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AMINATION OF DIMETHYL ETHER ON ZEOLITE CATALYSTS 1. INFLUENCE OF ALKALI-CATION CONTENT OF T-ZEOLITE ON THE DIMETHYL ETHER CONVERSION AND METHYLAMINE DISTRIBUTION

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T-zeolites with different H^+-exchange degrees (0, 44, 68 and 89%) were used for the amination of dimethyl ether in the temperature range of 603 to 703 K. On a Na, K-T-zeolite sample (synthesis form) at low dimethyl ether conversion high selectivities of lower methylated amines were observed and methanol was formed as by-product. By proton exchange the conversion could be enlarged, but the selectivity distribution was shifted to trimethylamine.

Keywords: Alkali zeolites, acid zeolites, proton exchange, phase selectivity, methylated amines

1. Introduction

The three methylamines, i.e. monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA), are important chemical intermediates and commercially manufactured by the reaction of methanol (MeOH) and ammonia. The methylamines are prepared in fixed-bed reactors at reaction temperatures ranging from 623 K up to 723 K under pressures of 15 to 30 bar. In all cases, ammonia is employed in excess [1,2]. Amorphous silica-alumina is widely used as catalyst. The reaction proceeds towards a TMA-rich product stream with a thermodynamically predicted distribution of 17, 21 and 62 mole% for MMA, DMA, and TMA, respectively, at complete MeOH conversion. The global market, however, demands amounts of 33, 53, and 14 mole% (MMA, DMA, TMA) [3]. In most cases, TMA and excess ammonia were recycled to reach a higher yield of lower alkylated methylamines.

Owing to their shape-selective and acid-base properties, zeolite catalysts have been used in a wide range of organic syntheses [4,5]. In the last ten years, some efforts have been made in methylamine synthesis with MeOH as feed to increase the yield of DMA by using zeolite catalysts. In addition to alkali-exchanged mordenites and Y-type zeolites, narrow-pore zeolites, such as erionite, RHO, T, ZK-5, and chabazite in the protonated form, have been used [6–12]. On these zeolites DMA selectivities of 40% up to 70% have been realized at 90% MeOH conversion. Weigert [7] and Ashina et al. [8] were able to produce DMA with an increased selectivity on sodium-containing mordenite. Keane et al. [10–12] used narrow-pore zeolites in the protonated form, such as RHO, ZK-5, and chabazite (synthetic and natural samples), to increase MMA and DMA selectivity. Additionally, a large number of different procedures has been described in the patent literature (e.g. [13–15]).

Our investigations illustrate some aspects of the connection of shape-selective and acid-base properties of zeolite catalysts in several organic reactions starting with methylamine synthesis. Depending on whether dimethyl ether (DME) or MeOH is used as feed, some differences in the reaction regime are expected. This applies in particular to the different sorption behavior of DME or MeOH, the sequence of pathways in the reaction mechanism, and the different catalytic influence of the acid sites on the formation of methyl cations. Owing to the double control of the reaction regime by the zeolite properties (acidic and shape-selective) the influence of the number and strength of acid centers on ether hydrolysis and ammonia alkylation during DME conversion should additionally result in overcoming of product distribution determined by the thermodynamic equilibrium.

Owing to the different possible reaction pathways (fig. 1), the amination may be used as a model for studying the influence of zeolite catalyst properties on the reaction mechanism in dependence on the feed used. These reaction pathways should be applicable to the amination of DME or MeOH based on the existence of methyl cations formed during ether hydrolysis or MeOH dehydration. Feed conversion should depend on the number and strength of acid sites, whereas the amine product distribution should be determined by pore geometry and possible diffusional limitations.

This paper is a first report describing the influence of the alkali content of the narrow-pore erionite-rich zeolite T on the product distribution during the amination of DME.

