INFLUENCE OF CHROMIUM CATIONS ON PROPERTIES OF STABILIZED AND NON-STABILIZED FORMS OF Y-ZEOLITES

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Differences in the behaviour of the non-stabilized form and of stabilized forms of the Y-type zeolite with Cr^{3+} in the interaction with ethylene were investigated. While with the stabilized forms the polymerization of ethylene takes place with initial rates $r_0 = 9-12 . 10^{-2}$ $g(C_2H_4)g^{-1}$ (zeolite) min^{-1}, the initial rate of polymerization with the non-stabilized zeolite containing Cr^{3+} is by two orders of magnitude lower. In the infrared spectra of OH stretching vibrations of the zeolites with Cr^{3+} cations two new bands were found at 3 660 and 3 550 cm^{-1}, in comparison with the initial samples. These bands were ascribed to hydroxocomplexes of chromium.

A considerable attention has been paid to stabilized and non-stabilized complexes of zeolites in the H^+-form as far as their preparation and properties, in particular their reactions with ethylene, are concerned. This subject has been treated in several recent reviews[1-5]. However, the possibilities of transforming these newly modified zeolite types back to their cationic forms, namely by the exchange with transition metal cations[6,7], have been studied but scarely. Transition metals, as generally known, may exhibit specific catalytic properties. Their presence in stabilized structures of zeolites may lead to new forms of zeolites exhibiting interesting catalytic properties. This contrasts with ultra-stable H^+-form zeolites, where mainly catalytic effects of their acido-basic centers play a role.

The aim of this paper has been to check the possibility of preparing stabilized zeolites with the Cr^{3+} cation, to investigate possible differences between the stabilized and non-stabilized zeolites containing Cr^{3+}, and to determine differences between the stabilized H^+-form zeolites and those with Cr^{3+} cations. In order to achieve this aim adsorption properties of the above mentioned zeolites and their catalytic activity in polymerization of ethylene was measured (the latter served as a model reaction sensitive both to the presence and to the valence state of chromium); in addition, the mechanism of ethylene sorption was studied.

EXPERIMENTAL

NH_4 70-Y *Zeolite* (serial number 00052/1), produced by the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava, was used as the initial material. The zeolite was stabilized in a small quartz reactor under so-called self-steaming conditions at 570°C for the USC zeolite (linear temperature increase of 4 K/min and 2·128 kPa water vapour pressure), and 770°C for the USE zeolite (linear temperature increase of 6 K/min, 2·128 kPa water vapour). The exchange to the Cr^{3+} form was carried out in the same way with both the two stabilized forms and the non-stabilized form: from a 0·02—0·01 mol/l $CrCl_3 . 6 H_2O$ solution at the room temperature. After the exchange the samples were filtered, rinsed by water until negative reaction on the presence of Cl^- was reached, and dried on air at the room temperature. Their analytical composition is given in Table I. All samples were crystalline; this follows from X-ray measurements.

The sorption capacity was measured by argon at —195°C on the samples previously activated at 350°C overnight. Their hydration in hydration-dehydration cycles was carried out by admitting water vapours at the room temperature and the following dehydration, again at 350°C overnight. Table II shows the sorption capacity changes after two hydration-dehydration cycles. With the exception of the $NH_4$70-Y zeolite the sorption capacity of the investigated samples does not change.

The thermal stability measurements showed that the lattice collaps occurs with the NH_4/70/Cr/30/-Y zeolite at approximately 1050°C, with the initial samples $NH_4$70-Y at about 800°C. With the stabilized forms, both the initial sample and that one with Cr^{3+}, the lattice collaps occurs at the same temperature of about 1 100°C. This follows from DTA measurements.

