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PREPARATION OF ALKYL-1,4-DIAZABICYCLO[2.2.2]OCTANES OVER ZSM-5 ZEOLITE

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Abstract

Research in the possibility of alkyl-1,4-diazabicyclo[2.2.2]octanes preparation using C-alkyl piperazines and ethylendiamine on zeolite ZSM-5 with a ratio Si/Al = 120 was carried out. It was found out that 2-methyl and 2-ethyl-1,4-diazabicyclo[2.2.2]octanes can be formed on ZSM-5. On the contrary, *cis* and *trans*-2,3-dimethyl -1,4-diazabicyclo[2.2.2]octanes are practically not formed due to steric constraints of these molecules.

Keywords: ZSM-5; alkylpiperazine; alkyltriethylendiamine; zeolite; catalyst.

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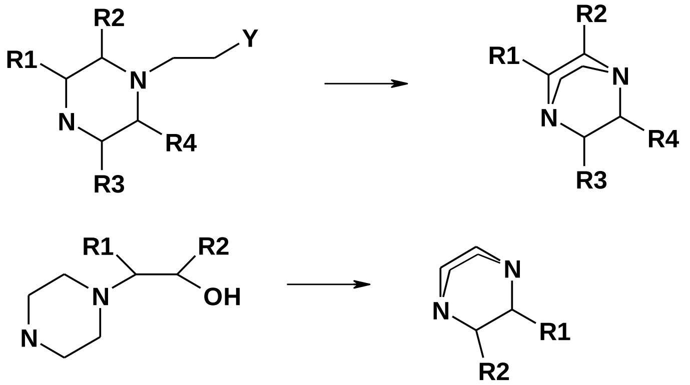
1. Introduction

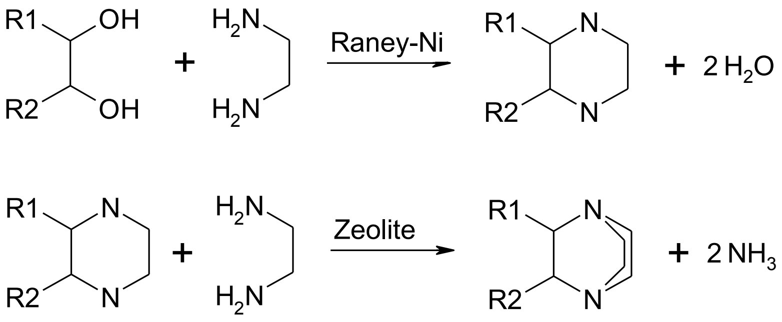
1,4-diazabicyclo[2.2.2.]octane (TEDA) is a white crystalline and hygroscopic compound with a melting point of 158-160°C and a boiling point of 173-174°C. It is an excellent catalyst for the formation of polyurethane substances (PUR). Due to the small difference in the melting and boiling points of TEDA and also its inclination to sublimation, its manipulation is not an easy task. Mostly it is used as an aqueous solution or in a suitable organic solvent. It is a disadvantage in the production of special PUR which require anhydrous conditions. On the other hand, 2-methyl-1,4-diazabicyclo[2.2.2]octane (2-MTEDA) is a colourless liquid with a melting point below 0°C and a boiling point of 184-186°C. It is less hygroscopic and its manipulation does not require special measures, yet the activity of 2-MTEDA for PUR applications is similar to that of TEDA. Other alkyl derivatives of TEDA for example, 2-ethyl and 2,3-dimethyl are likewise suitable [1].

The raw materials for the preparation of TEDA alkyl derivatives can be divided into two groups. They are 1-(2-aminoethyl) and 1-(2-hydroxyethyl) derivatives of C-alkyl piperazines and 1-(2-hydroxyalkyl) derivatives of piperazine (Scheme 1). In patent literature the procedures for the production of TEDA alkyl derivatives in the gaseous and also in the liquid phase are described. Kaolines [2], aluminosilicates, aluminophosphates [3] and also phosphoric acid modified titanium dioxide [4] are used as catalysts for the gas phase preparations. For the reactions in the liquid phase sodium and potassium salts of carboxylic acids and derivatives of phosphoric acid [5] are used.



Scheme 1. Different structures of piperazine derivatives used in the preparation of alkyl TEDA. R1-R4 alkyl or H, Y is an OH or an NH_2 group.

