

INVESTIGATION OF THE DEACTIVATION OF MORDENITE CATALYSTS BY COKE DEPOSITION AND THEIR REGENERATION

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ABSTRACT

Reaction parameter and pretreatment of zeolite catalysts used in this investigation were varied in order to obtain information about the possibilities to reduce deactivation by coke formation. Hydroisomerisation of n-hexane was used as a test reaction to study activity and deactivation of various synthetic and natural mordenites. Improvement of conversion and time on stream could be achieved for the synthetic mordenites by steaming at 450°C and by strong dealumination using HCl to get $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios up to 77. These zeolites could be regenerated several times without losing activity. Natural mordenites from the Tokaj-mountains (Hungary) gave satisfying results only after doping with platinum. Indications were obtained that the isomerisation reaction and the coking reaction proceed independently.

INTRODUCTION

Today zeolite catalysts are mainly applied for acid catalytic cracking and isomerisation reactions because of their strong acidity and their shape selectivity. However, during these reactions coke is formed by undesired side reactions. Coke, according to Venuto and Habib [1], is a high polymer deposition on the catalyst surface with a high carbon content. The nature and the chemistry of formation of these deposits are hitherto largely unknown. For this reason deactivation of a zeolite catalyst by coke deposition was studied using the hydroisomerisation of n-hexane on various modified mordenites as an example.

The mordenite which is rich in silicon exhibits a comparatively

high stability at high temperature and when treated with acid. Therefore it can be modified by various means without losing crystallinity. The mordenites used in this investigation were modified by exchange with Pt-complex compounds, by acid treatment and following calcination or by ammonia exchange and following defined steaming.

Isomerisation of n-hexane was chosen because this reaction can easily be handled and is almost isothermal. At the same time this reaction exhibits all features necessary to study the capabilities of zeolite catalysts. Publications about kinetics and mechanism of this reaction are available [2,3,4], yet little has been published about deactivation by coking during this reaction. Therefore, this investigation aims to prolong the time on stream by modifying natural and synthetic mordenites and by adjustment of the reaction parameters. At the same time the yield of branched hexane isomers should be as high as possible. Furthermore, these catalysts were tested with respect to their stability for regeneration by burning off the coke.

EXPERIMENTAL

Reactions were performed in an isothermal differential tube reactor. Products were analysed by gaschromatography. The regeneration of the coked catalysts was possible "in situ" by burning the coke in a stream of 5% oxygen in nitrogen at 550°C. Amounts of CO and CO₂ produced by this were determined by an infrared analyser. From this the original amount of coke could be calculated.

3 g mordenite were used for each run; when applying the natural Tokaj-mordenite a larger amount was used corresponding to the impurities. The reaction conditions held constant for all runs are shown in table 1.

Table 1
Reaction conditions for all runs

Flow of n-hexane	0.2 ml/min
Flow of hydrogen	200 ml/min
Total pressure	25 bar
Temperature	280°C
Time on stream	4 or 4.5 h
WHSV	2.64 g/g·h

The catalysts were activated inside the reactor by a hydrogen flow at 350°C for 1.5 hours.

Synthetic mordenite "Zeolon 100 H" from Norton and natural mordenite from the Tokaj-mountains (Hungary) were the basic materials from which modifications were obtained. Part of this material was treated with 1 N or 6 N HCl under reflux for various lengths of time. This was followed by "deep bed" calcination at 550°C for 16 hours. Another part of Zeolon 100 H was exchanged by ammonium nitrate and thereupon hydrothermally treated between 300 and 600°C whereupon the H-form was rebuilt. This steaming was performed in a special quartz tube with heaters through which air (55 l/h) loaded with water vapor was passed [5]. The partial pressure of the water was 306 Torr. 8 g of NH₄-mordenite were steamed for 4 hours at a time.

