

Preparation of synthetic zeolite ZSM-5

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The synthesis of zeolite ZSM-5 in the presence of ethylamine in aqueous medium was investigated. It was found that well crystallized zeolite of the ZSM-5 type originated from the sol of silicic acid and sodium aluminate in the presence of aqueous solution of ethylamine at the temperature of 150°C in the course of seven days if the ratio $n(\text{ethylamine}) : n(\text{SiO}_2)$ was equal to 1.7. The proposed procedure yields zeolites with high degree of crystallinity.

Исследован синтез цеолита ZSM-5 в присутствии этиламина в водной среде. Обнаружено, что если исходить из золя кремниевой кислоты, алюмината натрия и в присутствии водного раствора этиламина, то хорошо выкристаллизованный цеолит типа ZSM-5 получается при температуре 150°C в течение 7 дней при соотношении $n(\text{этиламин}) : n(\text{SiO}_2) = 1,7$. Предлагаемый метод синтеза позволяет получать цеолиты с высокой степенью кристалличности.

ZSM-5 is a representative of a new class of high-siliceous zeolites which exhibit exceptional catalytic properties and a high temperature stability resulting from their structure [1, 2].

The skeleton of zeolite contains two systems of channels with ten-membered ring holes. These channels run across each other. Owing to the diameter and shape of channels, ZSM-5 excels in shape selectivity which is used for catalyzing several important industrial processes, *e.g.* isomerization of xylenes [1, 3], disproportionation of toluene [3, 4], alkylation of toluene with methanol [3, 4], and alkylation of benzene with ethylene [4]. Recently, the process of gasoline production from methanol (MTG process) involving the use of some catalysts on the base of zeolite ZSM-5 [3—5] attracted attention all over the world.

Tetrapropylammonium compounds are used for forming the crystal structure of zeolite ZSM-5 according to the original procedure of Mobil Oil Co. [6]. However, these compounds are expensive and difficult to obtain and for this reason, a convenient substitute is searched for. Recent investigations show that the quaternary ammonium compounds are not necessary for forming the crystal structure of this zeolite [7]. It may be obtained in the presence of aliphatic amines [8], diamines [9—11], alkanol amines [12], glycerol [13], aliphatic alco-

hols and amonia [14], dodecylbenzenesulfonate [15], and a great number of other substances.

In this study, attention was paid to the preparation of zeolite ZSM-5 in the presence of ethylamine which proved to be one of the convenient substitutes for the hardly available tetrapropylammonium compounds [16]. Such replacement could give opportunity of eventual realization of the research results because ethylamine belongs among quite easily available aliphatic amines and is used for some products of organic chemical industry in CSSR. The aim of this study has been to find out an appropriate procedure and conditions for the preparation of this zeolite.

Experimental

Chemicals

The hydrosol of silicic acid ($w = 29.7$ mass % of silicon dioxide) (Research Institute of Crude Oil and Hydrocarbon Gases, Bratislava), sodium aluminate prepared in the Department of Chemical Technology of Silicates of the Slovak Technical University ($w = 52.3$ mass % of aluminium oxide and $w = 47.7$ mass % of sodium oxide), and aqueous solution of ethylamine ($w = 40.1$ mass %) (J. Dimitrov Chemical Works, Bratislava) were used. Other chemicals were common anal. grade products of Lachema, Brno.

Apparatus

Steel pressure ampoules with a teflon insert of free volume of 120 cm^3 which were placed in a heating block were used for preparation of the zeolites. The heating was electrical (resistance heating) and the temperature was controlled by means of a transistor regulator. The temperature in ampoules was measured with a platinum thermometer. The operation proceeded under static conditions.

Working procedure

The hydrosol of silicic acid was dropwise added into the aqueous solution of amine and sodium aluminate. The prepared mixture was homogenized for 20 min at laboratory temperature and poured into an ampoule where it was kept at a given temperature for a certain time (according to real conditions of experiments). After cooling, the crystalline portion was filtered off, thoroughly washed with distilled water, and dried for 4 h in vacuum drier at 110°C . The quality of the zeolites thus prepared was valued by the

X-ray diffraction analysis and the content of individual components was determined by chemical analysis.

