Oxidation and ammoxidation of toluene and benzyl alcohol over silico-aluminophosphate and metal–silico-aluminophosphate catalysts [1,2]

S.J. Kulkarni [a,*], R. Ramachandra Rao [a], M. Subrahmanyam [a],
A.V. Rama Rao [a], A. Sarkany [b], L. Guczi [b]

[a] *Indian Institute of Chemical Technology, Hyderabad 500007, India*
[b] *Institute of Isotopes, Budapest, Hungary*

Abstract

The silico-aluminophosphate (SAPO), vanadium–aluminophosphate (VAPO) and vanadium–silico-aluminophosphate (VSAPO) catalysts were synthesized by hydrothermal method. Depending on silicon and vanadium content, the as-synthesized molecular sieves were thermally stable or unstable up to 400–450°C. The catalysts were characterized by XRD, IR, TG and sorption methods. The oxidation and ammoxidation reactions of toluene and benzylalcohol were carried out over SAPO, VAPO and VSAPO catalysts. The catalysts were selective in the oxidation and ammoxidation of toluene. The yield of benzonitrile was 20–92 wt.-%. The vanadium and Sb_2O_3 modification enhances the yield of benzonitrile substantially. The benzoic acid was not observed in the products. In the ammoxidation of benzylalcohol, the yield of benzonitrile was 18%–74%. The selectivity of benzonitrile was comparatively lower. The reaction scheme is discussed. We report silico-aluminophosphate, VSAPO and TiSAPO, as-synthesized molecular sieves, as a new and novel class of oxidation and ammoxidation catalysts.

Keywords: Toluene ammoxidation; Benzyl alcohol; Benzonitrile; Ammoxidation; SAPO; Vanadium

1. Introduction

Zeolites and recently metal–silico-aluminophosphate molecular sieves are being used in the synthesis of speciality and fine chemicals [1–15]. The

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oxidation reactions have been reported over vanadium- and titanium silicalites [16–18]. We have reported the ammoxidation of ethanol to acetonitrile over silico-aluminophosphate (SAPO-40-type) with high yield (> 98%) and selectivity. Silico-aluminophosphate (SAPO) molecular sieves are mild and selective oxidation and ammoxidation catalysts. The ammoxidation of picolines over SAPO resulted into the corresponding nitriles with low yields (< 40%) and high selectivity [19,20]. The main purpose in using modified molecular sieves in these ammoxidation reactions is to lower the exothermicity and to reduce the high-boiling products in the reaction using the shape selectivity.

In the presently known processes, the ammoxidation of toluene has been carried out over non-uniform porous V_2O_5 or $VOPO_4$ supported over various supports like Al_2O_3, Al_2O_3–SiO_2, TiO_2, Cr_2O_3, ZSM-5, zeolites [21–40], etc. The catalysts were promoted by Sb, Bi, Fe, K, etc. compounds. The yield of benzonitrile vary from 70% to 92%.

In this paper, we report the synthesis, physicochemical characterization and the oxidation and ammoxidation of benzylalcohol and toluene over thermally stable and unstable silico-aluminophosphates (SAPO), vanadium–silico-aluminophosphate (VSAPO) and vanadium–aluminophosphate (VAPO) catalysts of molecular sieve type.

2. Experimental

The SAPO, VSAPO and VAPO type crystalline and amorphous catalytic materials are hydrothermally synthesized using aluminium sulphate, phosphoric acid, sodium silicate, vanadium pentoxide, with or without sodium chloride and tetrapropylammonium bromide (TPA), tetrabutylammonium bromide (TBA), tri-n-propylamine (TriPA), di-n-propylamine (DPA) for SAPO(TPA), SAPO(TBA), SAPO(TriPA) and SAPO(DPA), respectively [41]. The synthesis was carried out at 200°C for 24–80 h at autogenous pressure. All chemicals are LR or AR grade. The synthesis procedure is reported by Borade and Clearfield [41].

X-ray diffraction patterns were taken using Phillips instrument with Fe K α ($\lambda = 1.9359$ Å) and Cu K α ($\lambda = 1.5418$ Å) radiation from $2\theta = 4$ to 70. FT-Infrared spectra were recorded using KBr pellet on Nicolet 740 model (USA). The thermogravimetric studies have been carried out in the temperature range of 50 to 600°C of SAPO(TPA), VSAPO(A) and VAPO(B) catalysts. The ammonia was adsorbed from 1% ammonia in argon and detected by TCD. The temperature programmed desorption (TPD) of ammonia over SAPO(TPA), VSAPO(A), VAPO(B), VAPO(C) and VAPO(D) catalysts was carried out from 26 to 500°C in presence of helium. The n-butylamine (nBA) sorption was carried out over VSAPO(A), VAPO(D), SAPO(TPA), VAPO(C), VAPO(B) and SAPO(TBA) in the temperature range of 25 to 400°C. The catalysts were

activated at 450°C for 1 and 2 h for NH_3 and nBA sorption, respectively. The nBA was sorbed at 30 mm pressure of nBA and the desorption of nBA was carried out in the temperature range of 25 to 400°C under 10^{-5} Torr pressure.

The temperature programmed reduction was carried out in the 9.2 vol.-% H_2 in argon in the temperature range of 25 to 500°C over VAPO(C), VAPO(D) and V_2O_5 catalysts.

