HYDROISOMERIZATION AND HYDROCRACKING OF n-PARAFFINES ON ZEOLITE CATALYSTS

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ABSTRACT

　　　In technical gasolines the n-paraffines are the hydrocarbons with the lowest octane number. To convert them into components with higher octane level two different processes are used depending on their C-number: The hydroisomerization of the light gasoline and the shape selective hydrocracking of the n-paraffines of the reformate.

　　　For the development and application of catalysts for both processes two different principles of catalysis on zeolites have been followed. Activity and selectivity of the light petrol isomerization catalyst are based on the formation of BRÖNSTED centres with a specific acid strength in Y zeolites by special ion exchange and activation methods. On the other hand the very shape selective behaviour of H-erionite against n-paraffines even at reforming temperature was used for the development of a zeolite catalyst for the upgrading of reformates.

　　　Details of the zeolite catalysts developed for and applicated in both processes on industrial scale in the G.D.R. are given.

INTRODUCTION

　　　Usually the light gasoline (boiling range about 310 up to 360 K) and the heavy gasoline (boiling range about 370 up to 455 K) are processed separately because of the different potential to get aromatics. However, in the whole gasoline range the n-paraffines are the hydrocarbons with the lowest octane level (see Table 1).

　　　In the light gasoline fraction the aim of processing is the isomerization of the n-paraffines into iso-paraffines. The thermodynamic equilibrium between the n- and iso-paraffines [2] requires

Table 2

Specification of a technical light gasoline to be isomerized

component	mass-%	component	mass-%
$C_3 + C_4$	11.3	benzene	2.4
i-pentane	11.5	toluene	0.3
n-pentane	18.3	RON_{clear}	70.0
dimethylbutanes	1.0	RON_{leaded}	85.5
methylpentanes	20.4	S-content, ppm	5.0
n-hexane	19.0	H_2O-content, ppm	50
naphthenes	8.2		

ming process. The Selectoforming process of Mobil [3] describes
the removal of these n-paraffines from the reformate by hydro-
cracking on metal containing narrow porous zeolites on the basis
of the works of Maziuk et al. [4 - 6]. The narrow porous zeolite
should possess real shape selective properties for n-paraffines
even at the usual reforming temperature, should be highly active
and thermostable, should be available, and should stand the re-
forming catalyst life time at least. For this purpose mordenite,
offretite, erionite, and ZSM-type zeolites are to taken into
account.

Y ZEOLITE CATALYSTS FOR THE ISOMERIZATION OF LIGHT GASOLINE

        In the hydroisomerization of n-pentane and n-hexane the
acid Brönsted centres are of essential importance, if the metal
function is well established. We took care for this in all our
experiments by loading all zeolite catalysts with 0.5 % Pt and
by a careful air treatment followed by a slowly reduction with
hydrogen. So properties of the zeolite component became deter-
mining activity and selectivity, i. e. its acid properties.

        Fig. 1 shows the dependence of the Brönsted acid centres
concentration on the exchange degree of different cations in Y
zeolite. The Brönsted centres concentration has been measured
by I.R. spectroscopic determination of the extinction of the
pyridinium ion band (1550 cm^{-1}) of the pyridine adsorbed under
standard conditions. In all cases the concentration of acid
Brönsted centres increases with the exchange degree. The highest
concentration was found at the HNaY followed by the CeNaY zeo-

Table 1

Research octane numbers of some hydrocarbons [1]

$n-C_4$	93.6	$i-C_4$	99.0	2,2-DMP	80.0
$n-C_5$	61.5	$i-C_5$	99.5	benzene	98.5
$n-C_6$	29.0	2-MP	69.0	toluene	123.5
$n-C_7$	0.0	3-MP	85.5	m-xylene	120.0
$n-C_8$	< 0	2,2-DMB	97.0	cyclohexane	109.5

a temperature as low as possible but often the catalyst activity does not meet this demand.

In literature processes for low temperature isomerization using halogen containing catalysts are described. As far we know in all cases a lot of corrosion problems arose due to traces of water in the feedstock as well as other problems. The less sensitive high temperature processes (680 K) use noble metal/alumina catalysts.

The development of catalysts containing zeolites led to milder conditions (520 to 600 K). The required temperature depends on the type of alumosilicate and the process conditions like water, sulphur, and pressure of the recycle gas and on the feedstock composition.

