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Infrared Spectroscopic Investigations Relating to Coke Formation on Zeolites

I. Adsorption of Hexene-1 and n-Hexane on Zeolites of Type Y

D. EISENBACH AND E. GALLEI*

Institut for Chemische Technologie, TH Darmstadt, Petersenstraße, 6100 Darmstadt, West Germany

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The adsorption of hexene-1 and *n*-hexane on HY, CaY, and Pt/CaY has been studied by means of the transmission technique at various temperatures. Especially elucidated was the interaction between the functional OH groups on the internal and external surface and hexene-1 or n-hexane. Primarily not only at low but also at high temperatures a linear surface species is formed, which starts to rearrange at higher temperatures ($T \geqslant 400$ K) to branched species with tertiary carbon atoms. Further heating is accompanied by the appearance of a "coke" band at 1585 cm^{-1}. By dynamic and static adsorption experiments the importance of the gas phase and of the surface OH groups with bands at 3640 and 3740 cm^{-1} has been proved for the formation of coke. The influence of the external OH groups (3740 cm^{-1}) on coke formation is very low below 773 K and the $\mathrm{Ca(OH)^+}$ (3585 cm^{-1}) groups do not participate at all in the coking reaction. The highest activity for coking is shown by the OH groups in the supercages (3640 cm^{-1}).

INTRODUCTION

In recent years zeolite catalysts have become more and more important in modern oil refining and in the petrochemicals industry. In addition to cracking (*1*), bifunctional zeolite catalysts are used in hydrocracking (*2–4*), hydroisomerization (*5, 6*), and in so-called "selectoforming" (*7*). Another industrial process in which zeolites are employed is the low-temperature isomerization of aromatic hydrocarbons and toluene disproportionation (*8*). This broad range of application of zeolites for many catalytic processes is mainly due to their framework structure (*9*).

In hydrocarbon conversion reactions over zeolitic catalysts carbonaceous materials gradually deposit on the catalyst surface (*10*). These deposits tend to lower the catalytic activity due to poisoning of the catalytically active centers and due to a change in the macro- and micropore structure of the catalyst pellets (specific surface area, specific pore volume, and mean pore radius). From time to time these "coke deposits" have to be removed from the catalyst surface by burning. Many efforts have been made to hamper these coke producing reactions, and to obtain a closer insight into the mechanisms of reactions yielding carbonaceous materials.

Many studies have been concerned with coking kinetics (*11–15*) or with the inter-

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* To whom correspondence concerning this paper should be addressed.

* Present address: BASF A.G., M 301, 6700 Ludwigshafen/Rhein, W. Germany.

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TABLE 1

Analysis of Zeolites on Anhydrous Basis

Sample	SiO_2 (wt%)	Al_2O_3 (wt%)	Na_2O (wt%)	CaO (wt%)	NH_4^+ (wt%)
NaY	64.3	21.9	13.8	—	—
CaY	65.0	22.1	3.5	9.4	—
NH_4Y	64.8	22.2	3.8	—	9.2

relations between diffusion and coking (*16, 17*). There have been surprisingly few detailed investigations of the possible chemical mechanisms of coke formation. One relatively detailed study is that of Appleby *et al.* (*18*), in which aromatic structures were proposed as intermediates in coke formation. The publications of Ruderhausen and Watson (*13*) and of Eberly *et al.* (*14*) deal with investigations of the chemical reaction mechanism in coke formation and coke structure, respectively. But none of these studies contribute much to elucidating the interaction between the adsorbed hydrocarbons as possible coke precursors and the functional groups of the catalyst surfaces, e.g., OH groups.

Therefore in the present paper the chemical reactions occurring on faujasite zeolite surfaces during the adsorption of n-hexane and hexene-1 have been examined with respect to coke formation. Furthermore the interactions of the various acidic surface hydroxyl groups with n-hexane and hexene-1 adsorbates were elucidated together with the role of the gas phase surrounding the catalyst.

EXPERIMENTAL METHODS

Materials

The NH_4^+ and Ca^{2+} zeolites were prepared from the parent sodium form of faujasite (Linde SK 40) by ion exchange with 0.1 *N* solutions of analytical grade NH_4NO_3 and $Ca(NO_3)_2$ obtained from Merck Germany. The analysis of NaY and CaY zeolites on an anhydrous basis are given in Table 1. The degree of ion exchange was determined by analysis for sodium by flame spectrometry.

Platinum-containing CaY zeolites were prepared by ion exchange of NaY zeolite with 0.1 *N* $Pt(NH_3)_4Cl_2$ solution, reduction with hydrogen at 570 K, and subsequent ion exchange with $Ca(NO_3)_2$ solution. The platinum content was 0.5% by weight.

Analytical grade hexene-1 and n-hexene (Merck Germany) were used after further purification by distillation and storage over molecular sieve 4A.

Hydrogen and nitrogen (Messer Germany) were 99.995 and 99.999% by volume pure and were dried over "sicapent" before use.

