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Use of AlPO-11, SnAPO-11, SAPO-31 and SAPO-41 Elaborated Solid Materials as Catalysts in Ammonia Alkylation Reaction

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Abstract: The present study deals with the synthesis of octylamines by ammonia alkylation with octanol-1 in gaseous phase using solid microporous materials as AlPO-11, SnAPO-11, SAPO-31 and SAPO-41. They were prepared by hydrothermal process in Teflon steel less reactor under autogenic pressure and at determined temperatures. SAPO-31 material was obtained using HF acid and without fluoride media. The materials have presented a catalytic activity in the study reaction. Primary isomers (MOA) were obtained with better selectivity of about 85 to 99%. Silicium and tin are the origin of the acidity and are responsible to the activity catalytic of SnAPO-11 and SAPO-31 materials.

Key words: AlPO-11, SnAPO-11, SAPO-31, SAPO-41, ammonia alkylation, solid material

INTRODUCTION

SAPO-n and MeAPO-n known as silicoalumino-phosphates and metalloalumi-nophosphates have similar zeolites properties. They lasts are used in separation and purification of molecular species like sorbants and catalysts or catalytic supports (Amokrane *et al.*, 2001). Baiker (1985 and 1994) has used classical zeolites as ZSM-5, ZSM-11 and ZSM-21 and some aluminophosphates and alumino-magnesiens in tertiary amine synthesis by octanol amination with primary and secondary amines. The catalytic performances of NaY previously impregnated with aqueous wastes containing mainly UO_2^{2+} cations were studied in n-octanol amination and showed interesting catalytic activities (Azzouz *et al.*, 1991; Nibou *et al.*, 1996a, b). Recently, SAPO-5, SAPO-11, SAPO-31 and SAPO-34 were also studied in the same reaction (Amokrane *et al.*, 2001).

The present study was carried out in order to investigate the catalytic performances of AlPO-11, SnAPO-11, SAPO-31 and SAPO-41 in ammonia alkylation with octanol-1 in gaseous phase.

MATERIALS AND METHODS

Samples preparation: AlPO-11, SnAPO-11, SAPO-31 and SAPO-41 samples were prepared using a hydrothermally process. Phosphorous acid (85%, Fluka), ludox (Si: 41.6%), alumina (77%, Vista), dipropylamine (DPA, Merck) and tetrabutylammonium hydroxyde (TBAOH, Merck) were used as reagents.

The hydrothermal synthesis was run in Teflon steel less reactor under autogen pressure and at different temperatures. The elaboration methods are adapted from the process described by Khemaissia *et al.* (2007). The elaboration of different samples was carried out heating gels of molar composition as shown in Table 1. The obtained powder samples were characterized by X-ray diffraction using a Philips diffractometer type APD PW 1710 using copper Kα radiation, scanning electronic microscopy using Philips EM 420 T equipment. The acid properties of materials were characterized by infra-red spectroscopy using FTIR Philips PU 9800 equipment. The chemical analysis was released by inductively coupled plasma (ICP) and polarography.

Alkylamines synthesis procedure: The alkylation reaction was run in tubular reactor containing a fixed bed of catalyst. The alkylamines synthesis were investigated at the following operating conditions: temperature, 300°C; atmospheric pressure; ROH/NH₃ mole ratio, 1/3; weight hourly space velocity, 8 h⁻¹; carrier gas, 0, 2 mL sec⁻¹ of nitrogen and 0.2 g of catalyst.

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Table 1: Description of the most representative elaborations

No.	Sn	Si	Al	P	DPA	HF	H₂O	t (h)	T (°C)	XRD results
				Molar composition Condition						
S1	-	-	1.0	1.00	1.0	1.0	50	24	170	AlPO-11
S2	0.2	-	1.0	1.00	1.0	0.5	50	24	170	SnAPO-11
S2'	0.2	-	1.0	1.00	1.0	1.0	50	24	170	SnAPO-11
S3	-	0.4	1.2	1.03	1.7	1.0	62	24	200	SAPO-31
S4	-	0.4	1.2	1.03	1.7	-	62	24	200	SAPO-31
S5	-	0.4	1.0	1.00	1.0*	-	100	72	200	SAPO-41

*: TBAOH

The obtained reaction product were analysed by gaseous chromatography (PYE UNICAM series 304 Philips) with FID detector and using a column of 1.83 m composed of carbowax 20 M like stationary phase and diatomite CAW DMSC 100-120 mesh and 5% of KOH as support.

