

COKE FORMATION ON ZSM-5 AND MODIFIED Y ZEOLITES IN THE REACTION OF ETHYLENE

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ABSTRACT

The effect of the acidity and pore size on the coking process in the reaction of ethylene at 670 and 770 K was studied for AlHY, dealuminated Y, HZSM-5 and AlHZSM-5 zeolites using several experimental techniques: gravimetry for kinetic measurements of the surface species formation, mass spectrometry for analysis of the gas phase, infrared spectroscopy for identification of zeolitic OH groups and the composition of coke, temperature programmed desorption of ammonia for determination of acidity. Deactivation effect of coke was tested using oligomerization of ethylene at 300 K. The relation between the nature and strength of the acid sites and conversion of ethylene was found to hold also for the coking rate on the Y zeolites. The ZSM-5 zeolites with the highest activity exhibited the lowest coking tendency, attributed to the effect of the shape selectivity properties. This factor appeared also to be responsible for the composition of the coke and the pathway of the coke formation, which is different in Y and ZSM-5.

INTRODUCTION

The formation of a carbonaceous deposit represents a serious problem in catalysis on zeolites being associated with a decrease in the catalytic activity and with altered selectivity. The role of coke in a catalytic process consists mainly in poisoning of active sites on the zeolites, choking their channels, reducing the intercrystalline volume and direct involvement in the transformation of the reactants. Numerous studies were devoted to the deactivation of zeolites (1), however, the coking process is still far from being fundamentally understood. Even such questions as the chemical nature of coke, the role of acid sites in coke formation, the poisoning effect of coke and many others still remain to be answered.

In the present paper, we have attempted to contribute to the solution of some of the above problems by studying coke formation in the reaction of ethylene on Y and ZSM-5 zeolites differing not only in their structure and pore size but also in their acidity. Ethylene is a simple molecule with low basicity, whose reactivity is very sensitive to the nature and strength of the acid sites (2,3) and therefore permits study of the effect of both the shape selective factor and the presence of proton-

-donor and electron-acceptor sites. In the studied zeolites, a variation in the acid properties was achieved by a change in the Si/Al ratio in the lattice and by introduction of cationic Al into the cavities.

Several experimental techniques were used in this study: i) gravimetry to monitor the kinetics of zeolite weight-gain, ii) mass spectrometry to analyse the composition of the gas phase, iii) infrared spectroscopy (IR) to determine the nature of surface species and the zeolite OH groups and iv) temperature programmed desorption (TPD) of ammonia to follow changes in acidities. In this paper the term coke refers to compounds which cannot be removed from the zeolites at a temperature of 670 - 730 K.

EXPERIMENTAL

$\text{Al}_{12}\text{Na}_{25}(\text{NH}_4)_{40}\text{Y}$ was obtained from $(\text{NH}_4)_{70}\text{Na}_{30}\text{Y}$ using cationic exchange with $\text{Al}(\text{NO}_3)_3$. The sample denoted as deal Y was prepared from NaY by SiCl_4 dealumination at 670 K followed by NH_4^+ exchange (4). ZSM-5 zeolites were synthesized in the usual way (5), calcinated at 870 K and exchanged with NH_4^+ . Further exchange with Al^{3+} yielded $\text{AlNH}_4\text{ZSM-5}$. Good crystallinity of all the samples was evidenced with X-ray diffraction patterns, IR spectra and sorption capacities. The latter values are listed in Tab. 1 together with the Si/Al total value, concerning all respective atoms in the zeolites, and $(\text{Si}/\text{Al})_l$ in the lattice (4). Prior to measurements, the zeolites were dehydrated and deammoniated in vacuo at 670 K (Y) and 770 K (ZSM-5) for 18 hrs.

The weight gain resulting from the adsorbed species was measured with a quartz balance within an error $\pm 3 \times 10^{-5}$ g, using a 0.1 g zeolite plate in a reaction volume of 700 cm^3 . Oligomerization of ethylene (5.3 kPa) inside the cavities was investigated at 300 K over 30 min. In the high-temperature experiments, 5.3 kPa of ethylene was allowed to react with the Y and ZSM-5 zeolites at 670 and 770 K, respectively, the weight gain was measured at desired time intervals. Small amounts of the gas phase were withdrawn and analyzed using a mass spectrometer (MI 1305, USSR). In some experiments, the sample was filled with oligomers at 350 K prior to the reaction at the high temperature. The amount of coke reported in mg per g of the zeolite was determined from the zeolite weight after 30 min evacuation at 670 and 730 K for Y and ZSM-5 zeolites, respectively.