For determining the degree of crystallinity of the prepared zeolites we developed a method based on the comparison of intensity of the three diffraction maxima typical of the high-crystalline ZSM-5 in the region $2\theta = 22.5^\circ$ — 25° with the diffraction maximum of cristobalite used as an internal standard. The method of determination will be published in the subsequent paper. The conditions used for diffraction analysis were as follows: instrument DRON — 2.0; radiation $\text{CuK}\alpha$; C-monochromator; rate (2θ) $1^\circ \text{min}^{-1} \text{cm}^{-1}$; sensitivity $2 \times 10^3 \text{imp s}^{-1}$. The reproducibility of results showed an error up to $\pm 5\%$.

Results and discussion

In searching for a possible replacement of hardly available tetrapropylammonium compounds needed for the preparation of zeolites of the ZSM-5 type, we have disclosed that the performance of the hydrothermal synthesis in the presence of ethylamine gives rise to zeolites with a high portion of crystalline phase the X-ray diffraction pattern of which is identical with that of ZSM-5. An X-ray diffraction pattern of zeolite ZSM-5 synthesized in the presence of ethylamine (Table 2, experiment P₈) is represented in Fig. 1.

The influence of temperature, reaction time, ethylamine admixture, and reactor filling was examined in this study. We worked under static conditions at the pressure which corresponded to the pressure of the system at the investigated temperature (there was no possibility of measuring the pressure in ampoules).

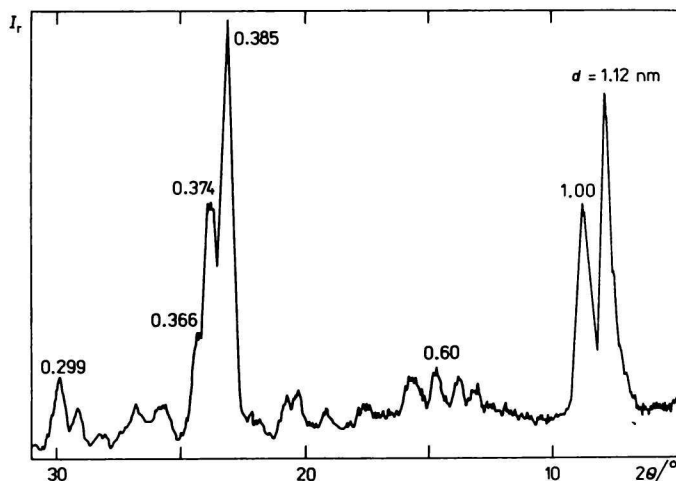


Fig. 1. X-Ray diffraction pattern of zeolite ZSM-5 ($m = 25.4$) prepared in experiment P₈ (Table 2).

One of the important factors which significantly affect the hydrothermal synthesis of zeolites is reaction temperature. The influence of temperature was investigated in the temperature range 135°C—195°C. We started from knowledge predominantly found in patent literature which referred to the preparation of ZSM-5 in the presence of tetrapropylammonium compounds. The reaction conditions, composition of starting mixture, and quality of the product as a result of the influence of reaction temperature are given in Table 1.

Table 1

Influence of temperature on the formation of zeolite ZSM-5

Experiment	P ₁	P ₂	P ₃	P ₄	P ₅
Reaction temperature/°C	135	150	165	180	195
Reaction time/day			6		
Charge put into reactor/g			100		
Filling of reactor/%			85		
Composition of starting mixture					
$n(\text{EtNH}_2)/n(\text{SiO}_2)$			2.1		
$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$			23.2		
$n(\text{Na}_2\text{O})/n(\text{SiO}_2)$			0.064		
$n(\text{Na}_2\text{O})/n(\text{Al}_2\text{O}_3)$			1.5		
$n(\text{H}_2\text{O})/n(\text{SiO}_2)$			18.2		
Composition of product					
$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$	25.68	24.93	24.9	25.57	17.41
$n(\text{Na}_2\text{O})/\text{mol}$	0.83	0.65	0.8	0.81	0.82
Result of X-ray diffraction analysis	ZSM-5	ZSM-5	ZSM-5	ZSM-5	Other structure
Crystallinity/%	63	88	85	70	

The first-quality zeolite was obtained under the investigated conditions at the temperature of 150°C, which is in good agreement with literature [6] referring to the preparation of ZSM-5 in the presence of quaternary ammonium compounds. As results from further our measurements, the temperature interval 150°C—170°C appears to be the best for the preparation of zeolite under given reaction conditions.