The reaction was carried out using a fixed-bed, down-flow, tubular pyrex reactor with 20 mm id. The amount of catalyst was 4 g and activated at 420°C for 4 h, before reaction. The reaction was carried out in the temperature range of 300–400°C, 0.25 to 1 h^{-1} weight hourly space velocity (WHSV). The reaction mixture was fed from the top using a syringe pump (Sage Instruments, USA). The product was cooled using ice-cooled water and collected at the bottom. The ammonia and air were passed through the calibrated manometer and flow-rates were measured. The products were analyzed by SE-30 (30%) and OV-17 columns. The analysis was confirmed by mass spectrometry and GC-mass spectrometry. The mass balance was 90%.

3. Results and discussion

The chemical composition of the catalysts is given elsewhere [19,20]. All the as-synthesized catalysts are crystalline materials. The typical XRD of SAPO(37-type), SAPO(TriPA), SAPO(DPA), SAPO(TBA), VSAPO(TBA) and TiSAPO(TBA) catalysts are given in Figs. 1 and 2. The catalysts with Al/Si > 10 are not thermally stable above 400°C, under our experimental conditions. The IR spectra of SAPO-37, SAPO(DPA), SAPO(TriPA), SAPO(TBA), VSAPO(TBA) and TiSAPO(TBA) catalysts are reported in Figs. 3 and 4. The IR spectra show characteristic patterns corresponding to zeolite molecular sieve. The thermogravimetric (TG) analysis of SAPO(TPA), VSAPO(TPA-A) and VAPO(TPA-B) corresponding to the removal of tetrapropylamine (template) are depicted in Fig. 5. Most of the template is removed up to 450–500°C [41]. The weight loss due to template in the temperature range of 25–500°C was 10.8, 9.9 and 6.3 wt.-% for SAPO(TPA), VAPO(B) and VSAPO(A) catalysts, respectively. The number of tetrapropylamine cationic species corresponding to this weight loss were $3.782 \cdot 10^{20}$, $3.493 \cdot 10^{20}$ and $2.229 \cdot 10^{20}$ molecules per g, respectively. The occlusion of template and the temperature at which the template decomposes compare to literature, indicating that the as-synthesized material was of molecular sieve type which may be destroyed during the removal of template.

The temperature programmed desorption (TPD) of ammonia for SAPO(TPA), VSAPO(TPA-A), VAPO(B), VAPO(C) and VAPO(D) catalysts is depicted in Fig. 6. The amount of ammonia desorbed (molecules per g) in the different temperature ranges from various VAPOs and SAPO(TPA) is given in Table 1. The total number of ammonia molecules sorbed were $8.7 \cdot 10^{19}$, $5.3 \cdot 10^{19}$,
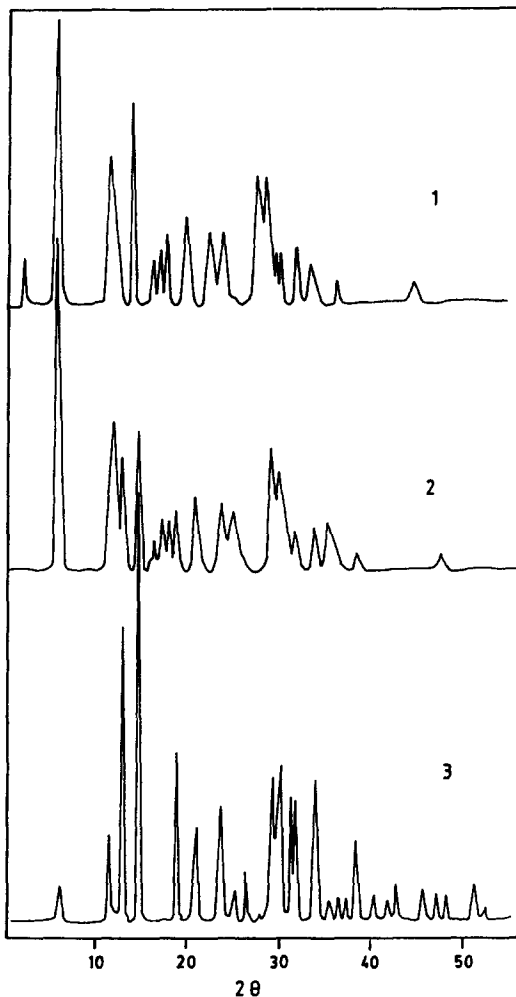
Fig. 1. X-ray powder diffraction profiles of (1) SAPO-37, (2) SAPO(TriPA), (3) SAPO(DPA).