Apparatus

The spectra were recorded on Perkin–Elmer grating spectrophotometers 421 and 325. The spectral slitwidth used was about 5 cm^{-1} and the scan speed 30 cm^{-1}/min.

High-temperature infrared transmission cells with CaF_2 windows (*19*) were employed. A dosing system for dosing hydrocarbons into the preevacuated cells and a flow system to feed hydrocarbons and hydrogen together with nitrogen as carrier gas in a continuous stream into both ir cells were used.

Procedures

The powdered zeolite samples were pressed under a pressure of 3700 bar to thin transparent pellets with a weight of about 7 mg/cm^2. In the cells the pellets were outgassed at 570 K for 3 hr. Ammonium faujasite decomposes under these conditions to HY zeolite. Platinum containing pellets were heated for about 1 hr in a hydrogen atmosphere to free them from adsorbed oxygen. Afterwards, to desorb the remaining hydrogen, they had to be activated at 570 K and 10^{-4} Pa for 3 hr.

After cooling the pretreated samples to the desired temperature the spectra were recorded. For adsorption experiments the vaporized hydrocarbons were brought into contact with the pellets either by leaving them for different periods in the closed cells at a pressure of 6.6×10^3 Pa (static experiments) or by passing them through the cells with a space velocity of 25 (g hydrocarbon)/(g catalyst·h) and a H_2/HC ratio of 5 (dynamic experiments).

Temperature radiation of the sample was checked by blocking the sample beam and recording the emission spectra. The corresponding transmission spectra were corrected for this emission. The temperature dependence of the extinction coefficients was determined for O–H and C–H vibrations by heating the samples to 570 K and observing the extinction change while cooling to "ambient" temperature. "Ambient" temperature stands for temperature of the sample in the incident ir beam and was about 323 K for our experiments.

RESULTS AND DISCUSSION

ADSORPTION OF HEXENE-1 ON Y ZEOLITES AT VARIOUS TEMPERATURES

Adsorption at Ambient Temperature

After the adsorption of hexene-1 on Y zeolite containing Ca^{2+} ions (CaY) the ir spectra show characteristic absorption bands at 2965 and 2925 cm^{-1}, correlated to asymmetric CH_3- and CH_2-stretching vibrations, respectively, and a band at 2860 cm^{-1}, which is due to the symmetric C–H vibrations. The bands of the CH_3- and CH_2-deformation modes are observed at 1460 and 1380 cm^{-1}. However, the absorption band at 3640 cm^{-1} assigned to the OH-stretching vibrations disappeared together with all olefinic bands of hexene-1. From these results one can conclude that saturated hydrocarbon species are present on the zeolite surface and were formed by interaction of the olefinic π system of hexene-1 with acidic OH groups. For the adsorption of hexene-1 on decationated zeolite qualitatively the same spectra were obtained. On zeolites with high OH-group concentrations such as CaY or HY zeolite the adsorbate hexene-1 is probably adsorbed in the same way, as can be concluded from the equal number and identical position of the absorption bands. Further evidence is given by evaluating the ratio of the intensities of the band at 2965 cm^{-1} ($\nu_{as.}$ CH_3) to the band at 2925 cm^{-1} ($\nu_{as.}$ CH_2). According to Jones (*20*) this value gives some information regarding the structure of a hydrocarbon molecule. For hexene-1 adsorbed on CaY- or HY-zeolite this value was determined as 0.71 and corresponds to a ratio of CH_3/CH_2 groups of 0.3. These data can be explained by the assumption of a linear adsorbed hydrocarbon species, formed by interaction of the strong acidic OH groups with the π electrons of hexene-1 according to the equation

$$\wr\, O{-}H + CH_2 = CH\,(CH_2)_3 - CH_3 \rightleftharpoons \wr\, O^{\ominus} + {}^{\oplus}CH_2\,(CH_2)_4{-}CH_3$$

However, it has to be kept in mind that the CH_3/CH_2 group ratios of Jones were determined for a homogeneous phase.

Heating the CaY-zeolite sample under vacuum merely produces changes in the intensities of the individual bands. As the intensities of the CH bands decrease so the intensity of the OH band at 3640 cm^{-1} increases, as can be seen from Fig. 1. This result confirms that by increasing the

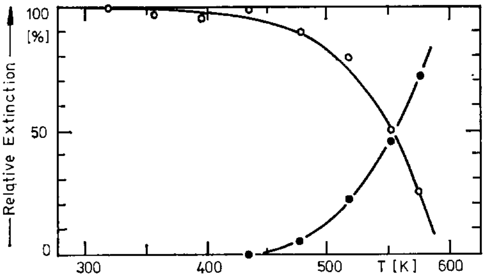


FIG. 1. Temperature dependence of the intensities of O–H and C–H stretching vibration bands after adsorption of hexene-1 on CaY at ambient temperature followed by evacuation. ○ C–H stretching vibration at 2965–2860 cm^{-1}. ● O–H stretching vibration at 3640 cm^{-1}.

temperature the structure of the adsorbed hydrocarbons species will not be changed and no coke formation will occur. The temperature rise only causes a partial desorption of the hydrocarbon species from the zeolite surface and consequently a reappearance of the OH bands at 3640 cm^{-1}. Identical results were obtained for HY zeolite.

