

## CONVERSION OF ALKYLAROMATICS ON HIGH-SILICA MORDENITES

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### ABSTRACT

Comparison is made on the acidity and catalytic behaviours during toluene and o-xylene conversion on silica-rich mordenites with close chemical compositions obtained by direct synthesis or by dealumination with HCl and EDTA. The samples acidity is studied by the TPD of  $\text{NH}_3$ . The catalytic activity is measured in a flow reactor at temperatures between 453 and 513K and atmospheric pressure in presence of  $\text{H}_2$  or Ar as carrier gases. It is found, that samples obtained by direct synthesis possess a higher disproportionation activity and are deactivated much more rapidly than the mordenites dealuminated with HCl and EDTA. On the basis of the results obtained some differences and peculiarities in the catalytic action of the mordenite samples with nearly the same chemical composition, prepared in various ways were interpreted.

### INTRODUCTION

The discovery of the new class of high-silica zeolites of the ZSM-5 type have rekindled the interest in the silica-rich mordenites too. The catalytic activity of these mordenites can be influenced by varying the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio over a very large interval using dealumination with mineral acids or chelating agent /1/. Another possibility to reduce the aluminium content is the direct synthesis, varying the composition of the initial gel /2, 3/. Thus, silica-rich mordenites appear to be a suitable model system for studying the effect of the preparation method on the catalytic performance of zeolites with equal crystalline structures. The increasing interest in these systems is also due to recent data concerning the differences in Al distribution in the zeolite crystal depending on the preparation conditions /4, 5/. In other words, high silica mordenites present a possibility to investigate the effect of both the content

and the distribution of aluminium on its properties. In the literature there are no comparative data on the catalytic behaviour of silica-rich mordenites prepared by direct synthesis and by dealumination excepting the data from the systematic studies of Minachev et al. on o-xylene conversion /5/ and ethylene aromatization /2/.

The catalytic action of the H-forms of mordenites with close chemical composition synthesized in different ways are compared in the present paper with respect to the conversion of toluene and o-xylene. The sample used had a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio ranging from 11 to 18, achieved by direct synthesis (designated as MS) and dealumination of NaM with HCl and EDTA (MD). Special attention was paid to the disproportionation reaction since it is assumed to be especially sensitive to zeolite treatments which modify the acid center concentration /6/. The acidic properties of the samples were also characterized by TPD of ammonia.

## EXPERIMENTAL

Table 1  
Chemical composition of the catalysts used

Samples	$\text{SiO}_2/\text{Al}_2\text{O}_3$ mol ratio	$\text{NH}_3$ mmol/g	Mode of preparation
MS <sub>11,7</sub>	11,7	-	Direct Synthesis
MS <sub>15,7</sub>	15,7	0,96	
MS <sub>18,2</sub>	18,2	0,98	
MD <sub>14,4</sub>	14,4	-	2,2M HCl
MD <sub>14,7</sub>	14,7	1,05	6,0M HCl
MD <sub>17,4</sub>	17,4	0,99	6,0M HCl
MD <sub>15,3</sub>	15,3	-	EDTA
MD <sub>12,1</sub>	12,1	0,94	EDTA

Table 1 presents the chemical composition of the samples. The Na-forms of MS were obtained by direct synthesis at 423K in an autoclave with stirring /2/. MD were prepared from NaM with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 10 by dealumination with EDTA or with 2,2 and 6,0 M HCl at 358K /7/. The preparation of the H-forms of MS and MD (dealuminated with EDTA) was achieved by ion exchange with 2M  $\text{NH}_4\text{Cl}$  solution followed by thermal treatment of the ammonium modifications at 723K for 6 h in air.

The phase purity and the crystallinity of the samples were controlled with a DRON-1 diffractometer using  $\text{CuK}_\alpha$  radiation and electron

microscopy /8/.

The samples acidity was determined by TPD of  $\text{NH}_3$ . The procedure employed was described in /9/. The catalytic studies were carried out in a flow reactor at atmospheric pressure in presence of  $\text{H}_2$  and Ar as carrier gases, the gas: hydrocarbon ratio being 10. The temperature varied between 453 and 513K. WHSV of  $1,1 \text{ h}^{-1}$  was used.

## RESULTS

### Toluene disproportionation

The H-forms of the mordenite type zeolites are known to possess a high acidity and catalytic activity with respect to the conversion of alkylaromatic hydrocarbons, but are very rapidly deactivated /10, 11/. For this reason, a study of the catalytic performance of samples with practically the same chemical composition, obtained in different ways required selection of the experimental conditions ensuring a correct comparison of their catalytic activities. The reaction temperatures usually applied to toluene disproportionation proved to be inappropriate in this case due to pronounced side reactions. For this reason we used an approach allowing a study of the activity change with the time on stream at a gradually increase of temperature up to values at which some of the samples showed offset of deactivation (Fig.1).