$2.7 \cdot 10^{19}$, $3.1 \cdot^{19}$ and $2.9 \cdot 10^{19}$ per g over SAPO(TPA), VSAPO(A), VAPO(B), VAPO(C) and VAPO(D) catalysts, respectively. The trend corresponding to the acidic strength of catalysts is as follows SAPO(TPA) > VSAPO(A) $\simeq$ VAPO(C) $\simeq$ VAPO(D) > VAPO(B). The NH_3-TPD curves also showed the same trend and indicates that SAPO(TPA) is the most acidic with respect to number and strength of acidic centres. The incorporation of vanadium does not increase the acidity. Borade and Clearfield [41] reported the TPD of ALPO-5, SAPO-5, -11, 34 and 37 molecular sieves. The medium-strong acidic centres are present over SAPOs. Su and Barthomeuf [42] reported that the heating of SAPO-37 at 700°C results into the transformation of some acidic centres to stronger acidic centres than those in HY. The results of sorption of nBA over SAPO and VAPOs are given in Table 2. The total number of nBA molecules per
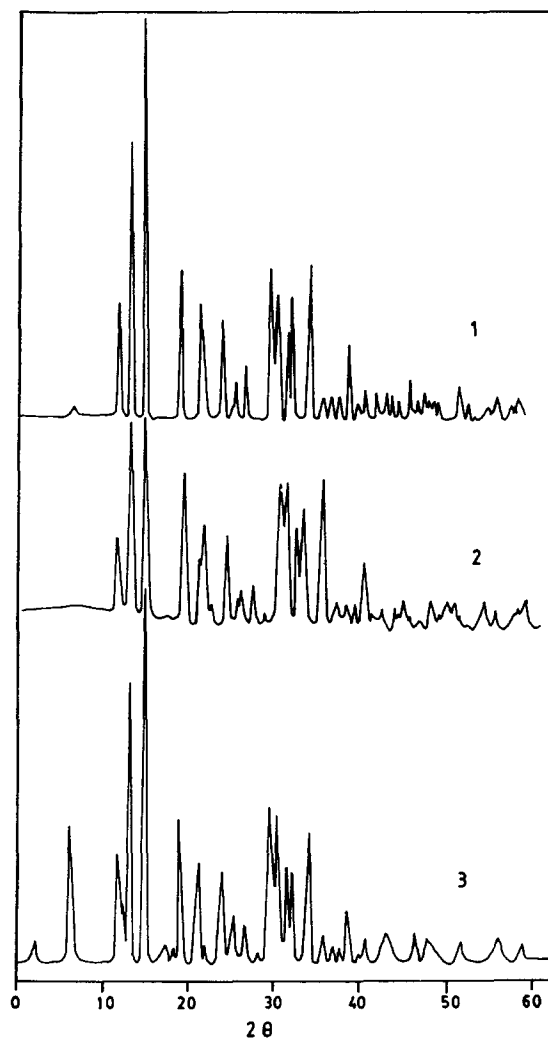
Fig. 2. X-ray powder diffraction profiles of (1) SAPO(TBA), (2) VSAPO(TBA), (3) TiSAPO(TBA).

g, sorbed over SAPO(TPA), SAPO(TBA), VSAPO(A), VAPO(B), VAPO(C) and VAPO(D) were $13.6 \cdot 10^{19}$, $6.7 \cdot 10^{19}$, $3 \cdot 10^{19}$, $1.9 \cdot 10^{19}$, $1.4 \cdot 10^{19}$ and $1.8 \cdot 10^{19}$, respectively. The acidity trend for various catalysts is similar in case of nBA and ammonia. During the desorption of nBA some interesting observations were made. In case of SAPO(TPA) and VAPO(D) catalysts, the desorption of nBA up to 300°C takes place depending upon acidic strength of active centres. In case of VSAPO(A), VAPO(B), VAPO(C) particularly, nBA was decomposed in the temperature range of 100–200°C. The loss of catalyst weight was observed in case of VSAPO(A) and VAPO(B) and VAPO(C) catalysts, if heated up to 300°C after the sorption of nBA. This was due to the removal of
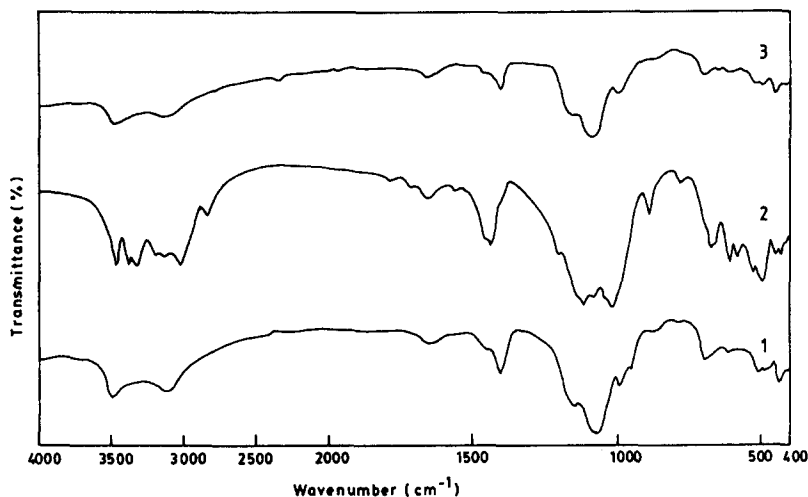
Fig. 3. IR spectra of (1) SAPO-37, (2) SAPO(DPA), (3) SAPO(TriPA).

framework oxygens which are strongly interacting with basic molecules like nBA. This observation may be possible only in case of the catalyst being very active in oxidation and ammoxidation reactions, indicating the presence of labile framework oxygen which can be exchanged with atomic oxygen. The temperature programmed reduction of VAPO(C), VAPO(D) and V_2O_5 was carried out in presence of 9.2 vol.-% H_2 in argon. For all the three materials, the peak position was the same at ca. 450°C. This indicates that vanadium in these catalysts cannot be reduced easily and is stable under the reducing conditions.

3.1. Ammoxidation of toluene

The ammoxidation of toluene was carried out over SAPO and VSAPO molecular sieves at 400°C and 0.5 h^{-1} WHSV and the results are given in Table 3. The maximum yield corresponding to the time on stream is reported. The yields of benzonitrile were 21.6, 28.7, 61.2 and 8.9 wt.-% at 23.1%, 29.8%, 63.5% and 18.3% conversions over SAPO-37, VSAPO-37, VSAPO(TriPA) and SAPO(DPA) molecular sieves, respectively.

