ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 905–910. © Pleiades Publishing, Ltd., 2009.
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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Densification Products in Conversion of Ethylene on a High-Silica Zeolite Catalyst

F. A. Gashimov

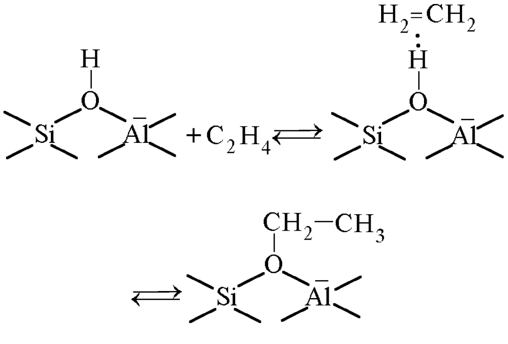
Azerbaijani State Petroleum Academy, Baku, Azerbaijan

Received July 30, 2008

Abstract—Fundamental aspects of the conversion of ethylene on a high-silica zeolite catalyst in the temperature range 200–400°C were studied. The methods of differential-thermal and X-ray phase analysis were employed to examine the formation of coking products on the surface of the zeolite catalyst in the conversion of ethylene at 350–450°C

DOI: 10.1134/S1070427209050309

As is known, high-silica zeolites are active catalysts in conversion of low-molecular-weight olefins [1–3]. These reactions occur at acid centers whose role is played by tricoordinated lattice atoms of aluminum and silicon, formed in high-temperature dehydroxylation of zeolites [4]. Adsorbed carbenium ions are conventionally regarded as active intermediate structures in these reactions [5, 6].



In the ionic mechanism of interaction between acid OH groups of a high-silica zeolite Pentasil and ethylene molecules, an intermediate complex with a hydrogen bond is formed and then transformed to the ethoxyl structure [4]:

Further, the carbon chain grows and the oligomer is subsequently desorbed from the catalyst surface [4, 7]. Analysis of published data shows that the mechanism of oligomerization of low-molecular-weight olefins on zeolite catalysts has been studied in sufficient detail.

In addition to the formation of various gaseous and liquid products, the conversion of hydrocarbons on catalysts is frequently accompanied by deposition of coking products (CPs) on the catalyst surface [8]. The effect of these products on the occurring reactions has not been entirely elucidated, and the available published data are occasionally contradictory [9–14].

In this context, a study of the conversion of low-molecular-weight olefins on zeolite catalysts and elucidation of the nature of CPs and their role in these reactions are a topical task.

This study is aimed to analyze the conversion of ethylene on a high-silica zeolite catalyst and to elucidate the nature of coking products and their role in this process.

EXPERIMENTAL

As object of study served a decationated high-silica zeolite of the Pentasil type, NVTsK ($SiO_2/Al_2O_3 = 60.3$, $N_2O < 0.1\%$). A modified catalyst with a ZnO content of about 8 wt % was prepared by impregnation of the starting H-form of the zeolite with an aqueous solution of $Zn(NO_3)_2$ and subsequent calcination in air at $T \approx 550°C$ for 6 h. Prior to experiments, the zeolite catalyst was dehydrated at 500°C in a flow of air, with oxygen removed by a flow of nitrogen. To completely remove the residual oxygen in the gas mixture, nitrogen was passed through a reactor with a copper catalyst heated to

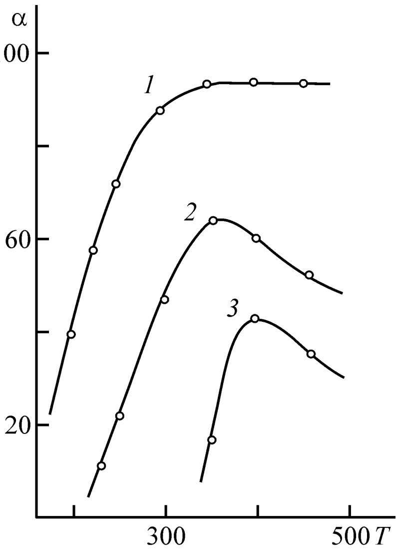


Fig. 1. Ethylene conversion α on NVTsK vs. temperature *T* at a volumetric flow rate $W = 240$ h^{-1}. (*1*) Conversion, (*2*) yield of liquid products, and (*3*) yield of aromatic compounds.