Up till now, we were concerned only with OH groups in the supercages giving rise to an absorption band at 3640 cm^{-1}. In addition there are OH groups in the zeolite faujasite framework structure, which are located in the cubooctahedra and give rise to an absorption band at 3540 cm^{-1}, and on the external zeolite crystal surface correlated to a band at 3740 cm^{-1} (*21*). These three OH groups interact in different ways with hydrocarbon molecules during the adsorption process.

The ir spectrum of a CaY-zeolite sample activated at 570 K only shows absorption bands at 3740 and 3640 cm^{-1}, correlated to OH groups on the external surface and in the supercage. As can be seen from Fig. 2, both OH groups interact with hexene-1. During the adsorption the OH bands disappear and arise again if the sample is heated. But the band at 3740 cm^{-1} reappears at much lower temperatures, indicating that the adsorbed hydrocarbon molecules desorb easier from this OH site.

This effect becomes even more distinct for the zeolite of type HY because of the higher concentration of the OH groups. In addition, HY zeolite possesses before the adsorption three OH groups related to absorption bands at 3740, 3640, and 3540 cm^{-1}. Containing the HY sample with hexene-1 causes a disappearance of the bands at 3740 (external OH) and at 3640 cm^{-1} (supercage OH), whereas the band at 3540 cm^{-1} (cubooctahedra OH) is much less changed.

The reason for this behavior may be the critical dimension of the hexene-1 molecule (~5 Å), which does not allow the hydrocarbon molecule to enter the cubooctahedra through the six membered rings with 2.5-Å diameter. An interaction between hexene-1 molecules in the supercages and the cubooctahedra OH groups

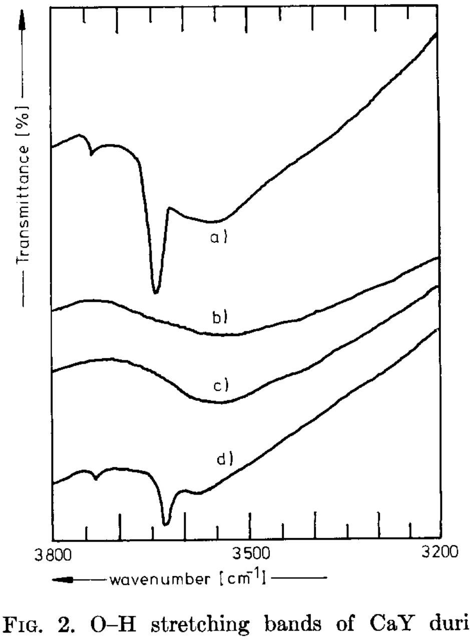


FIG. 2. O–H stretching bands of CaY during adsorption of hexene-1 at ambient temperature (a) before adsorption of hexene-1, (b) after adsorption of hexene-1 in the presence of the gas phase, (c) after adsorption and pumping off the gas phase, (d) after adsorption, pumping off, and heating to 570 K.

adjacent to the six-membered rings (window effect) is responsible for the decrease, the slight shift to lower wavenumbers ($\sim$10 cm^{-1}) and the broadening of the 3540-cm^{-1} band (Fig. 3). Pumping off the gas phase makes the band of the external OH groups reappear almost in its original intensity, whereas the intensity of the 3640-cm^{-1} band is only slightly increased. A subsequent temperature rise of the sample increases the intensity of the latter band very drastically as already observed for CaY zeolite. An explanation for the absence of absorption bands in Fig. 2, especially after pumping off, could be the lower OH concentration on zeolite CaY in comparison with zeolite HY (curve c).

The intensity of the 3740-cm^{-1} band remains almost unchanged. The desorption of hexene-1 from external OH sites at lower temperatures than from internal OH sites bands gives further support to the conclusion that the external OH groups possess a lower affinity toward olefins than those in the supercages.

The lower affinity of the external OH groups with absorption bands at 3740 cm^{-1} can be explained by their different surrounding, in comparison with OH groups inside the zeolitic faujasite framework.

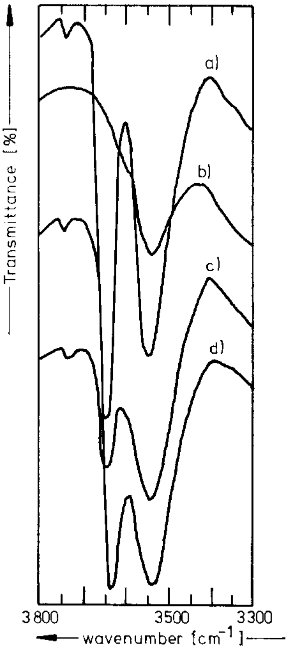
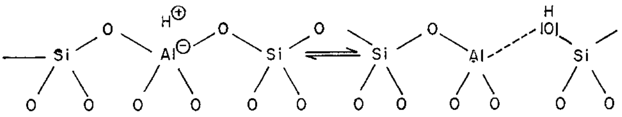


FIG. 3. O–H stretching band of HY during adsorption of hexene-1 at ambient temperature (a) before adsorption of hexene-1, (b) after adsorption of hexene-1 in the presence of the gas phase, (c) after adsorption and pumping off the gas phase, (d) after adsorption, pumping off and heating to 570 K.