The ammoxidation of toluene was carried out in presence of ammonia and air at 420°C and 0.5 h^{-1} WHSV over amorphous (thermally unstable) SAPO catalysts and the results are depicted in Table 4. The catalysts reported in Table 4 were amorphous with a probable presence of microcrystallinity. The materials were synthesized by the same hydrothermal method and as-synthesized catalysts were crystalline showing mostly molecular sieve structure with some phase impurities. The yields of benzonitrile were 23.5, 56.7, 47.6, 43.5 and 30.2 wt.-% at 25.2%, 67.8%, 50.9%, 46.6% and 31.5% conversion over SAPO(TPA), SAPO(TriPA), SAPO(DPA), SAPO-37 and SAPO(TBA) catalysts, respectively.
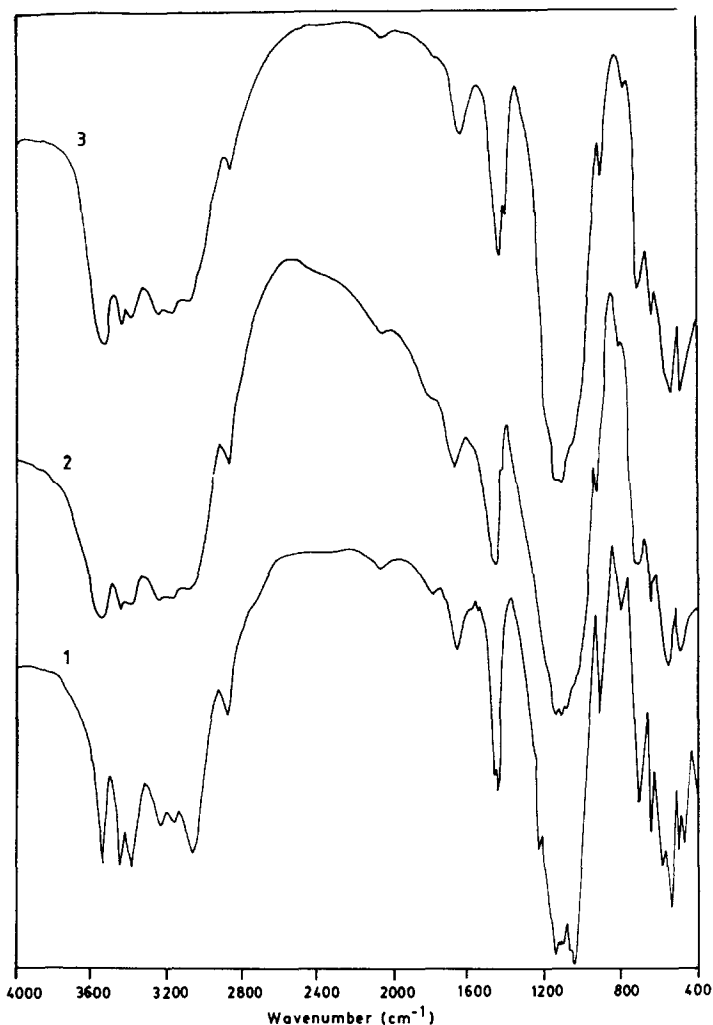
Fig. 4. IR spectra of (1) SAPO(TBA), (2) VSAPO(TBA), (3) TiSAPO(TBA).

The ammoxidation of toluene was carried out at 420°C and 0.5 h^{-1} WHSV over various vanadium modified aluminophosphate catalysts. The as-synthesized catalysts reported were crystalline composites. After calcination at 420°C for 4 h, the catalysts in Table 5 became mostly amorphous with a probable presence of microcrystallinity. The yields of benzonitrile were 94.7%, 61.9% and 68.9% at 97.3%, 71.9% and 73.3% conversion over Sb_2O_3–VSAPO(A), VSAPO(A) and VAPO(B) catalysts, respectively. The vanadium and antimony showed strong promoting effect in enhancing the ammoxidation activity.

The influence of temperature over the ammoxidation activity of Sb_2O_3–VSAPO(A) was studied and given in Table 6. The yields of benzonitrile were 53.1, 69.4 and 94.7 wt.-% at 71.5%, 70.5% and 97.3% conversion at 350, 380
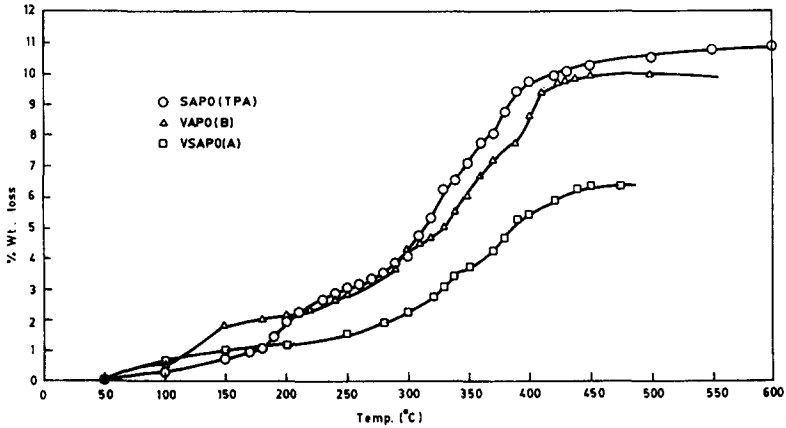
Fig. 5. Thermogravimetric analysis of the SAPO(TPA), VAPO(TPA-B), VSAPO(TPA-A) as-synthesized catalysts.

and 420°C, respectively. In case of non-zeolitic, conventional catalysts, the formation of carboxylic acid and CO_2 was observed. On the other hand, in case of VSAPOs or VSAPO-type materials, carboxylic acid or amide was not formed as a result of oxidation. This leads to the improvement of selectivity of benzonitrile and exothermicity is reduced. The effect of WHSV in the ammoxidation of toluene over Sb_2O_3–VSAPO(A) was studied and results are given in Table 7. The WHSV was varied from 0.25 to 1 h^{-1}. The yield and selectivity of

Fig. 6. Temperature-programmed desorption of ammonia.