A part of the acid treated Tokaj-mordenite was afterwards doped with platinum in the following way: The mordenite was stirred for 24 hours in a cold water solution of Pt(NH₃)₄Cl₂ corresponding to 0.5 w.% whereby the exchange resulted quantitatively. Reduction in a stream of hydrogen at 200 and 400°C followed. The catalyst material was pelletized to pellets with a mean diameter of 2.5 mm. Table 2 summarizes all used catalyst modifications.

Table 2
Modifications of mordenites used

H-mordenite	modulus ^x	23.3, 34.1, 59.2, 68.6, 77.8
NH ₄ -mordenite	steamed at	300, 400, 450, 500, 600°C
Tokaj-H-mordenite	modulus	23, 34
0.5 w.% Pt-Tokaj-mordenite	modulus	23, 34

^x Modulus is defined as molar ratio SiO₂/Al₂O₃

RESULTS AND DISCUSSION

Synthetic H-mordenites

Typical Features of Deactivation

A typical example of rapid deactivation is shown in fig. 1.

Activity of the H-mordenite with a modulus of 23.3 decreases to 50% after 30 minutes and to 25% after 2 hours. The exponential falling-off of the conversion is accompanied by an increase of the formed amount of coke. Strong coking at the beginning of the reaction is striking. So, after 10 minutes 50% of the final amount of coke is formed. Only little increase of the amount of coke can be observed after 2 hours because conversion has already reached a low level. A similar course of coke production was obtained by Shiring et al. [6].

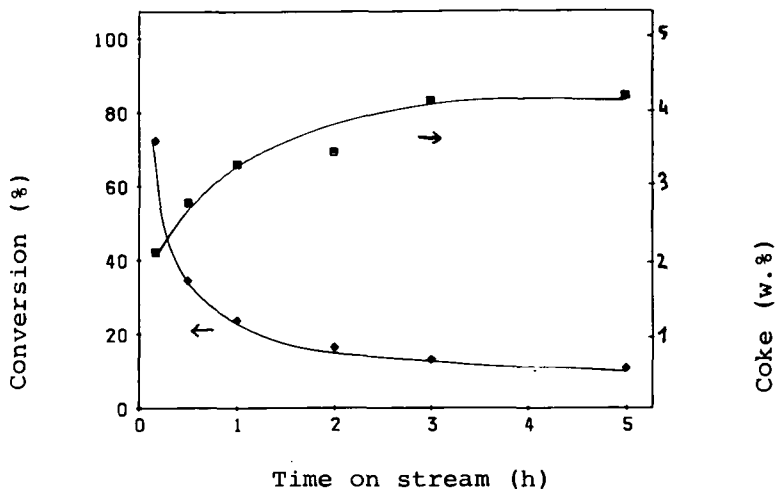


Fig. 1. Conversion and amount of coke vs. time on stream

It seems to be plausible that initially certain active centers of the catalyst are blocked. This effects cracking- and isomerisation processes quite differently as can be seen in fig. 2 which shows product yields of cracking and isomerisation. Coke deposition during the first hour of reaction causes a very strong decrease of cracking activity of the catalyst. Isomerisation conversion even shows a little increase during this time but it is usually only slightly influenced by coke formation. Yet, a strong correlation between coke formation and cracking activity is to be noted. It can therefore be assumed that by decrease of cracking activity less coke will be produced and at the same time the deactivation will be lowered. By this the selecti-

vities of hexane isomers will be raised.

