CATALYTIC CUMENE CRACKING ON H-ZSM-5 TYPE ZEOLITES

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ABSTRACT

The effect of cation exchange degree of H-ZSM-5 type zeolite the
mode of its decationation and its granulation on the zeolite catalytic
activity in the case of cumene cracking was investigated. Besides ben-
zene and propylene the main products of this reaction butenes and pen-
tenes as well as n-propylbenzene appeared as the products of side
reactions. Owing to the shape selectivity no saturated hydrocarbons
(except traces of butane) nor ethylbenzene and toluene were forming
which are typical products of side reactions on HNaY zeolites. Gene-
rally the H-ZSM-5 zeolites decationated by the substitution of Na^+ by
NH_4^+ are more active than those decationated by the treatment with hydro-
chloric acid solution exhibiting comparable content of Brönsted acid
sites.However this effect was definitely more distinct in the case of
highly exchanged zeolites (cation exchange degree about 90 %).

INTRODUCTION

Despite the fact that cumene cracking belongs to the frequently
used catalytic test reactions it has not been more thouroughly studied
on the ZSM-5 type zeolites. Nayak and coll. [1] described a series of
experiments in which cumene conversion was determined at 673 K on a
series of H-ZSM-5 zeolites differing by the cation exchange degree.
The present authors [2] compared the behaviour of HNaY and H-ZSM-5 type
zeolites as the catalysts of cumene cracking and stated distinct diffe-
rences in the yield and the composition of the side reactions products.
The aim of the present investigation was to study the catalytic cracking
of cumene on H-ZSM-5 type zeolites of different cation exchange degree
the acid properties of which were well characterized. Simultaneously
the effects of the decationation mode and the granulation of the
samples were investigated.

EXPERIMENTAL

   The samples of ZSM-5 type zeolite (Si/Al molar ratio equal to 47) were obtained at the Institute of Industrial Chemistry, Warsaw, as described in [3]. The decationation was carried out by J. Datka either via substitution of Na^+ ions with NH_4^+ (symbol NZ) or by the treatment with hydrochloric acid solution (symbol HZ). The samples with the highest cation exchange degree were also obtained in the case of which both methods of decationation were applied one after another but in different sequences (symbols HNZ and NHZ). The acid properties of the same samples were investigated in this laboratory by J. Datka and Tuż-nik and are described by them in full detail in their paper presented at this conference [4] and also in ref. [5] and [6]. The main data characterizing the samples are given in the Table. The numbers in the symbols of samples give the percentage of cation exchange. Strong Brönsted acid centres are formed by OH groups with the stretching frequency 3609 cm^{-1} Catalytic tests were carried out using either the samples not granulated containing crystallites of $\sim 1 \mu$m or the samples obtained by pressing the same fine crystalline powder, crushing the pellets and selecting the sieve fraction of grains 90-190 μm.

Table

Sample and cation exchange degree %	Apparent activation energy kJ mol^{-1}		Concentration of acid center per unit cell[x]				Rate constant of cumene cracking min^{-1}			
			Brönsted			Lewis	K_{670}		K_{630}	
	powder	granul.	strong	weak	total		powder	granul.	powder	granul.
NZ-31	62	39	0.29	0.30	0.59	0.10	70	100	31	59
NZ-43	54	44	0.47	0.36	0.83	0.15	144	145	85	88
NZ-83	52	30	0.85	0.39	1.24	0.18	238	218	135[xxx]	152
HZ-42	58	49	0.38	0.35	0.73	0.14	143	179	70[xx]	115
HZ-81	35	38	0.82	0.26	1.08	0.18	129	205	77	136
HZ-88	30	37	1.03	0.30	1.33	0.17	168	242	126	167[xx]
HNZ-90	38	35	0.96	0.22	1.18	0.10	115	209	72	140
HNZ-88	55	36	1.04	0.21	1.25	0.13	183	278	115	196

x - Determined by J. Datka and E. Tużnik [5,6] ; xx - Extrapolated ; xxx - Interpolated.

Catalytic tests were carried out in a pulse microreactor connected on line with a gas chromatograph. Helium was used as a carrier gas into the flow of which ($1200 \ cm^3h^{-1}$) the doses of 3 μl of cumene were introduced. The samples 0.02 g of catalyst diluted with 0.1 g of powdered quartz were activated "in situ" for 2 h at 720 K in the stream of helium. Analytically pure cumene (POCh Gliwice, Poland) was kept over metallic sodium and distilled before experiments. A Giede 18.6 Gas Chromatograph with programmed heating was used for the analysis of the reaction products applying a chromatographic column (length 2.5 m, diameter 4 mm) filled with Chromosorb W covered with 14 % of silicon oil DC 200. Katharometric detection was applied. The reaction products were identified using Mass Spectrometer LKB 9000 s.

