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Letter

Dehydrogenation of 2-picolyl alcohol to pyridine-2-carboxaldehyde over modified silico-aluminophosphate catalysts

R. Ramachandra Rao, S.J. Kulkarni^{*}, M. Subrahmanyam, A.V. Rama Rao

Indian Institute of Chemical Technology, Hyderabad-500 007, India

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Abstract

The dehydrogenation of 2-picolyl alcohol was carried out over modified and unmodified amorphous/crystalline silico-aluminophosphate catalysts. The silico-aluminophosphates are mild and selective oxidation catalysts. The best catalytic performance is shown by Sb-K-SAPO (DPA) with the formation of 81.9% pyridine-2-carboxaldehyde. Pyridine and 2-picoline were also observed as byproducts.

Keywords: Silico-aluminophosphate catalysts; Dehydrogenation; 2-Picolyl alcohol; Pyridine-2-carboxalde-hyde

1. Introduction

Zeolite molecular sieves are being used in the syntheses of specific and fine chemicals [1-17]. 2-Picolyl alcohol (2-pyridylmethanol) and pyridine-2-carboxaldehyde (pyridine-2-carbaldehyde) are useful intermediates in pharmaceuticals [18]. Pyridine-2-carboxaldehyde is used in the preparation of pralidoxime methiodide which is an antidote for poisoning by organophosphate acetylcholinesterase inhibitors. Pyridine-2-carboxaldehyde is also used in the production of bisacodyl, a laxative [18]. Papodopoulous et al. [19] reported the

^{*} Corresponding author.

synthesis of pyridine-carboxaldehyde from picolyl alcohol over manganese dioxide and Subrahmanyam and Prasad [20] over V-Mo oxide catalyst. Pyridine-2-carboxaldehyde is also synthesized from 2-picoline [21].

In this paper we report the synthesis of pyridine-2-carboxaldehyde from 2-picolyl alcohol over crystalline and amorphous silico-aluminophosphates (SAPO) and modified SAPO catalysts.

2. Experimental

The silico-aluminophosphate (SAPO), and vanadium-silicoaluminophosphate (VSAPO) were synthesized using aluminum sulphate, phosphoric acid, sodium silicate, vanadium pentoxide with or without sodium chloride and tetrapropylammonium bromide (TPA), tetrabutylammonium bromide (TBA), tri-n-propylamine (Tri-PA), or di-n-propylamine (Di-PA) for SAPO (TPA), SAPO (TBA), SAPO (Tri-Pa) or SAPO (Di-PA) catalysts, respectively. The detailed procedure of synthesis is reported in the literature [22–24].

The silico-aluminophosphate-37 (SAPO-37) molecular sieve was synthesized as follows. The composition of the initial slurry was as follows: $1 \text{ Al}_2\text{O}_3$:1 P₂O₅:0.4 SiO₂:1 TPABr:0.05 TMABr:0.02 M where M is the transition metal cation if present. The nitrates of transition metals were used for synthesis. For a typical synthesis, 31.5 g of $Al_2(SO_4)_3 \cdot 16H_2O$ or 20.4 g of aluminum isopropoxide was dissolved in 100 ml distilled water. 9.8 g of orthophosphoric acid was added slowly and stirred well. 26.6 g of tetrapropylammonium bromide and 0.77 g of tetramethylammonium bromide were added and stirred for about 2 h. 11.3 g of sodium silicate or 8.3 g of tetraethylorthosilicate or 2.4 g of colloidal silica was taken in 50 ml distilled water in a beaker and added slowly with stirring to the above mixture. The pH of the slurry was adjusted to 6.7 using ammonia solution. The slurry was stirred for about 4 h. Then the slurry was transferred to the autoclave. The crystallization was carried out at 200°C for 24-80 h at autogenous pressure. All chemicals were LR or AR grade. After cooling, the material was washed with distilled water and dried in an oven. All catalysts were calcined at 400-450°C for about 12 h to remove the template. In the synthesis of MSAPO-37, the nitrate solution of transition metal was added just before the addition of templates to the reaction mixture. For the syntheses of all the silico-aluminophosphates the same initial composition was used. The physico-chemical characterization is reported elsewhere [22,23].