As it is well known by literature, the isomerization of n-paraffines follows the classical mechanism with carbenium ion intermediates. The selectivity for the prefered isomerization depends on the strength of the acid Brönsted centre involved in the carbenium ion formation, if other rate limiting steps are excluded. The problem is how to avoid the nonselective hydrocracking which is also possible under isomerization conditions by a parallel reaction. Especially, this fits in case of the isomerization of a technical light gasoline containing higher hydrocarbons (see specification in Table 2). Therefore we followed in our work of the development of isomerization catalysts the way of creation of enough Brönsted centres of an optimal acid strength by special ion exchange and activation methods of Y zeolites. The pore diameter of Y zeolites allows the fast diffusion of n-paraffines and i-paraffines as well. Furthermore, a lot of details is known of the dependence of the surface chemical properties on the ion exchange.

In reforming products a content of about 5 to 10 % of the low octane level n-paraffines (Table 1) remains after the refor-
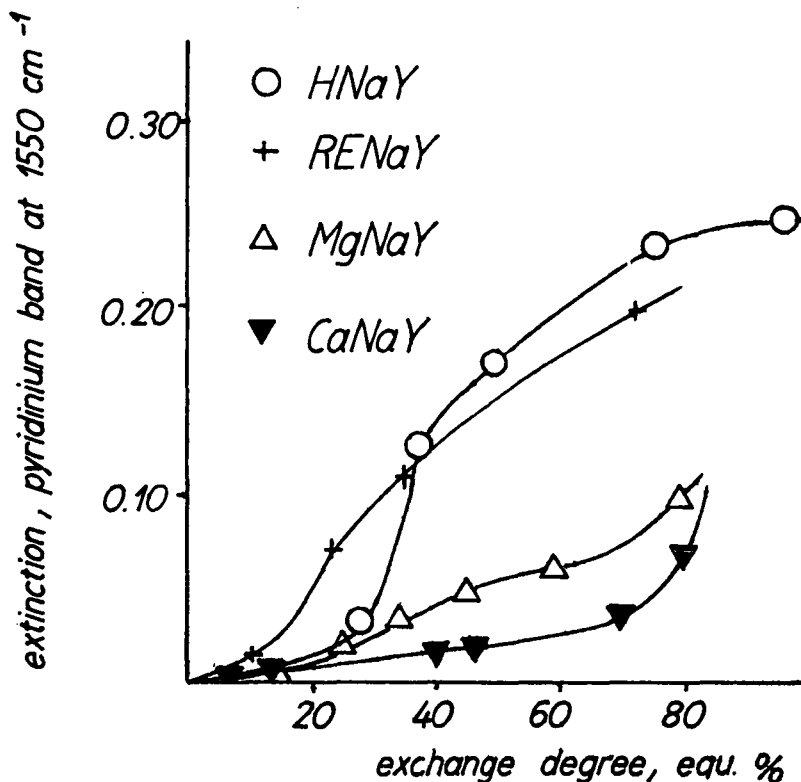
Fig. 1. Dependence of the concentration of Brönsted acid
centres on the exchange degree of Y zeolites [7]

lite. One could expect on these results, that the HNaY zeolite
would be the most active catalyst in the isomerization. This
only refers to the activity but not to the selectivity in the
n-hexane isomerization [8]. Due to the parallel hydrocracking
of part of the higher hydrocarbons this applies to the hydro-
isomerization of a technical gasoline especially.

　　　Therefore we concentrated our efforts on the development
of an isomerization catalyst on the basis of RENaY zeolite. We
found that a RENaY zeolite catalyst consisting of 0.5 % Pt and
with an exchange degree of about 65 equiv. % (specification
see Table 3, performance see Table 4) works at satisfactory
conditions as working temperature, octane level of the product,
and liquid yield. The results are remarkable better than those
of the formerly used Pt/Al$_2$O$_3$ catalyst (Table 4).

　　　During its technical application the RENaY catalyst was
slowly (within a period of about six month) desactivated and
its original activity could not be regained by a conventional
oxydative regeneration [9]. Investigating the desactivated ca-

Table 3

Specification of Leuna isomerization catalysts with zeolites

	Kt. 8815	Kt. 8850	Kt. 8851	Kt. 8852
composition	Pt/Al_2O_3	Pt/RENaY	Pt/MgCaNaY	Pt/RECaNaY
binder	-	clay	Al_2O_3	Al_2O_3
specific weight, g/l	700	870	580	580
form, diameter, mm	extrudates, 2	cylindric pellets, 5 x 5	extrudates 3	extrudates 3