RESULTS AND DISCUSSION

The most representative elaborations are described in Table 1. From these gels (samples No. S1 to S5), fully crystallized samples of AlPO-11, SnAPO-11, SAPO-31 and SAPO-41 were obtained. The diffractograms of powder samples were compared and identified with those given by Treacy *et al.* (2001).

Figure 1 shows the X-ray diffractogram of as-made and calcined samples S1 and S2. Figure 2 shows also the X-ray diffractogram of as-made and calcined sample S3.

The negative charges of the lattice in samples (S2 to S5) are shown in Table 2.

The generation of negative charge per TO₂ tetrahedron (T = Si, Al, P) was reported by Flanigen *et al.* (1998).

Si and Sn substitutions into a hypothecal AlPO₄ framework could occur via following mechanisms: Si substitutes for P according to $Si^{4+} + R^+ = P^{5+}$ and Sn substitutes for Al according to $Sn^{2+} + R^+ = Al^{3+}$, where R^+ is usually the organic templating cation. After calcination of the material to remove the template, the charge compensating cation R^+ will result in a proton attached to the framework as bridging OH groups. Thus, the obtained results show that Si and Sn incorporations occur via this mechanism.

The results of infrared spectroscopy investigations showed different absorption bands. These vibrations correspond to acidic sites present in samples. We can observe the 3500-3620 cm⁻¹ absorption bands, which may be related, respectively to P-OH, Si-OH and Al-OH linkages. Khemaissia (2002) have also reported the same infrared absorption bands found in SAPO-5, SAPO-31 and SAPO-34 structures.
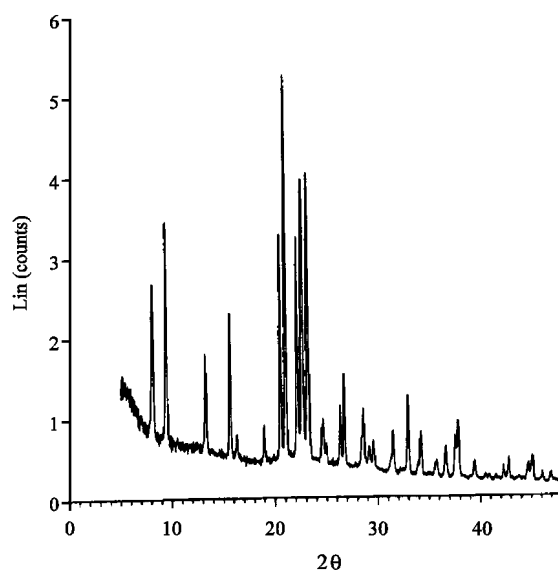

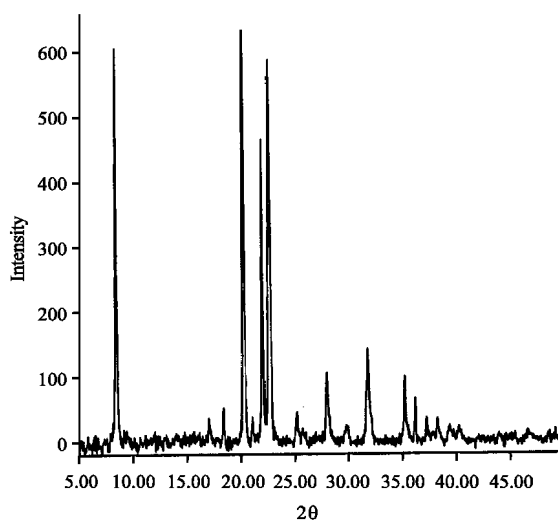Fig. 1: X-ray diffraction patterns of as-made AlPO-11 and SnAPO-11 samples S1 and S2, respectively

Fig. 2: X-ray diffraction patterns of as-made SAPO-31 samples S3

Table 2: Chemical composition of the most representative synthesis

| Sample | Chemical composition | | | | Al/P | Charge TO_2^{-1} | Acidity mmol BNH_2 g^{-1} |
	Al	P	Si	Sn			
S1	0.499	0.498	-	-	1.002	0.000	0.8
S2	0.304	0.500	-	0.196	0.609	-0.196	3.8
S2'	0.403	0.490	-	0.107	0.822	-0.127	3.4
S3	0.500	0.480	0.020	-	1.040	-0.020	3.3
S4	0.487	0.406	0.106	-	1.199	-0.085	3.7
S5	0.500	0.425	0.075	-	1.176	-0.075	3.5

Sample S1

Sample S3

Fig. 3: Scanning electronic micrographs of as-made AlPO-11 and SAPO-31 samples S1 and S3, respectively

Table 2 also shows the acidities values of samples indicating that SnAPO-11, SAPO-31 and SAPO-41 are acidic catalysts.

