# POLYFUNCTIONAL ZEOLITE CATALYSTS IN THE BENZENE-OLEFIN-HYDROGEN SYSTEM

I.I.LISHCHINER, V.A.PLAKHOTNIK, D.Z.LEVIN, E.S.MORTIKOV
Institute for Organic Chemistry of the Academy of Sciences, USSR, Moscow, USSR

## ABSTRACT

Benzene alkylation by $C_2$-$C_4$ olefins at 537 K and 3MPa over a polyfunctional zeolite catalysts has been studied.

It has been established that the admission of hydrogen to the reaction mixture in case of ethylene and butylene promotes chiefly olefin hydrogenation, while in case of propylene alkylation primarily proceeds. The correlation between acidic and catalytic properties of the catalyst in question has been revealed.

## INTRODUCTION

The literature available deals with alkylation and cracking processes able to proceed in hydrogen which promotes a higher zeolite catalysts stability [1,2]. We have found that using polyfunctional zeolite catalysts makes their stability and alkylation selectivity considerably higher if the process occurs in hydrogen [3].

In this paper the alkylating and hydrogenating properties of polyfunctional zeolite catalysts in the benzene-olefin-hydrogen system were studied depending on the olefin nature and the catalyst acidic properties.

## EXPERIMENTAL

The experiments were carried out in a 2,5-4,5 $cm^3$ tubular flow circulation stationary catalyst bed reactor. A mixture of benzene and olefin in the required proportion was pumped into the reactor with simultaneous admission of hydrogen. The amount of the admitted hydrogen was controlled by a highly sensitive flowmeter [4]. An Y-type zeolite, containing La, Ca and Ni-cations and prepared according to the technique [5] was used as a catalyst. A portion of this catalyst was subjected to 100% steam treatment at 873 K. The physico-chemical parameters of the zeolite catalysts were determined by X-ray

analysis, IR-spectroscopy [6,7] and TPD of ammonia in chromatographic [8] and thermogravimetric [9] methods.

The action of catalyst pyridine poisoning on the behavior of a polyfunctional catalyst in conditions of competitive processes of alkylation and hydrogenation was investigated. The pyridine adsorbed portion in n-heptane solution was determined by the difference in its concentration before and after its contact with the catalyst.

## RESULTS

Fig.1 gives the results on the investigation of CaLaNiY-activity in benzene alkylation by $C_2-C_4$ olefins depending on the catalyst thermo-steam pretreatment (TST) and hydrogen presence in the reaction mixture.
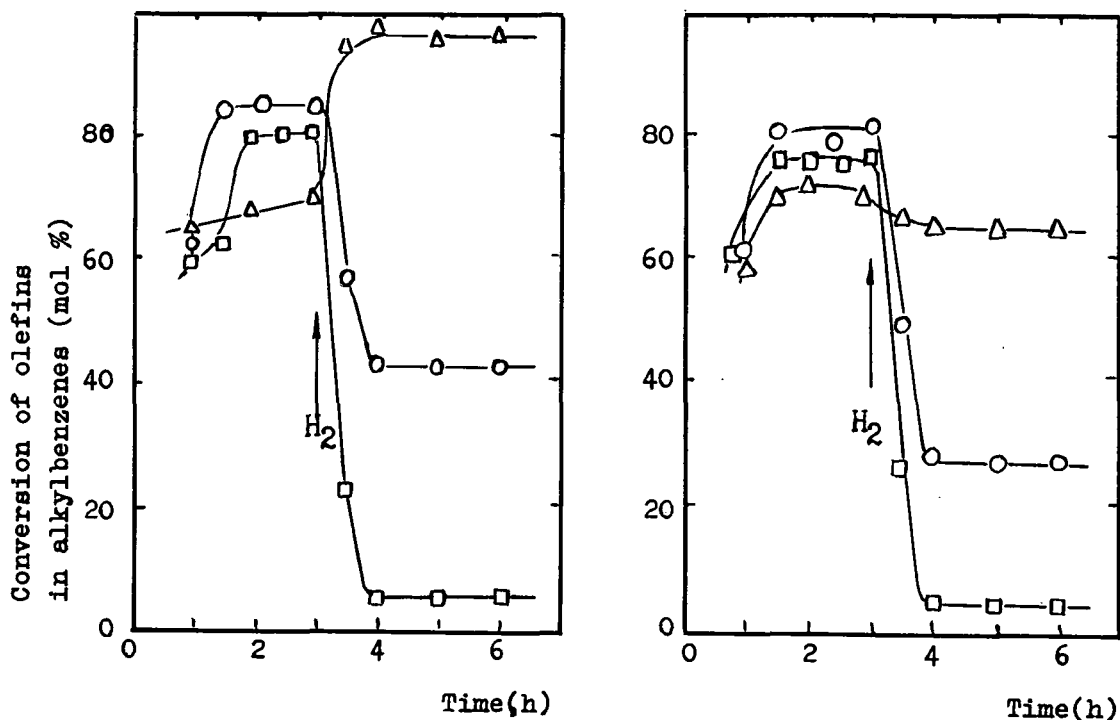