Table 1
Desorption of ammonia over SAPO and VAPO catalysts

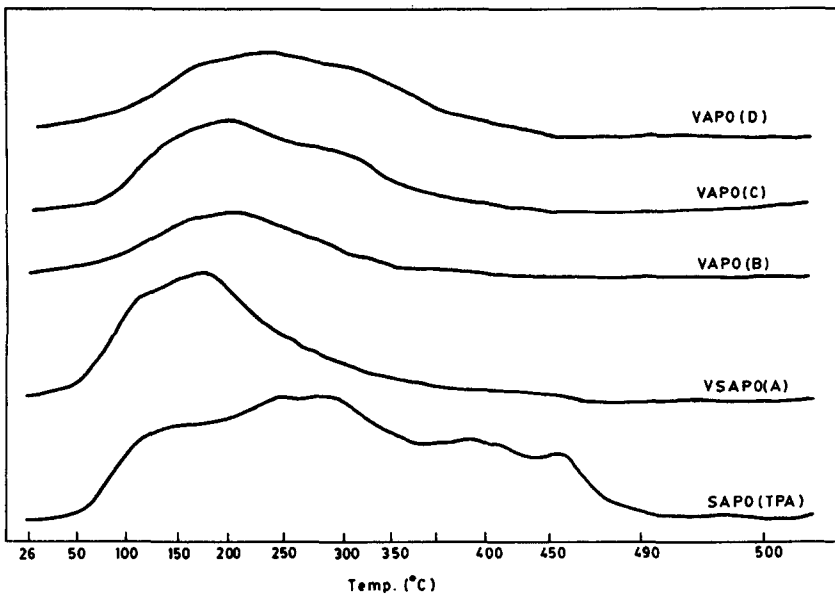| S. No.	Catalyst	Ammonia molecules desorbed per g ($\times 10^{19}$ mol/g)				
		20–150°C	150–250°C	250–350°C	350 and above	Total No. of molecules sorbed at 20°C
1	SAPO(TPA)	1.8	2.0	1.7	3.2	8.7
2	VSAPO(TPA-A) (11.7%V)	2.1	1.9	0.8	0.5	5.3
3	VAPO(TPA-B) (8.5%V)	1.0	0.9	0.3	0.5	2.7
4	VAPO(TPA-C) (2.4%V)	0.9	1.0	0.9	0.3	3.1
5	VAPO(TPA-D) (3.2%V)	0.8	0.9	0.9	0.3	2.9

Table 2
Sorption of nBA over SAPO and VAPO catalysts

S.No.	Catalyst	No. of nBA molecules sorbed per g			
	Temperature (°C)	25	100	200	300
1	VSAPO(TPA-A)	$3 \cdot 10^{19}$	$1.2 \cdot 10^{19}$	$5.1 \cdot 10^{19}$	–
2	VAPO(TPA-B)	$1.9 \cdot 10^{19}$	–	–	–
3	VAPO(TPA-C)	$1.4 \cdot 10^{19}$	$1 \cdot 10^{19}$	$0.74 \cdot 10^{19}$	–
4	VAPO(TPA-D)	$1.8 \cdot 10^{19}$	$0.74 \cdot 10^{19}$	$0.5 \cdot 10^{19}$	$0.4 \cdot 10^{19}$
5	SAPO(TPA)	$13.6 \cdot 10^{19}$	$9.7 \cdot 10^{19}$	$7.9 \cdot 10^{19}$	$6.2 \cdot 10^{19}$
6	SAPO(TBA)	$6.7 \cdot 10^{19}$	–	–	–

Table 3
Ammoxidation of toluene over SAPO and VSAPO molecular sieves

S. No.	Catalyst	Time on Stream (h)	Conversion of of Toluene (%)	Yield (wt.-%) [a]	
				Benzonitrile	Other products
1	SAPO-37	2 + 3	23.1	21.6	1.5
2	VSAPO-37	4	29.8	28.7	1.1
3	VSAPO(TriPA)	4	63.5	61.2	2.3
4	SAPO(DPA)	4	18.3	8.9	9.4

[a] Based on toluene.
Reaction temperature = 400°C; catalyst = 4 g; WHSV = 0.5 h^{-1}; toluene:NH_3 = 1:5 (molar); air flow 60 ml/min.

Table 4
Ammoxidation of toluene over different SAPO catalysts

S.No.	Catalyst	Time on Stream (h)	Conversion of Toluene (%)	Yield (wt.-%) [a]	
				Benzonitrile	Other products
1	SAPO(TPA)	4	25.2	23.5	1.7
2	SAPO(TriPA)	5	67.8	56.7	11.1
3	SAPO(DPA)	2	50.9	47.6	3.3
4	SAPO-37	4	46.6	43.5	3.1
5	SAPO(TBA)	3	31.5	30.2	1.2

[a] Based on Toluene
Reaction temperature = 420°C; catalyst = 4 g; WHSV = 0.5 h^{-1}; toluene:NH_3 = 1:5 (molar); air flow = 60 ml/min.