2. Experimental

Three H/Na,K-containing T-zeolites were prepared starting from an industrial erionite-rich T-zeolite (Chemie AG, Bitterfeld-Wolfen). The particular batch of T-zeolite, being a structural intermediate of erionite and offretite, was synthezised under conditions which favour the preferred formation of the erionite structure. The Si/Al ratio of the synthezised product was ca. 4.2 with a crystallite size of 2–3 μm. Sodium and potassium were exchanged by NH_4^+ (0.5 N NH_4NO_3 solution) at 353 K for several times and one sample was additionally treated by intermediate calcination steps to obtain a higher degree of exchange. Subse-

I. Amination reactions

$(CH_3) + NH_3 \rightarrow CH_3NH_2 + (H^+)$ *)
$(CH_3) + CH_3NH_2 \rightarrow (CH_3)_2NH + (H^+)$ *)
$(CH_3) + (CH_3)_2NH \rightarrow (CH_3)_3N + (H^+)$ *)

II. Disproportionation of amines

$2\ CH_3NH_2 \rightarrow NH_3 + (CH_3)_2NH$
$2\ (CH_3)_2NH \rightarrow CH_3NH_2 + (CH_3)_3N$
$CH_3NH_2 + (CH_3)_2NH \rightarrow (CH_3)_3N + NH_3$

III. Side reactions

$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$
$2\ CH_3OCH_3 \rightarrow 2\ CH_3OH + C_2H_4$

*) methanol feed–reaction product: water; dimethyl ether feed–reaction product: methanol.

Fig. 1. Possible reaction pathways during the amination of methanol or dimethyl ether on zeolites.

quently, the samples were calcined up to ca. 773 K to remove ammonia. All calcination treatments were carried out under shallow-bed conditions and temperature-programmed to remove water in the lower temperature range. After calcination, each zeolite powder was treated with pure silica (65 wt.-% zeolite and 35 wt.-% SiO_2) to shape catalyst pellets. Table 1 shows the catalysts used, the corresponding pretreatment conditions as well as Na/K-contents.

All experiments were carried out in a bench-scale reactor (quartz glass, catalyst volume ca. 30 ml) under atmospheric pressure. DME and ammonia were fed directly into the reactor after the flow controller and gas mixing system. The reaction products were analyzed by on-line gas chromatography, using a 3 m * 3

Table 1
Applied T-zeolite samples, pretreatment conditions and Na/K content

Sample	Exchange time (2 hours each)	Na/K content (wt.-% Na_2O)	Exchange degree (%)
TA	–	8.8	0
TB	1×	4.9	44
TC	4×	2.8	68
TD	8× *	1.0	89

* Intermediate calcination was performed after every two exchange procedures at 773 K.

mm stainless-steel column packed with Chromosorb W/AW (80–100 mesh) (Serva) coated with 2% Na_3PO_4 (Lachema) and 10% PG 400 (Merck), at 333 K with flame ionization detector and argon as carrier gas.

The catalytic results given in the figures were obtained after ca. two hours time on-stream. The total selectivity of the three methylamines describe the sum of the single selectivities of MMA, DMA, and TMA and refer to converted DME. The single selectivities of MMA, DMA, and TMA are calculated in the same way. After the reaction, the zeolite catalysts could be regenerated by air at ca. 723–773 K. In the subsequent reaction cycles the catalysts reached almost the same activity and selectivity they had prior the regeneration.

We have investigated the product distribution during DME amination as a function of reaction temperature (603 to 703 K). In general, a feed ratio of ammonia-to-DME of 2 and a WHSV of ca. 0.5 h^{-1} were used.

3. Results and discussion

Fig. 2 depicts the DME conversion. As expected, the conversion on the non-exchanged sample TA is very low. With ion exchange and transformation of the Na/K-form into the H-form, the DME hydrolysis is favoured, and with increasing reaction temperature the conversion rises up to 95%. Under the reaction conditions applied it seems that the exchange degree of the used H^+-containing samples is not important for the conversion rate as long as it is greater than 44%.

The total selectivity of the three methylamines is represented in fig. 3. The decrease in methylamine selectivity depends on the exchange degree: the higher