Lately, highly selective catalysts based on zeolite ZSM-5 are used for the TEDA synthesis. In addition, this particular catalyst enables the processing of a wide range of compounds like ethylenediamine (EDA), piperazine (PIP) and their 2-hydroxyethyl and 2-aminoethyl derivatives [6]. In our work we paid attention to ways of alkyl TEDA synthesis over zeolite HZSM-5 from a mixture of C-alkyl piperazines and ethylendiamine (scheme 2).



Scheme 2. C-alkylTEDA derivates synthesis. R1 = methyl or ethyl group, R2 = methyl group or hydrogen

2. Experimental

2.1. Chemicals

The zeolite catalyst ZSM-5 Si/Al = 120 extruded to a size of 1.6 mm using SiO_2 was supplied by SüdChemie.

2-methylpiperazine (2-MPIP) was prepared by reductive amination of 1,2-propanediol with ethylendiamine (EDA). 130 g of a 60% solution of 1,2-propanediol in dioxane and 12 g Raney-Ni (Degussa) were placed into a stainless steel autoclave (Riedel-de Haen). The hydrogen pressure in the autoclave was raised to 4 MPa and the temperature was maintained at 215°C. To limit the formation of piperazine (PIP), EDA (Fluka) was fed to the reactor at a rate of 0.2-0.3 ml/min up to a mole ratio of EDA : diol = 4 : 5. The resultant mixture was distilled in a column with 30 TP (Sulzer DX packing) and the fractions which contained 88 % 2-MPIP and 12 % PIP were collected in the temperature range of 153-158°C.

2-ethylpiperazine (2-EPIP) was prepared from 1,2-butanediol (Fluka) using the same procedure as that of 2-MPIP. The resultant mixture was distilled and the fractions which contained 93.5 % 2-EPIP and 6.5 % PIP were collected in the temperature range of 176-187°C.

Cis a *trans*-2,3-dimethylpiperazine (*cis*-2,3-DMPIP and *trans*-2,3-DMPIP) were prepared using the same procedure from 2,3-butanediol (Fluka) which contained *threo* and *meso* isomers in the ratio 33:67. The resultant mixture was distilled. Fractions which contained 95.5 % *cis*-2,3-DMPIP and 4.5 % PIP were collected in the temperature range of 162-165 °C. The second fraction which contained 50.5 % *cis* and 49.5 % *trans*-2,3-DMPIP was collected in the temperature range of 167-170°C.

2.2. Analytical methods

Quantitative analysis of reaction mixtures was carried out by means of the gas chromatograph SHIMADZU-GC-17 with an FI detector. The capillary column DB-5 (30 m x 0.32 mm, film 1 μm) was used. The carrier gas was nitrogen. Qualitative analysis of reaction mixtures was carried out by means of gas chromatograph GCMS-QP 2010 SHIMADZU equipped with a MS detector. The capillary column DB-5 (60 m x 0.32 mm, film 1 μm) and helium as the carrier gas were used. All the samples were diluted with methanol in the ratio 1:2 by weight and the feed to the gas chromatography was always 0.3 μL.

2.3. Catalytic test

The reactor was a glass tube with an internal diameter of 2 cm and length 55 cm. 1/3 of the tube was filled with porcelain fillings and on it a catalyst bed was formed. The remainder of the reactor after the catalyst bed was again filled with porcelain fillings. The reactor temperature was maintained at 360°C using an electrical heating jacket. Temperature was measured by means of a thermocouple, which was located in a thermo well (4 mm) located in the reactor axis. The reactants from a reservoir placed on digital balances were fed through the top of the reactor by a piston pump. The carrier gas (ammonia) from a gas cylinder was introduced through a regulation valve and a flow meter into the reactor co-currently with the reactants. Ammonia was fed in a mole ratio of 1:1 to the ethylene unit (EDA+alkyl-PIP). The reaction mixture flowed from the reactor to a Y-section and a water cooler where it condensed into a collection vessel. The gaseous fraction was vented off.