Table 5
Ammoxidation of toluene over various catalysts

S. No.	Catalyst	Time on Stream (h)	Conversion of Toluene (%)	Yield (wt.-%) [a]		
				Benzaldehyde	Benzonitrile	▶ Others
1	Sb_2O_3–VSAPO(A)	1	97.3	–	94.7	2.6
2	VSAPO(A)	2	71.9	–	61.9	10
3	VAPO(B)	3 + 4	73.3	–	68.9	4.4
4	VAPO(C)	2	30.5	9.4	19.8	1.3
5	VAPO(D)	2	15.1	–	12.4	2.7
6	VSAPO(TBA)	4	26.0	–	24.0	2.0
7	TiSAPO(TBA)	4	37.4	–	35.5	1.9

[a] Based on Toluene
Reaction Temperature = 420°C; Catalyst = 4 g; WHSV = 0.5 h^{-1}; toluene:NH_3 = 1:5 (molar).

Table 6
Ammoxidation of toluene at different temperatures over Sb_2O_3–VSAPO(A) catalyst

S. No.	Temperature (°C)	Time on Stream (h)	Conversion of Toluene (%)	Yield (wt.-%) [a]	
				Benzonitrile	other products
1	300	2 + 3	24.9	24.9	–
2	350	3	71.5	53.1	18.4
3	380	4	70.5	69.4	1.1
4	400	4	73.8	71.4	2.4
5	420	1	97.3	94.7	2.6

[a] Based on Toluene
Catalyst = 4 g; WHSV = 0.5 h^{-1}; toluene:NH_3 ratio = 1:5 (molar); air flow = 60 ml/min.

Table 7
Ammoxidation of toluene over Sb_2O_3–VSAPO(A): Effect of WHSV

S. No.	Catalyst	WHSV	Time on Stream (h)	Conversion of Toluene (%)	Benzonitrile (wt.-%)	Others [a]
1	Sb_2O_3–VSAPO(A)	0.25	3	100	77.4	22.6
2	Sb_2O_3–VSAPO(A)	0.37	3	72.2	65.8	6.4
3	Sb_2O_3–VSAPO(A)	0.50	1	97.3	94.7	2.6
4	Sb_2O_3–VSAPO(A)	0.75	3	95.3	80.5	14.8
5	Sb_2O_3–VSAPO(A)	1.0	1	45.2	39.2	7.8

[a] Aliphatics.
Reaction Temperature = 420°C; catalyst = 4 g; air flow = 60 ml/min.

benzonitrile increased from 0.25 to 0.5 h^{-1} and then decreased above 0.5 h^{-1} WHSV. The ammoxidation of toluene was carried out over SAPO(TriPA) at 400°C and 0.5 h^{-1} WHSV for 10 h on stream. During 10 h on stream, the yield of benzonitrile varied from 46 to 55.0 wt.-% and the catalyst showed no deactivation for at least 10 h. The results are given in Table 8.

Table 8
Ammoxidation of toluene over SAPO(TriPA) catalyst: Time on stream

Time on stream (h)	Conversion of Toluene (%)	Yield (wt.-%) [a]	
		Benzonitrile	Others
1	36.8	35.1	1.7
2	48.7	46.5	2.2
3	53.4	48.2	5.2
4	51.3	50.0	1.3
5	56.8	55.7	1.1
8 + 9	51.3	50.2	1.1
10	56.5	55.3	1.2

[a] Based on toluene.
Reaction temperature = 420°C; WHSV = 0.5 h^{-1}; air flow = 60 ml/min, toluene:NH_3 = 1:5 (molar).

The oxidation of toluene to benzaldehyde was carried out at 420°C and 0.5 h^{-1} WHSV. The results are given in Table 9. The yields of benzaldehyde were 12.5, 6.1, 9.0, 8.1 and 19.4 over SAPO(TPA), SAPO(TBA), SAPO(TriPA), SAPO(37) and VSAPO(A) catalysts, respectively. The lower yields of benzaldehyde indicates that the oxidation step is rate controlling in the ammoxidation of toluene.

3.2. Ammoxidation of benzylalcohol

The ammoxidation of benzylalcohol was carried out at 420°C and 0.5 h^{-1} WHSV. The maximum yields of benzonitrile were 14.6, 29.7, 23.8, 30.2 and 32.8 wt.-% at 28.0, 39.0, 41.3, 40.3 and 75.4% conversions over SAPO(TPA), SAPO(TBA), SAPO(TriPA), SAPO(DPA) and SAPO-37 catalysts, respectively. The results are depicted in Table 10. The side products were toluene and benzene. The SAPOs, thermally stable and unstable, catalysts are mild oxidation

Table 9
Oxidation of toluene to benzaldehyde over various catalysts

S. No.	Catalyst	Time on Stream (h)	Conversion of Toluene (%)	Yield (wt.-%) [a]	
				Benzaldehyde	Others
1	SAPO(TPA)	2	16.7	12.5	4.2
2	SAPO(TBA)	1	13.9	6.1	7.8
3	SAPO(TriPA)	1	17.8	9.0	8.8
4	SAPO(DPA)	4	7.7	2.1	5.6
5	SAPO-37	4	11.9	8.1	3.8
6	VSAPO(TBA)	3	10.6	6.7	3.9
7	VSAPO(A)	3	32.0	19.4	12.6
8	Sb_2O_3–VSAPO(A)	1	23.0	7.9	15.1

[a] Based on toluene.
Reaction temperature = 420°C; WHSV = 0.5 h^{-1}.

