

Ammoxidation of 3-picoline over vanadium-modified zeolites and crystalline/amorphous silicoaluminophosphate catalysts

R. Ramachandra Rao, S.J. Kulkarni, M. Subrahmanyam, and A.V. Rama Rao
Indian Institute of Chemical Technology, Hyderabad 500 007, India

The oxidation and ammoxidation of 3-picoline over vanadium-modified NaY, H-ZSM-5 (Si/Al = 30), crystalline SAPO (37), and crystalline/amorphous V-silicoaluminophosphate catalysts have been carried out. The yields of 3-cyanopyridine for V-ZSM-5, V-SAPO (37), and V-NaY were 62.6, 76.0, and 1 wt%, respectively. The aluminophosphate framework of SAPO enhances the yield of 3-cyanopyridine, and because of the shape selectivity the high boilers have been decreased in the product. We report vanadium-modified crystalline silicoaluminophosphate as a new class of oxidation and ammoxidation catalysts and compare them with amorphous materials.

Keywords: Ammoxidation; 3-picoline; 3-cyanopyridine; VSAPO (37); V-ZSM-5

INTRODUCTION

Recently zeolite molecular sieves are being used in the synthesis of speciality and fine chemicals.¹⁻¹¹ The oxidation reactions have been carried out over vanadium and titanium silicalites.¹²⁻¹⁴ We have reported one-step ammoxidation of ethanol to acetonitrile over a silicoaluminophosphate (SAPO-40) type catalyst with high yield (>98%) and selectivity.¹⁵ The oxidation and ammoxidation of toluene and benzylalcohol over vanadium-silicoaluminophosphate (V-SAPO) and SAPO catalysts led to corresponding aldehydes and nitriles with high selectivity.¹⁶ Nicotinonitrile and isonicotinonitrile are the resulting nitriles in the ammoxidation of 3-picoline and 4-picoline, respectively. These are important intermediates in the synthesis of pharmaceuticals and agrochemicals.¹⁷ We have reported the oxidation and ammoxidation of 4-picoline to aldehyde and isonicotinonitrile, respectively, with high yield (>90%) and selectivity over V-SAPO catalysts.¹⁸ In the presently known processes, the ammoxidation of picolines has been carried out over non-uniform porous V_2O_5 or α -VOPO₄ supported on Al_2O_3 , $SiO_2-Al_2O_3$, Cr_2O_3 , TiO_2 , etc.¹⁹⁻²⁷ In this paper we report for the first time the oxidation and ammoxidation of 3-picoline over various modified zeolites and crystalline and amorphous SAPO and V-SAPO catalysts. The V-SAPO and VAPO catalysts are either vanadium impregnated and/or incorporated into the matrix or composite catalysts with SAPO molecular sieve as a matrix component.

EXPERIMENTAL

The SAPO molecular sieves are hydrothermally synthesized using aluminum sulfate, phosphoric acid, sodium silicate, with or without sodium chloride and a template at 200°C for 24–80 h at 20 atm autogenous pressure. In the case of V-SAPO, vanadium pentoxide was used. The various SAPOs were synthesized using templates such as tri-*n*-propylamine, di-*n*-propylamine, tetrapropylammonium bromide, and tetramethylammonium bromide, tetrapropylammonium bromide and tetrabutylammonium bromide for SAPO (TriPA), SAPO (DPA), SAPO-37, SAPO (TPA), and SAPO (TBA) types, respectively. V-SAPO(A), VAPO(B), VAPO(C), and VAPO(D) catalysts were prepared using tetrapropylammonium bromide as a template, and the wt% vanadium was 11.7, 8.5, 2.4, and 3.2, respectively. The XRD patterns and i.r. spectra indicate the presence of good crystalline materials. All chemicals were AR or LR grade.

The reaction was carried out using a down-flow, fixed bed, pyrex reactor of 20-mm internal diameter. The reaction mixture was fed from top using a syringe pump (Sage Instruments). Ammonia gas was used. The reaction was carried out in the temperature range of 300–420°C, and the weight hourly space velocity (WHSV) was varied from 0.25 to 1 h⁻¹. The amount of the catalyst was 4 g of 18–30 mesh size. The product was cooled using ice-cooled water and collected at the bottom. The required number of ice-cooled traps was used to collect the total amount of product. The products were analyzed by gas chromatography using a (30%) SE-30 column. The analysis was confirmed by mass spectra, GC-mass. The mass balance was about 90% unless there was extensive coking in presence of less water in the feed.

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Dedicated to Dr. A.V. Rama Rao on his 60th birthday.

Address reprint requests to Dr. Kulkarni.