Fig.1. The effect of hydrogen on the activity of CaLaNiY subjected to TST (a) and untreated (b) in benzene alkylation by $C_2-C_4$ olefins.

　　O-ethylene,　△-propylene,　□-isobutylene

　　Conditions: 523 K; 3 MPa; $C_6$:olefin:$H_2$= 4,2:1:5; $3h^{-1}$

In case hydrogen is not present the pretreatment of the catalyst does not effect olefins conversion to alkylbenzenes as compared with alkylation in hydrogen. The hydrogen admission into the reaction mix-

ture over the initial (untreaded) catalyst leads to a considerable decrease of olefins conversion to alkylbenzenes due to the competitive olefins hydrogenation to saturated hydrocarbons (fig.1, table 1).

Table 1

The effect of thermo-steam pretreatment on the CaLaNiY activity . Conditions: 523 K; 3 MPa; $C_6$:olefin:$H_2$= = 4,2:1:5; 3 $h^{-1}$

| Catalyst Olefin | | Olefin conversion, mol.% | |
|---|---|---|---|
| | | to alkylation products | to hydrogenation products |
| initial sample | ethylene | 26,7 | 67,0 |
| | propylene | 65,3 | 19,6 |
| | isobutylene | 1,8 | 90,0 |
| sample after TST | ethylene | 47,9 | 45,3 |
| | propylene | 94,7 | 1,5 |
| | isobutylene | 5,2 | 78,5 |

However, if the catalyst undergoes TS-pretreatment and alkylation proceeds in hydrogen, the degree of olefins hydrogenation decreases in the ratio:for ethylene and isobutylene by 1,1-1,4, whereas propylene is not practically hydrogenated in these conditions. Due to the decrease of the olefins hydrogenation degree, the yield of alkylbenzenes increases.

Under conditions unfavourable for alkylation (benzene is replaced by n-heptane) the pretreatment of the catalyst does not affect its hydrogenating activity. For example, the degree of propylene hydrogenation is 82,7% for both the initial and pretreated CaLaNiY - samples.

In order to compare the reactivity of different olefins the benzene alkylation by equimolar ethylene-propylene mixture in hydrogen was carried out (table 2). As is shown, about 90% ethylene used is converted to hydrogenation products whereas 15-20% propylene is converted to propane, and 75-80% - to alkylbenzenes.

The similar dependence is observed in benzene alkylation in hydrogen by propylene-isobutylene mixture. Propylene is almost completely alkylated, while isobutylene is only hydrogenated.

Table 2

Benzene alkylation by ethylene-propylene mixture in
the presence of hydrogen over CaLaNiY - catalyst
after TST

Conditions: 3MPa, $3h^{-1}$, $C_6:C_2:C_3=2:1:1$; $H_2:C_2+C_3=3:1$

| NN | Temperature, K | Ethylene conversion mol.% | | Propylene conversion mol.% | |
|---|---|---|---|---|---|
| | | to alkylben-zenes | to ethane | to alkylben-zenes | to propane |
| 1 | 453 | 7,2 | 87,8 | 80,4 | 15,0 |
| 2 | 483 | 6,3 | 76,7 | 74,5 | 17,1 |
| 3 | 523 | 7,7 | 87,3 | 73,5 | 19,6 |

To explain the TST effect on CaLaNiY catalytic properties in the competitive alkylation and hydrogenation processes it was necessary to study the changes which occur in the catalyst during the treatment, i.e. to study its hydroxyl covering, acidity and the crystal structure parameters.

The X-ray analysis data on CaLaNiY-samples before and after TST reveal the relative crystallinity remain unchanged after steam treatment. In determining the adsorption capacity of catalyst samples it was found that the benzene adsorption value as a result of TST does not alter either.

The comparison of IR-spectra of CaLaNiY samples investigated in the range of 450-1450 $cm^{-1}$ showed the frequencies and intensities of typical absorption bands in the range of 570-580 $cm^{-1}$, 750-800 $cm^{-1}$, and 1050-1150 $cm^{-1}$ being practically constant.