The IR spectra of the zeolite plates were recorded on a Fourier transform Nicolet MX-1E infrared spectrometer at ambient temperature. Those presented here are related to a sample thickness of 7 mg cm^{-2} . Spectra of the surface species alone and the difference spectra of OH groups were obtained by subtracting the spectrum of the original zeolite from the spectrum after the reaction. The experiments were carried out in the same way and under the same conditions (except the sample weight which equalled 25 - 30 mg) as in the gravimetric studies.

Table 1

Characteristics of zeolites and amounts of coke formed during the transformation of ethylene

Zeolites	(Si/Al) ₁ lattice	Si/Al total	Capacity (mmol Arg ⁻¹)	Reaction		
				T(K)	t(hr)	coke ₋₁ (mg g ⁻¹)
AlHY	2.5	2.2	10.5	670	2	4.6
deal Y	10.8	5.7	9.2	670	1	17.4
				670 ^a	1	45.7
HZSM-5(a)	13.5	13.5	5.6	770	19	8.5
HZSM-5(b)	19	19	5.5	670	2	<0.5
				770	19	14.1
AlHZSM-5(b)	19	17.5	5.6	770	19	7.5

^a-before the reaction at 670 K the zeolite was filled with oligomer at 350 K

Ammonia evolved during the TPD measurements (18 μmol of NH₃ preadsorbed at room temperature on 10 mg of the zeolite, either in fresh form or after the coke formation) was pumped through the mass spectrometer. The samples were preheated in vacuo at 670 K for 18 hrs, the heating rate was 6 K min⁻¹.

RESULTS

Zeolite acidity. Various OH groups were found on the studied zeolites, nevertheless, only those located on the framework in positions accessible for the reactant can be considered most important for the reaction, as they possess a high acid strength depending on the (Si/Al)₁ (6). Therefore, the ZSM-5 zeolites, with (Si/Al)₁ equal to 13.5 and 19 and with hydroxyls characterized by a band at 3610 cm⁻¹, exhibit very high acid strength (6), while the AlHY contains considerably less acidic framework hydroxyls vibrating in large cavities at 3640 cm⁻¹ (7). In the deal Y with (Si/Al)₁ = 10.8, the hydroxyls similar both to those of AlHY and HZSM-5 appear, manifested by

Table 2

Reaction of C₂H₄ - composition of the gas phase (Vol %)

Zeolite	reaction conditions		ethylene	aliphatics	aromatics
	T(K)	t(hr)			
AlHY	670	2	91	9	-
deal Y	670	1	91.7	8.3	-
HZSM-5(b)	670	1	73	16.8	10.2
HZSM-5(b)	770	1	9.8	-	88

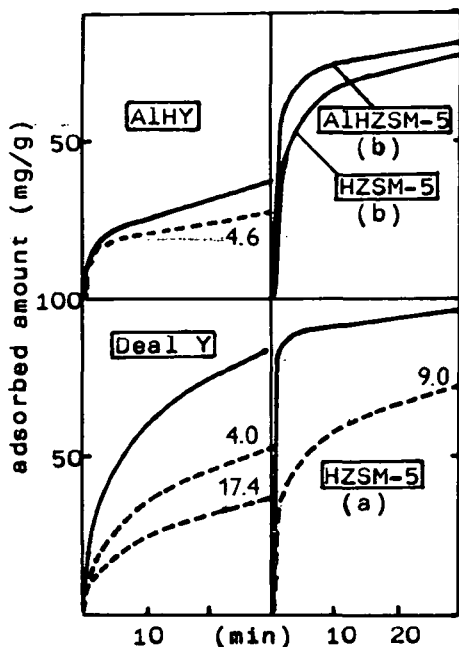


Fig. 1. Ethylene oligomerization on zeolites at 300 K: — original zeolite; ---- zeolite with coke in mg g^{-1} .