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Table 1 Ammoxidation of 3-picoline over various vanadium-modified zeolites

Serial no.	Catalyst	Time onstream (h)	Conversion of 3-picoline (wt%)	Yield (wt%)		
				Pyridine	3-Cyanopyridine	Others
1	V-SAPO-37 (10% V)	3	84.5	6.6	76.0	1.9
2	V-SAPO-37 (5% V)	3 + 4	6.2		5.1	1.1
3	V-SAPO-37 (1% V)	1	7.5	0.5	4.1	2.9
4	V-Ti-ZSM-5	4	7.9	0.8	5.9	1.2
5	V-ZSM-5 (10% V)	3 + 4	88.2	19.1	62.6	6.5
6	V-NaY (5% V)	1	35.0	27.7		7.3
7	V-NaY (10% V)	1	37.4	33.6		3.8
8	V-SiO ₂ -Al ₂ O ₃ (10%)	1	39.7	12.4	20.8	6.5

Reaction temperature 400°C; WHSV, 0.5 h⁻¹; 3-picoline:H₂O ratio, 1:3 v/v.

Table 2 Ammoxidation of 3-picoline: Variation of catalysts

Serial no.	Catalyst	Time onstream (h)	Conversion of 3-picoline (wt%)	Yield (wt%)	
				3-Cyanopyridine	Pyridine
1	SAPO (TPA)	1	13.5	10.1	3.4
2	V-SAPO (TPA-A) (11.7% V)	2	52.1	37.2	14.9
3	VAPO(B) (8.5% V)	1	59.0	58.8	0.2
4	VAPO(C) (2.4% V)	1	31.2	30.2	0.9
5	VAPO(D) (3.2% V)	3	16.0	15.9	0.1
6	Sb ₂ O ₃ -VSAPO(A)	1	36.9	35.3	1.6
7	SAPO-(TPA)	2	7.1	6.2	0.2
8	SAPO-(DPA)	2	5.6	5.5	0.1
9	SAPO-37	2	2.5	2.1	0.1
10	SAPO (TBA)	4	5.4	3.8	1.6

Reaction temperature, 420°C; WHSV, 0.5 h⁻¹; catalyst, 4 g; 3-picoline:NH₃, 1:16 molar; 3-picoline:H₂O ratio 1:3 v/v; air flow, 60 ml/min.

Table 3 Ammoxidation of 3-picoline over VAPO(B): Effect of temperature

Serial no.	Temperature (°C)	Time onstream (h)	Conversion of 3-picoline (%)	Yield (wt%)	
				3-Cyanopyridine	Others
1	300	1	6.4	2.2	4.2
2	350	1	28.6	14.7	13.9
3	380	2	44.0	41.8	2.2
4	420	1	59.0	58.8	0.2

WHSV, 0.5 h⁻¹; catalyst 4 g; picoline:NH₃, 1:16 molar; airflow, 60 ml/min; picoline:H₂O ratio 1:3 v/v.

Table 4 Ammoxidation of 3-picoline over V-SAPO-37 (10 wt% V): Effect of weight hourly space velocity

WHSV (h ⁻¹)	Time onstream (h)	Conversion of 3-picoline (wt%)	Yield (wt%)		
			Pyridine	3-Cyanopyridine	Other products
1	4	6.2	0.5	3.0	2.7
0.5	3	84.5	6.6	76.0	1.9
0.25	3 + 4	25.0		19.0	6.0

Reaction temperature, 400°C; 3-picoline:H₂O ratio, 1:3 v/v; atmospheric pressure.

Table 5 Oxidation of 3-picoline: Variation of catalysts

Serial no.	Catalyst	Time onstream (h)	Conversion of 3-picoline (wt%)	Yield (wt%)		
				Pyridine 3-carboxaldehyde	Pyridine	Other
1	V-ZSM-5 (10 wt% V)	3	59.4	14.5	35.8	9.1
2	V-SAPO-37	1	12.4	6.2	4.1	2.1
3	VAPO(B)	2	70.9	45.6	18.1	7.2
4	V-SAPO(A)	1	22.6	15.0	4.5	3.1
5	Sb ₂ O ₃ -V-SAPO(A)	(1 + 2)	36.0	33.5	2.5	
6	SAPO(TPA)	3	9.2	4.3	2.7	2.2
7	SAPO(TBA)	3	5.6	1.6	3.2	0.8

Reaction temperature, 420°C; WHSV, 0.5 h⁻¹; picoline:NH₃, 1:16 molar; catalyst, 4 g; picoline:H₂O ratio, 1:3 v/v.

RESULTS AND DISCUSSION

The results of the amoxidation of 3-picoline to 3-cyanopyridine over V-SAPO-37, ZSM-5, and Y zeolites are given in *Table 1*. The amoxidation of 3-picoline, ammonia, water, and air was carried out at 400°C, 0.5 h⁻¹ WHSV; the picoline:H₂O volume ratio was 1:3. The yields of 3-cyanopyridine were 76.0, 62.5, and ~0.0 over V-SAPO-37, V-ZSM-5, and V-NaY zeolites, respectively. The basically favorable structure of SAPO¹⁵ was modified further with vanadium for the amoxidation of 3-picoline. The selectivity for 3-cyanopyridine over V-SAPO is higher compared with that in V-ZSM-5. All catalysts in the *Table 1* are highly crystalline, and V-SAPO catalysts had ~80% crystallinity.

