FORMATION OF DEPOSIT AND AROMATICS ON HNaY ZEOLITE

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ABSTRACT
    Formation of deposit /i.r. band 1600 cm^{-1}/ and aromatics or
their precursors such as cyclic oligomer /1500 cm^{-1}/ through a
common oligomer on HNaY zeolite was studied using i.r. spectroscopy.
Olefins, isopropanol, aromatics and unsaturated aliphatic cyclo-
compounds were used as adsorbates in the range 301-673 K. Deposit
formation preceded aromatics, which were never observed before
appearing of deposit. Aromatics were not formed from deposit but
always in the presence of it and were not necessary for deposit
formation. There are two paths of oligomer transformation: one to
deposit and the second, after a suitable modification of HNaY
zeolite by deposit, to aromatics. The two processes can be sepa-
rated at relatively low temperature but they occur very fast at
673 K before the full deactivation of HNaY zeolite.

INTRODUCTION
    Our earlier investigations of the adsorption of alcohols,
ethers and olefins on ZSM-5 and HNaY zeolites showed that olefins
play an important role in transformations of alcohols and ethers
into hydrocarbons /1/.
    Olefins are transformed into desorbable species characterized
by i.r. absorption band about 1500-1518 cm^{-1} and to carbonaceous
deposit called also coke /i.r. band about 1600 cm^{-1}/.
    Formation of oligomers and deposits from olefins and others
molecules on decationized zeolites was studied in many papers /2-14/
and different hypothesis were advanced as to the nature of the
deposit. It was described as aliphatic /polyens/ or /and, at least
at higher temperatures, aromatic/ hydrogen-poor condensed aromatics
or alkylaromatics non desorbable species/, which could be removed
from a zeolite only by burning with air or oxygen.

We assumed earlier that the band about 1500 cm^{-1} is due to a shift of double bond in an olefin and we assigned this band to an electron-deficient double bond or even to stabilized carbenium ion /15,16/.

An olefin adsorbed on decationized zeolite forms a carbo-cation and transforms into an oligomer /1,2/, clearly visible in the case of ethylene. This oligomer seems to be present in the form of stabilized carbo-cation /6/. The spectrum of a saturated species after adsorption of an olefin on decationized zeolite is then the spectrum of a stabilized alkyl carbo-cation without any i.r. bands about 1500 cm^{-1} /6/.

The results described in /1/ made us to conclude that the oligomer transforms into another species, the appearance of the 1500 cm^{-1} band being not due to the shift of double band, because diminishing intensities of oligomer bands indicated that some cyclization might take place. The region of 1430-1600 cm^{-1} is characteristic for the group frequencies of aromatic compounds which show the bands of the breathing vibrations at 1430-1500 and 1580-1600 cm^{-1}. Taking in to account that some authors /17,18/ assigned the band at 1500 cm^{-1} to aromatics and that the same band appears also at higher temperatures /without evacuation/, we assumed its appearance indicates the formation of aromatic species or at least their adsorbed precursors such as cyclic oligomers /possibly in form carbo-cations/, though the temperature is very low. In this connection we may quote /19/ the existence of an alkenyl carbo-cation with an intense band at 1533 cm^{-1}, the only band between 2850 and 1450 cm^{-1}. The 1500 cm^{-1} band and bands of oligomer disappear after evacuation and heating to about 523 K /in many cases oligomer is more strongly adsorbed than species with 1500 cm^{-1}/, but up to this temperature aromatics are not appearing in the products /7/. It could be supposed that species characterized by the band about 1500 cm^{-1} is at least an intermediate or precursor of aromatics which at higher temperature desorbs in form of aromatics. We shall thus call it "aromatics" although its nature is not yet fully known.

Proportions of aromatics and deposit depend on the type of zeolite. In preliminary experiments on HZSM-5 zeolite only the formation of aromatics was observed, whereas on HNaY zeolite mainly the deposit and only a small amount of "aromatics" were formed.

