest yields obtained are comparable (>90%) to those reported in literature²⁷.

At 420°C, in the range of 0.25 to 1 h⁻¹ WHSV and picoline: NH₃ molar ratio = 1:15, the yields of 4-cyanopyridine were >80 wt percent and can be increased >90 percent by increasing ammonia-flow¹⁶. The high activity of the catalyst was maintained for more than 10 hours on stream.

Table 5—Amoxidation of 4-picoline over VSAPO (A): Variation of WHSV

Temp. = 420°; picoline: H₂O = 1:5 (volume); catalyst = 4 g; atmospheric pressure; picoline: NH₃ = 1:16 molar

WHSV (h ⁻¹)	Time on stream (h)	Conversion of 4-picoline (wt%)	Yield (wt%) ^a	
			4-Cyanopyridine	Pyridine
0.25	4	98.6	96.5	0.5
0.5	2	89.7	81.4	3.4
1	1	97.0	82.8	3.7
1.5	3+4	41.1	37.7	0.9
2	4	48.1	45.3	0.5

(a) based on 4-picoline.

Table 6—Oxidation of 4-picoline

Catalyst	Temp. (°C)	Time on stream (h)	Conversion of 4-picoline (wt%)	Yield (wt%) ^b		
				4-Pyridine carboxyldehyde	Pyridine	Others
V-SAPO (A)	420	2	94.5	54.7	35.2	4.6
V-SAPO (A) ^a	400	1	80.9	58.5	11.8	10.6
VAPO (B)	420	1	73.3	57.9		14.2
Sb ₂ O ₃ -VSAPO (A)	420	3	98.9	70.1	26.7	2.0

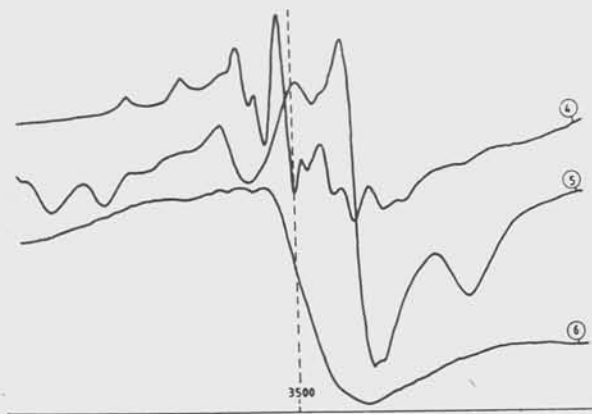
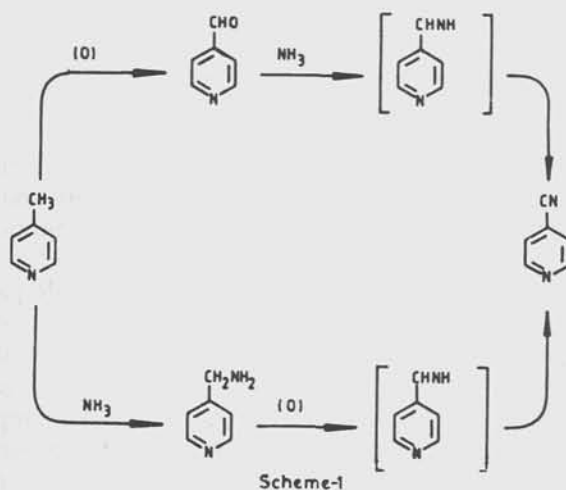
(a) 4-picoline: H₂O = 1:5 (volume); (b) based on 4-picoline.

Fig. 4—ESR spectra of as-synthesized (4) VAPO (TPA-D), (5) VAPO (TPA-D) calcined, and (6) V-SAPO (TPA-A) calcined

Oxidation of 4-picoline

The oxidation of 4-picoline using air and water at 420°C with 0.5 h⁻¹ WHSV over VSAPO (A), VAPO (B) and Sb₂O₃-VSAPO (A) was carried out; and the yields of pyridine-4-carboxaldehyde were 54.7, 57.9 and 70.1 wt percent respectively. The results are given in Table 6.



The reaction of 3- and 4-picolines with ammonia and water in the absence of air has been carried out over VSAPO and VAPO at 420°C and 0.5 h⁻¹ WHSV. But substantial (<5%) amount of 3- and 4-picolylamines was not observed in the products. Hence Scheme 1, reaction-route through aldehyde formation, is recommended. The corresponding carboxylic acid or amide was also not observed in the products. In the case of VSAPO,

tetrahedral V^{4+} , VO_4^- and acidic centres¹⁶ due to the substitution of silicon in place of phosphorus are the active centres and the catalyst is multifunctional. In the case of VAPO, $-VO_4^-$ species, evidenced ESR, are catalytically active in oxidation and ammoxidation reactions.

The ammoxidation of 3-picoline at 420°C and 0.5 h⁻¹ WHSV over VSAPO (A) and VAPO (B) leads to 37.2 and 58.8 wt percent yield of 3-cyanopyridine. The selectivities were > 90 percent for best catalyst. The oxidation of 3-picoline using water and air at 420°C with 0.5 h⁻¹ WHSV over VSAPO (A), VAPO (B) and Sb₂O₃-VSAPO (A) leads to 45.6, 15.0 and 83.3 wt percent of pyridine-3-carboxaldehyde, respectively¹⁶.

Thus we report and emphasize new and a novel class of oxidation and ammoxidation catalytic materials, namely, vanadium-silico-aluminophosphate, APO and SAPO catalysts. The oxidation and ammoxidation of aliphatic⁹, aromatic¹⁶ and heterocyclic alcohols and methyl-substituted compounds have been studied and can be extended for a wide variety of reactions.

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