Table 4

Catalytic performance of Leuna isomerization catalysts with zeolites

Reaction conditions: 2.5 MPa, space velocity 2 v/vh, gas liquid ratio 1000:1, industrial plant, gasoline see Table 2

	Kt. 8815	Kt. 8850	Kt. 8851	Kt. 8852
temperature, K	743	618	603	593
RON_{loaded}	89.5	90.0	90.5	91.0
liquid yield, mass-%	86.5	89.5	90.3	91.5
technical use	up to 1976	1976-1978	1978-1980	since 1980

talyst by means of ion exchange, catalytic and surface chemical methods we found a change in the cation distribution in the zeolite to be the reason. RE^{3+} ions located in the large cavaties and creating there acid Brönsted centres changed their positions with Na^+ ions coming from positions within the small cavaties.

Therefore we looked for a method to fix the cations creating catalytic active centres inside the large cavaties even under the reaction requirements as temperature and life time. At that time our bulgarian colleagues rendered assistance. They found, that it is possible to prevent the Na^+ ion migration into the large cavaties of Y zeolites if all the cation positions inside the hexagonal prisms are blocked by Ca^{2+} ions. This can be reached by simultaneous ion exchange of Ca^{2+} and Mg^{2+} ions at special conditions and cocentrations [10]. A Pt/MgCaNaY zeolite prepared in this manner is a very active and selective catalyst in the n-pentane isomerization [10].

On the basis of these results the Leuna-Kt. 8851 was deve-

loped [11]. Besides the new zeolitic component also the binder
was changed. Instead of pilling using a natural clay as binder the
Leuna-Kt. 8851 was formed by extrudation with a special activated
Al_2O_3 as binder. The main advantages of the changed forming method
consist in the lower specific weight (see Table 3), saved platinum
and higher porosity. The application of the Pt/MgCaNaY zeolite
catalyst in the industrial gasoline isomerization process brought
about higher efficiency (see Table 4). Above all no remarkable
desactivation could be observed.

Activity, selectivity as well as the altering resistance of
the Pt/MgCaNaY zeolite catalyst corroborated the availability of
the hypothesis, that it is necessary for good catalytic properties
to direct the highly charged cations in positions in the large
cavities and to fix them there too. According to this assumption we
introduced RE^{3+} ions into a CaNaY zeolite with high exchange deg-
ree replacing only part of the Ca^{2+} ions [12]. By this exchange
procedure OH groups acting as acid Brönsted centres are additio-
nally formed (see Fig. 2) in comparison with a 0.88CaNaY zeolite
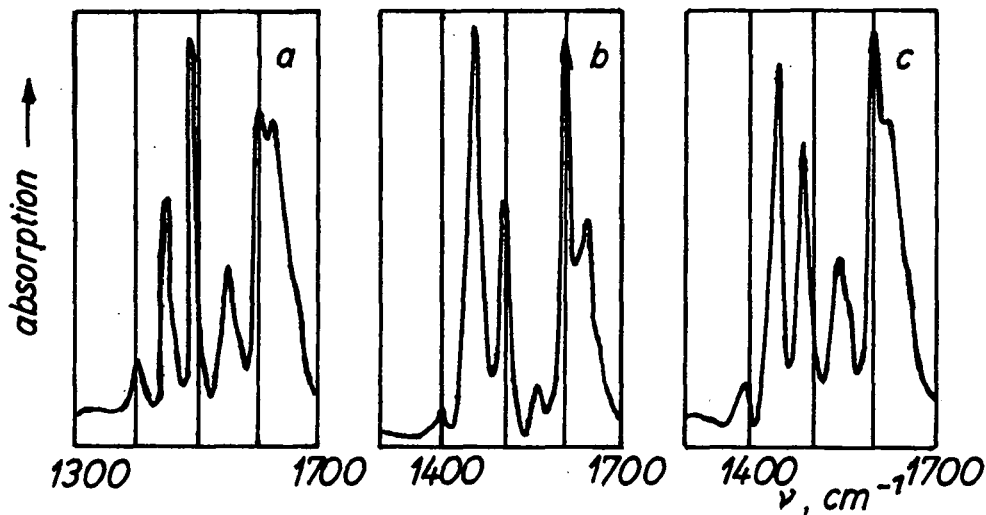and a 0.64 RENaY zeolite too.