Further parameter investigated in the synthesis of zeolite was reaction time. According to patent literature the hydrothermal synthesis of ZSM-5 takes place

Table 2

Influence of reaction time on the formation of zeolite ZSM-5

Experiment	P ₆	P ₇	P ₈	P ₉	P ₁₀	P ₁₁
Reaction time/day	5	6	7	8	9	11
Reaction temperature/°C			150			
Charge put into reactor/g			100			
Filling of reactor/%			85			
Composition of starting mixture						
$n(\text{EtNH}_2)/n(\text{SiO}_2)$			2.1			
$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$			23.2			
$n(\text{Na}_2\text{O})/n(\text{Al}_2\text{O}_3)$			1.5			
$n(\text{Na}_2\text{O})/n(\text{SiO}_2)$			0.064			
$n(\text{H}_2\text{O})/n(\text{SiO}_2)$			18.2			
Composition of product						
$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$	25.15	24.93	25.4	25.3	25.4	25.2
$n(\text{Na}_2\text{O})/\text{mol}$	0.61	0.65	0.69	0.68	0.65	0.6
Result of X-ray diffraction analysis			all ZSM-5			
Crystallinity/%	78	88	95	96	98	96

in the interval from several ten hours to several days consistently with other reaction conditions. A rough estimation of the preparation of ZSM-5 in the presence of ethylamine has shown that the time necessary for obtaining zeolite with high portion of crystalline phase is equal to six or seven days. We investigated the time interval between five and nine days. The use of shorter time resulted in insufficiently crystallized products. Table 2 contains reaction conditions, composition of starting mixtures as well as quality and composition of products for different reaction times.

It results from the measured results that the hydrothermal synthesis has to proceed for seven days if a first-quality zeolite is to be obtained.

Further investigated parameter was the amount of added ethylamine. It is used as a template for forming the crystal structure of zeolite owing to which its concentration in the reaction mixture immediately influences the quality of product. For this reason, it is necessary to know the optimum concentration of ethylamine in the reaction mixture and the economic aspects are also not negligible.

Table 3

Influence of ethylamine addition on the formation of zeolite ZSM-5

Experiment	P ₁₂	P ₁₃	P ₁₄	P ₁₅	P ₁₆
$n(\text{EtNH}_2)/n(\text{SiO}_2)$	0.79	1.23	2.12	3.0	3.08
Reaction temperature/°C			150		
Reaction time/day			7		
Charge put into reactor/g			110		
Filling of reactor %			93		
Composition of starting mixture					
$n(\text{SiO}_2) \ n(\text{Al}_2\text{O}_3)$			23.1		
$n(\text{Na}_2\text{O}) \ n(\text{Al}_2\text{O}_3)$			1.5		
$n(\text{H}_2\text{O}) \ n(\text{SiO}_2)$			18.1		
Composition of product					
$n(\text{SiO}_2) \ n(\text{Al}_2\text{O}_3)$	24.3	25.5	25.4	24.8	24.7
$n(\text{Na}_2\text{O}) \ \text{mol}$	0.56	0.66	0.69	0.7	0.67
Result of X-ray diffraction analysis					
	ZSM-5*		all ZSM-5		
Crystallinity %	68	88	94	100	96

The influence of the ethylamine addition was investigated for the ratio $n(\text{EtNH}_2):n(\text{SiO}_2)$ ranging from 0.79 to 3.08. The reaction conditions and results of experiments are given in Table 3.

Provided the ratio $n(\text{EtNH}_2):n(\text{SiO}_2) = 1.6\text{--}1.7$, the quality of the produced zeolite does practically not change with the amount of ethylamine in the reaction mixture.

A factor which affects the formation of zeolite is the filling of reactor. Ethylamine occurs in the reactor both in gaseous and liquid phase. In the scope of this study, the composition of phases and the influence of this circumstance could not be quantified. It has been ascertained that it is convenient to fill the reactor to 85 % not only from the viewpoint of obtaining a well crystallized product, but also from the viewpoint of security.

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