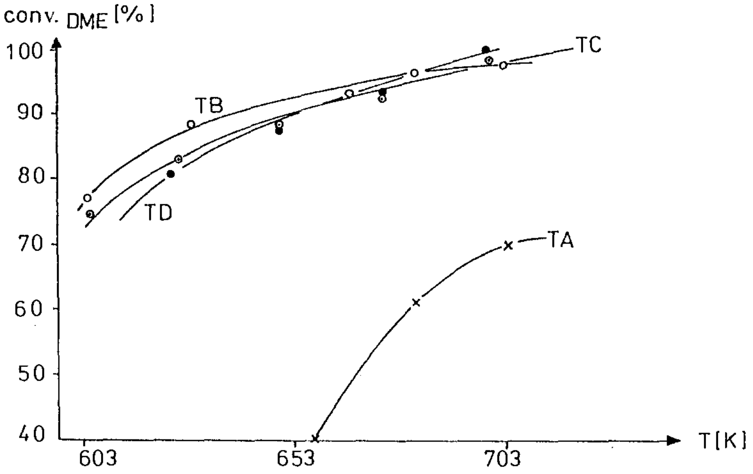

Fig. 2. DME conversion on T-zeolites: dependence on the reaction temperature (Ammonia-to-DME ratio = 2, WHSV = 0.5 h^{-1}, atmospheric pressure).

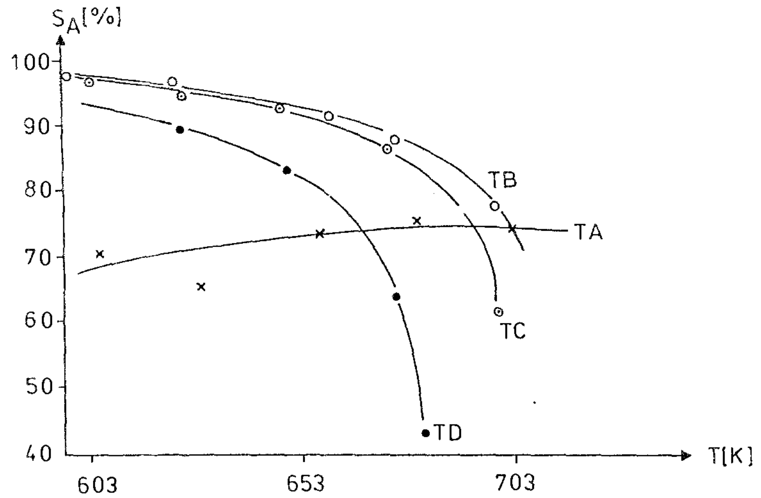

Fig. 3. Methylamine selectivities obtained on T-zeolites: dependence on the reaction temperature (Ammonia-to-DME ratio = 2, WHSV = 0.5 h^{-1}, atmospheric pressure).

the alkali content the lower the decline of selectivity. The total selectivity achieved on the catalyst TA is nearly constant at a level of 70% and is the lowest one compared with the exchanged catalysts. This could be explained by the slowest DME hydrolysis rate. The total selectivity obtained on the catalysts TB, TC, and TD decreases in dependence on the reaction temperature, in particular above 653 K.

Methyl cations are formed to a lesser extent on the TA catalyst than on the TD catalyst during DME hydrolysis. At lower temperatures they favourably react to amines, and at higher temperatures to hydrocarbons because ammonia could not be engaged in the reaction mechanism on acid sites at elevated temperatures (as found during TPDA and IR investigations and described in detail in [16]). In contrast, on the TA catalyst, the amine formation is constant due to the electrophilic methyl cation deficiency and the absence of Bronsted-acid sites; the selectivities of the by-products are however changed. The by-product selectivities (MeOH and hydrocarbons) of all samples investigated are summarized in table 2.

Beside disproportionations, parallel reactions and the formation of DMA and TMA (fig. 1) other possible reaction pathways in the system ammonia-DME are important for the explanation of the results obtained.

$$H_3C\text{-}O\text{-}CH_3 + NH_3 \rightarrow MMA + CH_3OH \quad (I)$$

$$H_3C\text{-}O\text{-}CH_3 + H_2O \rightarrow 2\ CH_3OH \quad (II)$$

$$CH_3OH + NH_3 \rightarrow MMA + H_2O \quad (III)$$

$$H_3C\text{-}O\text{-}CH_3 \rightarrow \text{Hydrocarbons} + H_2O \quad (IV).$$

According to eq. (I), DME amination leads to MMA and MeOH. MeOH could be additionally formed by ether hydrolysis (II). The MeOH formed and ammonia

Table 2
By-product selectivities (wt.-%) during the amination of DME on T-zeolite samples depending on the reaction temperature (ammonia-to-DME ratio = 2, WHSV = 0.5 h^{-1}, atmospheric pressure)