bands at 3630 and 3602 cm^{-1} , respectively, which was recently proved by adsorption of pyridine (7). However, the intensity of the latter band suggests that very strongly acidic hydroxyls are present in a smaller amount than on the HZSM-5 zeolite. The TPD curves of ammonia from fresh zeolites confirm the much higher acid strength of HZSM-5 and deal Y compared with AlHY: the maxima appear at 570, 630 and 450 K, respectively. IR spectra of OH groups and TPD curves of ammonia are depicted in Figs. 2-4, where they represent zeolites before coking. The electron-accepting properties of deal Y, AlHY and AlHZSM-5 zeolites originate from extralattice Al species formed either in the process of dealumination (4) or introduced into the latter two zeolites by ion exchange. The ratio (Al extralattice)/(Al lattice) amounts to 0.84, 0.12 and 0.06, respectively.

Oligomerization of ethylene at 300 K. The kinetic curves for the weight gain reflecting oligomerization activity of zeolites are depicted in Fig. 1. The oligomerization is clearly conditioned by the acidic properties of the individual samples, i.e. by the nature and strengths of acid sites. Thus, the ZSM-5 zeolites exhibit the highest activity caused by the dominant role of very strongly acidic hydroxyls. The rate of reaction then decreases in the sequence HZSM-5(a) > AlHZSM-5(b) > HZSM-5(b), which can be explained by the effect of the greater number of hydroxyls present on the HZSM-5(a) than on the HZSM-5(b) zeolite and by the participation of Al electron-accepting sites on the AlHZSM-5(b) zeolite. In contrast to HZSM-5, the HY zeolite (not shown here, see ref.(3)) is almost inactive. However, after the addition of cationic Al, oligomerization occurs, as demonstrated with AlHY, even though the rate is still low due to the relatively weak acid strength of the hydroxyls. This supports

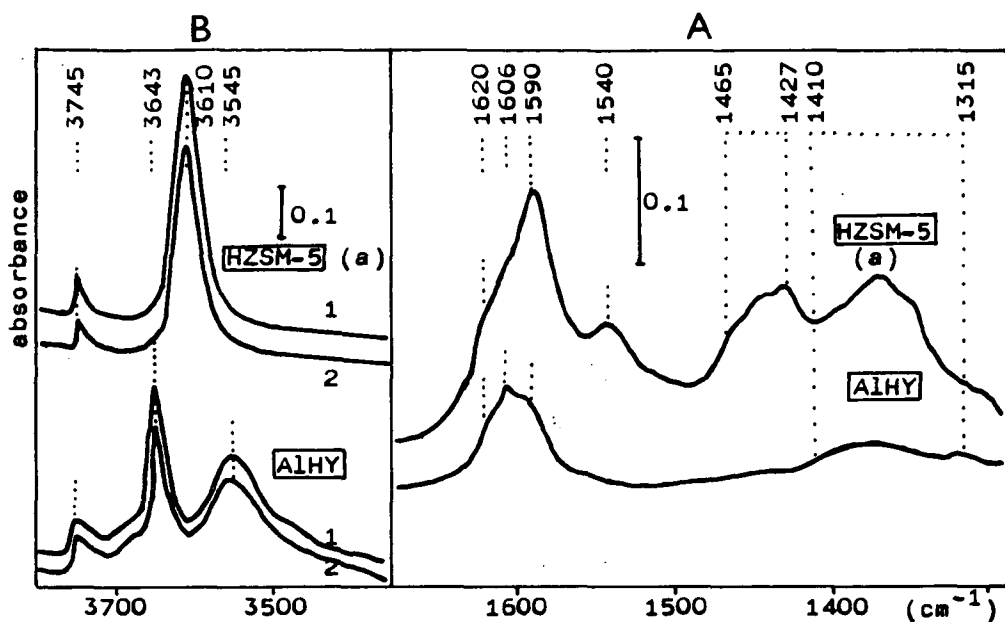


Fig. 2. IR spectra of the coke (A) and OH groups (B) of the HZSM-5 and AlHY zeolites: 1- original zeolite, 2- after coke formation caused by the reaction of ethylene, HZSM-5: 19 hr, 770 K, AlHY: 2 hr, 670 K.

the suggestion (3) of direct involvement of Al electron-accepting sites in the activation of ethylene. An appreciable increase in the oligomerization rate found for the deal Y zeolite can then be attributed to the presence of both very strongly acidic hydroxyls and Al electron-accepting sites.