The nature and concentration of the surface hydroxyl groups of a polyfunctional zeolite catalyst were investigated by diffuse reflectance IR spectroscopy in the range of main valence vibrations of OH-groups at 3000-4000 $cm^{-1}$ [10]. In the spectra of CaLaNiY-samples (fig.2) we observed four absorption bands: the high intensive band at 3540 $cm^{-1}$ attributed to OH-groups and bonded with La-atoms; the weak band at 3680 $cm^{-1}$ which according to [11], is assigned to OH-group, bonded with off-frame Al-atoms; two absorption bands of average intensity at 3645 and 3745 $cm^{-1}$, respectively. The absorption at 3645 $cm^{-1}$ is referred to structural OH-groups of bridge type [7]. In accordance with [12,13] the bridge hydroxyl groups which have vibration frequency in the range of 3610-3650 $cm^{-1}$, characterize Brendstad acidity of most zeolites. The frequency at 3745 $cm^{-1}$

is usually related to Si-OH groups of terminal type on the external zeolite surface or to silane groups of trace amorphous alumosilicate having greater contents of $Al_2O_3$ [10].
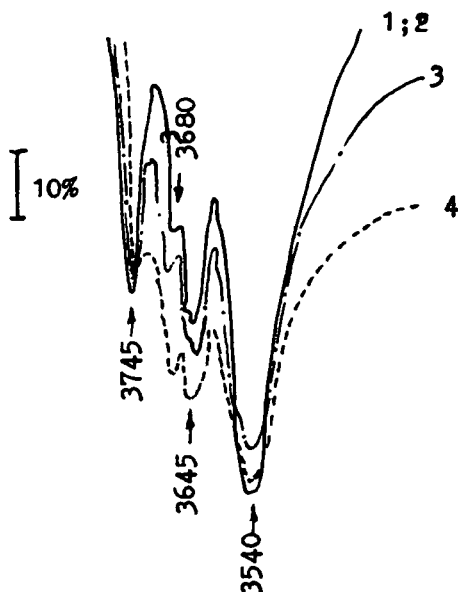


Fig.2. IR-CaLaNiY diffuse reflectance spectra 1-initial sample, 2 - after 2 h TST, 3- after 6 h TST, 4 - after 12 h TST.

The comparison of the spectra shows the spectrum of the initial CaLaNiY samples does not practically differ from those subjected to TST.

Using the programmed ammonia thermodesorption in a chromatographic regime we could investigate the change of CaLaNiY acidity as a result of TST (fig.3).
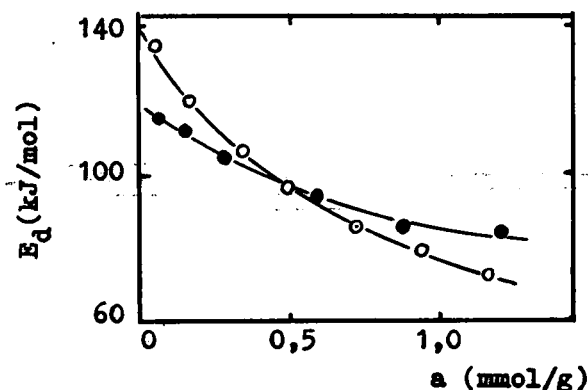


Fig.3. Activation energy of ammonia desorption ($E_d$) as a function of the amount of chemisorbed ammonium on the LaNiY catalyst: steam-treated (light points) and untreated (dark points)

It is shown that TST leads to the number decrease of strong acidic centres having $Edec_{NH_3}$ > 90 kJ/mol, and the increase of centres with $Edec._{NH_3}$ = 80-90 kJ/mol as compared with the initial catalyst.

These differences become more evident if we consider the dependence of chemisorbed ammonia amount on the temperature obtained by thermogravimetry. The thermograms calculation based on the integral curve (IC) shows that thermo-steam treatment does not influence the total amount of chemisorbed ammonia, i.e. the total CaLaNiY acidity does not alter in various TST conditions (Table 3). For the initial

Table 3

The effect of TST duration on acidic and catalytic
properties of CaLaNiY

| № | TST time, h | Total acidity, mmol/g | Temperature of ammonia desorption | Conversion of propylene to alkylbenzenes mol.% (A) | Conversion of propylene to propane, mol.% (B) | A/A+B 100% |
|---|---|---|---|---|---|---|
| 1 | - | 2,08 | 653,853, | 68,5 | 21,8 | 74,1 |
| 2 | 2 | 2,05 | 553,633, 813 | 71,5 | 18,5 | 78,0 |
| 3 | 6 | 2,05 | 453,553, 703 | 95,1 | 2,9 | 97,0 |
| 4 | 12 | 1,98 | 453,533, 693 | 96,0 | 2,5 | 97,5 |

catalyst the ammonia chemisorption on the active centres of the surface results in the formation of compounds which have the decomposition temperature 653 and 853 K. The initial catalyst TST, in case it is prolonged, can change DTA-curves. The two hour TST results in the formation of surface centres where the ammonia is desorbed at 553, 633 and 813 K. The six-hour TST provides the formation of centres where the ammonia desorption is observed at lower temperature.