Fig. 2. I.R. spectra of pyridine adsorbed on a) 0.64RENaY
b) 0.88CaNaY c)0.28RE0.60CaNaY zeolites
activation temperature 770 K, at 420 K 2.0 kPa pyridine
for 10 min, final evacuation at 420 K

The additionally formed Brönsted acid sites in the 0.28RE
0.60CaNaY zeolite possess mainly an acid strength in the region

of pK_a = -8.2 to -5.6 (see Fig. 3). Compared with the 0.88CaNaY zeolite the 0.28REO.60CaNaY zeolite has more and stronger acid centres. In no case the transformation of the used most acid indicator (anthraquinone pK_a = -8.2) has been observed.
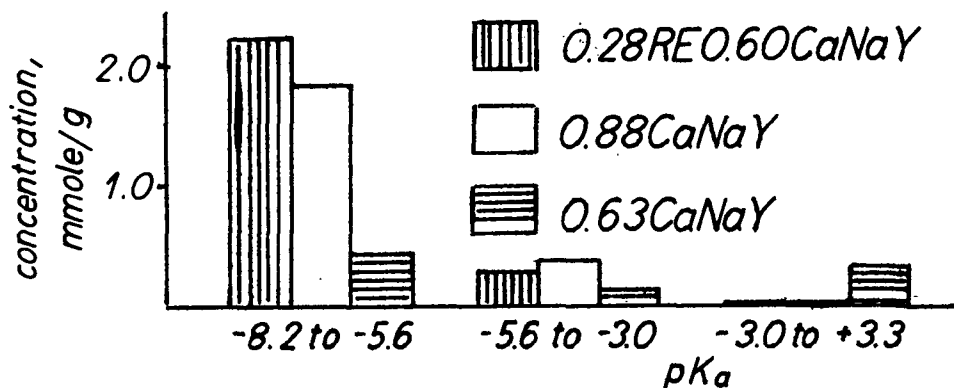

Fig. 3. Results of the titration with n-butylamine according to Benesi [13] using Hammett indicators

Obviously, the formation of more and stronger acid Brönsted sites on the 0.28REO.60CaNaY zeolite is due to the presence and
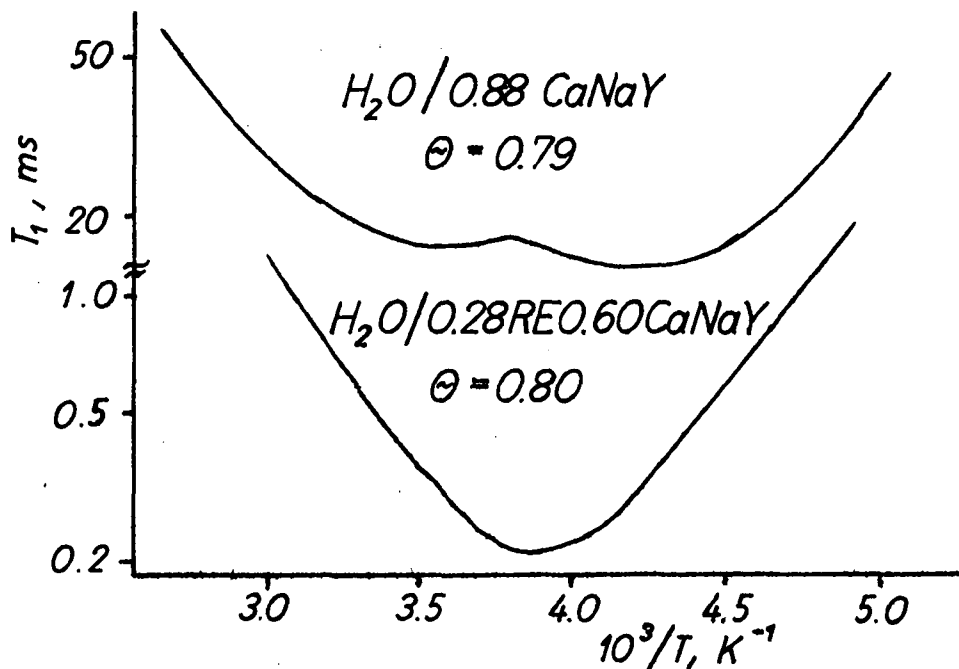