During the formation of internal OH groups, a threefold coordinated aluminum atom is produced according to the following reaction:



This electron-deficient aluminum atom interacts with the p-electrons of the oxygen atom of the new formed OH groups and consequently increases its affinity towards olefins.

The external OH groups terminating the zeolite crystals are not produced by a proton attack as shown in the above equation. Their nearest neighborhood does not have low-coordinated aluminum atoms, which are due to delocalization as in the case of internal OH groups (*22–25*).

Adsorption and Reaction at Higher Temperatures

When hexene-1 is adsorbed on CaY and Pt/CaY at higher temperatures ($T \geqslant 400$ K) and the surrounding gas phase interacts with the zeolite surface for some time, the changes in the ir spectrum are more drastic

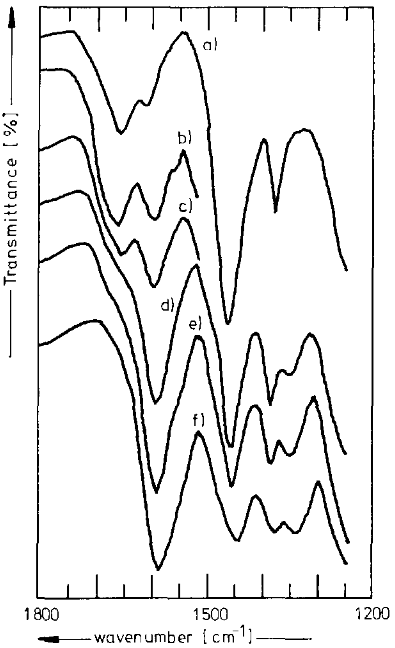
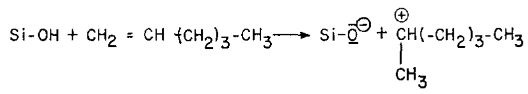


FIG. 4. Infrared spectra of the C–H deformation bands of hexene-1 after adsorption and reaction on Pt/CaY (a) at 400 K, (b) at 450 K, (c) at 490 K, (d) at 530 K, (e) at 570 K, (f) at 600 K.

the higher the adsorption temperature. The spectrum of the gas phase shows a strong CH_3-stretching band, but the CH_2-stretching band is visible only as a small shoulder. The olefinic C=C bands are no longer observable at higher temperatures. The spectra of the chemisorbed species reveal a strong intensity loss for the CH-valence and deformation bands. However, the decrease of the CH bands is not accompanied by the reappearance of the corresponding OH bands, as during heating after adsorption at ambient temperature. Furthermore the ratio of CH_3/CH_2 band intensities in the C–H stretching range is changed, and in the deformation range (Fig. 4) two new absorption bands at 1584 and 1345 cm^{-1} are observed. The intensities of these bands increased with rising temperature, though the CH band intensities decreased. The CH_3/CH_2 intensity ratio increased with the temperature. These results suggest that possibly an adsorbed species on the zeolite surface is formed as illustrated below:



$$\mathrm{Si{-}OH + CH_2{=}CH(CH_2)_3{-}CH_3 \longrightarrow Si{-}\underline{O}^{\ominus} + \underset{\displaystyle CH_3}{\overset{\oplus}{C}H}(-CH_2)_3{-}CH_3}$$

The absorption band at 1345 cm^{-1} can be assigned to vibrations of tertiary –C–H groups. The intensity ratio of the bands at 2965 cm^{-1} and 2925 cm^{-1} was determined to be 1. This value corresponds, according to Jones (*20*), to a CH_3/CH_2 ratio of 0.5 and comes very close to that of the above surface species. Further evidence for this surface species may be a band at about 1380 cm^{-1}, which can be assigned to the symmetric vibration of CH_3–C groups. The absorption band at 1585 cm^{-1} will be discussed later.

To clarify whether during adsorptions at higher temperatures the same surface species as at ambient temperature was primarily formed, hexene-1 was dosed in very short pulses and pumped off after a contact time with the sample of about 5 sec. The spectra obtained after this procedure did not differ from those obtained at ambient temperature. However, the interaction of the gas phase with the zeolite surface initiates consecutive reactions, which are due to a darkening of the zeolite catalyst pellet. This coke deposition on the catalyst surface will now be assessed more closely.