Scanning electronic micrographs of samples AlPO-11 (S1) and SAPO-31 (S3) are shown in Fig. 3.

Long prismatic crystals of sample S1 are observed. These latter have 40-70 μm in length and 5-10 μm in wide.

One can also observe six faces of individual prismatic crystals and the pyramid form at the end of prism. In the other hand, individual hexagonal prismatic crystals of about 5 μm in length are observed in sample S3. This crystal morphology is different from that described by Zubowa *et al.* (1990) for samples prepared in absence of HF. In the latter case 5-8 μm spherical agglomerates of crystals were obtained.

Results presented in Table 3 show clearly that the elaborated catalysts exhibit a catalytic activity in octanol amination reaction. The obtained reaction products are monooctylamine (MOA), dioctylamine (DOA), trioclylamine (TOA) and secondary products as (>C = C<) and (≡C-O-C≡) compounds. One can observe the highest selectivities for MOA isomer in this investigation.

Generally, the catalytic activity and the selectivity are strongly dependent on the type of catalyst and its acid properties. Thus, sample S5 is the most active and selective catalyst. Among the aluminophosphate catalysts, SnAPO-11 (S2) is the most active, but the selective is AlPO₄-11 (S1).

One can observe from Table 3 that, in all cases, the catalytic activity of catalysts is important and varies from 18-62%. But, the SAPO-31 (S3) catalyst gives a low conversion (less 11%) in this present reaction. It seems that the catalytic activity is greatly affected by the appearance of side reactions as shown in Table 3. It is also interesting to observe the highest selectivities of primary amines (MOA) obtained using these catalysts.

The selectivity of primary amines varies between 85-99% but of those of secondary (DOA) and tertiary (TOA) amines do no reach the value of 4 and 11%. It is well known that the formation of MOA, DOA and TOA isomers and other products occurs inside the microporous material. Only the products which critical dimensions are less than those of the catalysts pores can diffuse outside as MOA molecules. The other molecules or products are transformed by different reactions as disproportination. The selectivity of 11.52% of TOA obtained using SAPO-31 (S3) catalyst can be explained probably by its acidic external surface.

Table 3: Catalytic performances of catalysts

Sample	Octanol conversion (% Mass)	Isomers selectivity (% Mass)			Isomers yield (% Mass)			Mass (%)	
		MOA	DOA	TOA	MOA	DOA	TOA	Cocke	SP
AlPO$_4$-11 (S1)	18.08	99.40	0.60	-	74.44	0.44	1.42	0.12	4.53
SnAPO-11 (S2)	33.50	94.43	3.38	2.18	61.43	2.20	1.22	0.19	11.70
SnAPO-11 (S2')	49.12	96.42	1.93	1.63	72.00	1.45	1.22	0.17	12.43
SAPO-31 (S3)	10.51	85.99	2.47	11.52	21.50	0.62	2.88	0.15	7.88
SAPO-31 (S4)	27.07	99.75	0.24	-	90.32	0.22	-	0.19	2.54
SAPO-41 (S5)	62.77	93.84	3.18	2.97	73.80	2.50	2.34	0.31	13.38

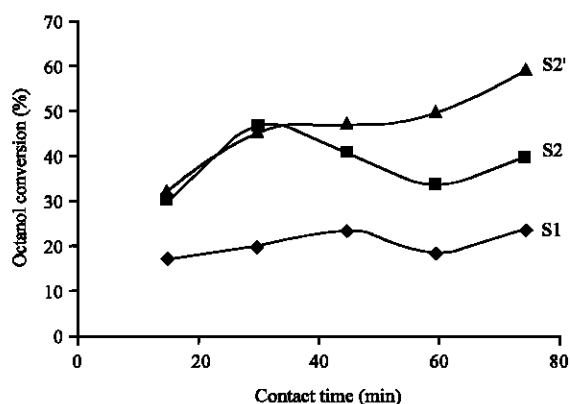(Conversions value taken at t = 60 min, %coke during 75 min, S.P: Secondary products)