Fig. 4. N.M.R. relaxation of water adsorbed on 0.88CaNaY and 0.28REO.60CaNaY zeolite, longitudinal proton spin relation time T_1 on reciprocal temperature, $\omega_1/2\pi$ = 90 MHz

fixation of part of the RE^{3+} ions within positions in the large
cavities (S_{II}). By N.M.R. relaxation measurements (T_1 of adsor-
bed water, see Fig. 4) [14] and by I.R. measurements in the lat-
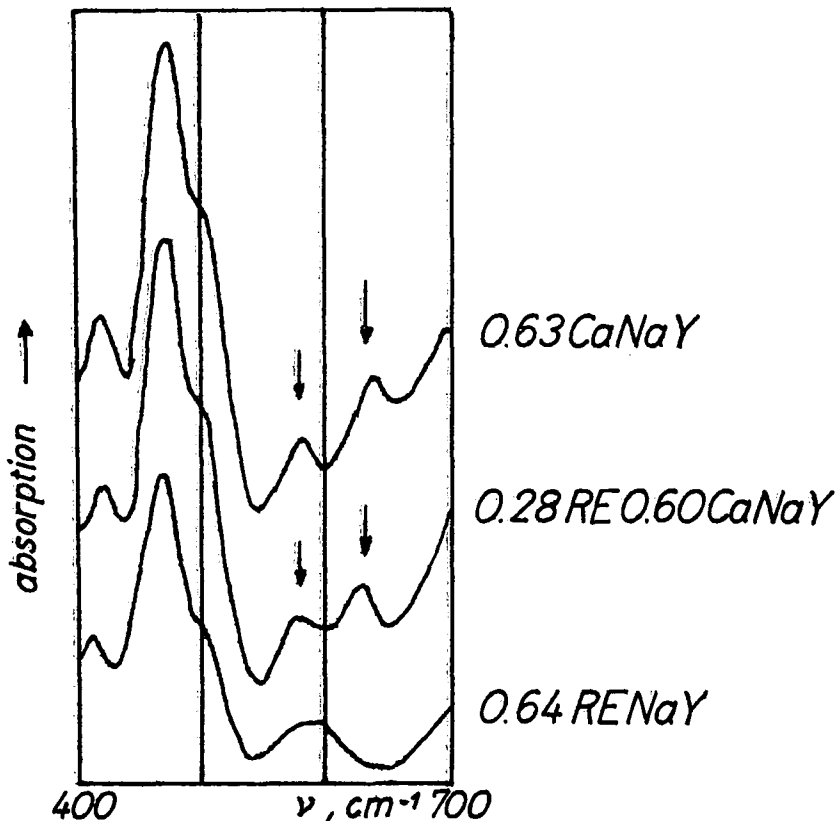tice vibration region [15] (see Fig. 5) it could be shown, that

Fig. 5. I.R. spectra of zeolites activated at 770 K,
10^{-2} Pa, 30 min, selfsupporting discs, <0.7 mg/cm^2

the RE^{3+} ions introduced into a 0.88CaNaY zeolite replace part of
the Ca^{2+} ions in the S_{II} positions and remain there after thermal
pretreatment also. In Fig. 4 it is demonstrated how the longitu-
dinal proton spin relaxation time of adsorbed water decreases, if
RE^{3+} ions (paramagnetic) are introduced in a 0.88CaNaY zeolite.
This effect is due to the proton paramagnetic ion interaction and
a proof of the presence of RE^{3+} ions within the large cavities.
    The results shown in Fig. 5 support the N.M.R. data also.
The I.R. spectra of unsupported discs (no binder) of the 0.63CaNaY
and the 0.28REO.60CaNaY zeolite [15] are quite similar in the re-
gion of the double six ring vibration (550 to 650 cm^{-1}). This

means, the RE^{3+} ions cannot be exchanged preferably into S_I po-
sitions (and only part of them may be located in $S_{I'}$ positions).

