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SYNTHESIS, CHARACTERIZATION AND CATALYTIC BEHAVIOUR OF SPECIAL TYPE OF SILICO ALUMINO-PHOSPHATE WITH OPAL STRUCTURE

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Abstract

In this study a special type of silicoaluminophosphate with opal structure (Opal-SAPO) was prepared under microwave condition using tetraethylorthosilicate (TEOS), triethanolamine (TEA), aluminiumisopropoxid and phosphoric acid 85%. The product was characterized by X-ray diffraction (XRD), thermogravimetric (TGA) and Fourier Infrared Spectroscopy (FTIR).The crystalline product showed a good activity and selectivity for regeneration of methylethylketone, benzaldehyde, and cyclohexanone from their semicarbazones derivatives.

Keywords: Silicoaluminophosphate; Opal; Template; Microwave radiation; Semicarbazones

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Introduction

The first microporous crystalline aluminophosphates (ALPO) was reported by Union Carbid researchers in 1982 [1]. Since then many works have been done to incorporate silicon atoms into the framework of AlPOs [2,3] such as silicoaluminophosphates (SAPOs) and metalloaluminom phosphate (MAPOs) [4,5]. Moreover, synthesis of SAPOs molecular sieves has been the subject of intense investigations.

During the past years, many types of SAPOs were hydrothermally synthesized in the presence of templates like amines or their derivatives as structure directing agents. For example, SAPO-5, SAPO-11 and SAPO-31 were prepared using diporopylamine as templates [6]. SAPO-34 [7], SAPO-39 [8], SAPO-43 [10] and SAPO-47 [11] have also been synthesized using various types of templates.

A wide range of templates which have been currently used in the synthesis of SAPOs include dipropylamine, isopropylamine, triethylamine, tetraalkylammonium hydroxide, cyclohexylamine, morpholine and sect-butyl amine [11].

In this study, we investigated the effect of microwave irradiation on the formation of silicoaluminophosphate. In fact by substitution of Si in the framework of AlPO molecular sieves imparts acidity to the material and makes it active for a variety of acid catalyzed reactions [12]. As known, phenylhydrazones, tosylhydrazones and semicarbazones are important derivatives of aldehyde and ketones. Extensive studies have been carried out using catalysts such as sodium bismuthate on wet silica [13], antimony trichloride under microwave condition [14], tetrabuthyl ammonium peroxy disulfate [15], quinolinium dichromate [16], and so on. Also we recently showed that metal exchanged zeolite Y successfully converts semicarbazones to the corresponding aldehyde and ketone [17], we decided to

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Table 1. Synthesis conditions for Opal-SAPO

Sample code	Al_2O_3	P_2O_5	H_2O	SiO_2	TEA	Time	Product
1	0.126	1	37.6	0.2	0.88	36″	Amorph
2	0.097	1	37.6	0.2	0.88	2′,10″	Amorph
3	0.132	1	37.6	0.184	1.2	4′,30″	Amorph
4	0.097	1	37.6	0.2	–	5′,20″	Amorph
5	0.097	1	37.6	0.2	0.88	8′,24″	Opal-SAPO

investigate the same transformation under the effect of (Opal-SAPO) as well.

Experimental Section

All the materials were purchased from Merk Chemical Company. The prepared samples were characterized by XRD (Philips, PW=1730, PW=1840) with Cu and Co Lamps, (X-360, Cambridge models). X-ray fluorescence XRF by Philips, PW=1400. Gas chromatography Philips PU 4400 chromatograph (1.5 m, 3% ov-17 column) and Gc-Mass Shimadzu-14 A (CBP-5-M25, capillary column, fused silica), Microwave MB 242.FTIR model PU-9800 Philips and Shimadzu corporation.

Synthesis Opal-SAPO

The optimal synthesis composition of the pure Opal-SAPO was according to the following molar ratios of the oxide: (0.098 Al_2O_3, 1 P_2O_5, 0.135 SiO_2, 0.88 TEA, and 7.64 H_2O). The standardized mixing procedure was as follows, phosphoric acid was mixed with appropriate amount of water in a plastic beaker. The aluminum isoperoxide was gradually added to this solution while vigorously mixing in order to get a homogeneous solution. Then tetraethylorthosilicate (TEOS) was added to this thoroughly mixed gel. Finally triethanol amine was slowly added to the above slurry solution. The resultant mixture was stirred for 10 more minutes. This mixture was transferred to a teflon-vessel, which was then put under microwave irradiation for few minutes. The obtained solid was filtered, washed with distilled water to pH=7 and then dried at 100°C.