The mechanism of formation of deposit and "aromatics" on HNaY zeolite is not yet fully understood and it seemed of interest to

study this mechanism by monitoring the transformations of some molecules on HNaY zeolite with i.r. spectroscopy.

EXPERIMENTAL

The decationized form of HNaY zeolite was obtained from the NaY parent zeolite of the composition: 0.87 $Na_2O \cdot Al_2O_3 \cdot 5.05$ SiO_2 x H_2O by exchange of ammonium ions /degree of exchange 71 %/. Samples were pressed into self-supported plates and placed in the high temperature vacuum cell /20/, connected to conventional vacuum apparatus. Adsorption and desorption of adsorbates were carried out at temperatures from 301 - 318 to 673 K and from several Torr to 10^{-1} - 10^{-5} Torr.

All the adsorbates were of pure grade: propene, but-1-ene, dec-1-ene, isopropanol, benzene, toluene, p-xylene, ethylbenzene, cumene, cyclohexene, cyclohexadienen /1,3/, methyl-1-cyclohexe-1-ene, methyl-1-cyclohexadiene /1,3/ and cyclopentene.

I.r. spectra were recorded on a double beam spectrophotometer UR-20 /Zeiss/.

RESULTS AND DISCUSSION

Adsorption of olefins on HNaY Zeolite

After adsorption of propene on HNaY zeolite, beside the i.r. absorption bands of the oligomer /1470 cm^{-1} and 2880-3000 cm^{-1}/ the band of deposit /1600 cm^{-1}/ /Fig.1/ was observed already at 301 or 318 K. On heating the i.r. bands of oligomer diminished and that of deposit increased. It is noteworthy that the band of the deposit appeared before the i.r. shoulder or band of "aromatics" /1500 cm^{-1}/ were formed in the range of 343-373 K. In the range of 348-423 K new i.r. bands about 1350 cm^{-1} appeared, which could be connected with isomerization of oligomer yielding more branched structures, containing tertiary groups. At 623 K "aromatics" desorbed, but oligomer remained in the zeolite. I.r. bands of OH groups were rebuilt after heating but they did not reach their initial intensities. After oligomer desorption a new band between 1350 and 1400 cm^{-1} developed which was earlier tentatively assigned by us as symmetric vibration of carboxylate species /1/.

On HNaY zeolite "aromatics" were never formed before appearing of the deposit. It may be thus concluded that deposit modifies the system of cages and channels of HNaY zeolite making possible the formation of small molecules, which can then desorb.
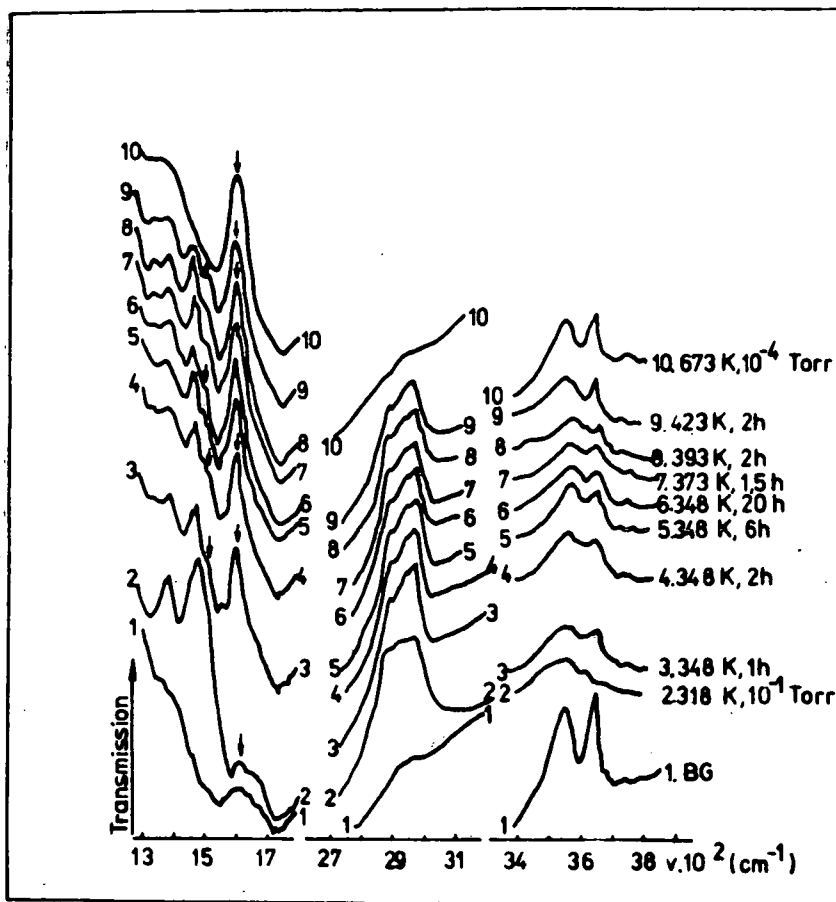
Fig. 1. Spectra of propene adsorbed on HNaY zeolite