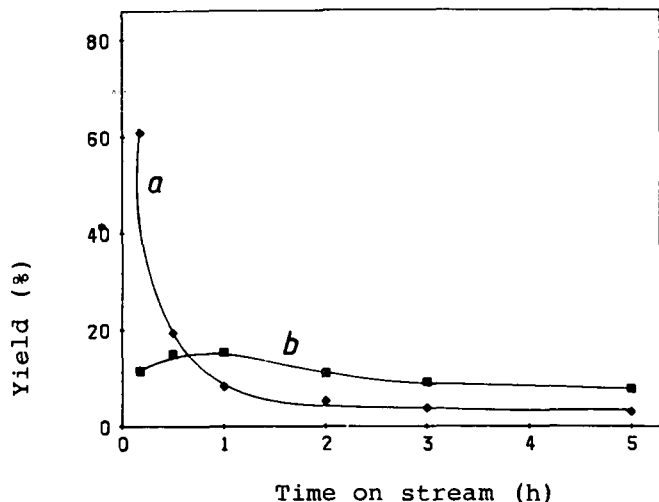


Fig. 2. Yields of cracking (a) and isomerisation (b) vs. time on stream

Influence of reaction parameters on deactivation

Much suppression of the cracking reaction can be achieved by lowering the reaction temperature. This can be seen in fig. 3 in which the ratio of hexane isomers to cracking products is drawn against time on stream. The modulus and reaction temperature were varied. The effects are so drastic that a logarithmic ordinate has to be chosen. The ratio of hexane isomers to cracking products covers the region between 0.1 and 100 for high temperatures as well as high initial conversions and for 250°C-reaction temperature as well as strong dealumination respectively. The four curves in fig. 3 nicely demonstrate the synergistic effect between reaction temperature and modulus. The mentioned ratio always decreases with increasing temperature; the decrease can partly be compensated by an increase of the modulus.

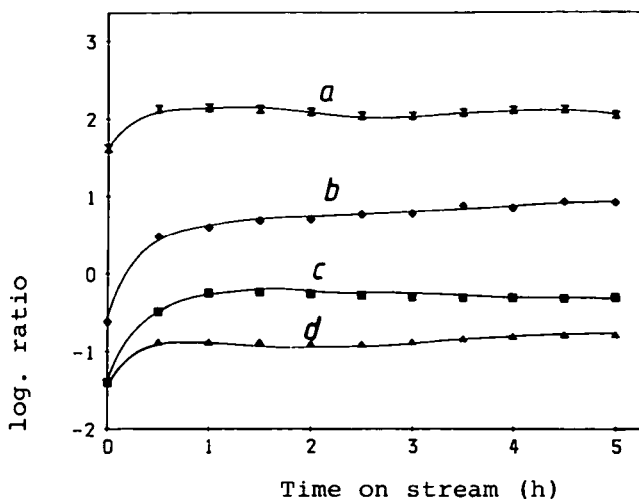


Fig. 3. Dependence of the ratio of n-hexane isomers/cracking products on modulus, reaction temperature and time on stream: a) modulus 77.8, 250°C, b) modulus 34.1, 250°C, c) modulus 77.8, 350°C, d) modulus 34.1, 350°C.

Suppression of cracking reactions by lowering the reaction temperature, however, causes a strong decline of conversion. Conversion can again be improved by an increase of total pressure and of the hydrogen partial pressure. Deactivation is also diminished by this. Optimization with respect to activity and time on stream can only be achieved in a limited way by variation of the reaction parameters. A real improvement can only be gained by modification of the zeolite structure. This is shown next with the example of hydrothermal treatment.

Influence of the modifications of the catalyst

In fig. 4 is shown how conversion and yields of cracking products and branched hexane isomers depend on steam temperature for an ammonia mordenite after 2 h time on stream. A distinct maximum can be seen at 450°C for all curves. The decrease of conversion at low temperatures is assumed to be due to the fact that ammonia is not completely decom-

posed and still blocks active centers. The decrease of conversion at higher steam temperatures on the other hand is caused by AlO^+ -cations occupying active centers which are produced by the dealumination process. It is interesting to note that all three curves are more or less parallel. The strong influence of the AlO^+ -cations should be mentioned; they cause the cracking reactions to stop because they apparently preferably block those centers that produce cracking products.