Oligomers on Y and ZSM-5 zeolites differ in their composition consisting of saturated branched and straight-chain hydrocarbons, respectively (2,3). On heating to 670 K, oligomers on Y zeolites yield coke (see below and ref. (8)) while on ZSM-5 zeolites are completely decomposed.

Fig. 1 also demonstrates the deactivation effect of coke. It can be seen that the presence of coke even in amounts below 10 mg g^{-1} considerably decreases the oligomerization rate on both Y and ZSM-5 zeolites. This decrease is most pronounced with very small amounts of coke as is evident from the activity of deal Y.

Reaction of ethylene at high temperatures. Coke formation. The gravimetric experiments indicate a continuous increase in the sample weight when ethylene reacts over the Y zeolites at 670 K. They point to coke formation at a rate appreciably higher on deal Y than on AlHY as is demonstrated in Tab. 1 with the amount of coke formed after 1 and 2 hrs. During this period, ethylene also yields aliphatics $\text{C}_3\text{-C}_5$, which are the main gas products at the ethylene conversion level of about 10 % (Tab. 2). ZSM zeolites exhibit the highest activity, however, coking does not proceed at a measurable rate. Even at 770 K, when ethylene is rapidly converted, mainly to

C₆-C₈ aromatics (Tab. 2), coking is a very slow process: coke appears after 19 hrs of reaction in amounts comparable with those reported above for the Y zeolites at 670 K after 1 and 2 hrs (Tab. 1).

It follows from the IR spectra in Figs. 2 and 3 that the composition of coke on Y zeolites is different from that of HZSM-5. It is also apparent from these data that coke formation leads to removal of part of the framework hydroxyls, namely those vibrating at 3640, 3602 and 3610 cm⁻¹ on the AlHY, deal Y and ZSM-5 zeolites, respectively.

The coke on Y zeolites is characterized by bands in the regions 1640 - 1590 and 1410 - 1315 cm⁻¹ which can be assigned to C=C and CH vibrations, respectively, of the unsaturated compounds, while the bands near 1460 and at 3000 - 2800 cm⁻¹ representing paraffinic CH₃ and CH₂ groups are very weak. In addition, the typical bands of aromatics, which should appear near 1500 cm⁻¹, are hardly visible in our spectra. It thus follows that the coke consists mainly of hydrogen-deficient polyene species. The band of the C=C vibration is composed of several components, of which the most prominent ones appear at 1595 and near 1610 cm⁻¹. A specific increase in the intensity of the latter band is observed when deal Y is filled with the oligomer at 350 K