Two series of catalytic tests were carried out. In constant temperature tests the dependence of activity and selectivity on the number of cumene pulses was investigated. In polythermic tests executed usually between 570 and 670 K at each temperature only one pulse was introduced in order to avoid the effects of ageing.

The rate constant of cumene conversion was calculated assuming 1st order of the reaction.

RESULTS AND THEIR DISCUSSION

Reaction products. Besides the main reaction products benzene and propylene some amounts of side reactions products were also detected : butenes, pentenes and n-propylbenzene but only traces of butane. The olefins were the products of the transformations of primary propylene as verified by the separate experiments in which pure propylene was introduced on the catalyst. The fact that olefins were the predominant products of propylene secondary reactions and only traces of alkanes (butane) were present which on the other hand are the main products of propylene secondary reactions on NaHY zeolites [2] is a typical shape selective effect. Presumably it is connected with different properties of propylene oligomer forming in both cases. In ZSM-5 zeolites the narrow pores allow only the formation of linear oligomer which, as it is supposed, decomposes into olefins of various chain length while the threedimensional oligomer forming in large cavities of faujasite type zeolites disproportionates into the hydrogen rich (alkanes) and hydrogen deficient precursor of the coke [7].

Only one aromatic product of side reactions was detected i.e. the n-propylbenzene which is the product of cumene isomerization. According to [8] the latter reaction occurs with the formation of monomolecular

transition complex. No ethylbenzene nor toluene were formed which were
observed in the case of NaHY zeolites. They are considered to be formed
via bimolecular transition complexes [8] which obviously can not be
formed in the narrow pores of H-ZSM-5 zeolite.

Ageing of the catalysts. The ageing of the catalysts was follo-
wed at 600 and 670 K. Fig. 1 (full line) shows that the deactivation of
the catalyst with the increasing number of cumene pulses was slow being
more distinct at lower temperature and in the case of the catalyst ex-
hibiting smaller cation exchange degree. The fact that deactivation was
slower at higher temperatures can be explained by a more rapid de-
sorption of precursors of the coke deactivating the catalyst. No influ-
ence of the granulation on the ageing of the catalyst (dashed lines on
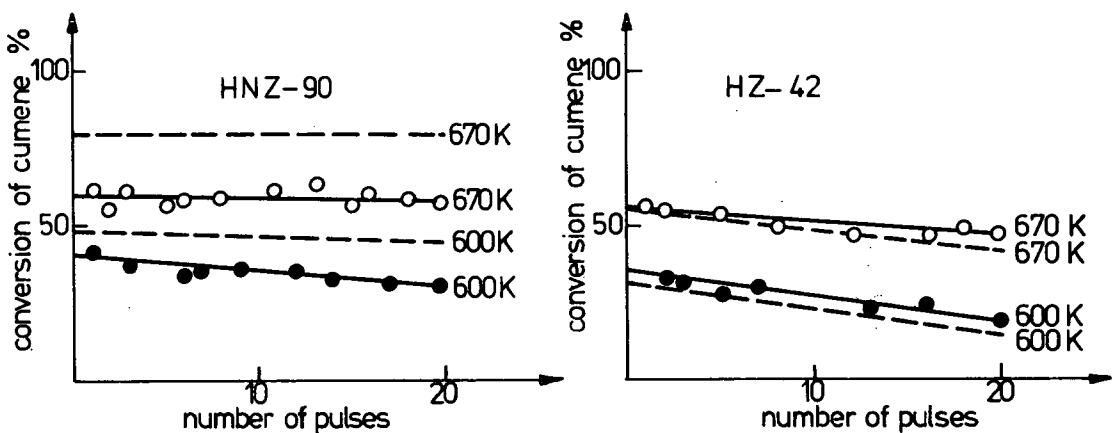Fig. 1) was observed.

Fig. 1. Conversion of cumene as the function of the number of
cumene pulses in the case of HNZ-90 and HZ-42 samples non-granulated
(full line) and granulated (dashed line).