The special distribution of the RE^{3+} ions in a RECaNaY
zeolite and the outstanding surface chemical properties caused
by it are the reasons for the high activity and selectivity of
a Pt/0.28RE0.60CaNaY zeolite catalyst in the n-hexane isomeriza-
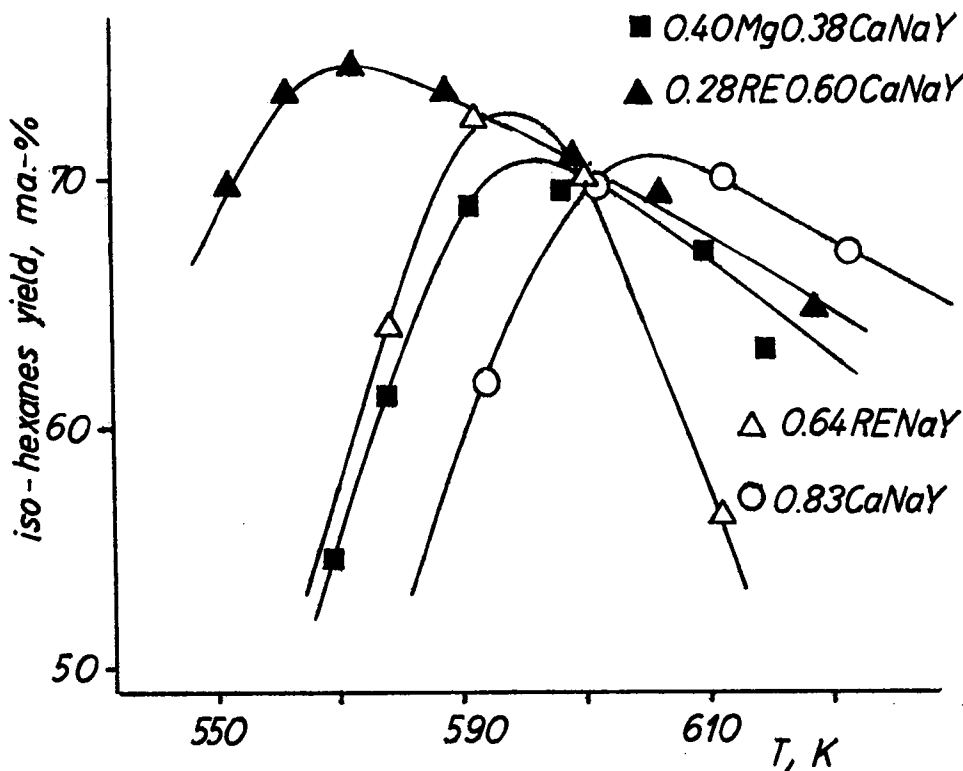tion (see Fig. 6). The data given in Fig. 6 show that the highest

Fig. 6. n-hexane isomerization activity of Y zeolites,
dependence on temperature, 2 cm^3 catalyst (0.2 - 0.3 mm)
H_2 : n-hexane = 5 : 1 mole/mole, LHSV = 1.5 v/vh, normal
pressure, 0.5 % Pt

yield of iso-hexanes at the lowest temperature are obtained on
the 0.5%Pt/0.26RE0.60CaNaY zeolite catalyst in comparison with
catalysts on the basis of 0.64RENaY, 0.83CaNaY, and 0.40MgO.38
CaNaY zeolites, respectively. Furthermore, the consecutive for-
mation of double branched iso-hexanes is much more higher on the
0.5%Pt/0.28RE0.60CaNaY zeolite catalyst [16].
On the basis of these scientific results the industrial catalyst
Leuna-Kt. 8852 was developed and applicated. Once again an in -

crease in liquid yield and higher quality at lower temperature
could be reached in comparison with its pecursors (see Tab. 4).

MORDENITE CATALYST FOR THE SHAPE SELECTIVE HYDRCRACKING OF
n-PARAFFINES

Due to the pores dimensions mordenite, offretite, erionite,
and ZSM-5 type zeolites are to taken into account as catalysts
for the shape selective hydrocracking of n-paraffines out of a
reformate hydrocarbon mixture.

According to the carbenium ion mechanism of cracking and
also of hydrocracking of n-paraffines the zeolite must be trans-
formed into an acid form to become actively. In case of mordenite
this can be reached by direct acid treatment. By leaching of sodi-
um mordenite with HNO_3 of different concentration it is possible
to influence the activity as well as the selectivity of the re-
sulting H-mordenite for the cracking of a 1 : 1 molar mixture of
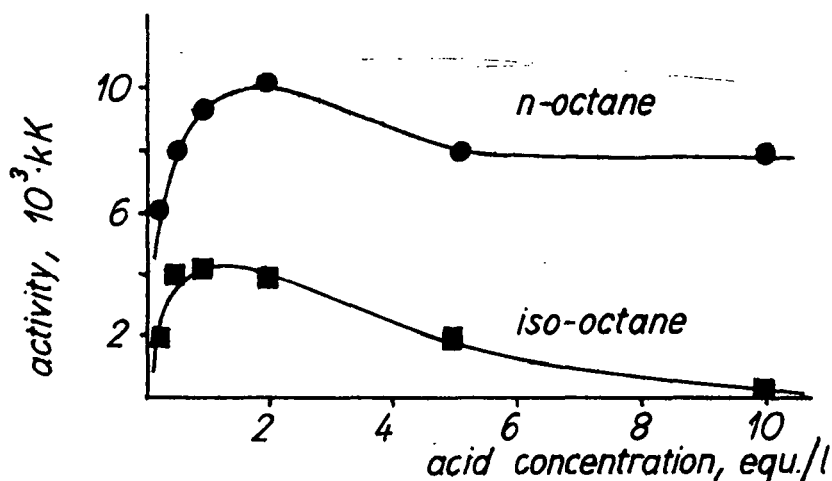n-octane and iso-octane (see Fig. 7).