INVESTIGATIONS OF THE MECHANISM OF COKE FORMATION ON CaY AND Pt/CaY

The above mentioned darkening of the catalyst samples is always accompanied by a drastic increase of the intensity of the absorption band at 1585 cm^{-1}. This band is still fairly weak at 380 K, as can be seen from Fig. 4, but becomes the dominant band at higher temperatures at which coke formation is increased. This result suggests a relation between the 1585 cm^{-1} band and coke formation on the catalyst surface. To prove this assumption, systematic ir studies were carried out on various activated carbon and soot samples (*26*). The data obtained made it possible to assign the 1585 cm^{-1} band to C=C stretching vibrations of microcrystalline graphitic carbon structures, which are present in polycyclic aromatic compounds, and which also make up the carbonaceous turbostratic deposits on catalysts (*27*). If the band at 1585 cm^{-1} can be assigned to a vibration mode of the coke structure, its intensity is a measure of the amount of coke deposited on the catalyst. Monitoring this absorption band makes it possible to follow spectroscopically the deposition of coke on catalyst surfaces.

INFLUENCE OF THE GAS PHASE

As already mentioned above, the coke formation at higher temperatures only can be observed if the surrounding gas phase is in contact for some time with catalyst surface. Consecutive reactions cause an obvious change of the corresponding ir spectra, as shown in Fig. 5. Curves a and b are almost identical. However, for longer contacting times of the hydrocarbon molecules with the catalyst surface a completely different spectrum arises (curve c), in which the absorption at 1585 cm^{-1} becomes the dominant band. The transformation of hydrocarbon surface species to coke is not only a function of the catalyst temperature, but also important is the presence of the gas phase, which is in contact with the zeolite surface. In this the chemical composition of the gas phase plays an

FIG. 5. Infrared spectra of the C–H deformation bands of hexene-1 adsorption on Pt/CaY followed by evacuation (a) adsorption at ambient temperature, (b) adsorption at 575 K in short pulses, (c) adsorption and reaction at 575 K.

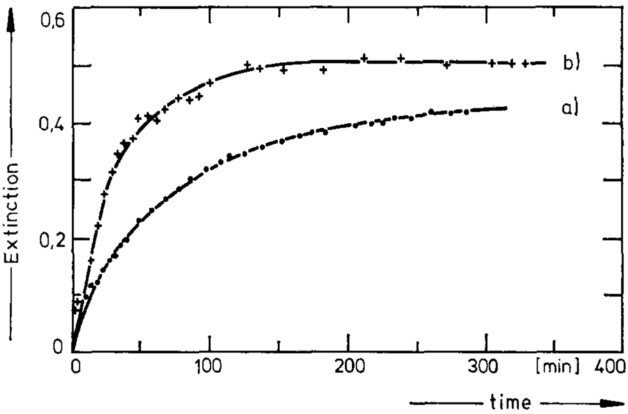


FIG. 6. Reaction of hexene-1 on Pt/CaY. Intensity of the 1585-cm^{-1} band as a function of time for dynamic experiments: (a) at 530 K, (b) at 600 K.

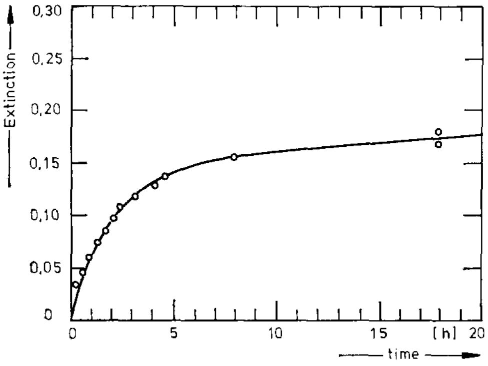


Fig. 7. Reaction of n-hexane on Pt/CaY. Intensity of the 1585-cm^{-1} band as a function of time at 600 K.

important role, as can be seen by a comparison of Fig. 6 with Fig. 7. Figure 6 shows the increase of the intensity of the 1585-cm^{-1} band as a function of time at 600 K for dynamic runs, with hexene-1 as adsorbate and Pt/CaY as adsorbent. In Fig. 7 the corresponding intensity time dependence for n-hexane as adsorbate is illustrated. Whereas for hexene-1 the intensity approaches its limiting value already after 2 hr, the corresponding curve with n-hexane after 2 hr shows only 30% of its maximum intensity. From these data we can conclude that the paraffinic gas phase shows a much lower coking rate than the olefinic one. Similar results were obtained for static experiments.