When small portions of propene were consecutively adsorbed on HNaY zeolite it was found that adsorption of about 31 molecules of propene per unit cell resulted in the complete disappearance of HF OH groups at 3650 cm^{-1}. It may be concluded that the oligomer contains on an average 12 carbon atoms, the same as that found in /2/ after adsorption of butene.

In the case of but-1-ene and dec-1-ene on HNaY zeolite, similarly as in case of propene the deposit appeared at 301 and 318 K and "aromatics" at 398 and 363 K respectively.

In the case of dec-1-ene the oligomer was formed instantaneously because dec-1-ene could directly form stabilized carbo-cation.

Adsorption of aromatics and alkylaromatics on HNaY zeolite

No i.r. band of deposit were observed in spectra after adsorption of benzene and toluene on HNaY up to 673 K, what rules out the

possibility that aromatics and alkylaromatics form deposit in this
temperature range.

Spectra recorded during adsorption of p-xylene on HNaY zeolite
showed that deposit band appeared from 533 K as a result of p-xylene
dealkylation and formation of reactive species as e.g. olefins.

Adsorption of ethylbenzene was carried out in such a way that
before every registration of spectrum with a change of temperature,
the sample was outpumped in order to expose deposit band screened
by the spectrum of ethylbenzene. The band of deposit /most probably
formed from ethylene/ was observed at 533 K, its intensity
increasing with temperature.

The procedure by adsorption of cumene was the same as for
ethylbenzene in order to expose the band of deposit which was
observed at 423 K. Some changes in the spectra after heating of
cumene were connected with its decomposition to benzene and propene.
A shoulder appearing at 533 K at 1500 cm^{-1} could be assigned to the
band of "aromatics" originating from propene.

It may be thus concluded that in the case of alkylaromatics
the deposit appears first at such a temperature, whereat
decomposition of alkylaromatics begins, resulting in the formation
of reactive species such as olefins.

Adsorption of isopropanol on HNaY zeolite

Bands of isopropanol, water and deposit were present in the
spectrum of adsorbed isopropanol /318 K/, which after heating to
353 K resembled the spectrum from olefins. At 373 K the intensity
of deposit band increased, whereas that of oligomer bands diminished
and a new band about 1350 cm^{-1} appeared. At 403 K a shoulder
appeared about 1500 cm^{-1}, becoming more pronounced at 443 K, the
band at 1350 cm^{-1} also increased in intensity and changed its
shape. Evacuation at 318 K caused disappearance of the band of water
and exposure of the big band of deposit. The band of "aromatics"
was clearly visible and reappearance of OH groups began. After
heating to 673 K following bands were only left: deposit, weakened
OH groups and the band about 1350 cm^{-1}.

Adsorption of isopropanol on HNaY zeolite resembles thus that
of olefins /oligomerization goes fast at 353 K/ but presence of
water hinders the formation of "aromatics" which become visible in
the spectrum only at 403 K.