400°C. The catalytic activity of NVTsK was studied in a flow-through laboratory setup in the temperature range 200–450°C under atmospheric pressure. The volume and the grain size of the catalyst in the reactor were 1 cm^3 and 2–3 mm, respectively.

The acid properties of the starting NVTsK catalyst were studied with a UR-20 spectrophotometer equipped with an adsorption-vacuum setup. Pyridine molecules were used as a probe. The accumulation of coking products on NVTsK in the conversion of ethylene and the adsorption of ammonia on the starting catalyst and that coked at various temperatures were examined on a gravimetric installation with a McBain balance with a quartz coil [15]. Ethylene was produced by dehydration of ethanol on γ-Al_2O_3 at a temperature of 375°C. The reaction products were analyzed with an LKhM-8 MD chromatograph. Gaseous products were analyzed using a column with a length of 6 m and diameter of 3 mm, packed with a sorbent (INZ-600 firebrick with 15% Vaseline oil), which enables separation of C_2–C_3 and all isomers of C_4H_{10} and C_4H_8 hydrocarbons. Aromatic hydrocarbons were analyzed with a column 3 m long and 3 mm in diameter, packed with a sorbent (15% dinonyl phthalate on dinochrome).

A differential-thermal analysis of samples of the starting catalyst and that carbonized at various temperatures was made with a MOM derivatograph (Hungary) in the temperature range 20–1000°C. Calcined α-Al_2O_3 served as reference. Weighed portions of the samples were taken in an amount of about 300 mg. An X-ray phase analysis was performed with a DRON-2 instrument (CuK_α radiation, NI filter).

It is known that olefin may undergo various transformations on zeolite catalysts: isomerization, oligomerization, and aromatization, which yields a large number of gaseous and liquid products. Figure 1 shows how parameters of ethylene conversion on high-silica zeolite catalysts depend on temperature. At 200°C, the conversion of ethylene is 40%, with only gaseous hydrocarbons formed as products. As temperature increases, the conversion of ethylene grows and reaches a maximum at 350°C and then remains almost unchanged. The yield of liquid products of ethylene conversion starts to be observed at 225°C; as temperature is raised to 350°C, it increases and then starts to decrease. The gaseous products are composed of C_2–C_4 hydrocarbons and a minor amount of C_5 hydrocarbons. The liquid phase of the reaction products formed in the temperature range 225–350°C is mostly composed of aliphatic hydrocarbons. Aromatic hydrocarbons start to be formed in the temperature range 300–350°C, with their yield reaching a maximum at 400°C. As temperature is raised further, the yield decreases, but the fraction of aromatic hydrocarbons in the liquid products somewhat increases. At a comparatively constant conversion of ethylene, the yield of gaseous products of ethylene conversion markedly grows at temperatures higher than 350°C, with the qualitative composition of the liquid phase of the products preserved.

It should be noted that, in these experiments, the catalyst retained its activity during a rather long time, despite the deposition of coking products on its surface. Commonly, the preservation of the catalytic activity by a coked catalyst is attributed to several reasons. First, the coke may be deposited on different parts of the catalyst: at pore mouths, in the outer sphere of a grain, over the entire internal surface of the pores, etc. The occurrence of a certain type of coking mainly depends on the nature of a catalyst (its structure and activity) and temperature [16]. Second, another form of influence exerted by CPs on the catalytic properties is their modifying effect, which results in a change not only in the activity of a catalyst, but also in its specificity [17]. Because the elucidation of the role of CPs in the conversion of ethylene on high-silica zeolite catalysts is among the goals of the study, this phenomenon was examined in more detail.

Figure 2 shows how the accumulation of CPs and the yield of liquid products of ethylene conversion depend on time at 350°C. It can be seen that, at this temperature, 7.8 wt % CP accumulate on the catalyst surface during 20 min from the beginning of the process, after which the rate of CP formation becomes zero. Liquid products start to be formed in noticeable amounts only 15 min after the beginning of the process, when the degree of coking reaches a value of 6.5 wt %. With further accumulation of CPs on the catalyst, the yield of liquid products grows and stabilizes after the accumulation of CPs terminates.

