EFFECT OF ZEOLITE ZSM-5 PARTICLE SIZE IN THE SYNTHESIS OF 1,4-DIAZABICYCLO[2.2.2]OCTANE

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The effect of the particle size of zeolite ZSM-5 in the synthesis of 1,4-diazabicyclo[2.2.2]octane from ethylenediamine was studied. The activity of the catalyst and its selectivity for 1,4-diazabicyclo[2.2.2]octane increase with decreasing particle size of zeolite ZSM-5.
Keywords: Zeolites; Particle size; 1,4-Diazabicyclo[2.2.2]octane.

Zeolites, crystalline aluminosilicates with precisely defined structure, have nowadays a broad field of the industrial application. Negative charge of aluminium in the crystalline structure is compensated by cations. For an acid catalysis, the zeolites are transformed into NH_4^+ form by means of an ion exchange. The NH_4^+ form of the zeolite is then consequently changed into acid H^+ form by heating. The transformation to H^+ form may be also provided by diluted acid for more stable zeolites (i.e. zeolites with higher Si/Al ratio)[1].

The effect of zeolite particle size has been studied mainly in alkylations of aromates. Olson and Haag[2] studied an influence of the zeolite particle size in disproportionation of toluene to benzene and xylenes. The authors found, with higher zeolite particle dimensions a formation of *para*-xylene is increased. Such behavior is caused by a prolongation of a diffusion pathway in bigger particles, which leads to preference of most compact para isomer. Another authors observed the same effect in alkylations of toluene by methanol[3] or ethylene[4]. Benchman et al.[5] explained, the increase in the para selectivity is not caused only by the diffusion pathway prolongation, but is given also by a decrease of the external/internal active sites ratio. Kono et al.[6] studied hydratation of cyclohexene to cyclohexanole in a liquid phase in the presence of ZSM-5 zeolite. The particles were larger than 1 μm,

the reaction rate was proportional to the external surface of the catalyst. The particles were smaller than 0.1 μm, the reaction rate was proportional to the acidity of the catalyst.

In this work, the attention is paid to the effect of the zeolite ZSM-5 particle size at a constant Si/Al ratio in the synthesis of 1,4-diazabicyclo[2.2.2]-octane (DABCO) from ethane-1,2-diamine (EDA). This crucial effect has not yet been described in literature.

DABCO is a white hygroscopic crystalline substance with the melting point 158–160 °C and boiling point 173–174 °C. It is used as an excellent catalyst for the production of polyurethane materials. The preparation of DABCO from several raw materials and with a number of catalysts is described mainly in the patent literature. Generally, the synthesis of DABCO can be considered as condensation reaction and, depending on the raw materials, also dehydration or deamination over acid catalysts. The process can be carried out either in the gas or liquid phase. The raw materials used for the production of DABCO can be divided into three groups:

1. piperazine and its 2-aminoethyl- or 2-hydroxyethyl derivatives
2. mono-, di- or triethanolamine and
3. polyethylenepolyamines H_2N-(-CH_2-CH_2-NH-)$_n$-H, or their 2-hydroxy-ethyl derivatives.

The compounds that frequently mentioned in literature in the synthesis of DABCO are *N*-(2-aminoethyl)piperazine (AEPIP), *N*-(2-hydroxyethyl)-piperazine (HEPIP), bis *N*,*N'*-bis(2-hydroxyethyl)piperazine (BHEPIP), 2-aminoethan-1-ol (AE) a ethane-1,2-diamine (EDA).

A large number of catalysts used in the synthesis of DABCO in the gas phase are mainly aluminosilicates (synthetic or natural), SiO_2, alumina, metal oxides and phosphates[7–17]. For the synthesis of DABCO in the liquid phase, organic acids are used[18–20].