Regeneration of Carbon Compounds from Semicarbazones: General Procedure

Mthylethylketones (mmol) in 5 ml CH_2Cl_2 was added to 0.3 g Opal-SAPO in 5 ml CH_2Cl_2, then it was refluxed for 6 h under nitrogen atmosphere. After filtration and washing with solvent, it was subjected to GC and GC-Mass analysis.

Results and Discussion

Table 1 reveals molar composition of the reaction mixture for the synthesis of silicoaluminophosphate under microwave condition. According to the results the reaction time has essential effect on product formation. It was observed that after 36, 150, 270 and 320 sec (runs 1-4), the crystalline phase of products was amorphous. By increasing the time of irradiation to 504 sec, a crystalline phase was obtained (run-5).

The powder XRD pattern of the product of run 5 is shown in (Fig. 1). It can be seen that, it is identical to that reported earlier for opal structure (Table 2) [18]. This result indicates that a special type of silicoaluminophosphate with opal structure was prepared under microwave conditions, which we named it Opal-SAPO. (Chemical analysis: SiO_2=1.12%, Al_2O_3=27.01%, P_2O_5=71.51%) The thermogravimetric (TGA) results are shown in Figure 2. From the TGA data, it reveals that the weight loss of water and triethanol amine is occurred in three stages and the total weight loss was around 9.2 wt%. In the first stage, the weight loss is 1.5% at the temperature range of 25°C to 207°C which is due to the desorption of physisorbed of water. The loss of 7.73 wt% occurs in the second stage from 200°C to 400°C, which corresponds to desorption of TEA. This decomposition is consistent with the behaviour of amine containing SAPO precursors [19] and TEA-analcime [20] and dipropylamine containing aluminophosphate [8]. In the third stage, the small weight loss of 1.44 wt% occurs in the 400-500°C range, which is due to the very slow desorption of TEA adsorbed strongly on acidic sites in Opal-SAPO type.

FTIR spectra of Opal-SAPO shows a broad band around ~3700-3600 cm^{-1} is assigned to X-OH (where X=Al, Si, P) groups. We also see strong bands at ~1400 cm^{-1} due to Bronsted acid sites and a weak band at 1620 cm^{-1} due to Lewis acid sites. The bands around 1250-1000 cm^{-1} and 800-650 cm^{-1} are assigned to the asymmetric stretching mode of TO_4 (T=Al, Si) and to the bending modes of TOT vibrations [8].

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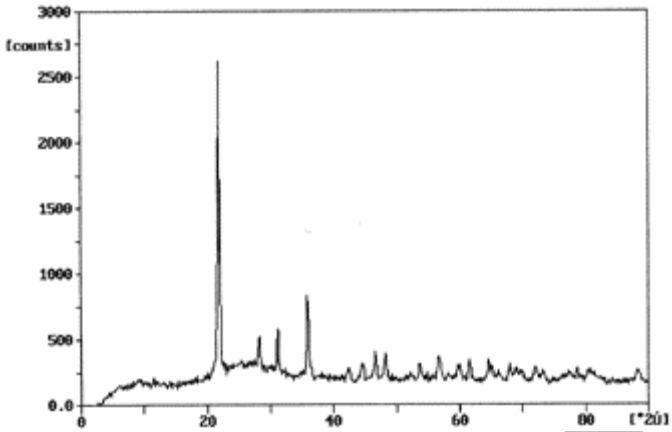

Figure 1. X-ray powder diffraction pattern (XRD) of as made Opal-SAPO type crystallized under microwave condition (run 5).