Similar results were obtained at temperatures of 400 and 450°C, for which the maximum degrees of catalyst coking were 6.5 and 6.2 wt %, respectively. At these two temperatures, chosen for the study, the liquid products were mostly composed of aromatic hydrocarbons. The maximum yields of the liquid products at 350, 400, and 450°C were 64.0, 42.0, and 39.2%, respectively, in good agreement with the data in Fig. 1.

The results obtained demonstrate that, in the temperature range studied, NVTsK starts to exhibit activity in formation of liquid products of ethylene conversion only after a certain amount of CPs accumulates on the catalyst surface. This may indicate that CPs show a catalytic activity in the process under consideration.

The nature of the forming coking products can be studied in experiments on regeneration of a catalyst. Figure 3 shows results of these experiments for catalysts coked at various temperatures (350–450°C).

It can be seen from these data that CPs can be partly removed from all the catalysts by simple heating in a flow of nitrogen. It can be assumed that, in this case, the high-molecular-weight compounds contained in CPs are thermally decomposed to give gaseous products. As the temperature of CP formation increases, the fraction of such CPs decreases. At the same time, the fraction of products that can be removed from the catalyst surface only by oxidative regeneration (with oxygen or air) grows. Irrespective of the CP formation temperature, complete burning-out of CPs is achieved only on raising the regeneration temperature to 550–600°C and keeping the catalyst at these temperatures for no less than 3 h.

The nature of the accumulated CPs was also studied by differential-thermal analysis of coked NVTsK samples. The samples were prepared by treating the starting catalyst with the reaction mixture in a flow-through integral reactor at temperatures of 350, 400, and 450°C for 20 h. Then the catalyst was cooled in the reactor in hydrocarbons to room temperature and its ~300-mg portion was taken, placed in the measuring cell of the derivatograph, and analyzed. The results of DTA of the starting catalyst and that treated at various temperatures are shown in Fig. 4.

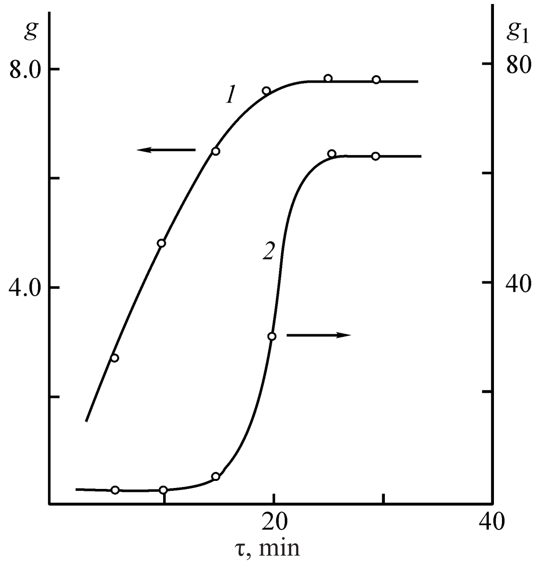


Fig. 2. (*1*) CP accumulation *g* and (*2*) yield of liquid products, g_1, vs. time τ in the conversion of ethylene on NVTsK. $W = 240$ h^{-1}, $T = 350$°C.

The TG curve of the starting sample (Fig. 4a) shows a noticeable decrease in its mass at comparatively low temperatures, which is accompanied by a small endothermic effect peaked at 130°C. The most probable explanation of these changes consists in removal of water adsorbed on the zeolite. As temperature increases further, the rate at which the sample mass decreases becomes substantially lower in the absence of any noticeable heat effects. In this case, the decrease in mass is presumably due to a gradual dehydroxylation of the catalyst surface in the temperature range 650–800°C.