Catalyst	TA		TB		TC		TD	
temperature (K)	MeOH	HC *	MeOH	HC *	MeOH	HC *	MeOH	HC *
603	30	2	1	3	tr.	4	tr.	8
628	28	2	1	4	1	4	tr.	10
653	25	6	1	9	2	6	tr.	13
678	14	11	tr.	12	tr.	14	tr.	34
703	10	16	tr.	21	tr.	43	tr.	64

* Hydrocarbons (methane, C_{2-4} paraffins and olefins).

could react again into MMA and water (III). As a side reaction, DME could react to hydrocarbons and water (IV) (MTG, MTO), particularly on acid sites at higher temperatures.

On the non-Bronsted-acid sample (TA) considerable amounts of MeOH were observed, caused by the formation of MeOH according to eqs. (I) and (II). On non-Bronsted-acid sites the excess of MeOH could not be converted to methylamines neither could it react to DME again to a sufficient degree. Only at higher reaction temperatures were some hydrocarbons formed according to eq. (IV).

On the acidic samples TB to TD, the DME conversion was high and methylamines were formed in high selectivities according to eq. (I) and (III). The whole amount of the "in-situ" formed MeOH was converted into reaction products on acid sites and were not observed in the product stream. At higher reaction temperatures, where the ammonia chemisorption on Bronsted sites should be more difficult, considerable amounts of hydrocarbons (MTG reaction) were formed on acid sites and only traces of MeOH could be detected. Generally, the decline in amine selectivity caused by the increased formation of hydrocarbons at elevated temperatures is reflected by the selectivities of the single methylamines.

Fig. 4 mirrors the selectivity of MMA on the applied catalysts. The selectivity on the sample TA is very high, starting at 65% and declining to 35% with a rise in reaction temperature. In contrast to it, the observed selectivities on the catalysts TB and TC are lower, but more constant. They decreased solely in the upper temperature range. The selectivity curve of the sample TD shows the same behaviour, but the selectivity data are lower compared to the results obtained on the catalysts TB and TC.

Fig. 5 depicts the observed DMA selectivities. Whereas the selectivity of DMA on the TA sample was increased, the values obtained on the other samples were distinctly diminished. The highest selectivities for DMA up to ca. 40% were reached on the zeolite sample TA.

The development of TMA selectivities on the four catalysts as a function of the reaction temperature is demonstrated in fig. 6. No TMA was formed on the

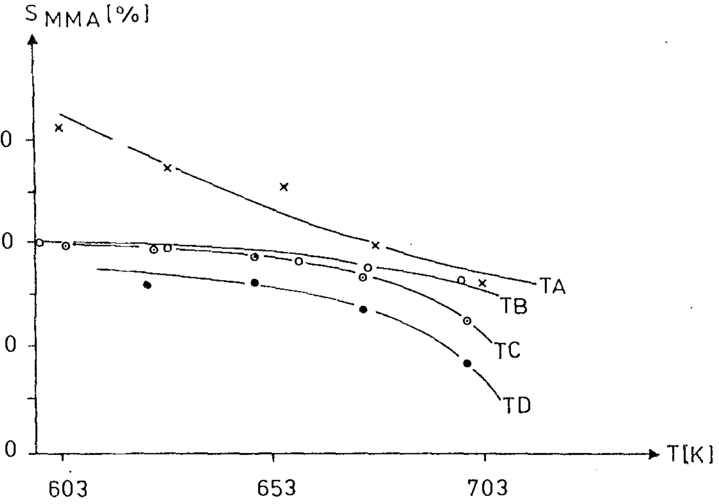

Fig. 4. Selectivity of MMA on T-zeolites: dependence on the reaction temperature.

sample TA below 653 K and a selectivity of only ca. 10% was obtained at 703 K. Higher selectivities were reached on the acidic samples TB and TC, but they decreased with rising temperatures and enlarged hydrocarbon formation. The higher amounts of TMA formed on acidic catalysts could result from the concentration of the acid character of the zeolites by higher proton content connected with a better accessibility of the pore system and the pore mouths of zeolite T. These considerations concerning the TMA selectivity are clearly reflected in the case of sample TD. The highest TMA selectivity was observed on the catalyst with the lowest alkali content (up to 45%).