The data of the thermogram calculations based on the conclusions of the paper [14] enable us to make a diagram of distribution the centres according to their acidic level (fig.4) in coordinates $\Delta m / \Delta H_0 - H_0$, where $\Delta m / \Delta H_0$ - the number difference of acidic centres which corresponds to the small interval of change in Hammett acidity function $H_0$. It is seen that after the catalyst TST the number of centres with $H_0 \sim$ ranging from -8 to -14 (which corresponds to the ammonia desorption temperature 473-673 K) decreases as compare with the initial catalyst. At the same time the number of centres having $H_0$ from -6 to -8 (433-473 K) sharply increases and the centres be-
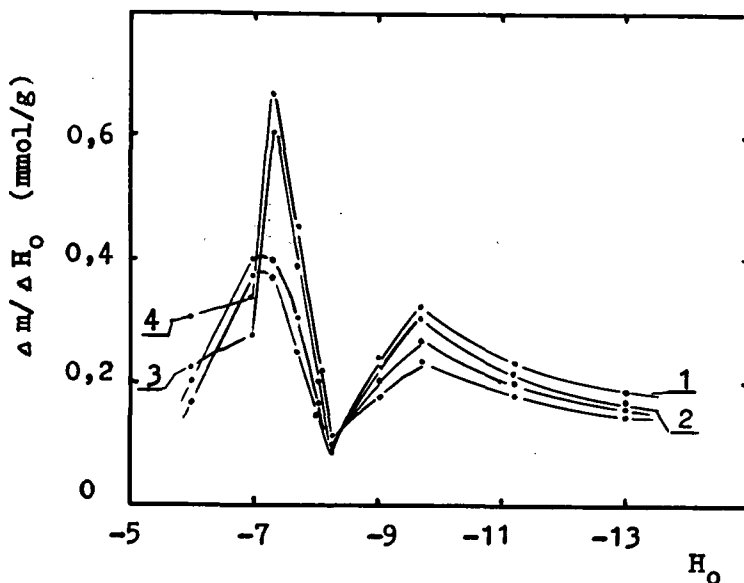
Fig.4. The centres distribution by acidic levels

come more homogeneous by their level with prolonging the TST dura-
tion, the number of centres with $H_o < -8$ increases even more at the
expense of the number decrease of centres with $H_o$ from $-8$ to $-14$.

In order to clear up the correlation of acidic and catalytic
properties of a polyfunctional zeolite catalyst the latter was sub-
jected to a subsequent poisoning by pyridine (fig.5).

After the sorption of 0,018 mmol pyridine/g catalyst the alkyla-
ting activity of CaLaNiY is lowered half as much as compared to the
initial sample, and the hydrogenating activity grows 7 times as much.
After the sorption of 0,09 mmol pyridine the conversion of propylene
into alkylbenzenes lowers from 75 to 20%, and in case to propane it
grows to 64%.

The 0,45 mmol base sorption leads to nearly a complete catalyst
deactivation in the alkylation process, hydrogenating activity is
remaining as high as in propylene hydrogenation in heptane solution
(the conversion to propane 81,5%).

