

ISOMERIZATION OF XYLENES ON H-MORDENITE AND H-CLINOPTILOLITE OF NATURAL ORIGIN

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There are large deposits of two important zeolites, clinoptilolite and mordenite, in Hungary in the rhyolite tuffs of the Tokaj mountains as microcrystalline rock-forming minerals. The H-derivatives of these zeolites prepared by Ag⁺-exchange and subsequent reduction are very active and stable catalysts in xylene isomerization, as opposed to the H-derivatives obtained by acid treatment or ion-exchange with NH₄⁺ ions. By means of TG—MS measurements we have established the concentration of OH groups in the various catalysts prepared, the conditions of their formation and their thermal stability. The experimental results help explain the differences between the catalytic properties of the Ag→H-mordenite and those of the other H-mordenites.

Introduction

On the H-forms of zeolite catalysts the following reactions of C₈ alkylaromatic compounds occur depending on the conditions: isomerization of xylenes into each other, metathesis, partial or complete dealkylation of xylenes and of ethyl-benzene. The acidic insulator catalysts are active without regeneration only for a very short time (between a few seconds and 1-2 days). Their activity can be stabilized by the incorporation of metals or metal oxides into their structure. This, however, requires consideration of active centers other than those of the acidic type, which may promote additional reactions. In this paper the catalytic properties of acidic derivatives of natural clinoptilolite and mordenite prepared in different ways are described. Our aim was to obtain zeolites in the H-form with a stable activity and selectivity in order to study the isomerization of xylenes, regarding the other possible processes as undesirable side-reactions.

Experimental

Preparation and characterization of the catalysts

There are large amounts of microcrystalline mordenite and clinoptilolite in Hungary as rock-forming minerals. The mordenite and clinoptilolite content of these sedimentary rocks varies but in samples from certain locations may be as high as 70—80%. On the basis of X-ray diffraction and electron microscopic data, we have established that in both zeolite-containing rocks, used as starting materials for

the catalysts, the main crystalline non-zeolitic mineral is quartz (occasionally some feldspar); the rock contains also amorphous rock glass.

Table I shows the chemical composition of the rock rich in mordenite and clinoptilolite. It is seen from Table I that the rocks contain a small amount of iron oxide, too. When using natural zeolites as catalysts, it is often feared that the non-zeolitic



Fig. 1. Transmission electron micrograph of a mordenite-containing rock (the bar denotes 1 μm)

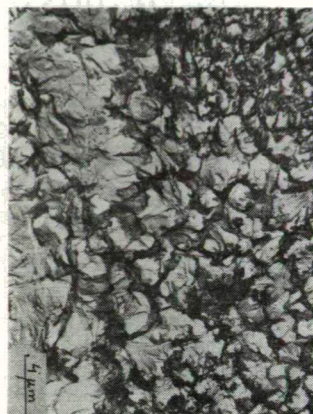


Fig. 2. Transmission electron micrograph of a clinoptilolite-containing rock

components may have a disturbing effect. We have proved experimentally that in our case these components — including iron oxide — do not influence the catalytic behaviour of the rock and do not lead to aging of the catalysts, either.

By means of electron microscopy we have established the shape and size of the zeolite crystals (Figs. 1—3). In Fig. 1 well developed mordenite crystals, 5—10 μm in length and a few tenth of a μm in width and thickness, are to be seen. On transmission electron micrographs the clinoptilolite crystals are not clearly seen (see Fig.

Table I
Composition (wt. %) of the rocks
containing mordenite
(MR) and clinoptilolite (CR)

Component	MR	CR
Na ₂ O	1.37	0.24
K ₂ O	4.11	3.24
MgO	0.28	0.89
CaO	1.87	1.82
Al ₂ O ₃	10.78	10.12
SiO ₂	70.93	70.96
Fe ₂ O ₃	1.41	1.30
TiO ₂	—	0.07
Weight loss on heating at 1000 °C	9.23	11.28

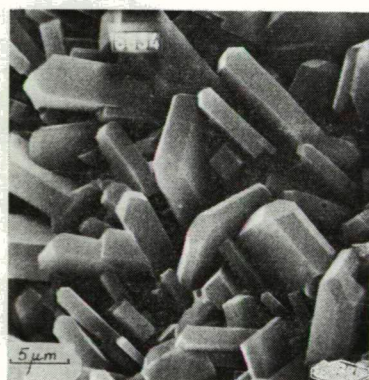


Fig. 3. Scanning electron micrograph of a clinoptilolite-containing rock

2), but scanning electron microscopy permits to obtain pictures of a crystalline region (Fig. 3).