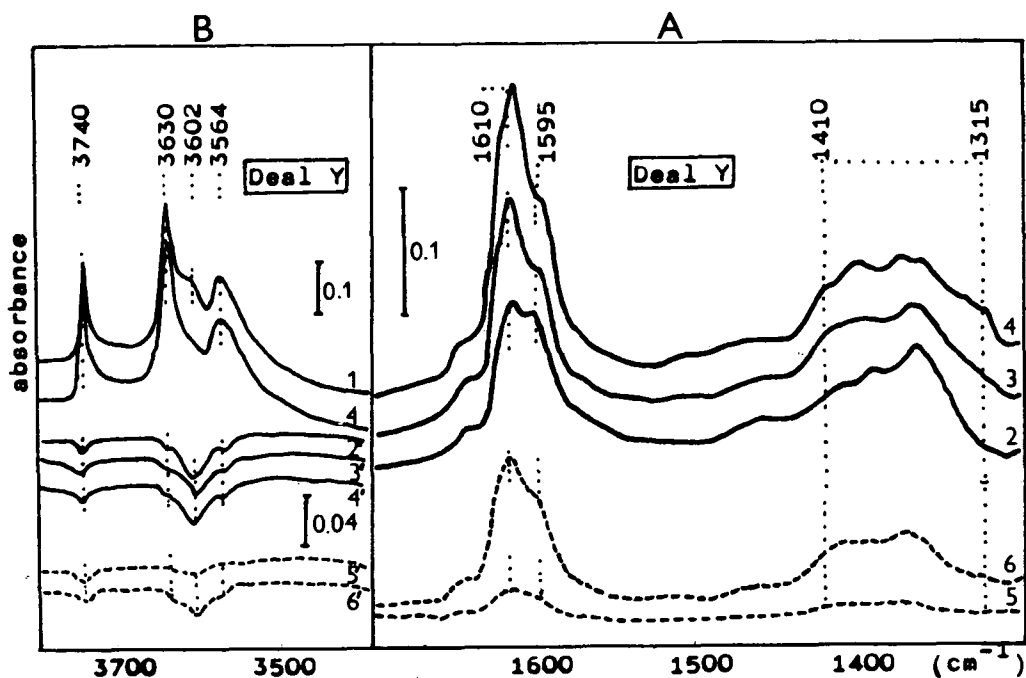


Fig. 3. IR spectra of coke (A) and OH groups (B) of the deal Y zeolite.

1- original zeolite, 2,3,4- after transformation of low-temperature oligomers and reaction of ethylene at 670 K for 15, 30 and 60 min., respectively, 5,6- after reaction of ethylene with fresh zeolite at 670 K for 15 and 60 min., respectively; 2'-6'. difference spectra of OH groups.

prior the reaction of ethylene at 670 K. Then the coke formed at the expense of the oligomer substitutes the most acidic hydroxyls at 3602 cm^{-1} giving rise to the appearance of both the 1595 and 1610 cm^{-1} bands. Further coking is not associated with changes in the composition of the OH groups, but leads to the most pronounced increase in the intensity of 1610 cm^{-1} band (Fig. 3). Thus it can be assumed that the 1595 cm^{-1} band represents polyene species in an intimate contact with the lattice, while the band at 1610 cm^{-1} corresponds to the component of the coke which might be responsible for the pore chocking. Fig. 3 also shows that the reaction of ethylene with the fresh sample at 670 K is accompanied by a simultaneous increase in intensity of both the bands of coke and a decrease of the 3602 cm^{-1} band of most acidic hydroxyls. This result should be interpreted as implying continuous poisoning of the acid sites and pore chocking from the beginning of reaction.

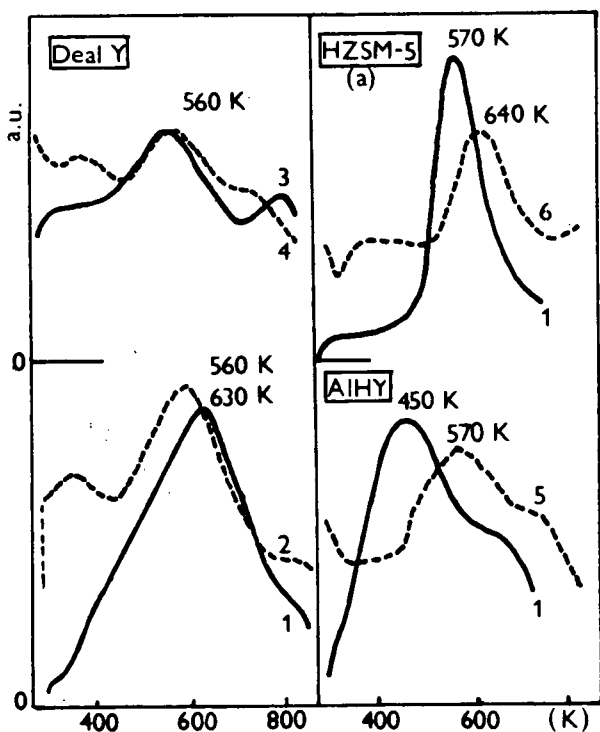


Fig. 4. Effect of coke on the TPD of ammonia from the deal Y, AlHZSM-5 and AlHY zeolites. 1- original zeolite, 2,3,4,5,6- zeolites with coke in amount of 3, 9.7, 19.2, 6.7 and 7.4 mg g^{-1} , respectively.

In contrast to Y zeolites, the ZSM-5 zeolites contain coke consisting apparently of polyene chains and bulky aromatics and exhibiting a higher H/C ratio. This is evidenced by bands at 1590 , 1540 and $1465 - 1315\text{ cm}^{-1}$ (Fig. 2) representing vibrations of C=C, the aromatic ring and CH_n groups, respectively.