Table 10
Ammoxidation of Benzyl alcohol over various SAPO catalysts

S. No.	Catalyst	Time on Stream (h)	Conversion of Benzyl alcohol (%)	Yield (wt%) [a]	
				Benzonitrile	Other products [b]
1	SAPO(TPA)	4	28.0	14.6	13.4
2	SAPO(TBA)	1	39.0	29.7	9.3
3	SAPO(TriPA)	1	41.3	23.8	17.5
4	SAPO(DPA)	2	40.3	30.2	10.1
5	SAPO-37	1	75.4	32.8	42.6

[a]) Based on Benzyl alcohol; b) Toluene is the major product (> 90%).
Reaction temperature = 420°C; WHSV = 0.5 h^{-1}; catalyst = 4 g; Benzyl alcohol: NH_3 ratio = 1:5 molar.

Table 11
Ammoxidation of Benzyl alcohol over different modified catalysts

S. No.	Catalyst	Time on Stream (h)	Conversion of Benzyl alcohol (%)	Yield (wt%) [a]		
				Benzonitrile	High boilers	Other products
1	VSAPO(TPA-A)	1	92.0	73.7	–	18.3
2	VSAPO(TPA-B)	1	68.8	29.7	22.3	16.8
3	VAPO(TPA-C)	2	95.8	34.7	29.1	32.0
4	VSAPO(TPA-D)	1	75.1	53.7	–	21.4
5	Sb_2O_3–VSAPO(TPA)	2	91.8	51.5	26.5	13.8
6	TiSAPO(TBA)	1	63.1	58.7	–	4.4
7	VSAPO(TBA)	1	30.4	18.2	–	12.2

[a]) Based on benzylalcohol; Reaction Temperature = 420°C; WHSV = 0.5 h^{-1}; Catalyst = 4 g; Benzyl alcohol:NH_3 = 1:5 (molar); Air flow = 60 cc/min.

catalysts. The selectivity for benzonitrile was reduced due to the acid catalysed reactions like dealkylation.

The results of ammoxidation of benzylalcohol over vanadium modified SAPO/APO catalysts are given in Table 11. The yields of benzonitrile were 73.7, 53.7 and 51.5 wt.-% at 92.0, 75.1 and 91.8% conversions over VSAPO(A), VAPO(D) and Sb_2O_3–VSAPO(A), respectively, at 420°C. This indicates that incorporation of vanadium increases the ammoxidation of benzylalcohol. On the other hand, the promoting effect of Sb_2O_3 was more pronounced in toluene ammoxidation. In case of benzylalcohol ammoxidation the by-products were more, 12% to 32%, than those observed in toluene reaction. This may be because of the VSAPO catalysts showed mild and selective in toluene ammoxidation, while strongly active and less selective in benzylalcohol reaction.

The oxidation of benzylalcohol was carried out at 420°C and 0.5 h^{-1} WHSV over SAPO and VSAPO catalysts and results are given in Table 12. The yields of benzaldehyde were 49.1, 35.2 and 28.4 wt.-% at 59.1, 51.5 and 48.5% conversion over SAPO(TBA), SAPO-37 type and VSAPO(TPA-D) catalysts, respectively. It is evident from the data in Tables 11 and 12 that TiSAPO is

Table 12
Oxidation of Benzyl alcohol to Benzaldehyde over various catalysts

S.No.	Catalyst	Time on Stream (h)	Conversion of Benzyl alcohol (%)	Yield (wt%)	
				Benzyldehyde	Others [a]
1	SAPO(TBA)	1	59.1	49.1	10.0
2	VSAPO(TBA)	2	19.5	11.3	8.2
3	TiSAPO(TBA)	3 + 4	36.8	35.6	1.2
4	SAPO(TriPA)	2	31.8	25.3	6.5
5	SAPO(TPA)	4	38.8	9.8	29.0
6	SAPO-37	2	51.5	35.2	16.3
7	VAPO(TPA-D)	2	48.5	28.4	20.1

Reaction temperature = 420°C; WHSV = 0.5 h^{-1}; Catalyst = 4 g; Air = 60 ml/min. a) including Toluene (> 90%).

more selective than VSAPO in oxidation and ammoxidation, while VSAPO is more active.