TABLE I

Chemical Composition of the Zeolites Studied

$NH_4$70-Y	$0.31\ Na_2O . 0.65\ (NH_4)_2O . Al_2O_3 . 5.22\ SiO_2$
NH_4(70)Cr(30)-Y	$0.24\ Na_2O . 0.41\ (NH_4)_2O . 0.102\ Cr_2O_3 . Al_2O_3 . 4.93\ SiO_2$
USC-Cr30	$0.10\ Na_2O . 0.071\ Cr_2O_3 . Al_2O_3 . 4.51\ SiO_2$
USE-Cr30	$0.09\ Na_2O . 0.079\ Cr_2O_3 . Al_2O_3 . 4.67\ SiO_2$

TABLE II

Sorption Capacity (mmol/g) for Ar at —195°C and 1·33 kPa and the Stability of the Zeolites under the Hydrothermal Conditions

Zeolite	Initial	1st Cycle hydration-dehydration	2nd Cycle hydration-dehydration
$NH_4$70-Y	12·03	9·37	3·35
USC	10·36	10·41	10·32
USE	9·61	9·69	9·49
NH_4(70)Cr(30)-Y	11·18	11·04	10·50
USC-Cr30	9·36	9·43	9·37
USE-Cr30	8·64	8·69	8·73

Ethylene and propylene used in the experiments were sampled into glass ampoules and purified by multiple freezing.

Infrared spectra were measured on a Perkin–Elmer 621 spectrometer using a standard procedure with the double slit. The description of the apparatus, sample preparation, and measuring conditions were described earlier[8]. The sample thickness varied between 8 and 12 mg/cm^2, the samples were activated overnight at 350 and 500°C under vacuo of about $1{\cdot}33 \,.\, 10^{-3} - 1{\cdot}33 \,.\, 10^{-4}$ Pa. The ethylene sorption was carried out at the spectrometer beam temperature.

Kinetic curves of ethylene polymerization were measured on a quartz balance with a sensitivity of $\pm 0{\cdot}03$ mg. The sample weight was about 100 mg. To remove the effects caused by the transport of ethylene in the zeolite layer and those connected with the released polymerization heat, the samples were pressed into thin pellets. A similar experimental arrangement was successfully used in the study of the kinetics of physical adsorption[9]. The compressing pressure was about 1 000 kg/cm^2, the pellet thickness was 0·4 – 0·8 mm. The activation was carried out overnight at 350°C at $1{\cdot}33 \,.\, 10^{-2} - 1{\cdot}33 \,.\, 10^{-3}$ Pa. Ethylene was sorbed at 77·0°C, the temperature was maintained by a water thermostat. Kinetic curves of the sorption of propane were measured in the same way. Propane was sorbed at 0°C, the temperature was kept constant by a water-ice bath.

RESULTS

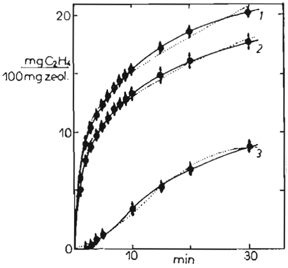
Experimental measurements were aimed, on the one hand, at the quantitative evaluation of the initial rates of ethylene polymerization on the zeolites under study, on the other hand, at the investigation of the mechanism of adsorption and polymerization of ethylene in the adsorbed state, using the infrared spectroscopy method.

In order to characterize the samples of the zeolites USC-Cr30, USE-Cr30, and NH$_3$/70/Cr/30/-Y, the time dependence was investigated of the weight increment of the zeolite under study during its interaction with ethylene in the pressure interval 5·32 – 6·65 kPa and at the constant temperature of 77·0°C. The kinetic curves obtained are shown in Fig. 1. Curve *3* corresponding to the NH$_4$/70/Cr/30/-Y zeolite gives