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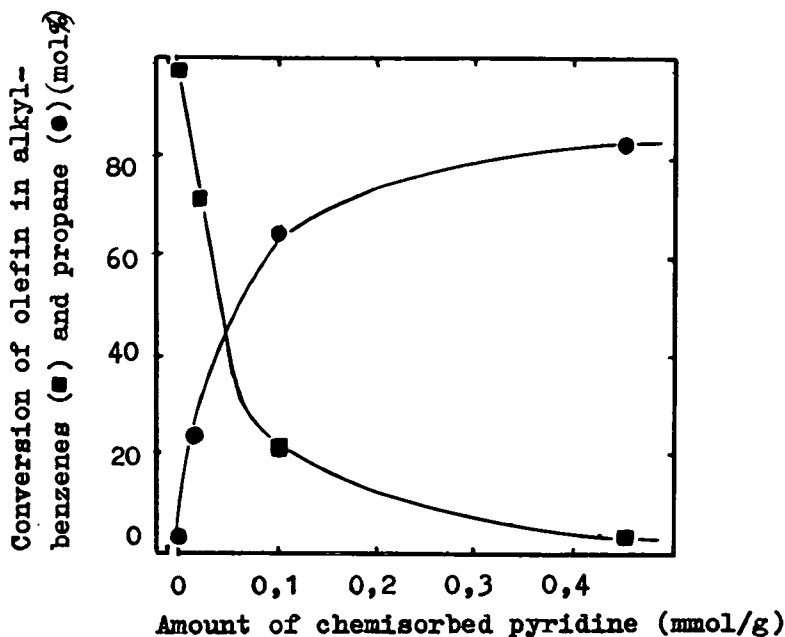UR - spectra were measured by Kustov L.M. and Borovkov V.Yu.

Fig. 5. The dependence of alkylating and hydrogenating activity
on the chemisorbed pyridine amount.
Conditions: 523 K; 3MPa; 3 $h^{-1}$; $C_6$:$C_3$:$H_2$=4,2:1:4,2

## DISCUSSION

From the data of fig.1 and table 1 it follows that thermo-steam
treatment effects a polyfunctional zeolite catalyst activity in alky-
lation in hydrogen, and promotes a considerable lowering the degree
of the $C_2$–$C_4$ olefins hydrogenation and increasing the alkylbenzenes
yield.

In order to explain the effect of the catalyst TST in the com-
petitive alkylation and hydrogenation reactions it is important to
consider the CaLaNiY physico-chemical parameters and their altera-
tion during TST. The X-ray data and IR-spectroscopy, as well as the
results of the catalyst sorption capacity determination show that
as a result of TST, irrespective of its duration, the crystal cata-
lyst structure, the $SiO_2$/$Al_2O_3$ ratio, and also the hydroxyl surface
groups nature and concentration do not change while the zeolite aci-
dic properties are altered.

The ammonia thermodesorption data indicate that in the process
of TST the redistribution of acidic centres, possessing different
levels, is observed. The comparison of CaLaNiY catalytic activity
with the change in the catalyst acidity spectra (table 3 and fig.4)
shows that TST results in increasing the number of acidic centres

with $H_o$ < -8° (as related to the "weak"), and correspondingly, the growth of alkylating activity is observed. After achieving the optimal distribution of acidic centres of different levels at $-6 < H_o < -8$ and $-8 < H_o < -14$, CaLaNiY catalytic properties stop changing and as it follows from table 3, the definite ratio between alkylation and hydrogenation reactions is established.

It should be taken into account that a polyfunctional zeolite catalyst hydrogenating activity is determined by presence of a metal while alkylating activity is connected with acidic properties of a catalyst. In favour of this there are      data which confirm the change of the alkylating and hydrogenating activity of the catalyst which underwent a subsequent poisoning by pyridine. As poisoning the acidic centres of the catalyst its activity dropped in the alkylation process, while in hydrogenation reaction it rose (fig.5).

Hence, one can assume that the acidic centres of different levels are responsible for the alkylation reaction. However, the advantageous preferred alkylation in the conditions of its competition with hydrogenation over the catalyst, subjected to TST, can be explained by increasing the number of relatively "weak" acidic centres which are apparently determining in alkylation professes.

Thus, thermo-steam treatment allows in the conditions of competitive alkylation and hydrogenation reactions to control purposefully the activity of a polyfunctional zeolite catalyst.

Considering the behaviour of $C_2$-$C_4$ olefins in benzene alkylation in hydrogen one can note the following according to [15] , the $C_2$-$C_4$ olefins by their reactivity in benzene alkylation over zeolite catalysts can be arranged in the row:ethylene < propylene ~ isobutylene At the same time the hydrogenation rate of individual $C_2$-$C_4$ olefins is approximately similar [16]. The results which we have obtained on benzene alkylation by individual olefins and their equimolar mixtures show that in hydrogen media the olefins sequence changes as related to their reactivity in alkylation process over zeolite catalysts:

isobutylene < ethylene < propylene

This change might be due to the difference in hydrogenation and alkylation rates, and also in polymerization,which makes the alkylation process more complicated. According to polymerization, rates over zeolites, containing transition metals cations, the olefins are located [17]: isobutylene > ethylene > propylene

In the presence of hydrogen in the reaction mixture the olefins hydrogenation is suppressed, though for each individual olefin it is

likely to be different, and this effects their reactivity in the al-kylation process.

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