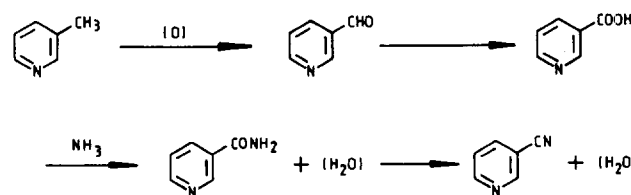
All as-synthesized catalysts in *Table 2* are crystalline. Except for SAPO-37, all other catalysts were almost amorphous after calcination at >400°C. Characterization was done by XRD, i.r., e.s.r., and sorption methods discussed elsewhere.¹⁸ The e.s.r. spectra showed hyperfine splitting and the presence of V⁴⁺ in V-SAPO and VAPO catalysts. The results of the amoxidation of 3-picoline to 3-cyanopyridine over various amorphous V-SAPO catalysts are given in *Table 2*. The reaction of 3-picoline, ammonia, water, and air was carried out at 420°C, 0.5 h⁻¹ WHSV, and the picoline:H₂O volume ratio was 1:3. The yields of 3-cyanopyridine over VAPO(TPA-B), V-SAPO(TPA-A) and Sb₂O₃-V-SAPO(TPA-A) were 58.8, 37.2, and 35.3 wt% based on 3-picoline, respectively. The yield of 3-cyanopyridine was 2–10 wt% over various unmodified amorphous SAPO catalysts.

The effect of reaction temperature in the amoxidation of 3-picoline is depicted in *Table 3*. The yield of 3-cyanopyridine varied from 2.2 to 58.8 wt% in the temperature range of 300–420°C, over amorphous VAPO(B) catalyst. The amoxidation of 3-picoline was studied at various WHSVs over V-SAPO-37 catalyst at 400°C, under identical conditions; the results are shown in *Table 4*. The yields of 3-cyanopyridine were 19.0, 76.0, and 3.0 wt% at 0.25, 0.5, and 1 h⁻¹ WHSV, respectively. The selectivity of 3-cyanopyridine was >75%. At lower (0.25 h⁻¹) WHSV, the selectivity to 3-cyanopyridine was lower, whereas at higher (1 h⁻¹) WHSV the percent conversion of 3-picoline was lower. The highest selectivity and yield for 3-cyanopyridine were obtained at 0.5 h⁻¹ WHSV, as shown in *Table 4*. The reaction of 3-picoline, ammonia, air, and water was

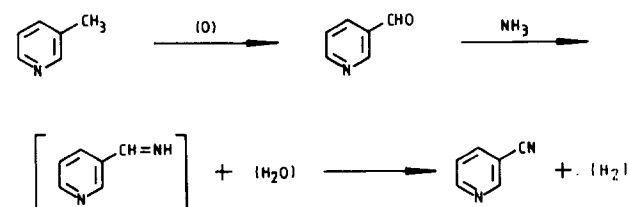
carried out at 420°C and 0.5 h⁻¹ WHSV, as shown in *Table 4*. The reaction of 3-picoline, ammonia, air, and water was carried out at 420°C and 0.5 h⁻¹ WHSV over VAPO(B) catalyst for 15 h onstream. Typically, for the 1st and 3rd onstream, the yields of 3-cyanopyridine were 58.8 and 52.9 wt%, respectively, which decreased to about 30 wt% after the 10th h onstream.

The oxidation of 3-picoline in the presence of air and water was carried out at 420°C and 0.5 h⁻¹ WHSV, and the results are shown in *Table 5*. Over amorphous VAPO(B), 45.6 wt% pyridine 3-carboxaldehyde based on 3-picoline was obtained at 70.9% conversion. The dealkylation of 3-picoline resulted in 18.1 wt% pyridine, but a negligible amount of the corresponding carboxylic acid was observed. The reaction of 3-picoline, ammonia, and water was carried out over the VAPO(B) catalyst at 420°C under identical conditions, but a substantial amount (5 wt%) of 3-picolyamine was not ob-

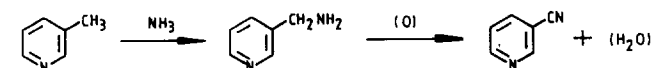
Route (a)



Route (b)



Route (c)

**Figure 1**

served in the products. In brief, the reaction routes are depicted in *Figure 1*. As the corresponding carboxylic acid, amide, and 3-picolylamine were not observed in the products in various reactions by changing feed, the routes (a) and (c) cannot be considered. The presence of 3-pyridine-carboxaldehyde is confirmed in the products. So route (b) in *Figure 1* through carboxaldehyde is recommended. Compared with conventional catalysts such as Bi-Sn-V-Al₂O₃, the side products like carboxylic acid and CO₂ were almost not observed over our catalysts. Similarly, high boilers were reduced because of the shape selectivity of these catalysts. The enhanced selectivity is the major advantage. Thus we report and emphasize the new and novel class of oxidation and ammoxidation catalytic materials, vanadium zeolites and amorphous and crystalline V-SAPO, VAPO and SAPO catalysts. The oxidation and ammoxidation of aliphatic, aromatic, and heterocyclic alcohols and methyl-substituted compounds have been studied and can be extended to a wide variety of reactions.

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