ZSM-5 zeolite has been used mainly because of its high selectivity. Primary building unit of the ZSM-5 zeolite is a five-membered ring composed of tetrahedra (SiO_4 or AlO_4^-). Secondary building unit is doubled primary unit. ZSM-5 has a system of channels built from 10 tetrahedra arranged in a ring. Direct channels are elliptical with the dimensions 5.1 × 5.5 Å. The cross channels are sinusoidal with the almost circular shape (5.4 × 5.6 Å). Both systems hold a 90° angle.

Several of ZSM-5 modifications have been described to increase its selectivity for DABCO [21–23]. Ion exchanges with alkaline metal ions[24], selection of a suitable template[25] for the synthesis of the zeolite and different calcina-

tions methods[26] have been described. Furthermore, the processing of zeolite with NaOH [27], oxalic acid as a complexation agent[28] or organosilicon containing compounds to lower the acidity of the external surface[29] have been mentioned. Attention is also devoted to a suitable binder[30].

Reichle[31] devoted his work to the selection of a suitable Si/Al ratio, in terms of the catalyst activity and selectivity, zeolite ZSM-5 with a Si/Al ratio of ca. 200 seemed the most suitable. Reichle also proposed mechanism of DABCO and pyrazines (by-products) formation based on reaction of protonated vinylamine with piperazine and dehydrogenation of EDA over acid catalyst, respectively.

We discovered the mechanism of DABCO and pirazines formation is quite different based on elimination, condensation, cracking and proton transfer reactions[32].

EXPERIMENTAL

Chemicals

Ethylenediamine of 99% purity was obtained from Sigma–Aldrich Co. The catalysts were obtained from Research Institute of Inorganic Chemistry Ústí nad Labem (Table I). The catalysts which were not in the H-form were subjected to multiple ion exchanges by 1 M NH_4NO_3 and subsequently calcined at 550 °C. The particle size was estimated by electron microscopy. The catalysts without a binder were tabletted in the presence of 2% graphite as a lubricant. After tabletting the catalysts were ground to the desired size (1.6–1.8 mm)

TABLE I
Zeolite catalysts used

| Catalyst	Si/Al mass ratio	Crystal size, μm
A1	40	0.2
A2	36.7	0.5–1
A3	38	1–1.5
A4	39.8	1.5–2.5
A5	42.8	2–3
A6	38.1	2.5–3.5
A7	40	4

Analytical Methods

Quantitative analysis of reaction mixtures was carried out by gas chromatography (Shimadzu-GC9 with a flame ionization detector). A capillary column HP-PONA (50 m × 0.2 mm, film 1 μm) was used. Helium was the carrier gas. Qualitative analysis of reaction mixtures was carried out using a gas chromatograph GC MS-QP 2010 Shimadzu equipped with an MS detector. A capillary column DB-5 (60 m × 0.32 mm, film 1 μm) and helium as the carrier gas were employed. The samples were homogenized with methanol and analyzed by the method of internal standard. The correction factors were determined using pure standards.

Catalytic Test

The experiments were carried out in a fixed-bed tubular reactor. The length of the reactor was 70 cm and its internal diameter was 1.4 cm. Temperature was probed with a thermocouple in a thermowell (4 mm) axially placed along the reactor. The first 50 cm of the reactor was filled with ceramic packing and served as an evaporator. The next 10 cm was filled with 6.5 g of the catalyst. The final 10 cm of the reactor was filled with ceramic packing. The evaporator and the catalyst bed were heated separately. The chosen temperature was maintained at ±2 °C along the catalyst bed. A sampling vessel immersed in an ice bath was placed beneath the reactor. The reactants were fed with a piston pump. The catalyst was activated in a flow of dry air at 75 l/h with a 5 °C/min temperature rise to 450 °C within 3 h. In all the experiments the reaction temperature was 360 °C. The inlet raw material was 50 wt.% a water solution of EDA.