Adsorption of unsaturated aliphatic cyclocompounds on HNaY

It seemed interesting to investigate adsorption of some unsatu-

rated aliphatic cyclocompounds on HNaY zeolite to explain their role
as possible precursors of aromatics in the reaction sequence:
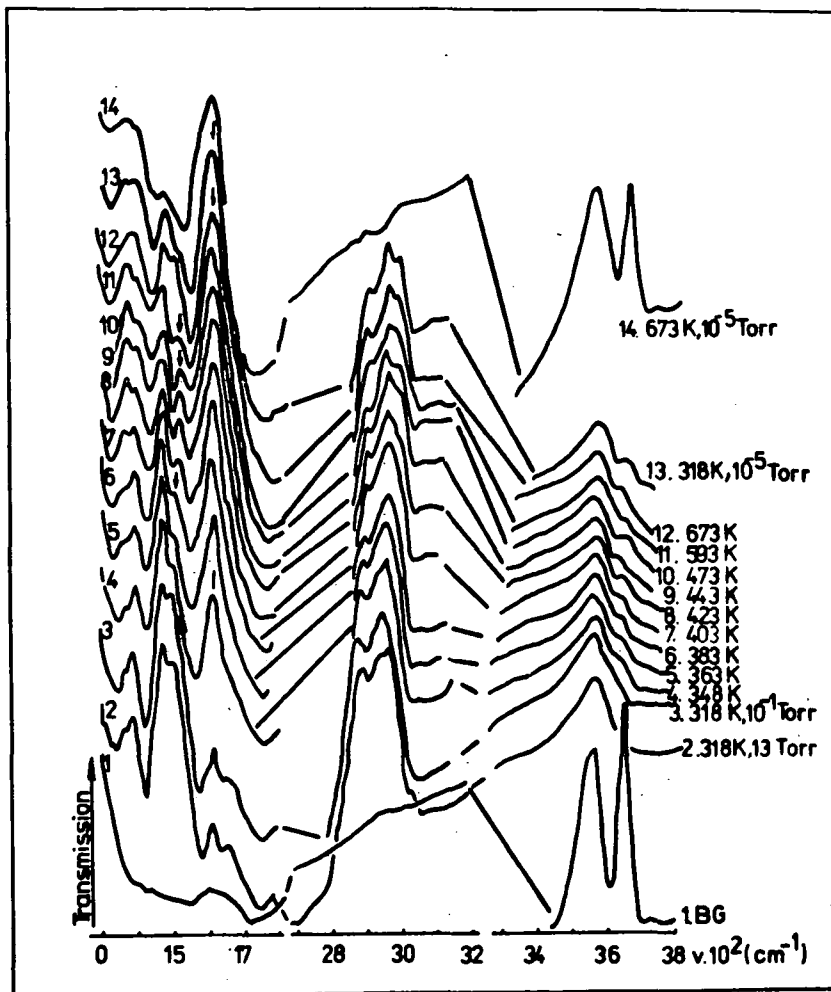cyclohexene ⟶ cyclohexadiene ⟶ benzene.

Fig. 2. Spectra of methyl-1-cyclohex-1-ene adsorbed
on HNaY Zeolite

The set of i.r. bands characteristic for adsorbed methyl-1-cy
lohex-1-ene is very similar to that of an oligomer formed from an
olefin on HNaY /Fig.2/ and behaves in a way similar to that of an
oligomer, revealing that deposit and "aromatics" are formed on
heating. It may be thus concluded that after adsorption of methyl-1-
cyclohex-1-ene an appropriate type of oligomer is formed. The band
at 1490 cm^{-1} not observed before could belong to this type of
oligomer, but its intensity diminished much faster that those of

other bands of oligomer and disappeared below 373 K, "aromatics" beginning to appear above this temperature.

Heating to 348 and 363 K caused the decrease of all oligomer bands /the band at 1490 cm^{-1} most rapidly/ and considerable growth of deposit band. At 373 K the band of "aromatics" appeared at 1503 cm^{-1}, its intensity increasing at 403 K. The oligomer bands diminished, that of deposit grew and a group of bands at 1360 cm^{-1} increased and changed its pattern. After heating to 423 K the band of "aromatics" /1510 cm^{-1}/ and that at 1360 cm^{-1} increased, the former reaching its maximum at 443 K. The group of bands at 1360 cm^{-1} was at its maximum at 473 K. After evacuation at 673 K only following bands remained: strong deposit, one at 1350 cm^{-1} and weakened OH groups.