FIG. 1

Kinetic Curves of Polymerization of Ethylene on Zeolites

1 USE-Cr30, *2* USC-Cr30, *3* NH$_4$(70).Cr(30)-Y; ——— Experimental curves, ······ calculated curves using constants $a_0 = 15{\cdot}00$ [g(C$_2$H$_4$)g^{-1} (zeolite) . 10^{-2}], $c = 79{\cdot}49$ (dimensionless) for USE-Cr30, $a_0 = 13{\cdot}17$, $c = 69{\cdot}05$ for USC-Cr30; $b_1 = 0{\cdot}13$ [g(C$_2$H$_4$)g^{-1} (zeolite) . 10^{-2} min^{-1}], $b_2 = 2{\cdot}27 \,.\, 10^{-2}$ [g(C$_2$H$_4$)g^{-1} (zeolite) . 10^{-2} min^{-2}], $b_3 = -5{\cdot}91 \,.\, 10^{-4}$ [g(C$_2$H$_4$)g^{-1} (zeolite) . 10^{-2} min^{-3}] for NH$_4$(70)Cr(30)-Y.



the irreversible adsorbed fraction of ethylene after the correction on physical adsorption (*i.e.* the amount that could be desorbed at 77°C during several minutes after the adsorption was terminated). The remaining curves *1*, *2* concern the zeolites USC-Cr30 and USE-Cr30, and show pure chemisorption; physical adsorption was not observed. The points plotted in Fig. 1 represent the arithmetic mean of values of at least three measurements, vertical arrows show the values of the standard deviation.

The initial reaction rate was chosen as the measure of estimating the catalytic activity of the zeolites studied. For this purpose empirical functions were fitted to the experimental kinetic curves by the least square, namely curves 1 and 2 were fitted using the expression

$$a_t = a_0 \frac{c\tau}{(1 - \tau)(1 - \tau + c\tau)}, \qquad (1)$$

where $a_0(\mathrm{g}[\mathrm{C_2H_4}]\,\mathrm{g}^{-1}$ (zeolite) $10^{-2}]$, and c (dimensionless) are constants, $a_t[\mathrm{g}(\mathrm{C_2H_4})\,.\,\mathrm{g}^{-1}$ (zeolite) $10^{-2}]$ is the amount adsorbed in time t (min), $\tau = t/100$. Curve *3* was described in a similar way by the expression

$$a_t = b_1 t + b_2 t^2 + b_3 t^3, \qquad (2)$$

where $a_t[\mathrm{g}(\mathrm{C_2H_4})\,\mathrm{g}^{-1}$ (zeolite) $10^{-2}]$ is the amount adsorbed in time t (min), and $b_1[\mathrm{g}(\mathrm{C_2H_4})\,\mathrm{g}^{-1}$ (zeolite) $10^{-2}\,\mathrm{min}^{-1}]$, $b_2[\mathrm{g}(\mathrm{C_2H_4})\,\mathrm{g}^{-1}$ (zeolite) $10^{-2}\,\mathrm{min}^{-2}]$, $b_3[\mathrm{g}(\mathrm{C_2H_4})\,\mathrm{g}^{-1}$ (zeolite) $10^{-2}\,\mathrm{min}^{-3}]$ are constants. Fig. 1 gives the values of the constants of the above mentioned empirical relations. By means of the empirical equations $(\mathrm{d}a_t/\mathrm{d}t)_{t=0} = a_0 c/100 = r_0$ and $(\mathrm{d}a_t/\mathrm{d}t)_{t=0} = b_1 = r_0$ values of the initial rates of the interaction ethylene — studied zeolite were calculated

TABLE III

Relative Filling of Zeolite Cavities by Ethylene

Zeolite	Polyethylene ($\varrho = 0.92\ \mathrm{g/cm^3}$)			Liquid ethylene ($\varrho = 0.39\ \mathrm{g/cm^3}$)		
	5 min	10 min	30 min	5 min	10 min	30 min
USC-Cr30	0·44	0·57	0·75	1·05	1·33	1·77
USE-Cr30	0·56	0·70	0·93	1·34	1·67	2·19
$\mathrm{NH_4}$(70)Cr(30)-Y	0·04	0·12	0·31	0·09	0·28	0·73

$$\text{USC-Cr30} \qquad r_0 = 9{\cdot}09 \,.\, 10^{-2}\,[\mathrm{g(C_2H_4)\,g^{-1}\,(zeolite)\,min^{-1}}]$$

$$\text{USE-Cr30} \qquad r_0 = 11{\cdot}92 \,.\, 10^{-2}\,[\mathrm{g(C_2H_4)\,g^{-1}\,(zeolite)\,min^{-1}}]$$

$$\mathrm{NH_4/70/Cr/30/\text{-}Y} \qquad r_0 = 0{\cdot}13 \,.\, 10^{-2}\,[\mathrm{g(C_2H_4)\,g^{-1}\,(zeolite)\,min^{-1}}]$$