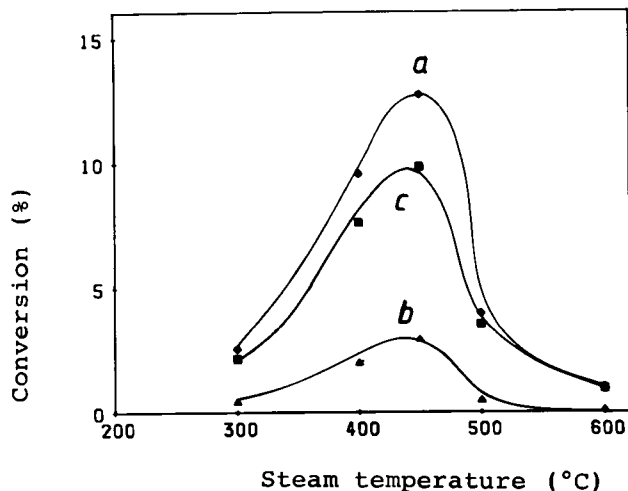


Fig. 4. Dependence of conversion (a) and yields of cracking (b) and isomerisation (c) on steam temperature

An increase of n-hexane isomer yields in connection with diminishing deactivation can also be achieved by strong dealumination of the mordenite by HCl. This treatment causes an increase of strong Brønsted acid sites while the total number of OH-groups decreases [7]. Fig. 5 shows the yields of cracking products and branched hexane isomers and the conversion in dependence of the modulus after 2 h time on stream. Conversion and yields decrease slightly with increasing degree of dealumination for lower values of the modulus. However, for strong dealumination yields for branched hexane isomers increase, this in turn causes conversion to increase in spite of decreasing cracking activity. If the modulus is larger than 68 the catalyst exhibits a substantially

smaller tendency to coke and the amount of coke produced is essentially less. So, the mordenite with a modulus of 68.6 still shows a conversion of 14% even after 4 h time on stream. For the two most dealuminated mordenites even after 4 h the yields for n-hexane isomers are still between 10 and 11%.

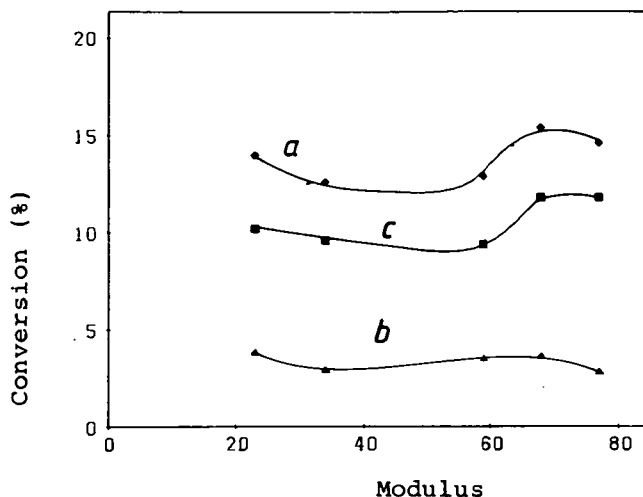


Fig. 5. Dependence of conversion (a) and yields of cracking (b) and isomerisation (c) on modulus.

Natural Tokaj-mordenite

While in the case of synthetic mordenites even small dealumination results in a decrease of conversion, the activity of natural Tokaj mordenites can be increased by raising the modulus from 23 to 34. This is probably due to a slight widening of the pores by acid treatment which is not observed with the synthetic mordenite. However, the activity of the Tokaj-mordenite is substantially lower than the synthetic mordenite. It can be increased by addition of platinum to a degree that is comparable with strongly dealuminated synthetic mordenites. This treatment almost completely suppresses the cracking activity and conversion is more stable. However, even with this catalyst constant conversion for a longer period could not be achieved.

Comparison of the various catalyst modifications

For the final discussion of the catalyst modifications the selectivities after 1.5 h time on stream of five selected mordenites are compared in fig. 6. It can be seen, that the selectivities of hexane isomers can be improved by stronger dealumination as well as be steaming at 450°C when compared with a catalyst of a low modulus of 23. It can also be noticed that of the catalysts tested the Tokaj-mordenite shows the lowest selectivities in spite of low conversion-rates. However, the selectivity is better than that of a steamed synthetic catalyst when the Tokaj-mordenite is doped with platinum. The trend of these selectivities is also reflected by the deactivation behaviour. The three catalysts with the lowest cracking selectivities exhibit the highest stability of conversion while mordenites with high cracking activity distinctly deactivate faster.