Fig. 7. Activity of Ni/H-mordenite in the hydrocrac'.ing of
a 1 : 1 molar mixture of n-octane and iso-octane, dependen-
ce on the HNO_3 concentration used in the leaching treatment,
pulse reactor, 573 K, 3 l/h H_2, 5 μl pulses, 100mg catalyst
The dependence of the selectivity on the acid treatment con-
ditions can be explained by the prefered dealumination of the
shells of the mordenite crystallites. The shape selectivity of mor-
denite for n-paraffines in a mixture with iso-paraffines is only
based on the slowlier diffusion of the latter, because iso-paraf-

fines can enter the mordenite channel system too. By the peri-
pherical dealumination the acid centres in the outskirts, where
the iso-paraffines could be converted, are removed preferably.

The best results are obtained by leaching with concentra-
ted HNO_3 followed by supporting 5 ma.-% Ni. Investigating the
hydrogen reduction process of the Ni^{2+} ions introduced in the
H-mordenite by impregnation we found an interesting effect [17].
At temperatures above 770 K we observed a reduction degree of
the supported Ni^{2+} of more than 100 percent. A blank test gave
the surprising result that even the H-mordenite free of Ni strong-
ly chemisorbs hydrogen at temperatures above 720 K (see Fig. 8).
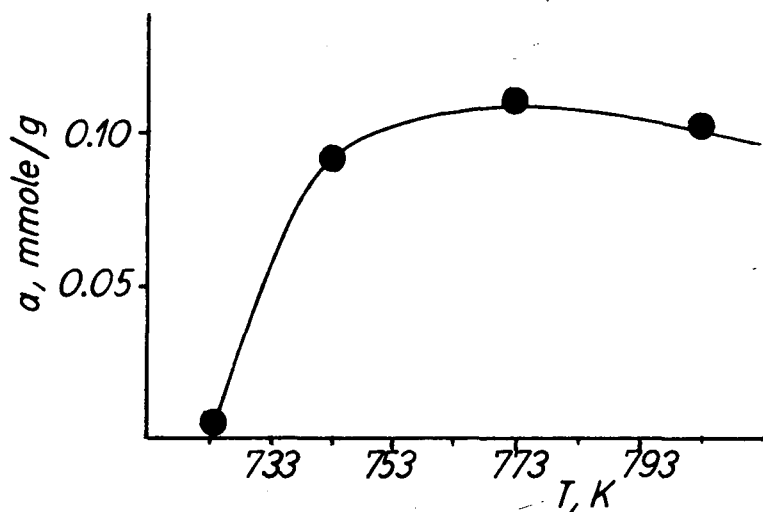

Fig. 8. Hydrogen chemisorption on H-mordenite

These data were obtained by a volumetric method as follows: Ac-
tivation of the mordenite sample in air for 3 h with 3 l/h at
the later reduction temperature, treatment for 2 h with 3 l/h
H_2 at the given temperature, treatment for 1 h with 3 l/h Ar at
the same temperature, cooling down to room temperature, evacu-
ation to 10^{-2} Pa, adding of outgassed HCl, measurement of the H_2
evolved.

On the basis of such experimental results the Leuna-Kt.
9561 has been developed [18]. Its performance in a pilot reactor
is shown in Table 5. The results show, that the Ni/mordenite
catalyst is able to improve the octane level by about five units
without large loss in liquid yield. The relationship one RON unit

Table 5

Performance of the Leuna-Kt. 9561 in a pilot plant

Reaction conditions: 4.0 MPa, 670 K, LHSV = 3.0, gas liquid - ratio = 1000 : 1 m^3/m^3, feed: reformate		
	feedstock	product
density, g/cm^3	0.759	0.748
liquid yield, ma.-%	-	96.5
RON$_0$	81	86
aromatics, vol.-%	38.0	42.5
naphthenes, vol,-%	7.0	8.5
paraffines, vol.-%	55.0	49.0
sulphur, ppm	3	-
light fraction to 100°C, vol.-%	18.5	23.5

gain per 0.7 ma.-% loss in liquid yield is satisfactory for usual reforming.