RESULTS AND DISCUSSION

With starting reactant EDA, the synthesis of DABCO involved four consecutive reactions. In the first step diethylenetriamine (DETA) was formed from EDA. In the second step was DETA cyclized to PIP. In the third step AEPIP was formed which finally cyclized to DABCO in the fourth step (Scheme 1).
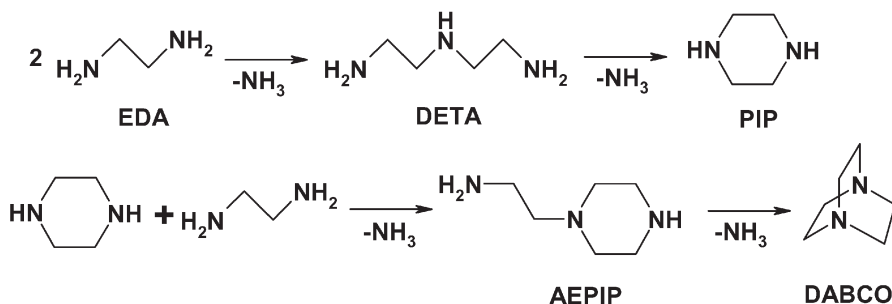
SCHEME 1
Main reactions in the synthesis of DABCO

In addition to the above mentioned compounds the reaction mixture also contains minor products. According to literature these compounds are mainly pyrazines (pyrazine (PYR), methylpyrazine (MPYR), ethylpyrazine (EPYR), 2,3-dimethylpyrazine (2,3-DMPYR)) and piperazine derivatives *N*-methylpiperazine (N-MPIP) and *N*-ethylpiperazine (N-EPIP).

The activity of zeolite ZSM-5 depends on the number of inlets in the pore structure. The catalyst deactivation occurs mainly by blocking of the pore inlets on the zeolite ZSM-5 surface with carbonaceous deposits. Two catalysts with different particle sizes the same amount of carbonaceous deposits in the same catalyst mass, the catalyst with larger particles would deactivate faster (Fig. 1).

The idea about the effect of particle size on the activity and deactivation of the zeolite catalysts was experimentally confirmed with a number of catalysts we studied (Table II). Two catalysts with different particle sizes were compared at the similar weight hourly space velocity (WHSV), A7 (4 μm, WHSV = 5.25 g/h and conversion 64.5%) and A1 (0.1–0.2 μm, WHSV = 5 g/h and conversion 98.8%). It is clear that the activity of a catalyst with smaller particles was much greater.

A rapid catalyst deactivation was observed during the testing of the first three catalysts with the largest crystals (A7, A6 and A5). The test method was subsequently modified in order to quantify the extent of catalyst deactivation. Thus, at the end of testing catalysts (after ca. 8 h) using different catalyst loads (WSHV), the starting WHSV was set. For the remaining four catalysts (Table II) it is apparent that with decreasing particle size the extent of catalyst deactivation decreased.
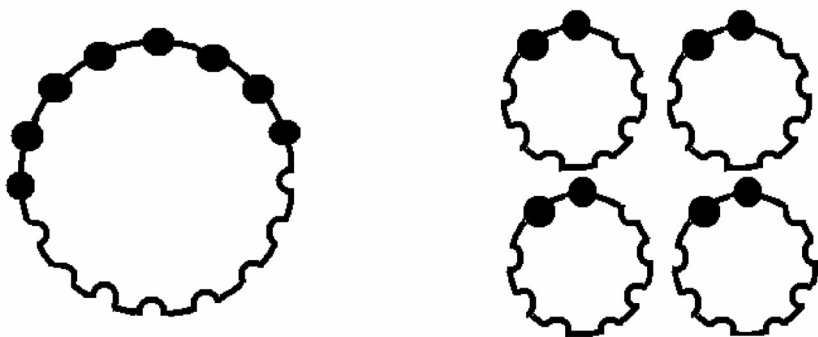

F_IG. 1

Comparison of different sizes of zeolite ZSM-5 particles in terms of numbers of pore inlets and deactivation