The reaction was carried out using a fixed-bed, down-flow, tubular pyrex reactor with 20 mm internal diameter. The amount of catalyst was 4 g (18–30 mesh size) and activated at 400°C for 4 h before the reaction. The reaction temperature, weight hourly space velocity (W.H.S.V.) were varied for a typical catalyst. The reaction mixture was fed from top using a syringe pump (Sage

Sl. no.	Catalyst	Time on	Conversion	Yield (wt%)				
		stream (h)	of 2-picolyl alcohol (%)	Pyridine	2-Picoline	Pyridine-2- carboxal- dehyde	Other	
1	SAPO (TPA)	1	29.6	1.1	0.9	20.7	6.9	
2	SAPO (DPA)	4	99.9	13.5	14.8	69.1	2.5	
3	SAPO (Tri-PA)	3	95.1	10.3	13.3	65.4	6.1	
4	SAPO-37	3 + 4	100.0	19.2	25.9	53.2	1.7	
5	VSAPO (TBA) (5 wt% V)	1	100.0	14.3	35.8	10.4	39.5	
6	VSAPO (TPA.A) (11.7% V)	1	98.8	50.5	20.6	22.5	5.2	
7	SAPO (Tri-PA) ^a	3 + 4	83.5	1.0	43.8	35.5	3.2	
8	K-SAPO (DPA) (5% K)	(3+4)	100.0	14.7	9.7	70.6	5.0	
9	Sb-K-SAPO ^b (DPA) (5% K, 1% Sb)	2	98.0	7.2	5.3	81.9	3.6	
10	HZSM-5 (30) ^b	2	98.2	76.3	12.9	1.4	7.6	
11	V-TiZSM-5 ^b (3% V, 3% Ti)	2	100.0	45.9	31.3	2.2	20.6	

Table 1 Dehydrogenation of 2-picolyl alcohol: variation of catalysts

Reaction temperature = 400°C, 2-picolyl alcohol: $H_2O = 1:3$ volume ratio, WHSV = 0.5 h⁻¹, flow rate of air = 6 ml/min.

^a Air was not used.

^b Reaction temperature = 380°C.

Instruments, USA). The product was cooled using ice-cooled water and collected at the bottom. The air was passed through the calibrated manometer. The products were analyzed by GC using SE-30 (30%) column. The analysis was confirmed by mass spectra and GC-mass. The mass balance was > 90%.

3. Results and discussion

All the as-synthesized catalysts in Table 1 were crystalline, but after removal of template (> 400°C in air) they lost 90% crystallinity. SAPO-37 was > 80%, and HZSM-5 catalysts were > 95% crystalline and are typical molecular sieves. The ESR spectra showed hyperfine splitting and the presence of V⁴⁺ oxidation state in vanadium modified catalysts [23]. The g_{\perp} and g_{\parallel} values of VSAPO (TPA.A) are typically 2.044 (g_{\perp}) and 2.0221 ($_{\parallel}$). The g values indicate the presence of V–O bonding. The presence of broad singlet in ESR of calcined VSAPO (TPA.A) is due to the dipole–dipole interaction in V–O–V linkages with 5.1 Å distance between vanadium ions [22]. In case of SAPO catalysts, Bronsted and Lewis acidic centres [24] are the active centres, which is due to the

SI. no.	Catalyst	Temper- ature (°C)	Time on stream (h)	Conversion of 2-picolyl alcohol (%)	Yield (wt%)			
					Pyri dine	2-Pico line	Pyridine-2- carboxal- dehyde	Other
1	V-SAPO-37	380	1	100	15.0	48.1	31.4	5.5
2	Mn-SAPO-37	380	3 + 4	93.4	7.6	12.0	65.9	7.9
3	Co-SAPO-37	380	1	69.8	5.7	13.3	38.6	12.2
4	Ni-SAPO-37	380	3+4	97.8	17.3	11.7	68.4	0.4

 Table 2

 Reaction of 2-picolyl alcohol over SAPO-37 modified with first transition series elements

WHSV = 0.5 h⁻¹, feed = 2-picolyl alcohol: $H_2O = 1:3$ volume ratio, $M^{n+} = 1$ wt.-%.

substitution of silicon in place of phosphorous, the mild basic centres which are discussed by Akolekar et al. [25] and probably oxygen vacancies. In case of VSAPO catalysts, tetrahedral V^{4+} , $-VO_4-$, $-VOPO_4-$, acidic centres and oxygen vacancies are the active centres and are obviously multifunctional catalysts. The presence of V^{4+} species is particularly supported by ESR [22,23]. The test reaction of cyclohexanol at various temperatures has been carried out over some SAPO and VSAPO catalysts [26,27]. The presence and nature of acidic centres in HSAPO-37 has been reported by Su and Barthomeuf [28]. As reported in the literature amorphous or crystalline SAPO catalysts are mild and selective oxidation and ammoxidation catalysts [11,22,23].