Comparison of the data on the catalytic activities of the two samples with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  about 18 showed MD to have a lower catalytic activity than MS but to be much more stable at temperatures of 453 - 493K (Fig.1 A). A similar situation was observed with MD (prepared under mild conditions - with 2,2M HCl) having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of about 15 in comparison to MS (Fig.1 B).

To check the validity of what was established above, concerning the lower activity of MD than that of MS, we prepared a series of samples dealuminated also with EDTA. The results showed that irrespective of the way of dealumination all the MD probes had a lower activity and a better stability than the MS (with an analogous modulus, (Fig.1 B and C). In addition, it should be noted that due to the rapid ageing of MS samples at higher temperature (513K) the dealuminated materials become more active which could cause some misunderstandings. As the linear relationship between  $\ln k - 1/T$  in the Arrhenius plot shows, there are no diffusional limitations for all the dealuminated samples investigated.  $E_a$  ranges from 14 up to 19 Kkal/mol.

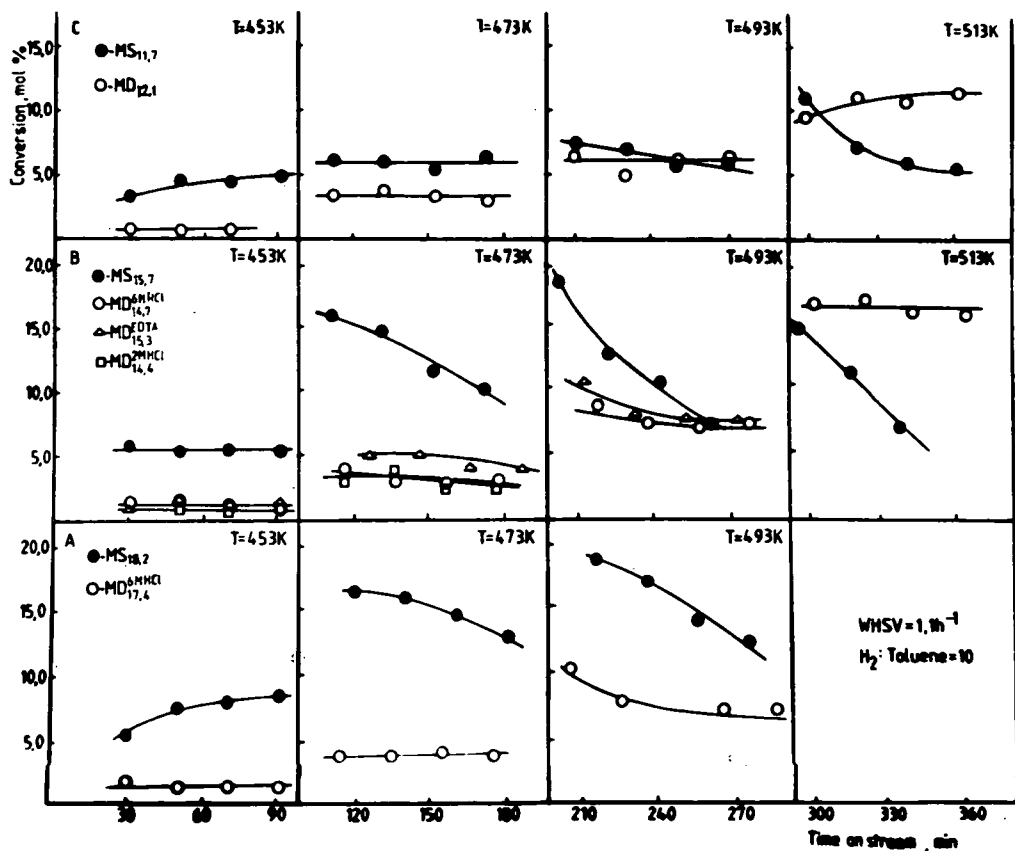


Fig.1. Toluene conversion over differently prepared mordenites with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios about:  
 A-18, B-15 and C-12

Another interesting result from the comparison of the catalytic action of directly synthesized and dealuminated samples is that MD have a considerably higher selectivity with respect to the disproportionation reaction. At higher temperatures the benzene: xylenes ratio is about 0,8 - 0,9 for MD whereas with MS it is considerably lower (0,6 - 0,7). It indicates a higher degree of dealkylation on MS. As far as this result presupposes the presence of more acidic centers in MS, it was of interest to compare the acidity of the series of samples with close  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. Since the couples of mordenites being investigated had nearly the same aluminium contents, differences in the total number of acidic centers were not to be expected. Indeed,  $\text{NH}_3$  adsorption at 573K (a temperature at which adsorption is assumed to proceed at the strongly acidic centers) gave practically the same amounts of ammonia adsorbed on the samples

being compared. The shapes of the thermodesorption curves were also analogous (Fig.2). The broad maximum at the thermodesorption curves observed with MS can be indicative of a larger number of strongly acidic centers.