TABLE II
Effect of catalyst load on conversion for various crystal sizes of zeolite ZSM-5

Catalyst	WHSV, g/h	Conversion EDA, %
A7	5.25	64.5
(4 μm)	4.15	69
	3.08	73
	1.8	84.6
A6	4.88	66.7
(2.5–3.5 μm)	6.25	55.4
	3.38	72.6
	5	61.3
A5	3.88	75.8
(2–3 μm)	2.28	82.6
	2.59	72.8
A4	4.75	89.2
(1.5–2.5 μm)	6.25	75.5
	7.5	68.8
	4.75	80.3
A3	5.13	87.9
(1–1.5 μm)	6.13	77.9
	3.5	92.1
	5.13	81.3
A2	5.13	94
(0.5–1 μm)	6.25	84.9
	7.5	80.4
	5.13	89.9
A1	5	98.8
(0.2 μm)	7.13	93.4
	9.9	88.2
	5.4	97.6

Effect of the active sites on the particles external surface was also tested. Acidity of the external surface was measured by means the 4-methyl-quinoline TPD technique described elsewhere[33]. External surface of catalyst A3 was dealuminated[28] with 1 M oxalic acid at 80 °C for 5 h. It was seems the acidity of the external surface decreased to 2% of the original one but the effect to the catalyst activity and selectivity was negligible from which results the active sites on the particles surface did not play an important role.

Although, the activity and the catalyst deactivation are important process parameters, the selectivity for DABCO and PIP is the decisive factor. In the synthesis of DABCO using EDA, these are two types of competing reactions, substitution and elimination. The substitution reactions are desirable leading to DABCO through intermediates like DETA, PIP and AEPIP. On the other hand, the elimination reactions lead to undesired products such as pyrazines and alkylpiperazines. These compounds arise by the elimination of ammonia from a molecule of EDA. Therefore, the rate of elimination is first order with regards to the concentration of EDA. The substitution reaction leading to DETA is of the second order with respect to EDA It is well known that in a system where side reactions with different reaction orders take place and reaction rates are influenced by mass transfer, the reaction with a lower reaction order is preferred. In our case, it can be assumed that the larger the zeolite particles the longer the diffusion paths to the active sites in the particles and the more significant are the effect of mass transfer. Hence, we can assume that the ratio elimination/substitution would change with an increase in the particle size and thus, the selectivity for DABCO would decrease. This was confirmed and it was also observed that the yields of DABCO and PIP increase with a decreasing particle size (Fig. 2). At high EDA conversions (about 70%) DETA and AEPIP concentrations are very low and the main products are DABCO and PIP. Consequently, we chose the sum of the theoretical yields of DABCO and PIP for comparison of the catalysts.

If the elimination occurs to a smaller extent on small particals, the by-products, pyrazines and alkylpiperazines, would also be formed in smaller amounts. That was confirmed (Fig. 3) and that leads to the conclusion that the formation of pyrazines and alkylpiperazines is caused by elimination reactions which is in agreement with our previous work[32].