3.3. Reaction scheme and mechanism

The reaction scheme considered in the reaction of toluene to benzonitrile is depicted in Fig. 7. In our studies, we have not observed benzoic acid or amide as by-products. In the oxidation of toluene in air and absence of ammonia, benzoic
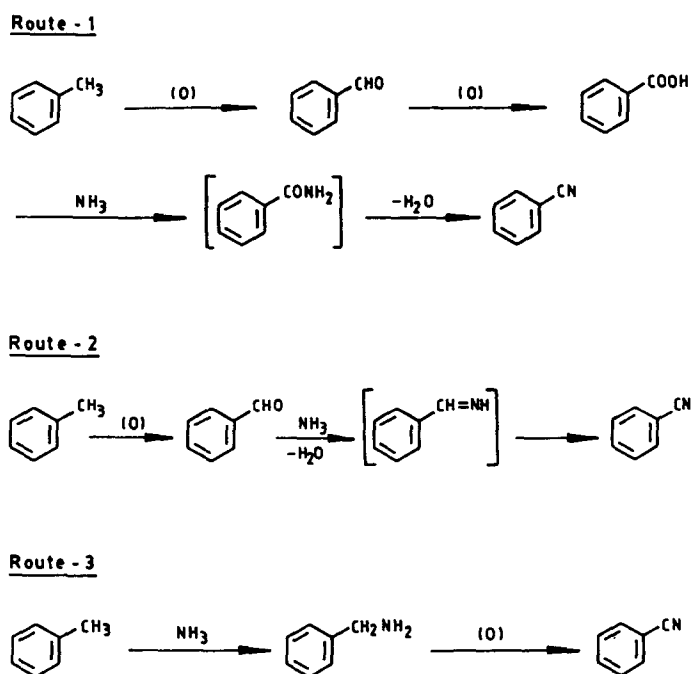

Fig. 7. Reaction routes considered in the reaction of toluene to benzonitrile.

acid was not observed. Similarly, in the reaction of toluene with ammonia, in the absence of air, benzylamine was not observed. This indicates that Routes 1 and 3 are not valid. We have observed the formation of benzaldehyde as reported. So, benzonitrile is formed from toluene and also benzylalcohol via the formation of benzaldehyde and corresponding imine and Route 2 is recommended. In case of non-zeolitic, mixed oxide catalysts, the presence of benzoic acid, CO_2 and benzoate ion as intermediate has been established [21].

In case of SAPO catalysts, Brønsted (and Lewis) acidic centres [41], due to the substitution of silicon in place of phosphorous, mild basic centres which are discussed by Akolekar et al. [43] and probably oxygen vacancies are the active centres. In case of VSAPO, tetrahedral V^{4+}, $-VO_4-$, acidic centres and oxygen vacancies are the active centres. While in case of VAPO catalysts V^{4+}, $-VO_4-$ species, Lewis acidic centres (mainly) and oxygen vacancies are the active centres in the oxidation and ammoxidation reactions. The catalysts are multifunctional. The presence of V^{4+}, VO^{2+}, V_2O_4 and $-VO_4-$species is predicted by ESR data, particularly [19,20]. The test reaction of cyclohexanol has been carried out over some SAPO and VSAPO catalysts [44,45]. The formation of cyclohexene and cyclohexanone indicates the presence of acidic and basic centres, respectively. The presence and nature of acidic centres in HSAPO-37 is reported by Su and Barthomeuf [42].

Kim and Chon [35] reported the ammoxidation of toluene over Cu-Na-ZSM-5. They have discussed the changes in the reaction pattern for ammoxidation of toluene in terms of the stability of $(Cu^{II}(NH_3(tol.))$ and the mechanism differs compared to the non-zeolitic catalysts. The nature of vanadium species and the reaction mechanism have been discussed in the literature [21]. The formation of benzaldehyde from toluene occurs particularly on V^{4+}, VO^{2+} or V_2O_4 type of species [29]. The presence of V^{4+} in VSAPO and VAPO catalysts have been confirmed by ESR studies [19,20]. On the other hand, the formation of benzoic acid from toluene occurs on V^{5+} or V_2O_5 species [29]. Another more important factor is the oxygen mobility and supply on the catalyst surface. Rizayev et al. [21] reported that the aromatic nitriles are produced as a result of the interaction of toluene, ammonia and active catalytic surface. The role of gas phase oxygen is to oxidize catalytic surface, i.e., to reduce V^{5+} to V^{4+} and fill the oxygen vacancies. The oxygen vacancies are also filled by bulk oxygen [21], through diffusion. The layered structure present in the ammoxidation catalysts like $V_2O_5-MoO_3$, $V_2O_5-P_2O_5$ or BiO_3-MoO_3 facilitates the diffusion of bulk oxygen to the external surface. Our VSAPO and VAPO catalysts are heterophasic and almost all the ammoxidation catalysts are having redox active centres and multifunctional. This indicates that along with the incorporation of vanadium or titanium into the framework of SAPO; the impregnation, particularly stepwise or simultaneous, with strong metal–framework interaction in SAPO, should be the properly tailored ammoxidation catalyst.

Due to the lack of specific and uniform geometrical structure in case of

non-zeolitic catalysts, the mechanism of alternate reduction and oxidation of the catalyst surface and oxygen migration at high temperatures ($> 400°C$) occur throughout the catalyst. This type of continuous variation of the catalytic surface may lead to rapid deactivation and sensitive to various parameters like pressure, temperature, etc. On the other hand, in general, zeolite framework is quite stable with respect to the redox conditions and oxygen is generally supplied to the surface from gas phase to the oxygen vacancies. Even the carbonaceous material deposited on the redox surface may be responsible for the ammoxidation activity [21], which is generally characterised by the increase in activity with time on stream. In addition, as a source of nitrogen ammonia reduces catalytic surface and reduces the strong acidic centres and helps in reducing side reactions in ammoxidation [21]. In absence of ammonia as a nitrogen source, the toluene deep oxidation may occur predominantly resulting into carbon dioxide. But, such possibility is very much reduced over promoted silicoaluminophosphates due to its mild and medium strength activity in the presence of ammonia.

Thus, SAPO, VAPO and VSAPO catalysts, thermally stable or unstable molecular sieves, synthesized by hydrothermal method, are good and a new class of oxidation and ammoxidation catalysts.

Acknowledgements

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