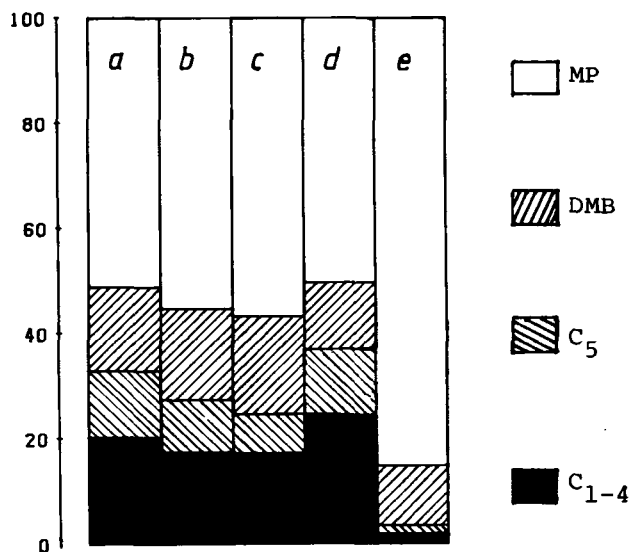


Fig. 6 . Selectivities of five selected mordenites after 1.5 h time on stream: a) H-mordenite modulus 23.3, b) H-mordenite modulus 68.6, c) NH₄-mordenite steamed at 450°C, d) Tokaj-mordenite modulus 23, e) Pt-Tokaj-mordenite modulus 23.

Behaviour on repeated regeneration

Final runs were undertaken to test the activity after repeated

regeneration. Furthermore the influence of residual amounts of coke on the initial activity of the catalyst was investigated. Residual amounts of coke could be realized by variation of the regeneration temperature between 450 and 550°C.

Fig. 7 shows the conversion after 1 h time on stream in dependence of the number of cycles and on the residual amount of coke. Furthermore the ratio methylpentanes/dimethylbutanes is shown which is related to the pore width of the catalyst at the beginning of each reaction period. Initially a pore widening is observed after the first cycle which also causes an increase of conversion. Regeneration was performed at 550°C for this first cycle. The regeneration temperature was lowered by 25°C after each of the following cycles. A distinct decrease of conversion - accompanied by a pore narrowing by residual coke - is only observed after the fifth cycle before which regeneration took place at 475°C. Before this cycle the initial activity was again attained. This proves that H-mordenite can repeatedly be regenerated without losing its activity.

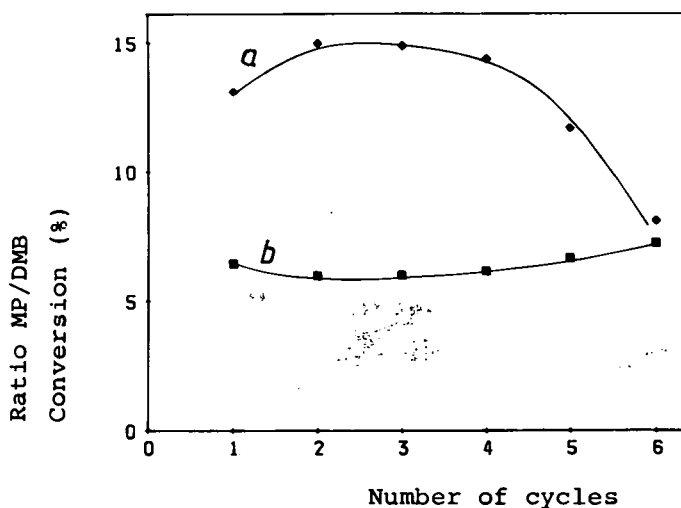


Fig. 7. Dependence of conversion (a) and MP/DMB ratio (b) on the number of cycles and the residual amount of coke.