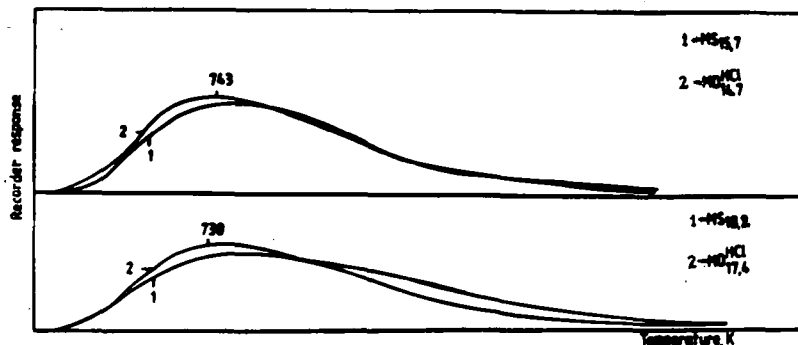


Fig.2. TPD chromatograms of  $\text{NH}_3$  adsorbed at 573K

### O-xylene conversion

It is known that the o-xylene molecule has a more basic character and a reactivity considerably exceeding that of toluene. This presupposes the proceeding of intensive xylene disproportionation along with isomerization on these strongly acidic catalysts. Hence, the study of o-xylene conversion allowed checking ones more the differences found in the disproportionation activities of MS and MD with respect to a higher - reactive hydrocarbon. On the other hand, comparison and differentiation between the performance of the samples in the two competitive reactions: disproportionation and isomerization can be made.

The results indicate a higher o-xylene total conversion in presence of MD at temperatures 443-473K, which was found to be close to that of MS at 503K. However, comparison of the disproportionation and dealkylation activities of MD and MS with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of about 18 showed a much larger contribution of these side reaction with respect to the total conversion at the very beginning of the experiment in the case of MS than in that of MD (55 and 50% respectively, Fig.3 A, 3 B). After the fast decrease in activity during the first twenty minutes of the experiment and the much more rapid deactivation of MS, MD exhibited higher disproportionation and isomerization ability. This is to be illustrated also by the presence of a maximum in the curves showing the change in the amount of the isomerization products (m- and p- xylenes) for the two samples being compared (Fig.3 C). Therefore, it can be stated that the trend to a very fast

ageing of MS disguises its considerably higher initial activity. In addition, this tendency is more pronounced with MS samples in both disproportionation (Fig.3 A) and isomerization (Fig.3 C).

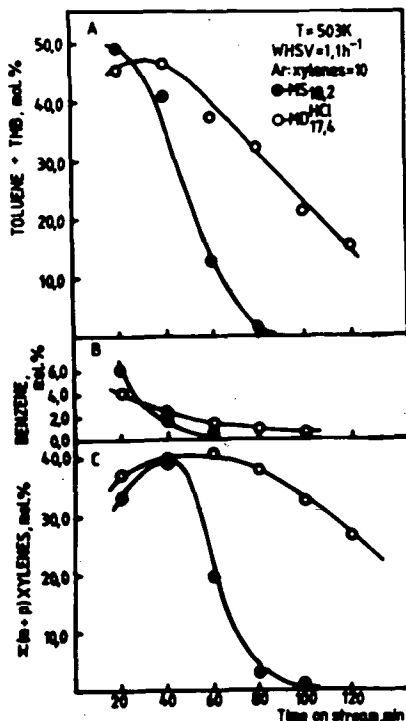


Fig.3. Conversion of o-xylene on dealuminated MD<sub>17,4</sub> and as-synthesized MS<sub>18,2</sub> at 503K

## DISCUSSION

Comparison of the data obtained during conversion of alkyaromatic hydrocarbons at relatively low temperature (where effects of rapid deactivation are absent) showed that the directly synthesized samples had a higher disproportionation activity but a lower stability than the dealuminated ones. A higher activity of MS compared to MD with a similar chemical composition was also found in other reactions such as C<sub>2</sub>H<sub>4</sub> aromatization /2/ and cracking of n-paraffines /12/. On the other hand, the studies of Minachev et al. /5/ showed a higher total conversion degree of o-xylene on MD. Therefore, irrespective of the close Si/Al ratio the samples prepared by various methods differed in their behaviours.