The results of the reaction of 2-picolyl alcohol over various modified and unmodified silico-aluminophosphate catalysts and HZSM-5 are given in Table 1. The reactions were carried out after removal of the template. The yields of pyridine-2-carboxaldehyde were 69.1, 65.4 and 53.2 wt.-% over SAPO (DPA), SAPO (Tri-PA) and SAPO-37 catalysts, respectively, at >95% conversion at 400°C reaction temperature, and 0.5 h⁻¹ weight hourly space velocity. Over HZSM-5 (Si/Al = 30) and V-TiZSM-5, ca. 2.2% pyridine-2-carboxaldehyde

Catalyst	Picolyl alcohol:H ₂ O volume ratio	Time on stream (h)	Conversion of 2-picolyl alcohol (%)	Yield (wt%)				
				Pyridine	2-picoline	Pyridine 2- carboxal- dehyde	Other	
SAPO (Tri-PA)	1:1 (1:5.5) ^a	2	100	13.0	35.2	28.7	23.1	
	1:3 (1:16.6)	2	98.0	32.1	27.2	22.5	16.2	
	1:4 (1:22.2)	3	97.0	65.6	9.4	5.1	16.9	
	1.5 (1:27.7)	4	100	75.7	9.2	9.8	5.3	

Table 3	
Dehydrogenation of 2-picolyl alcohol over SAPO (Tri-PA), effect of water-dilution	

Reaction temperature = 380°C, W.H.S.V. = 0.5 h⁻¹, catalyst = 4 g, air flow rate = 40 cc per min.

^a The molar ratio is given in brackets.

Catalyst	Temp. Time on (°C) stream (h)	Time on	Conversion of 2-picolyl alcohol (%)	Yield (wt%)				
		stream (h)		Pyridine	2-Picoline	Pyridine-2- carboxal- dehyde	Other	
SAPO (Tri-PA)	350	3	90.5	14.6	6.3	63.5	6.1	
	380	3 + 4	98.3	20.1	10.5	64.4	3.3	
	400	4	99.9	13.5	14.8	69.1	2.5	
	250 ^a	3 + 4	55.2	3.1	1.3	44.3	6.5	

Table 4Dehydrogenation of 2-picolyl alcohol: variation of temperature

2-Picolyl alcohol: $H_2O = 1:3$ volume ratio, air flow rate = 60 ml/min.

^a 2-Picolyl alcohol: $H_2O = 1:1$ volume ratio, WHSV = 0.5 h⁻¹.

was obtained and the major products were pyridine and 2-picoline, as given in Table 1. The dealkylation of picolyl alcohol leads to pyridine and the acidic centres are responsible for the process. To enhance the selectivity of picoline-2-carboxaldehyde, the amorphous silico-aluminophosphate (DPA) catalyst was further promoted by potassium (5 wt.-%) to reduce the acidic centres and antimony (1 wt.-%). As given in Table 1, the yield of pyridine-2-carboxaldehyde was 81.9% at 98% conversion over Sb-K-SAPO (DPA) at 380°C.

The reaction of 2-picolyl alcohol was carried out over amorphous MSAPO catalysts and the results are given in Table 2. The yields of pyridine-2-carbo-xaldehyde were 31.4, 65.9, 38.6 and 68.4% over amorphous VSAPO-37, MnSAPO-37, CoSAPO-37 and NiSAPO-37 at 380°C. The variation in the activity is due to the transition metal cations.

The effect of water dilution on the dehydrogenation of picolyl alcohol over amorphous SAPO (Tri-PA) is given in Table 3. The yield of pyridine-2-carboxaldehyde decreased with the increase of dilution of the feed. On the other hand the formation of pyridine increases. The effect of reaction temperature on the dehydrogenation of 2-picolyl alcohol is given in Table 4. The yield of pyridine-2-carboxaldehyde in the temperature range of 350° to 400°C was 63.0 to 69.1% over the amorphous SAPO (Tri-PA) catalyst. Over the vanadium (>15%) modified catalysts, the formation of other side products like carboxylic acid and CO_2 were observed due to the strong oxidizing nature of the active centre. In our studies we have not observed carboxylic acids CO_2 , etc. > 2% (significantly). As proposed in the literature [21], a redox system like vanadium is the active centre for the dehydrogenation. In case of $V^{5+} \leftrightarrow V^{4+}$ system, the oxidation states are stable and with the various coordination states for the formation of oxo and peroxo species [21]. In the literature over non-zeolitic catalysts, carboxylic acid and CO₂ were observed [20]. Thus the dehydrogenation of 2-picolyl alcohol to pyridine-2-carboxaldehyde has been carried out over crystalline and amorphous modified silico-aluminophosphate catalysts with high yield and selectivity.

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