TPD of ammonia. The TPD curves of ammonia evolved from AlHY, deal Y and HZSM-5 are depicted in Fig. 4. It can be seen that the presence of coke substantially changes the shape of the curves; the maximum effect is again reserved for the lowest amount of the coke. The original zeolites consume almost all the ammonia dosed at 295 K . Coked samples do not adsorb all the ammonia from the gas phase and the peak

heights are lower, indicating poisoning of the acid sites. For AlHY and HZSM-5, the peaks are shifted to higher temperatures. As it is hardly possible that this could be caused by increased acid strength, hindered ammonia desorption due to pore blocking could explain this shift. With deal Y, the maximum is shifted to lower temperatures, reflecting the poisoning of most of the acid sites. In addition, the desorption curves are also influenced by the limited diffusion caused by the coke.

DISCUSSION:

In the course of a catalytic reaction, several types of compounds can be found in the zeolite cavities. Some of them act as reaction intermediates and some represent reaction products with restricted diffusibility hindering their removal from cavities. The remaining species which are stable towards desorption at high temperatures and can be removed only by burning represent the actual coke considered in this paper.

It follows from the above results that the acidic properties of zeolites control the conversion of ethylene both in the low-temperature oligomerization and in the catalytic reaction at high temperatures: the higher the acid strength of the framework hydroxyls the higher is the reactivity of ethylene and the lower this acid strength the more important the role played by Al electron-accepting sites. Nevertheless, the catalytic power of the latter centres is much less than that of the strongly acidic hydroxyls of ZSM-5 and deal Y zeolites. The same factors were found to govern the coking of Y zeolites. However, ZSM-5 with the highest catalytic activity exhibited substantially lower coking tendency. This distinction supports the suggestion (1) that coking reactions are spatially demanding.

The typical features of this process, occurring on the Y and ZSM-5 zeolites, and reflecting a shape selectivity effect, can be characterized as follows:

i) For Y zeolites at 670 K, ethylene yields C_3-C_5 aliphatics in the gas phase while predominantly polyene species with low hydrogen content appear in zeolite. These species also can be obtained via direct transformation of low-temperature oligomer through heating. In addition, the coking tendency of the samples parallels their low-temperature oligomerization activity. Therefore, coking apparently proceeds via oligomerization, isomerization, hydrogen transfer and cracking steps, of which the first is most probably the rate determining one. ii) In contrast to Y zeolites, the oligomer formed from ethylene on ZSM-5 zeolites at a low temperature is decomposed at 670 K. Coking on ZSM-5 zeolite occurs at a measurable rate at 770 K, when ethylene is rapidly converted to C_6-C_8 monoaromatics, so that the deposit increases in an atmosphere of these substances. This ability to provide monoaromatics probably via rapid condensation of ethylene is apparently closely connected with the high coking tolerance of ZSM-5, as these products can diffuse out of the pores. Nevertheless, further reactions of aromatics can be considered to be responsible for coking. No special relationship was found between the amount of coke on various ZSM-5 samples and their low-temperature oligomerization activity. According to the IR spectra,

the carbonaceous residue is composed of bulky aromatics together with polyene- type structures.

It can thus be concluded that the shape-selectivity factor governs not only the coking tendency of zeolites but also the composition of carbonaceous residues as well as the pathway of their formation. This pathway probably proceeds through oligomer precursors on Y zeolites and through aromatics ones on ZSM-5.

The deactivation effect of even low amount of coke (below 10 mg g^{-1}), tested by the oligomerization of ethylene at 300 K, consists of both the poisoning of acid sites and the blocking of pores near the surface. This is reflected in the loss of part of framework hydroxyls and in the increased resistance to mass transfer (IR spectra, TPD of ammonia). For Y zeolites, two types of polyene coke species were found using IR spectroscopy. The first one, characterized by the band at 1595 cm^{-1} , is supposed to act in the poisoning of the acid sites while the second one, represented with the band at 1610 cm^{-1} , in the choking of the pores. In the ethylene reaction at 670 K, the formation of both coke species proceeds simultaneously.

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