Fig. 4: Effect of the contact time on the catalytic activity of AlPO$_4$-11(S1) and SnAPO-11(S2 and S2') catalysts. T = 300°C, Octanol/NH$_3$ = 3, WSHV = 8 h^{-1}
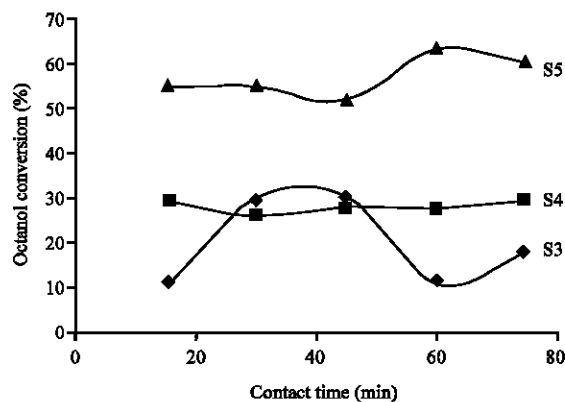
Fig. 5: Effect of the contact time on the catalytic activity of SAPO-31 (S3 and S4) and SAPO-41 (S5) catalyst. T=300°C, OCT/NH3 = 3, WHSV = 8 h^{-1}

One can observe from Table 3 that the obtained yield of primary amines is important and varies from 20-90%. But, the secondary and tertiary amines are obtained with a very low yield.

The effect of contact time on the catalytic properties of the samples catalysts was further investigated. Figure 4 (curves S1, S2 and S2') shows the catalytic evolution in time of AlPO$_4$-11 and SnAPO-11 catalysts.

One can observe from this figure that the activity of AlPO$_4$-11 is less affected by the increase of the contact time than those of other catalysts. In fact, after 30 min, the activity loss is about 5-10% for S2 catalyst, but it increases with increasing time for S2 catalyst (60%). This could be explained by the fact that S2 catalyst exhibits acidic sites with a very strong strength (3.8 mmol BNH$_2$ g^{-1}) and 0.19% of coke. This last is generally responsible for the decrease in activity of the zeolites. However, with S2 catalyst the initial deactivation by coking is not observed. Comparatively, it appears that S2 and S2' catalysts have different acidic sites. This difference is due probably to the Sn content incorporated in the AlPO$_4$-11 framework. This suggests that higher Sn concentration favours the deactivation of catalyst as S2 sample.

From Fig. 5, one can also observe the effect time on the catalytic activity of SAPO-31 (S3 and S4) and SAPO-41 (S5) catalysts. Sample S5 seems stable in time and very active after 75 min of reaction. However, it seems that SAPO-31 (S3) sample is not stable after 40 min of reaction and its activity is followed by a decrease. But, the catalytic activity of sample S4 is less affected after 75 min. The performance of this catalyst is strongly dependent on the nature of the acidic sites and the content of incorporated silicon. An increase of Si content improves the conversion and the stability, whereas a decrease of this last leads to a decay of the catalytic activity.

Figure 6 shows the distribution of the two isomers of octylamine obtained using SAPO-41 catalyst. One can observe the increasing of monooctylamine distribution in time and the decrease of that dioctylamine. This phenomenon is also observed when the other catalysts are used. The results of amine isomers distribution contain significant information and should correlate with the shape selectivity of catalysts. As shown by Fig. 4, the analysis of distribution curves S5 (MOA) and S5 (DOA) shows that MOA is selectively formed using SAPO-41 catalyst. In the other catalysts, the same isomers distribution id also observed.
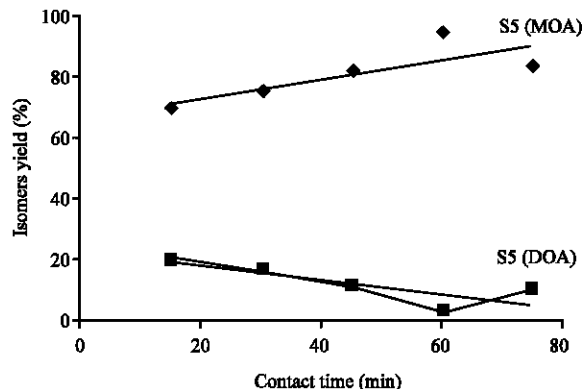
Fig. 6: Distribution of amine isomers SAPO-41(S5) catalyst. T=300°C, Oct/NH$_3$ = 3, WSHV = 8h^{-1}.

CONCLUSIONS

On the basis of these results, we may conclude that AlPO-11, SnAPO-11, SAPO-31 and SAPO-41 samples have presented a catalytic activity in amination reaction with octanol in gas phase. Primary isomers (MOA) were obtained with better selectivities of about 85-99%. Silicium and tin are responsible of the acidity and then of activity catalytic of SnAPO-11 and SAPO-31 catalysts.

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