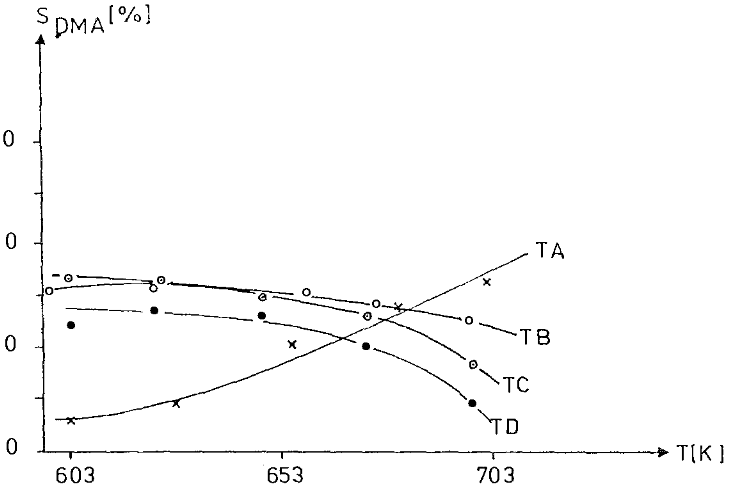

Fig. 5. Selectivity of DMA on T-zeolites: dependence on the reaction temperature.

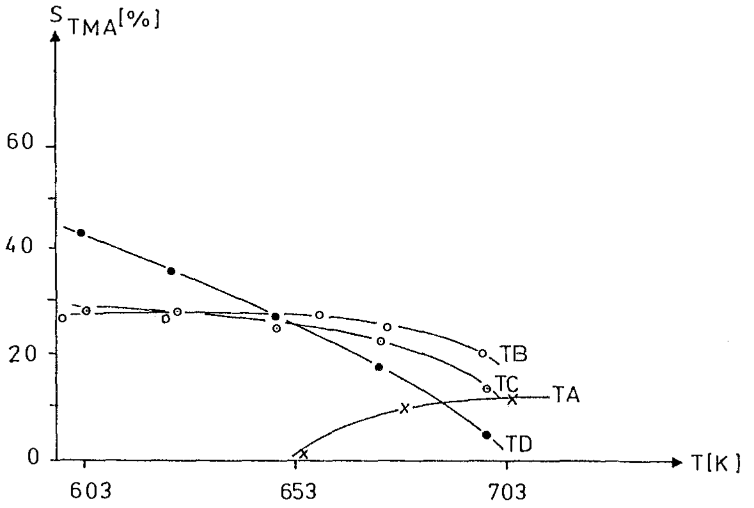

Fig. 6. Selectivity of TMA on T-zeolites: dependence on the reaction temperature.

Table 3 mirrors the normalized selectivities of the three methylamines expressed as the quotient of single methylamine selectivity (MMA, DMA or TMA) and total amine selectivity. It is clear that the change in selectivities is exclusively due to the product distribution of the methylamines and is a function of the proton content of the T-zeolite catalysts.

Summing up, we have shown the influence of different alkali contents in T-zeolites on their acidity and shape-selective behaviour in DME amination to methylamines. Although in the literature [9,10] the methylation of ammonia on erionite or erionite-like zeolite catalysts is described applying methanol as alkylating agent, the regioselectivity is nearly the same when dimethyl ether is used. On the non-exchanged catalyst high selectivities for the lower-methylated MMA and DMA were observed at low DME conversion. In addition to the hydrocarbons, MeOH is a major by-product. With increasing exchange rate the conversion of DME is increased but the product distribution then shifts to TMA. Above 653 K more hydrocarbon is formed owing to changes in reaction pathways.

Table 3
Normalized selectivities of the single methylamines

Catalyst temperature (K)	TA	TB	TC	TD	TA	TB	TC	TD	TA	TB	TC	TD
	S (MMA)				S (DMA)				S (TMA)			
603	90	40	42	32	10	33	32	27	0	27	26	41
628	83	41	42	34	17	32	32	30	0	27	26	36
653	60	42	41	36	30	31	32	30	10	27	27	34
678	51	41	42	37	35	31	31	30	14	28	27	33
703	42	43	43	53	45	30	31	28	13	27	26	19

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