Unfortunately the optimal working conditions of mordenite containing shape selective hydrocracking catalysts are about 670 K and a LHSV of about 3 v/vh. This means in case of technical application an additional reactor in the reforming plant is required, in which the special working conditions can be chosen. Especially the working temperature is nontypical of reforming. At higher temperature the selectivity rapidly decreases due to the origin of the shape selectivity of mordenite catalysts and the liquid yield/RON relationship becomes lower than in case of conventional reforming.

ERIONITE CATALYST FOR THE SHAPE SELECTIVE HYDROCRACKING OF n-PARAFFINES

In comparison with mordenite erionite possesses real shape selectivity due to its pores dimensions [19]. From the hydrocarbons contained in a reformate only the n-paraffines are able to diffuse into the erionite structure even at about 770 K.

By repeated ion exchange with ammonium salt solution and thermal decomposition it is possible to prepare a catalytically active form of synthetic erionite. After forming of the H-erionite and supporting 0.5 % Pt for instance by impregnation a very active and selective catalyst is obtained [20]. Similar to this

the Leuna-Kt. 9562 has been produced in 1978 and applicated on industrial scale up today in three reforming plants. Table 6 contains a comparison of usual reforming with a commercial Pt/Al_2O_3 catalyst and a sandwich combination of the same Pt/Al_2O_3 catalyst with the Pt/H-erionite catalyst Kt. 9562 in the same conventional reforming plant consisting of three reactors.

Table 6

Comparison of reforming and reforming/shape selective cracking with Leuna-Kt. 9562, industrial plant, 2.5 MPa, gas product ratio = 1000 : 1 m^3/m^3

	reforming	reforming/selective cracking	
		variant 1	variant 2
results after time on stream, h	4 200	3 900	3 100
inlet temperature, K			
1. reactor	766	743	748
2. reactor	771	747	751
3. reactor	779	725	757
at catalyst Kt. 9562	-	711	735
LHSV, v/vh	2.1	2.1/25.0	2.1/25.0
liquid yield, ma.-%	87.3	87.3	84.4
$RON_{0.04}$	89.6	89.9	94.7
aromatics, ma.-%	39.2	35.1	43.3
naphthenes, ma.-%	6.3	12.8	8.7
paraffines, ma.-%	54.5	52.1	48.0

In case of the combination only 10 % of the reforming catalyst have been replaced by the shape selective hydrocracking catalyst Kt. 9562, that the specific space velocity at the Kt. 9562 is about 25 v/vh.

The results listed in Table 6 show that the application of the catalyst Kt. 9562 in combination with conventional reforming enables

- at unusual low temperature the same reforming result (variant 1), saving of energy and increasing of the life time of the whole catalyst combination up to more than 20 000 h without regeneration

or

- at lower temperature as it is usually applicated in reforming

plants higher RON level at high liquid yields (variant 2).

These good results are due to the real shape selective hyd-
rocracking of the n-paraffines and an additional formation of
aromatics as is shown in Table 7. The data given in Tab. 7 are
in accordance to the results of the technical plant listed in
Tab. 6.

Table 7

Feedstock and products for reforming and its combination with
shape selective hydrocracking, results of capillary chromato-
graphy, reaction details see Tab. 6

hydrocarbon	feedstock	reforming	reforming/selective cracking	
			variant 1	variant 2
	ma.-%	ma.-%	ma.-%	ma.-%
n-pentane	0.02	1.3	1.6	1.9
n-hexane	2.0	2.2	1.6	1.3
n-heptane	5.8	4.0	2.3	1.7
n-octane	6.8	2.8	1.9	1.2
n-nonane	4.7	1.3	1.0	0.8
n-decane	2.1	0.4	0.3	0.2
iso-pentanes	0.03	1.8	1.6	2.4
iso-hexanes	0.9	2.9	2.8	2.5
iso-heptanes	6.8	8.7	8.6	7.4
iso-octanes	7.9	8.1	8.6	8.2
iso-nonanes	7.1	5.1	6.6	6.1
benzene	0.4	2.1	1.6	1.9
toluene		9.8	7.6	9.2
C_8 aromatics	2.4	14.6	11.6	17.3
C_{9+} aromatics	5.5	18.2	17.2	21.1

The main advantages of the application of the erionite cata-
lyst are :
  - large gain in octane number at only small loss in liquid yield
  - mild reforming conditions
  - long run without regeneration
  - energy economizing
  - rationalization of reforming plants without reconstruction.

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