Fig. 2 shows on the example of HZ-1 sample the effect of the de-
activation on the composition of reaction products. It is seen that the
mole % of benzene in the initial pulses exceeded the sum of mole % of
propylene unchanged and propylene transformed into butenes. The deficit
of propylene must be due at least partially to its irreversible ad-
sorption resulting in the slow catalyst deactivation but also some
amounts of it may be only slowly desorbed out of the catalyst and not
be included in the pulse of products introduced on the chromatographic
column. Similarily as it was observed in [2] catalyst deactivation
results in the diminishing of the amounts of side reactions   products :
increasing the content of propylene, decreasing the content of other
olefins. Simultaneously the relative content of benzene with respect to

the total content of propylene is decreasing and slowly approaching the molar ratio 1:1 thus indicating that the deficit of propylene is growing less and the catalyst is becoming more selective in respect to the main cracking reaction. This indicates that the secondary transformations of propylene occur on the acid centres – presumably the strongest ones – which are poisoned at first.
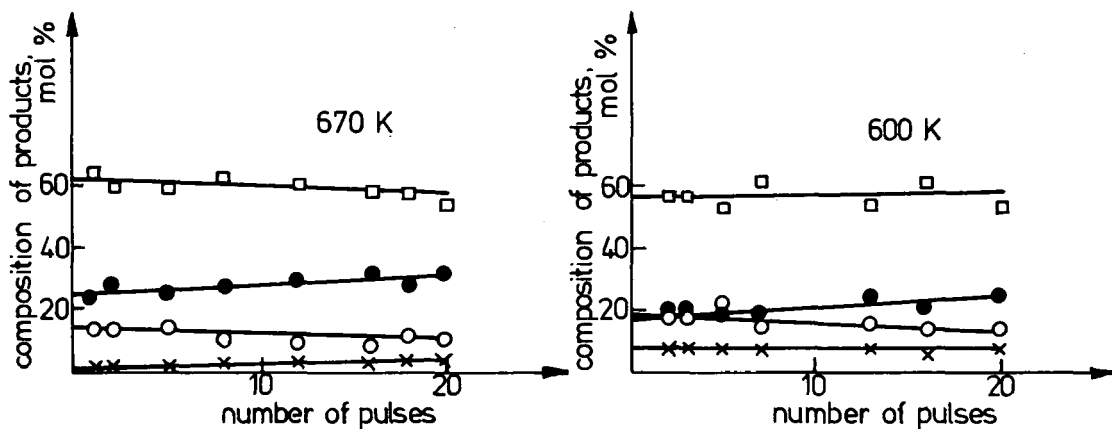

Fig. 2. Composition of the reaction products on the HZ-42 non-granulated at 670 and 600 K as the function of the number of cumene pulses (mol %).
   □ benzene
   ● propylene
   ○ butenes (expressed as the number of moles of converted propylene)
   × n-propylbenzene