Over the catalyst Pt/CaY the surface reaction of hexene-1 leads to a limiting value for the coke band, as can be seen from Fig. 6. For static experiments an explanation would be a change of the surrounding gas phase. To clarify this the spectrum of the originally olefinic hexene-1 gas phase was recorded after having reached the maximum intensity of the 1585-cm^{-1} band for various temperatures. Obviously a correlation exists between the increase of the coke band at 1585 cm^{-1} and the decrease of the olefinic =CH band at 3080 cm^{-1}. During the coke formation a hydrogen transfer from the zeolite surface to the olefinic gas phase must have occurred, changing the gas phase to a paraffinic one. Further support to this assumption is given by the generally accepted fact that hydrogen addition to the hydrocarbon gas phase decreases the coke

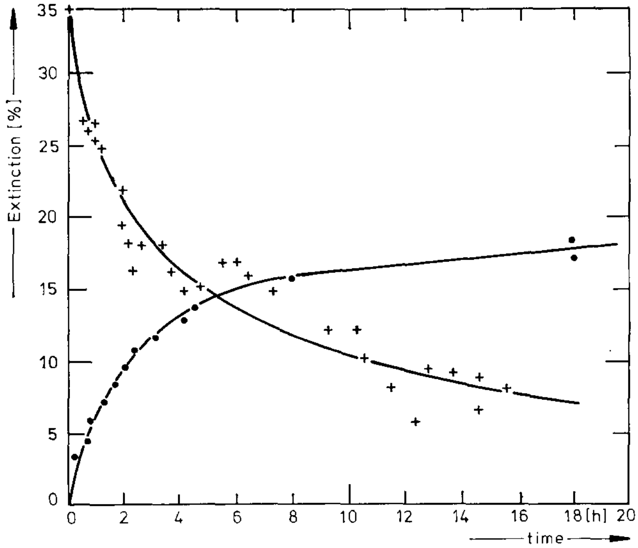


Fig. 8. Reaction of n-hexane on Pt/CaY at 600 K, intensities of the 1585-cm^{-1} band (• • •) and of the 3640-cm^{-1} band (+ + +) as a function of time.

formation rate, by possibly hampering the hydrogen transport to the gas phase.

However, the change of the gas phase (olefinic–paraffinic) does not explain the fact that in the case of dynamic experiments the same limiting value is obtained for the intensity of the 1585-cm^{-1} band, and that the deposition of coke can also be observed with paraffinic hydrocarbons. In addition there must be some functional groups on zeolites which are consumed during the coking reaction and hence causes the limiting value of the amount of coke deposited on the catalyst surface. For the system hexene-1–Pt/CaY the influence of OH groups is difficult to investigate by means of ir spectroscopy, because of the extensive interaction between olefinic hydrocarbon molecules and the surface zeolitic OH groups. The system n-hexane–Pt/CaY was therefore examined in connection with the influence of OH groups on coke formation. The intensity of the absorption band at 3640 cm^{-1}, assigned to very acidic OH groups in the supercages, was monitored together with the coke band at 1585 cm^{-1} as a function of time (Fig. 8). Figure 8 shows very clearly that at the time the intensity of the OH band reveals a drastic decrease, the corresponding coke band at 1585 cm^{-1} is strongly increased. This result supports the importance of acidic OH groups for the coking reaction. The OH groups react with adsorbed hydrocarbon species producing coke and thereby are consumed irreversibly. The rate of coke production is strongly dependent on the concentration of acidic OH groups, and the coke formation will stop first, when all reachable OH groups have reacted. There is no equilibrium concentration of coke for a given temperature, but the rate the maximum coke concentration will be reached is a function of temperature (Figs. 6, 7). In another study (*28*) we found, that over zeolite NaY, which contains very few acidic OH groups, no coke formation could be observed in the above temperature range. This is another support to the importance of acidic OH groups in coke formation.

The high influence of the OH groups can be explained by their bifunctional character. First, OH groups are adsorption sites, and second, they are very acidic sites, which induce the elimination of hydrogen and finally the coke formation. According to Olah *et al.* (*29*), who investigated the reaction of very strong acids (superacids) with paraffins, such a removal of hydrogen from saturated hydrocarbons can be initiated by very strong protonic acids.

Zeolites may act in the same way, because of very acidic OH groups the

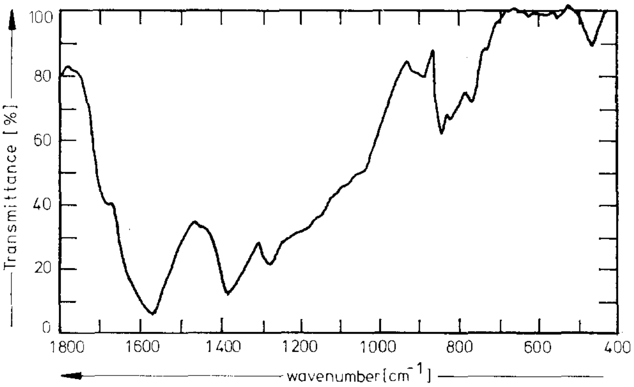


FIG. 9. Infrared spectrum of coke deposits from CaY, obtained by cracking of n-hexane at 770 K.

protons of which become more and more mobile at higher temperatures. However, one should keep in mind that the hydrocarbon surface species interact also with the surrounding gas phase, which takes up the removed hydrogen, even in the case of a paraffinic gas phase, as can be illustrated by studying the composition of the gas phase before and after coke formation.