It is known that the disproportionation activity of mordenite catalysts is directly associated with their Brønsted acidity /13-15/ or rather /14,15/ with the number of the strongly acidic centers of this type. Our results of TPD of ammonia at 573K showed nearly the same values of the total amount of  $\text{NH}_3$  adsorbed for the pairs of samples with a close silicate modulus (Table 1). However, it is difficult to state explicitly that there are different number of centers with diverse strengths. The data in Fig.2 only indicate this tendency. Obviously, as Jacobs et al. /16/ suggested, some slight differences in the acidity spectrum of samples with close compositions cannot be established by TPD of  $\text{NH}_3$ . For the present, measurements of the heats of ammonia adsorption /17/ have only permitted to state that there are some differences in acid strength distribution in MS (synthesized in the presence of a TEA-cation) and MD with an identical  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 20. However these differences alone cannot satisfactorily explain the effects on the catalytic activities observed by us.

The presence of a gradient in the concentration of the Al atoms and hence, of the active centers (depending on the preparation conditions of the samples) may be an additional reason for the different performance of the mordenites. On the basis of data from the literature, dealumination with mineral acids /1, 4, 5/ and EDTA /1, 18/ leads to preferential elimination of aluminium from the surface layers of the mordenite crystals. In addition, a model proposed by us /19/ have shown that the absolute number of aluminium atoms in the unit cell of the samples obtained by dealumination is lower than that in the corresponding directly synthesized samples with the same silicate modulus. As far as the MS studied by us are concerned, the XPS data /5/ indicate a uniform distribution of Al in the zeolite crystal.

Thus it can be assumed that depending on the method of preparation, zones with active centers differing in number and strength appear in the mordenite crystal. The presence of this microheterogeneity should affect the catalytic activity especially in cases when the reacting molecules and products have sizes comparable with those of the mordenite channels. Hence, appropriate variation of the experimental conditions and the kind of substrate used could give additional information on the existence of such a gradient in the concentration of the active centers.

Indeed, our data concerning the distribution of the products of xylene disproportionation - toluene and trimethylbenzenes (TMB) confirmed this assumption. At relatively low reaction temperatures (443K) in the absence of cracking products, the toluene : TMB molar ratio was to be equal to 1. This was actually observed with the directly synthesized samples only. On the contrary, at practically identical conversion degrees, this ratio was by about one order of magnitude higher for MD and only at 503K it became equal to that for MS. A similar increase in the toluene/TMB ratio was found with rising the contact time. Only at very low conversion degrees, after practically complete deactivation of the MD samples, the toluene : TMB ratio approached unity. It should be noted that the above factors (reaction temperatures, contact time and degree of deactivation) did not affect the value of the toluene : TMB ratio for the MS samples.

On the basis of the results obtained and the hypotheses suggested the different behaviours of MS and MD could be explained as follows. The higher concentration of active centers in the pore mouth of the MS zeolite facilitates its rapid interaction with the reacting molecules and determines the relatively higher initial disproportionation activity of this sample. As some authors proposed, bimolecular disproportionation needs a pair of nearly situated acid sites /13/, which density on the surface of MS probably is greater than on MD.

The faster deactivation compared to that of MD is an additional evidence of the prevailing participation of centers localized near the surface and of the relatively quick blocking of the access to the interior sites. A similar explanation of the effect of the acid center density on the stability of the catalytic activity can be found in the literature for highly dealuminated zeolites /18, 20/. With dealuminated samples disproportionation probably proceeds at a larger depth of the mordenite crystal due to the selective denuding of the surface layers and pore mouth sites in the process of dealumination /18/. This can be the reason for the lower disproportionation activity and enhanced toluene : TMB ratio during a reaction proceeding at lower temperatures. The processes of coke precursor formation also concerns a zone inside the zeolite crystal. Moreover, after being formed in the narrow mordenite channels, the large molecules of the polyalkylaromatic hydrocarbons (in which the TMB participate) would hardly be able to desorb out of these channels.



This may be an explanation for the observed higher toluene : TMB ratio. The restricted participation of the surface layers in these reactions in comparison with MS will lead to a much slower fouling rate for MD. Probably, the gradual elimination of the acid sites in the bulk of the crystal by deactivation results in disappearance of the initial inhomogeneity of the active centers distribution in MD and the toluene/TMB ratio approaches one, as in the case of MS.

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