3. Discussion

For the synthesis of alkyl-TEDA an aqueous solution of EDA (37 %) in which 13 % of the prepared fraction contained C-alkylpiperazine was on every occasion prepared. The samples from the reaction mixture were each time diluted with methanol in the ratio 1:2 and the amount of the sample injected into the chromatograph was always the same (0,3 µl). Thus, the area percentage of the individual substances from the results can be compared. 15.4g of zeolite catalyst ZSM-5 (Si/Al = 120, silica gel 20 %) was placed into the reactor. 3 samples of C-alkylpiperazine were taken at 3 different values of the feed 34.4 g/h, 25.2 g/h, 14.3 g/h and temperature 360°C for each mixture fed. From the results (see Tab 1.) it is apparent that TEDA and PIP are formed at a much higher rate than 2-MTEDA. These results could be expected because one methyl group makes the shift of the 2-MTEDA molecule sterically demanding in the pore system of the zeolite ZSM-5.

In addition to the observed products a number of other products are formed as a result of elimination, aldol condensation and hydrogen transfer reactions. Amongst them are alkyl piperazines and alkyl pyrazines [7]. Intermediates like N-aminoethyl-C-alkyl-piperazines were not detected at all.

Tab 1. Concentration of observed compounds in the reaction mixture for various catalyst loads of the inlet mixture containing 11.4 % 2-MPIP, 1.6 % PIP, 37 % EDA and 50 % water (15.4 g of catalyst ZSM-5 Si/Al = 120, 360 °C, the concentrations are given as area percentage, the MS spectrum of 2-MTEDA (m/z(rel.in), 126(63.3), 84(30), 72(36.2), 69(44.8), 57(36.5), 56(100), 55(33.7), 42(78.3), 28 (32.3))

WHSV ($g_{mix}.g_{cat}^{-1}.h^{-1}$)	2.25	1.64	0.90
EDA	4.01	1.35	0.22
PIP	21.10	19.70	17.01
2-MPIP	21.78	20.64	18.53
TEDA	40.38	43.23	45.55
2-MTEDA	7.74	9.08	11.24

In the experiments with a mixture of 2-EPIP, TEDA and PIP were formed faster than 2-ETEDA, much like in the previous case of 2-MPIP (Tab 2.). The comparison of these results with the results from the previous experiments, it is clear that the mole ratio TEDA/2-ETEDA is lower than the ratio TEDA/2-MTEDA, thus 2-ETEDA is formed faster than 2-MTEDA (Figure 1). It is interesting because the ethyl group has to be sterically strained than the methyl group.

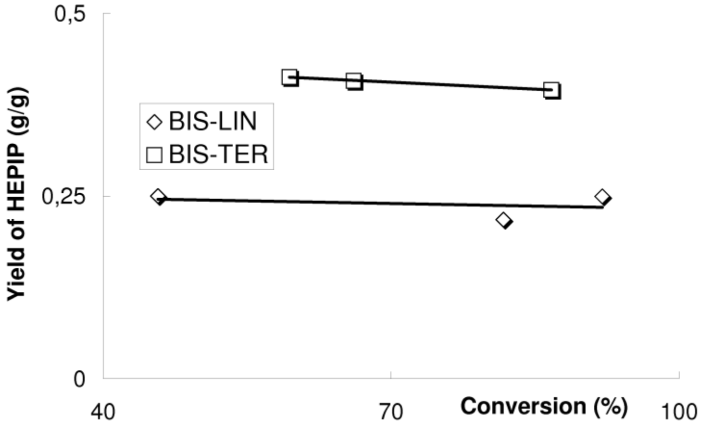


Figure 1. Comparison of mole ratios TEDA/2-MTEDA a TEDA/2-ETEDA for various reactor loads.

We assumed that the length of the alkyl chain would more or less hinder the diffusion, however, this was not confirmed. At this point, it is evident that another effect other than diffusion applies. The ethyl group can lead to a higher reactivity of 2-EPIP by increasing the electron density on nitrogen in the reaction with EDA and would be higher than that of the methyl group.