Starting from a 1.0—1.6 mm particle size fraction grist of the mordenite- and clinoptilolite-containing rock the partially or fully protonated H-forms were prepared in 3 different ways: by acid treatment with HCl, and ion-exchange with NH_4NO_3 and AgNO_3 solutions. (Acid treatment with 0.1 N, 1 N and 3 N hydrochloric acid, ion-exchange with 2 N NH_4NO_3 and AgNO_3 , 3×4 hrs with fresh solutions, were carried out by refluxing. For 100 g zeolite grist 400 ml solution was applied. From the NH_4 - and Ag-form we have prepared the H-forms by a deammoniation or reduction at a suitable temperature.) Comparative catalytic investigations were made on the three mordenite and clinoptilolite samples; the corresponding 2 samples were always prepared under the same circumstances. In all cases the mordenite catalysts proved to be more active and the aging experiments showed that the activity of the H-mordenite prepared by Ag ion-exchange practically did not change. The differences in the activity of clinoptilolite and mordenite catalysts are supposed to be due to differences in the structure, because the reaction occurs in both cases on the surface of the crystallites, and there are no significant differences between the surface of the various catalysts. (Earlier adsorption investigations have shown that natural mordenite is a narrow-pore solid [1]). Comparison of the activities shows that the most active are the H-forms prepared by Ag ion-exchange, a somewhat lower activity is observed for the derivatives prepared by NH_4NO_3 ion-exchange, and the acid treated forms have the smallest activity. Changes in the chemical compositions owing to various treatments were followed by X-ray microanalysis of the mordenite [2, 3] crystals, which can be readily indentified on the electron micrographs. The electron beam can be focused on a single crystal, thus permitting to analyze the zeolite phase proper. The measurements prove that by Ag^+ -exchange all K-, Na- and Ca-ions are removed, while treatment with NH_4NO_3 leads to a full exchange of Na, ca. 90% exchange of Ca and ca. 50% exchange of K. Upon acid treatment the extent of ion-exchange further decreases, thus the sequence of activity can be explained on this basis. The stable activity of the Ag^+ -exchanged derivatives in time is remarkable. The origin of this phenomenon was studied by TG—MS measurements with special reference to the formation and stability of the acidic centers. For elucidation of the mechanism of catalysis, the kinetics of xylene isomerization have been studied.

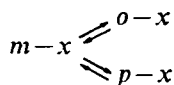
Xylene isomerization on H-mordenite catalysts

This reaction has been investigated by many authors because of its relevance to numerous petrochemical processes [4]. Also, it is very suitable test reaction for characterizing the activity of such catalysts (see *e.g.* [5]).

In our experiments isomerization was followed starting from the individual xylene isomers, in a flow reactor, at 200—400 °C and at total pressures of 5—60 atm and at various hydrogen/xylene partial pressures. By changing the space velocity, so called conversion isotherms were recorded. The following conclusions can be drawn partly from the direct conversion data, partly from the kinetic parameters calculated from the conversion isotherms:

a) Starting from each xylene isomer under the above circumstances on all three H-mordenite catalysts the main reaction is the intramolecular isomerization of xylenes, which is accompanied to a small extent by the metathesis of xylenes. (This does not exceed 5% for the equilibrium xylene composition.)

b) Starting from individual xylene isomers it has been established that the inter-conversion of the 3 xylene isomers follows the scheme:



there being no direct route from ortho to para xylene. The consecutive processes indicate that no equilibrium exists between the adsorbed species. In accordance with this, we have found that the initial rate of *m*-xylene isomerization can be described by a Langmuir isotherm which holds in the case of a rate-determining surface reaction.

c) The selectivity of *m*-xylene isomerization into *o*- and *p*-xylene (selectivity means here the ratio of *p*- to *o*-xylenes formed) is the same for all three H-mordenite catalysts and is independent of the temperature. The activation energy of *m*-xylene isomerization is also the same on the various H-mordenite catalysts: 38 kcal/mol, the chemisorption heat of *m*-xylene is 16 kcal/mol. From these facts one can conclude that on all three mordenite catalysts prepared in different ways, the adsorption of the xylene molecule occurs on the same Brönsted acid centers, *i.e.* the first step is a fast (equilibrium) adsorption of the species followed by the rate-determining surface reaction (1 → 2 methyl transfer along the ring), the catalytic cycle being closed by the fast desorption of the product.

The same selectivity and activation energy values on different H-mordenites permit the conclusion that metallic silver formed by the reduction of the Ag ion-exchanged form has no catalytic effect on the above reaction. This conclusion is supported by the fact that re-conversion of the H-form into the Na-form with a NaCl solution produces a fully inactive catalyst.

From the chemical analysis of ion-exchanged mordenite and its catalytic activity, it can be concluded that the acidic centers optimal in xylene isomerization with respect to their position and acid strength are only formed by total ion-exchange and they are responsible both for the high activity and stability.

Concerning the nature (characterized by thermostability) and quantity of acid centers on the three H-mordenite catalysts prepared in various ways, results were obtained by so-called TG—MS measurements.

Combined thermogravimetric-mass-spectrometric (TG—MS) measurements on the starting mordenite and the catalysts prepared from it

The literature discusses almost exclusively the thermostability of synthetic H-mordenites prepared by NH_4^+ -exchange [6—9]. BEYER *et al.* [10], however, discussed in detail the properties of a synthetic Ag(H)-mordenite obtained from Ag-mordenite, too.