The thermogram of a catalyst carbonized at 350°C (Fig. 4b) shows a small decrease in mass and insignificant endothermic effects at low temperatures (300°C), which can be attributed to desorption of hydrocarbons adsorbed on the sample in its cooling in the reactor. Further increase in temperature leads to a noticeable decrease in mass, accompanied by a broad exothermic effect with two peaks at 440 and 530°C. The existence of two peaks demonstrates that CPs contain at least two dissimilar components with different properties and chemical compositions. In addition, this may indicate that, in the course of oxidative regeneration, CPs undergo changes leading to their higher coking and to a higher C/H ratio in their composition at temperatures exceeding that of their formation.

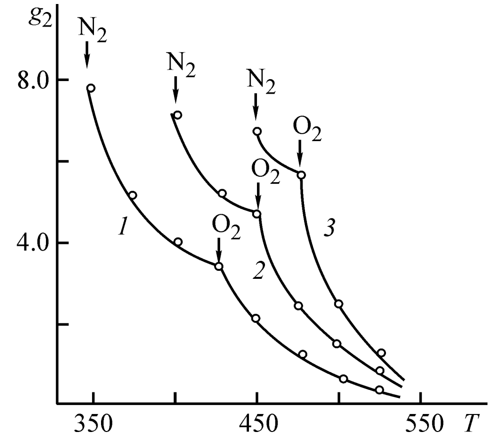


Fig. 3. Regeneration g_2 of CPs that accumulated in the conversion of ethylene on NVTsK at (*1*) 350, (*2*) 400, and (*3*) 450°C. (*T*) Temperature.

A similar pattern is observed for samples coked at 400 and 450°C (Figs. 4c, 4d). In these cases, there also occurs an exothermic effect that is associated with CP burning and has two peaks, with the positions of these peaks shifted to higher temperatures. For example, to these peaks correspond temperatures of 480 and 560°C for the CPs formed at 400°C, and 490 and 560°C for those formed at 450°C.

These results demonstrate that the CP formation temperature affects not only the maximum amount of CPs deposited on the catalyst, but also their physicochemical parameters. Presumably, an increase in temperature favors formation of more condensed structures in the composition of CPs.

The deposition of coking products on a catalyst may change its crystal structure. It was already shown that 7.8, 6.5, and 6.2 wt % CPs is deposited on the catalyst surface in conversion of ethylene on a high-silica zeolite catalyst at temperatures of 350, 400, and 450°C, respectively, during the first 20 min after the beginning of the process, after which the formation of CPs terminates. Only after that the catalyst acquires the maximum activity in the process under consideration. Apparently, the accumulation of CPs modifies NVTsK, with a change in the phase composition of the zeolite being a possible reason for this modification. To verify this assumption, the starting catalyst and that coked at various temperatures were subjected to X-ray phase analysis. It was found that the accumulation of CPs does not give rise to new crystalline phases. The native crystal structure of NVTsK is preserved even at the maximum amounts of CPs on a catalyst. Only a small decrease in the intensity separate peak and a certain increase in the absorption background are observed. The data obtained indicate that the crystal structure of the zeolite is insignificantly distorted by the deposition of CPs in the channels and voids of the zeolite matrix. The coking products themselves either have an amorphous structure or are constituted by a large number of very fine crystallites.

Transformations of hydrocarbons on zeolite catalysts are commonly related to the acid-base properties of these catalysts [2, 4, 7]. It was described above that hydrocarbons are adsorbed on acid centers of the surface, with those adsorbed on Lewis acid centers possibly undergoing deeper transformations than hydrocarbons adsorbed on Brønsted centers. The change in the catalytic activity of NVTsK in the conversion of ethylene may be due to the effect of CPs on the acid-base characteristics of the zeolite.

Figure 5 shows IR spectra of the starting NVTsK and that probed with pyridine molecules. It can be seen that, in the initial state, absorption bands at 3720, 3600, 1650, and 1630 cm^{-1} appear in the IR spectrum. The absorption bands at 3600, 1650, and 1630 cm^{-1} can be attributed to adsorbed water molecules. After a vacuum treatment of a catalyst sample at 500°C, the absorption bands of molecularly bound water disappear from the IR spectrum and absorption bands of thermally stable silanol Si–OH and acid –OH groups appear at 3720 and 3600 cm^{-1}, respectively. On bringing the catalyst surface in contact with a pyridine vapor, absorption bands of pyridine adsorbed on both Lewis and Brønsted acid centers appear in the IR spectrum at 1585 and 1440 cm^{-1}, respectively [18].