Tab 2. Concentration of observed compounds in the reaction mixture for various catalyst loads of the inlet mixture containing 12.2 % 2-EPIP, 0.8 % PIP, 37 % EDA and 50 % water (15.4 g of catalyst ZSM-5 Si/Al = 120, 360 °C, the concentrations are given as area percentage, the MS spectrum of 2-ETEDA (m/z(rel.in), 140(87), 98(86.6), 86(39.7), 83(52.9), 70(97.1), 57(62.1), 56(97.2), 55(52.5), 42(100), 41(40.7), 28(41))

WHSV ($g_{mix}.g_{cat}^{-1}.h^{-1}$)	2.25	1.64	0.90
EDA	7.27	2.42	0.25
PIP	20.25	19.30	16.73
2-EPIP	21.95	20.43	17.46
TEDA	33.62	38.22	41.16
2-ETEDA	11.25	13.36	15.72

For the preparation of 2,3-DMTEDA two mixtures with concetrations of 50 % water 37 % EDA and 13 % 2,3-DMPIP fraction were used. The first mixture only contained the *cis* isomer of 2,3-DMPIP with a 4.5 % PIP impurity and the second mixture had both isomers in an approximate ratio of 1:1. At this point, it is clear that the shift of the two methyl groups in 2,3-DMTEDA is restricted in both isomers. It is possible that the 2,3-DMPIP molecule does not diffuse into the pores of zeolite ZSM-5 or 2,3-DMTEDA cannot be formed inside the pores of the zeolite structure. The small amount of 2,3-DMTEDA detected in the reaction mixture is a result of the reaction on the surface of the zeolite crystals where there is no steric hindrance. The rate of formation of 2,3-DMTEDA isomers is more or less the same although it is apparent that *trans*-2,3-DMPIP reacts faster than the *cis* isomer to other products other than to *trans*-2,3-DMTEDA. The experimental results are summarized in tables 3 and 4.

Tab 3. Concentration of observed compounds in the reaction mixture for various catalyst loads of the inlet mixture containing 12.4 % cis-2,3-DMPIP, 0.6 % PIP, 37 % EDA and 50 % water (15.4 g of catalyst ZSM-5 Si/Al = 120, 360 °C, the concentrations are given as area percentage, the MS spectrum of cis-2,3-DMTEDA (m/z(rel.in), 140(41.2), 84(36.8), 72(40.3), 71(26.8), 69(33.6), 56(100), 42(41.7), 28(24.5))

WHSV ($g_{mix}.g_{cat}^{-1}.h^{-1}$)	2.25	1.64	0.90
EDA	3.47	1.40	
PIP	18.95	17.26	14.59
cis-2,3-DMPIP	33.86	33.69	33.24
TEDA	38.90	41.95	44.75
cis-2,3-DMTEDA	0.64	0.83	1.13

Tab 4. Concentration of observed compounds in the reaction mixture for various catalyst loads of the inlet mixture containing 6.5 % cis-2,3-DMPIP, 6.5 % trans-2,3-DMPIP, 37 % EDA and 50 % water (15.4 g of catalyst ZSM-5 Si/Al = 120, 360 °C, the concentrations are given as area percentage, the MS spectrum of *trans*-2,3-DMTEDA is similar to that of the *cis* isomer

WHSV ($g_{mix}.g_{cat}^{-1}.h^{-1}$)	2.25	1.64	0.90
EDA	2.35	0.90	
PIP	17.97	16.61	14.33
cis-2,3-DMPIP	16.53	16.36	16.11
trans-2,3-DMPIP	14.58	14.64	13.58
TEDA	42.04	44.22	46.32
cis-2,3-DMTEDA	0.35	0.44	0.58
trans-2,3-DMTEDA	0.31	0.38	0.49

4. Conclusion

It was found out that the catalyst with a ZSM-5 structure preferentially forms TEDA in contrast to all the observed alkyderivatives of TEDA. 2-MTEDA and 2-ETEDA are rather sterically hindered although it is possible to prepare them in good yield over zeolite ZSM-

5. It was also observed that 2-ETEDA forms at a higher ratio to TEDA than 2-MTEDA. On the contrary, both *cis* and *trans* 2,3-DMTEDA isomers are spatially demanding and therefore, it is impossible to prepare them in high yield over zeolite ZSM-5.

Symbols used

TEDA	1,4-diazabicyclo[2.2.2.]octane
2-MTEDA	2-methyl-1,4-diazabicyclo[2.2.2]octane
2-ETEDA	2-ethyl-1,4-diazabicyclo[2.2.2]octane
EDA	ethylenediamine
PIP	piperazine
2-MPIP	2-methylpiperazine
2-EPIP	2-ethylpiperazine
trans-2,3-DMPIP	*trans*-2,3-dimethylpiperazine
cis-2,3-DMPIP	*Cis*-2,3-dimethylpiperazine

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