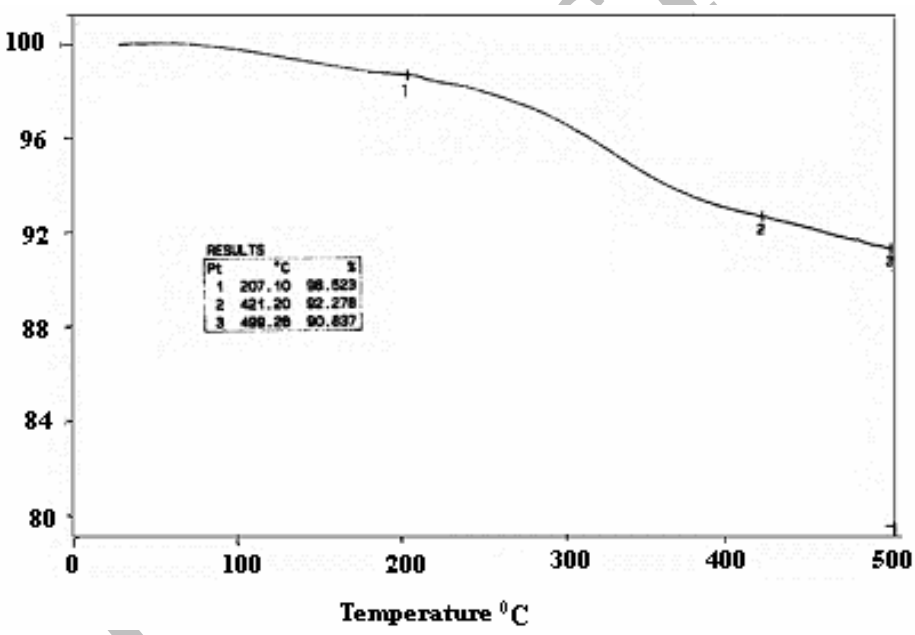

Figure 2. Thermogravimetric (TGA) analysis of as made Opal-SAPO type.

Table 2. The comparison between the XRD data of as made Opal-SAPO and Opal [18]

Peak intensity (I/I_0)	d	D (experimental)
100	4.08	4.068
30	2.51	2.504
10	2.86	2.81
9	3.14	3.153
5	1.93	1.95

Table 3. Conversion of semicarbazones with wet Opal-SAPO

Substrate	Product	Yield
Ethylmethylketone semicarbazone	Ethylmethylketone	94
Banzaldehyd semicarbazone	Banzaldehyde	81
Cyclohexanon semicarbazone	Cyclohexanone	70

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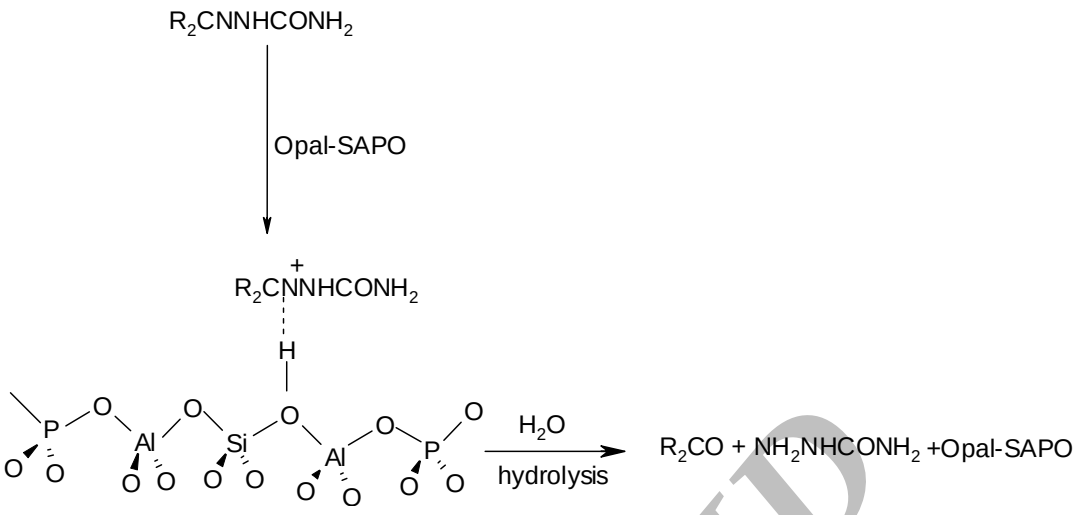

Scheme 1. Hydrolysis of semicarbazone on Bronsted acid sites.

The catalytic behaviour of Opal-SAPO on regeneration of mthylethylketone, benzaldehyde and cyclohexanone from the corresponding semicarbazones derivatives is given in Table 3. In fact, OH groups on Opal-SAPO surface provide Bronsted acidity to substrates. The first step in the regeneration of aldehydes or ketones from semicarbazone derivatives is chemisorbed of semicarbazones on the acid Bronsted sites. The carbon-nitrogen bond (C=N) cleavage is catalyzed by H^+ and the next step is hydrolysis by small amounts of water molecules. It was observed that in the absence of water no reaction is occurred. The plausible reaction mechanism is shown in Scheme 1. Therefore, the Opal-SAPO could be a candidate as easy made and active catalyst for this type of regeneration.

Conclusion

1- A special type of Silicoaluminophosphate with Opal structure (Opal-SAPO) was prepared under Microwave condition using TEOS, TEA, Aluminium-isoperoxid, H_3PO_4 (85%).

2- Opal-SAPO as a fast and easy made material is a good catalyst for regeneration of aldehydes and ketones from the corresponding semicarbazone derivatives.

3- It was found that the reactivity of Opal-SAPO toward the regeneration of carbonyls is as follow: Mthylethylketone>benzaldehyd>cyclohexanone.

Acknowledgements

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