The acid properties of the starting and coked catalysts were studied by measuring the adsorption of ammonia in the dynamic mode in a flow-through setup with a spring McBain balance. Prior to letting in NH_3, samples were blown with dried nitrogen to remove hydrocarbons and water vapor from the system. The adsorption was performed at room temperature. It was found that the adsorption of ammonia on the starting NVTsK sample reaches a value of approximately 10 wt %. In thermal desorption of NH_3, a break in the desorption curve is observed at 230°C, with adsorbed ammonia completely removed on heating the sample to 430°C.

On coked samples, up to 6 wt % NH_3 is adsorbed at room temperature, almost irrespective of the temperature at which CPs are formed, with the thermal desorption curve having no pronounced breaks and ammonia completely removed at 360°C.

The results obtained indicate that the surface of the starting zeolite catalyst is nonuniform in the strength of acid centers, in agreement with the IR data. Beyond any doubt, the coking is a catalytic reaction occurring at acid centers. The accumulation of CPs on a catalyst both reduces the total number of acid centers and lowers their strength. In addition, the surface of the coked catalyst is presumably more uniform.

As noted above, the role of coking products in the conversion of hydrocarbons has been disregarded in most of studies devoted to oligomerization and aromatization of olefins on zeolite catalysts, with only the formation of CPs as a by-product mentioned. At the same time, the results of this study demonstrate that CPs are not only formed in ethylene conversion on NVTsK, but also strongly affect this process. This effect is mainly constituted in that the acid properties of the starting catalyst are changed. Apparently, as shown by IR spectral studies, the NVTsK surface possesses acid properties due to the presence of both Lewis and Brønsted acid centers with various strengths. In addition, published data suggest that the firm adsorption of an olefin on strong acid centers results in that coking products blocking this center are formed. At the same time, Brønsted acid centers involved in the adsorption and conversion of the olefin may exist on the CP surface itself, i.e., the products themselves may exhibit a catalytic activity in the conversion of olefins. Presumably, the olefin is mostly adsorbed in the initial stage of the process on strong Lewis acid centers, which leads to a not too large degree of ethylene conversion, with coking products formed. New Brønsted acid centers responsible for "milder" conversion of ethylene to oligomers and aromatic hydrocarbons are formed on the CP surface. After all the acid centers are blocked, the formation of CPs terminates and the olefin is converted to gaseous and liquid products.

Despite that the suggested mechanism of the olefin conversion on a zeolite catalyst undoubtedly requires verification by direct experiments, it can be assumed that, with a high probability, coking products are directly involved in the ethylene conversion on NVTsK by affecting the acid-base properties of the zeolite catalyst. In addition, it can be assumed that the CPs possess their own activity in this process. Thus, the results obtained show that the concepts of the mechanism by which olefins are converted on zeolite catalysts should be revised by taking into account their conversion not only to gaseous and liquid hydrocarbons, but also to solid coking products.