The sequence given above resembles that obtained after adsorption of an olefin on HNaY zeolite: deposit is formed first, "aromatics" later.

Adsorption of cyclohexene on HNaY was quite similar to the case of methyl-1-cyclohex-1-ene. Deposit started to form at 318 and "aromatics" at 383 K.

Adsorption of cyclopentene is also similar to that of methyl-1-cyclohex-1-ene: deposit at 318 K and the band about 1500 cm^{-1} at 403 K. It is necessary to stress that the difference in the ring structure of the adsorptive does not influence the results.

Adsorption of methyl-1-cyclohexadiene /1,3/ on HNaY resembles that of methyl-1-cyclohex-1-ene: deposit is formed at 318 and "aromatics" from 383 K. Similarly cyclohexadiene /1,3/ gives deposit at 318 and "aromatics" at 363 K.

Results described above enable following conclusions to be formulated:

1. appearance of the deposit /the characteristic band at about 1600 cm^{-1}/ from the oligomer, formed earlier from: propene, but-1-ene, dec-1-ene, isopropanol, cyclohexene, cyclohexadiene /1,3/ methyl-1-cyclohex-1-ene, methyl-1-cyclohexadiene /1,3/ and cyclopentene on HNaY zeolite occurs in the temperature range 301-318 K and always precedes the formation of "aromatics" /the characteristic band about 1500 cm^{-1}/,

2. "aromatics" were formed at relatively low temperatures: from olefins at 348-363 K, from isopropanol at 403 K and from investigated unsaturated aliphatic cyclocompounds at 363-403 K,

3. "aromatics" were not observed before the appearance of the deposit, what indicates that "aromatics" were not the source

for deposit formation,

4. formation of "aromatics" from deposit was not detected,

5. deposit was not formed from benzene or toluene /up to 673 K/ but it was generated by adsorption of p-xylene and ethyl-benzene at 533 K and cumene at 423 K, i.e. at temperatures higher than those necessary for the formation of deposit and aromatics from olefins and unsaturated aliphatic cyclocompounds; it may be concluded that deposit was obtained from alkylaromatics only after their dealkylation and appearance of some reactive species as e.g. olefins,

6. only two central members of the sequence: cyclohexane $\rightarrow$ cyclohexene $\rightarrow$ cyclohexadiene $\rightarrow$ benzene can transform into deposit in mild conditions /at 318 K/,

7. in the case of unsaturated aliphatic cyclocompounds the ring structure does not influence their transformations,

8. a new band at 1350 cm^{-1} was observed at higher temperatures and its assignment is not clear; it may be assigned to carboxylate species though the appropriate asymmetric vibration band with few exception was not observed; it could be screened by very strong deposit band,

9. intensities of OH group diminish after deposit formation,

10. "aromatics" appear on HNaY zeolite always in the presence of deposit,

11. it can be assumed that at the beginning favourable conditions exist in supercages of HNaY zeolite for the formation of big molecules of deposit from the oligomer and these molecules have no possibility to leave the zeolit; by formation of the deposit the system of cages and channels of the HNaY zeolite is modified and in some regions conditions arise for oligomer transformation to small aromatic species which are able to desorb from the system.

This modyfication may consist e.g. in such distribution of the deposit that the resulting geometry of cages and channels resembles that existing in ZSM-5 zeolite. Thus, two paths of oligomer transformation exist: the first /especially fovoured in fresh samples/ to deposit and the second, after a suitable modification of supercages by the deposit earlier formed, to some desorbable species of aromatic character; these processes can be separated at relatively low temperature under nonstationary conditions when the coverage by the deposit has not yet caused the complete deactivation of HNaY zeolite, but they proceed very fast at 673 K.

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