The thermogravimetric experiments were carried out on a Mettler thermobalance combined with a Balzers mass spectrometer QMG—101, under N_2 atmosphere, with a heating rate of 4 °C/min.

Experiments were made with the original mordenite-containing rock and the above derivatives. (The Ag^+ -exchanged sample was reduced *in situ* and the measurement carried out under reductive conditions in order to prevent silver from reoxida-

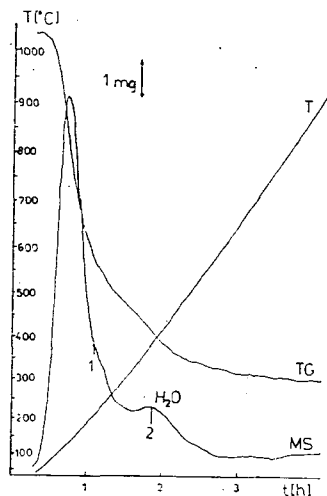


Fig. 4. TG—MS diagram of the original mordenite sample

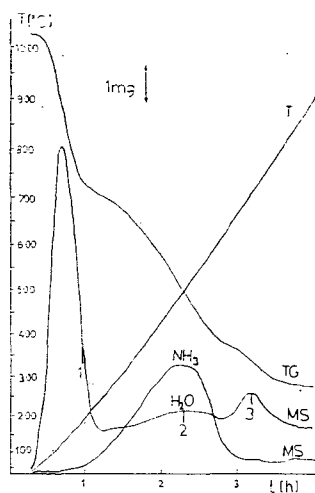


Fig. 5. TG—MS diagram of the NH_4^+ -exchanged mordenite

tion.) Figs. 4, 5 and 6 show TG—MS diagrams for the original, NH_4^+ -exchanged and Ag^+ -exchanged samples, respectively.

In the TG—MS diagram of the original mordenite (Fig. 4) three types of water are to be distinguished desorbing at various temperatures. The so-called zeolitic water, adsorbed physically, desorbs in two overlapping steps up to 250 °C (marked in Fig. 4 by 1); thereafter, in a third, better separated region the desorption of water bound to cations of the mordenite begins (marked by 2). For the lack of space the diagrams concerning the three acid-treated derivatives are omitted. The diagram shows the formation of various OH groups as a consequence of the acid treatment (quantitative data are summarized in Table II).

Table II

Concentration of acidic centers
in catalysts prepared in different ways

Preparation of catalysts from mordenite	Concentration of acidic centers (mmol/g)
Treated with 0.1 N HCl	0.2
Treated with 1 N HCl	1.0
Treated with 3 N HCl	0.8
NH_4^+ -exchanged	1.7
Ag^+ -exchanged	1.8

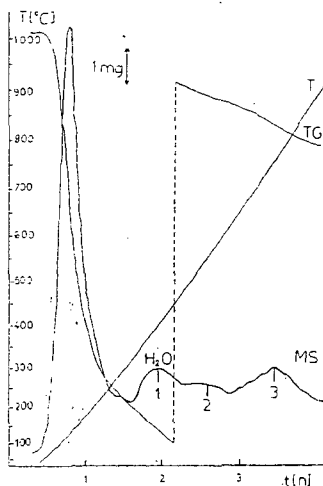


Fig. 6. TG—MS diagram of the Ag^+ -exchanged mordenite

Upon thermal decomposition of the NH_4^+ -mordenite (Fig. 5) the other product observed in addition to water was NH_3 . It is to be seen in Fig. 5 that the deammoniation begins after the removal of physically adsorbed water at ca. 200 °C and lasts till ca. 630 °C. In parallel to the deammoniation, part of the OH groups is immediately removed (region 2 in Fig. 5). The removal of water between 620 and 800 °C proves the presence of strongly bound structural OH groups.

In the TG—MS diagram of the H-mordenite produced by reduction of the Ag^+ -exchanged sample (Fig. 6), in addition to the desorption of zeolitic water, 3 different types of water are removed between 300 and 850 °C. The two overlapping peaks with the NH_4^+ -mordenite in region 2 correspond here to two clearly distinguishable steps.

The calculated concentrations of the OH groups for the three H-mordenite types prepared in different ways are presented in Table II.

Conclusions

a) By acid treatment — in our experimental conditions — the alkali and alkaline-earth cations can be only partially exchanged for protons.

b) Owing partly to unsatisfactory ion-exchange, partly to the high temperature needed for deammoniation (where dehydroxylation also occurs, consequently, the number of the acidic centers decreases), it is not possible to obtain the fully exchanged H-form from the NH_4^+ -form either. During its use as a catalyst only part of the OH groups originally amounting to 1.7 mmol/g, remains in the zeolite.

c) Presumably the H-mordenite formed by reduction of the Ag^+ -exchanged form, contains all the possible types of OH groups distributed in various positions, which is due partly to complete ion-exchange, partly to the low temperature (~ 320 °C) needed for reduction.

The above facts permit interpretation of the observed catalytic properties of the H-mordenites prepared in different ways.

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