If ethylenediamine is the starting material and conversions above 80% are obtained, PIP and DABCO would be the main stable cyclic products in the reaction mixture meanwhile DETA and AEPIP would occur in insignificant amounts. The choice of the zeolite particle size can influence the
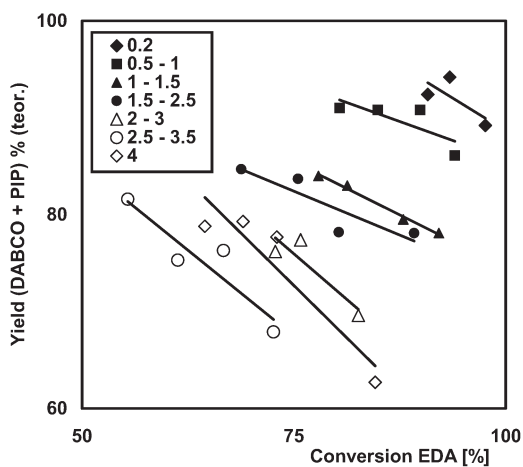
F<small>IG</small>. 2
Effect of the zeolite ZSM-5 crystal size (in μm) on the yield of DABCO and PIP
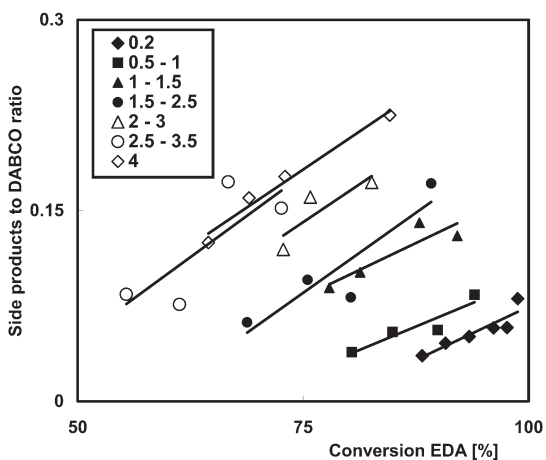

F<small>IG</small>. 3
Effect of the zeolite ZSM-5 crystal size (in μm) on the formation of side products (methyl-pyrazine, ethylpyrazine, 2,3-dimethylpyrazine, *N*-methylpiperazine and *N*-ethylpiperazine)

DABCO/PIP ratio. If we consider the size of corresponding molecules it is clear that DABCO would have a larger mean kinetic diameter than PIP, therefore it can be assumed that the DABCO molecule would slowly diffuse in the zeolite pores than PIP. With a decrease in the zeolite ZSM-5 particle size the difference in the diffusion of DABCO and PIP would cancel and the DABCO/PIP ratio would change in favour of DABCO. Such results were indeed observed (Fig. 4).

From thermodynamic calculations carried out using the Aspen plus program for the same reaction conditions as in experiments (360 °C, 101.325 kPa, 50% EDA water solution the ammonia feed mole ratio 1:1, DETA, PIP, AEPIP and DABCO considered as the only products) and after attaining thermodynamic equilibrium and complete conversion of EDA, the only products are DABCO and PIP in the mass ratio 10:1. Hypothetically, it can be assumed that if the zeolite ZSM-5 particle size decreases further below 0.2 μm the DABCO/PIP ratio in the reaction mixture would approach the computed ratio. Such a trend can be seen in Fig. 4.
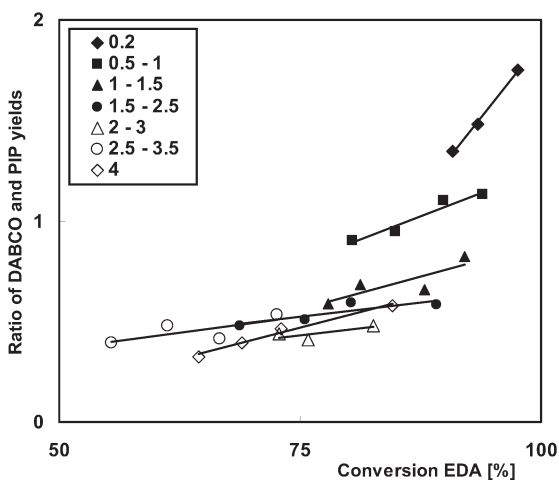

Fig. 4
Effect of the zeolite ZSM-5 crystal size (in μm) on the yield ratio of DABCO to PIP

CONCLUSIONS

From the results it is clear that the size of zeolite ZSM-5 particles is an important parameter which considerably influences the catalyst activity and, to a certain extent, its deactivation. The selectivity to DABCO and PIP increases with decreasing particle size. The DABCO/PIP ratio also increases with decreasing particle size.

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