The effect of cation exchange degree and the mode of decationation. Fig. 3 shows the dependence of rate constant on the temperature as obtained in polythermic tests carried out with not granulated samples. When comparing the activity of various samples the following statements can be done :
1. Within both series of zeolites NZ and HZ the catalytic activity is increasing with the increasing cation exchange degree and also with the acidity as given by the concentration Brønsted acid centres.
2. The effect of the decationation mode can be followed by comparing samples HZ-42 and NZ-43 with cation exchange degree 42 resp. 43 % and also on the samples HZ-88, HNZ-90 and NHZ-88 with 88-90 % of cation exchange. In the further case the activities of both samples are similar within the whole range of temperature but the sample NZ-43 with higher
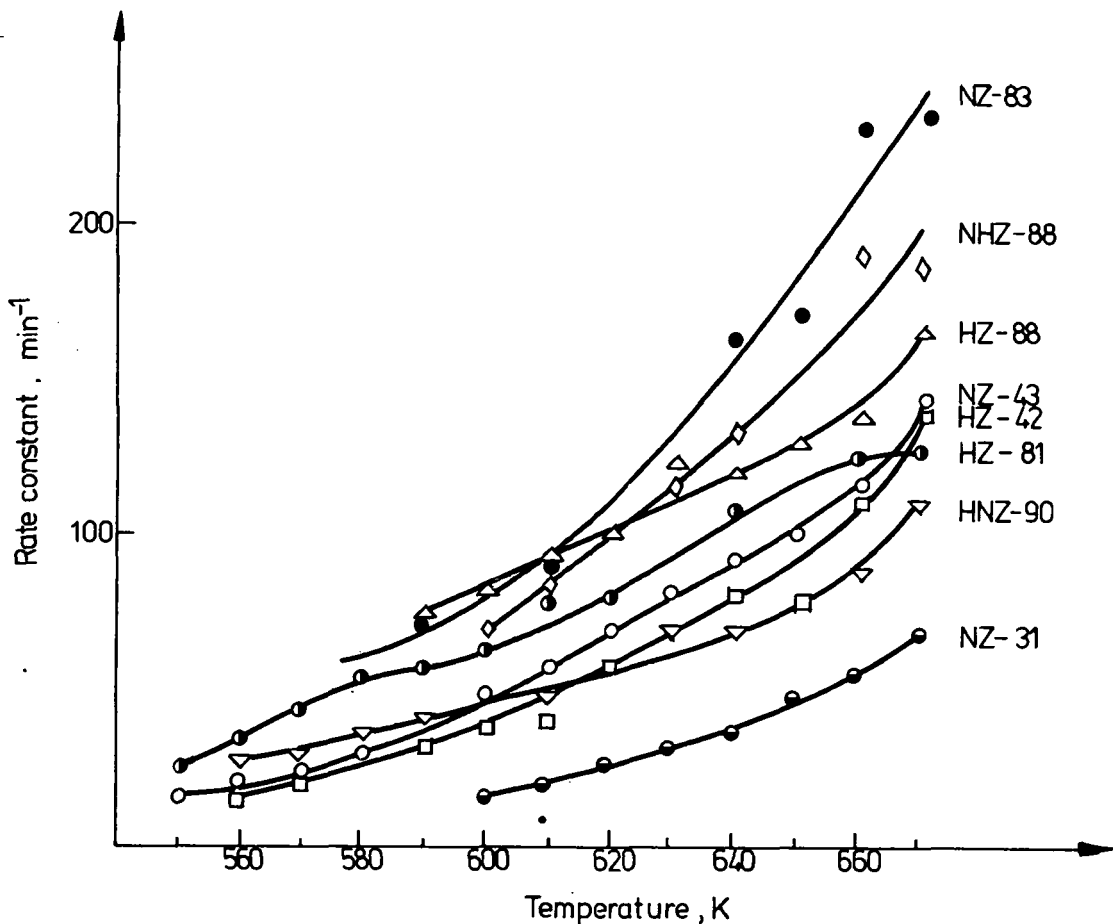
Fig. 3. Rate constant of the non-granulated catalysts as the function of temperature

content of Brönsted acid centres was always more active. In the latter case the discrepancies in the activity are much more pronounced and the sequence of activity HNZ-90   NHZ-88   HZ-88 corresponds well to the sequence of the total concentration of Brönsted acid centres. However it should be observed that the sample NZ-83 with 1.24 Brönsted acid centres per unit cell practically identical with that of the sample NHZ-88 is more active than all the other samples. The apparent activation energies of catalytic reaction of NZ-83 and NHZ-88 are not very much differing but the activation energy in the case of the latter sample is somewhat lower and the observed differences may be attributed to the higher activity of catalytically active Brönsted acid centres. However the second possibility is that in NHZ-88 sample the acid centres although accessible to pyridine molecules in the course of determination of their concentration, are only partially accessible to the cumene molecules. This

might be due to some structural changes in NHZ-88 sample.
3. The apparent activation energy of cumene conversion decreased within
both series of samples NZ and HZ with increasing cation exchange
degree. With the exception of NHZ-88 sample this rule seems to be also
approximately valid for the whole set of the results. The decrease of
activation energy with the decreasing cation exchange degree was also
observed in some other cases as e.g. in the case of butene isomeri-
sation on NaHY zeolites [9]. There are several possible reasons of
such effect. First of all the increasing number of acid centres
playing the role of catalytically active sites results in much faster
reaction in the zeolite pores and in such situation diffusion becomes
a factor influencing the overall rate of the process. Secondly the in-
creased acid strength of the Brönsted acid centres may lower the ener-
gy needed for the formation of transition complex. Finally the possible
increase of the adsorption heat of the substrate may cause the decrease
in the apparent energy of activation even if the true activation energy
remains unchanged.

The effect of sample granulation. is shown in Fig. 1 in which
full lines correspond to the not granulated samples and the dashed
lines to the granulated ones. It is seen that in the case of HZ-42
sample exhibiting relatively low activity the effect of granulation is
not pronounced. On the other hand in the case of highly active HNZ-90
sample the conversion on the granulated catalyst is definitely higher.
This can be attributed to the fact that the reagents penetrating into
the pores between particular crystallites remain for a longer period
of time in the contact with the catalyst and the effect is similar to
that obtained by the prolongation of contact time. The effect of diffusion
in the intercrystalline pores of the granules is the obvious reason
ahy granulating the samples lowers the apparent activation energy as it
is seen from the data presented in the Table.

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