The hydrocarbon molecules are dehydrogenated on the zeolite surface and gradually transformed to the energetically favorable turbostratic carbon structure. But this transformation does not occur completely, as can be seen from the ir spectrum of a coke sample (Fig. 9) which was isolated from a spent zeolite CaY catalyst pellet. The spectrum shows three sharp absorption bands between 900 and 700 cm^{-1}, which can be assigned to CH-wagging modes of polycyclic aromatic compounds (*30*) like pyrene, chrysene, etc. The same results have been obtained by Eberly (*31*). This provides evidence that the dehydrogenation of hydrocarbons to coke passes through polycyclic aromatic intermediates, which already contain a preformed graphitic structure.

Behavior of $Ca(OH)^+$ Groups

The ir spectrum of a Pt/CaY catalyst at temperatures up to 570 K shows four absorption bands in the OH-stretching region at 3740, 3640, 3585, and 3540 cm^{-1}. The assignment of these bands is clear except for the band at 3585 cm^{-1}. There are basically two possibilities for a proper correlation of this band: First, the 3585-cm^{-1} band can be assigned to a stretching vibration of a $Ca(OH)^+$ cation (*32*), and second, the OH groups in the supercage, the band of which is shifted by interaction with n-hexane, may be responsible for this band, as observed by Liengme and Hall (*33*) on a HY zeolite at 320 K. The latter assignment is supported by the fact that during adsorption of hexene on Pt/CaY at 530 K the decrease of the 3640-cm^{-1} band is accompanied by an increase of the 3585-cm^{-1} band.

However, much evidence is in favor of an assignment to a $Ca(OH)^+$-stretching vibration. When a stream of n-hexane passes over a Pt/CaY catalyst, weak interaction between the surface OH groups and the gas phase will occur and will cause a small shift of the OH-stretching vibration. According to the theory of bifunctional catalysis, the hydrocarbon molecules are dehydrogenated over platinum to olefines and the latter are isomerized over acidic sites (e.g., OH groups). So, the intensity of the OH band at 3640 cm^{-1} is decreased to 60% of its initial value, but remains afterwards unchanged, because of the absence of coking reactions.

During a dosage of n-hexane at 530 K the intensity of the 3585-cm^{-1} band increased and that of the 3640-cm^{-1} band decreased. However, after evacuation of the n-hexane gas phase the intensities of both bands at 3640 and 3585 cm^{-1} went up. If the assignment of the 3585-cm^{-1} band to a shifted OH vibration due to interaction with the gas phase would be correct, its intensity should decrease during evacuation. But the opposite happened, namely, an increase of the 3585-cm^{-1} band was observed. This behavior was qualitatively not changed at higher temperatures, even when coking occurred.

Thus the absorption band at 3585 cm^{-1} can be correlated with the OH-stretching vibration of $Ca(OH)^+$ groups, which are formed by a reaction between adsorbed water molecules and Ca^{2+} ions. The increase of this band during evacuation can be explained by the fact that by pumping off the gas phase the hydrocarbon molecules are preferentially removed from the zeolite surface and the remaining water molecules can interact more intensively with the Ca^{2+} ions producing more

$Ca(OH)^+$ according to the equation

$$H_2O + Ca^{2+} \rightleftharpoons Ca(OH)^+ + H^+.$$

With increasing temperature the intensity of the 3585-cm^{-1} band is lowered, because the $Ca(OH)^+$ ions are dehydrated to CaO. From the inert behavior of the OH vibration of $Ca(OH)^+$ ions one can conclude that these ions do not have any influence on the coking reactions.

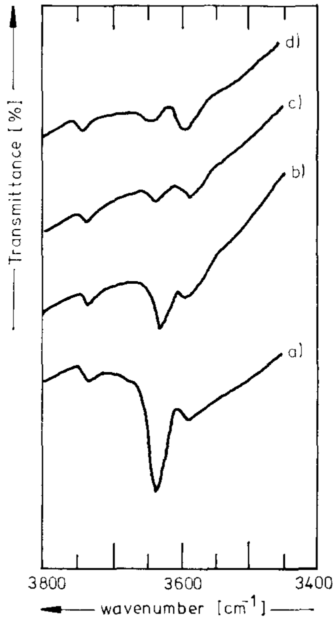


FIG. 10. Infrared spectra of the O–H stretching region during the adsorption and reaction of n-hexane on Pt/CaY at 625 K (a) before the adsorption and reaction, (b) after adsorption and 10 min of reaction time, (c) after adsorption and 22 hr of reaction time, (d) after adsorption and 22 hr of reaction time followed by evacuation.

Behavior of External OH Groups

The coking reaction is initiated by the interaction of hydrocarbon molecules with acidic OH groups. Acidic OH groups are located on the internal and on the external surfaces of zeolite crystals. So far we examined only the influence of internal OH groups on the formation of coke, and the role of external OH groups has still to be elucidated. Figure 10 shows the spectrum of the OH-stretching range of a Pt/CaY sample, during and after the reaction with n-hexane at 625 K. The intensity of the 3640-cm^{-1} band is reduced to half of its initial value during the hydrocarbon dosage. A further continuous decrease is observed during the reaction time of 22 hr. After evacuation the intensity of this band is again slightly increased. The decrease can be explained by a reaction of n-hexane with OH groups, and the increase by desorption of part of the n-hexane.