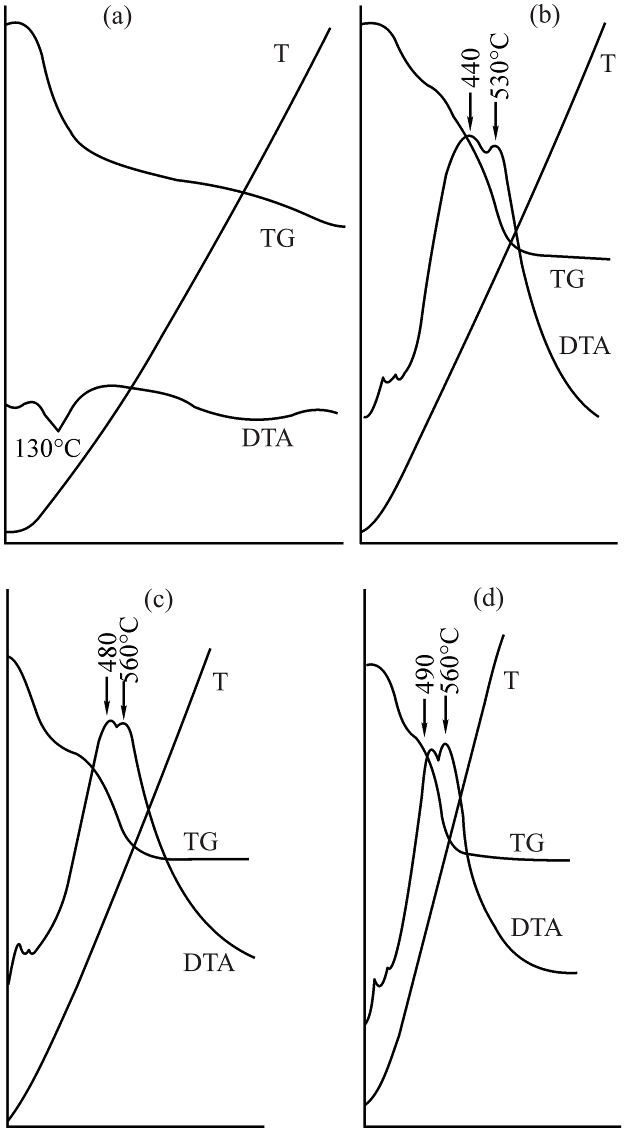


Fig. 4. Thermograms of (a) starting NVTsK catalyst and that coked in ethylene conversion at (b) 350, (c) 400, and (d) 450°C.

CONCLUSIONS

(1) The conversion of ethylene on a high-silica zeolite catalyst was studied in a wide temperature range (200–450°C). It was shown that the yield of reaction products is only observed after coking products are formed in an amount of 6–8% on the catalyst surface in the first 20 min after the beginning of the process.

(2) Liquid reaction products start to be formed at 225°C. The liquid phase of the reaction products formed is

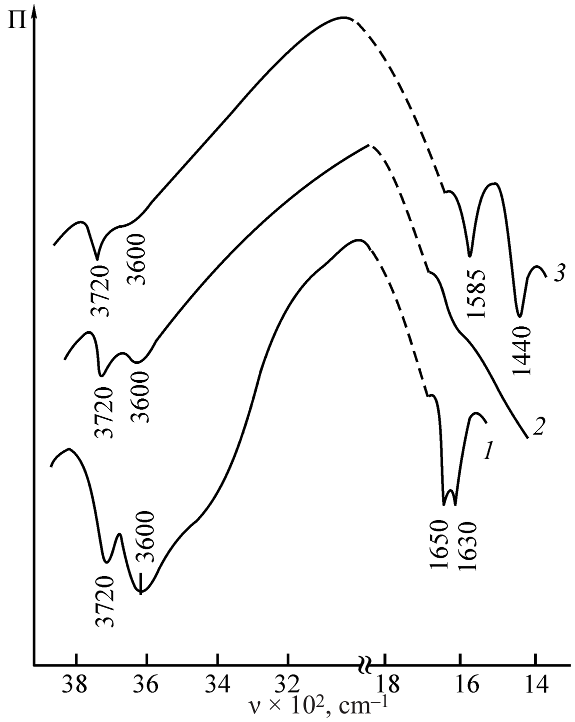


Fig. 5. IR spectra of an NVTsK catalyst modified with zinc oxide. (ν) Wave number. (*1*) Starting catalyst after a vacuum treatment at 10–5 mm Hg, (*2*) catalyst vacuum-treated at 500°C, and (*3*) catalyst upon adsorption of pyridine at room temperature in a vacuum.

mainly composed of aliphatic hydrocarbons at 225–350°C and aromatic hydrocarbons at 350–450°C.

(3) The coking products formed are inhomogeneous, which is indicated by two temperature peaks in the DTA curve, associated with the presence of two different thermally stable phases of coking products.

(4) The coking products affect the acid-base properties of the zeolite catalyst by reducing the number and strength of acid centers and are involved in ethylene conversion reactions.

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