The behavior of the external OH groups is much more difficult to examine because

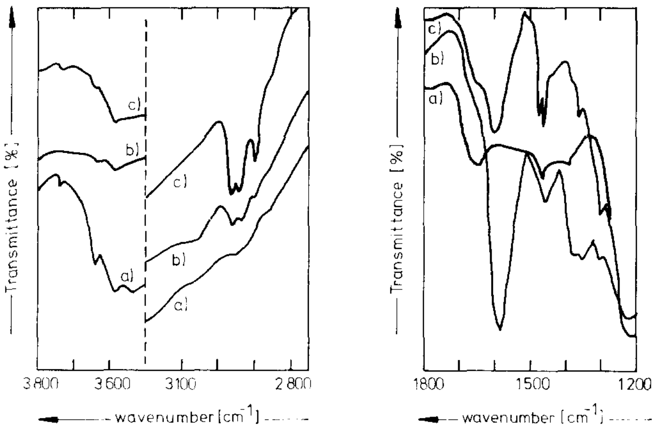


FIG. 11. Infrared spectra of used catalysts, (a) CaY contacted with n-hexane at 523 K, (b) CaY contacted with n-hexane at 773 K, (c) Pt/CaY contacted with n-hexane at 773 K.

of the low intensity of their absorption band. In spite of that difficulty, Fig. 11 shows a completely different behavior of the external OH groups at 3740 cm^{-1}. The intensity of the 3740-cm^{-1} band does not show any remarkable change during the reaction with n-hexane, but the band at 3640 cm^{-1} has decreased to 10% of its initial intensity.

Studies of chemisorption as already reported in this paper reveal that the external OH groups have a lower activity than the internal ones. Obviously the reactivity of the external OH groups is too low to break the σ bonds of n-hexane and so to inititate the coking reaction. The external Brønsted sites are not consumed during coke formation, and are still available as active sites on a coked catalyst. This is important for many hydrocarbon reactions which occur mainly in the macro- or transport pores of the catalyst pellets, that is to say, on the external surface of the zeolite crystals. Because of the very slow consumption of the external OH groups during coking the activity of a catalyst can be kept constant for a long time after having consumed the acidic OH groups in the supercages, which initiate the coking reaction already at fairly low temperatures of 625 K. But this does not mean that external OH groups are not consumed at all during coking, as can be seen from Fig. 11, which shows the ir spectra of various catalysts used in a bench scale reactor under different operation conditions. Curve a represents the spectrum of CaY zeolite which was treated under low severity conditions in the presence of n-hexane; consequently, no coke laydown was obtained. OH bands at both 3640 and 3740 cm^{-1}, for internal and external OH groups, respectively, are fully preserved. Curves b and c are spectra of zeolite samples which were heated up to 770 K in the reactor (high severity). In the case of Pt/CaY (c) the band at 1585 cm^{-1} is observed, which was correlated to the "coke" band. The OH band at 3640 cm^{-1} only shows a low intensity, whereas the intensity at 3740 cm^{-1} is almost unchanged. In the CaY sample without hydrogenation metal (b), for which a very strong coke band is observed, almost both OH bands have disappeared. This catalyst has lost all its activity.

CONCLUSIONS

From the CH_2/CH_3 intensity ratios we can conclude that during the adsorption of hexene-1 on CaY and HY zeolite primarily the same linear surface species are formed at ambient or higher adsorption temperatures. But at higher temperatures ($T \geqslant 400$ K) the interaction of the adsorbed species with the surrounding gas phase initiates rearangements on the zeolite surface producing branched hydrocarbon species with tertiary carbon atoms, which produce an absorption band at 1345 cm^{-1}.

With increasing temperature a band at 1585 cm^{-1} becomes more and more intense. This band can be assigned to a structural vibration of coke and is a good probe to follow the deposition of carbonaceous material on catalytic surfaces. From experiments with different contacting times and with different hydrocarbons as adsorbates (paraffins–olefines) the importance of the presence and of the composition of a gas phase around the catalyst sample was proved for the coke formation.

The simultaneous decrease of the OH band at 3640 cm^{-1} and the increase of the coke band at 1585 cm^{-1} in dynamic and static experiments gives evidence that OH groups act as active sites in coke formation and are irreversibly consumed.

The ir spectrum of coke between 900 and 700 cm^{-1} shows absorption bands for CH-wagging vibrations of polycyclic aromatic compounds. Therefore it seems likely that these compounds are precursors of carbonaceous deposits.

From the ir spectra it appears that the band at 3585 cm^{-1}, which can be assigned to the OH vibration of a $Ca(OH)^+$ ion, does not have any influence on the formation of coke.

External OH groups (3740 cm^{-1}) possess lower activity than internal ones and are consumed only at temperatures as high as 773 K, but not at 625 K.

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