Further results characterizing differences in the behaviour of the studied zeolite in the interaction with ethylene are given in Table III. In this table the respective columns show the relative filling of zeolite cavity volumes at t = 5, 10, and 30 min, assuming the adsorbed ethylene density to be $\varrho = 0{\cdot}39\ \mathrm{g/cm^3}$ (liquid ethylene) and $\varrho = 0{\cdot}92\ \mathrm{g/cm^3}$ (polyethylene). These data were calculated from the over-all value of the cavity volume in 1 g of zeolite, obtained from the experimental data of sorption capacity as measured by argon (Table III), assuming the cavity volume filled by ethylene of the given density equals unity.

Under similar conditions kinetic curves of sorption of propane on the studied types of zeolites were measured. The results show that – unlike with ethylene – with propane only physical adsorption takes place, with the same rate on all the samples. In this way it was confirmed that the differences in the kinetics of ethylene sorption are not due to steric, transport influencing, effects. The adsorbed amount of propane corresponds to the sorption capacity of the particular zeolite types as measured by argon.

The mechanism of sorption of ethylene was studied on the zeolites in question by the infrared spectroscopy method. Table IV shows the position of bands in the region of OH stretching vibrations of parent zeolites and the studied $\mathrm{Cr^{3+}}$-containing zeolites, activated at 350°C overnight. The behaviour of all the three samples during the dehydration at 500°C overnight is shown in Fig. 2.

TABLE IV

Wave Numbers ($\mathrm{cm^{-1}}$) of Stretching Vibrations of OH Groups of Initial and Studied Zeolites

$\mathrm{NH_470\text{-}Y}$	$\mathrm{NH_4(70)Cr(30)\text{-}Y}$	USC	USC-Cr30	USE	USE-Cr30
3 740	3 740	3 740	3 740	3 740	3 740
3 640	3 640	3 680	3 680	3 680	3 680
—	3 660	—	3 660	—	3 660
3 550	↑	3 600	3 600	—	3 610
	3 550				
—	↓	—	3 550	—	3 550

Figs 3*a*,*b*,*c* show the spectra of these samples after the adsorption of ethylene. The spectra cover the region of OH stretching vibrations, ν(C—H) in CH_3 and CH_2 groups; they illustrate clearly the differences in the behaviour of the stabilized and non-stabilized zeolite forms. In the infrared spectrum of ethylene adsorbed on the stabilized forms there are missing the bands at 3080 cm^{-1} (characterizing the stretching vibration ν(C—H) in the $=CH_2$ group) and the band at 1460 cm^{-1} in the region of bending vibrations δ(C—H) (refs[10,11]). These bands can be seen in the infrared spectra of the non-stabilized forms of zeolites with Cr^{3+} cations.

DISCUSSION

It follows from Table II, from the DTA measurement, and the X-ray data that in a simple way, by ion exchange, stabilized forms of the Y-type with Cr^{3+} cations (USC-Cr30, USE-Cr30) can be prepared, by substituting the rest of Na^+ cations with Cr. The sorption capacity of these zeolites is the same as that one of the corresponding initial zeolites (USC, USE). No change of this capacity was found even after the hydrothermal treatment: under these conditions they behave in the same way as the initial sample (USC, USE). The non-stabilized zeolite with Cr^{3+} cations, NH_4/70/Cr/30, shows the same behaviour under the hydrothermal conditions as the stabilized forms either with H^+ or Cr^{3+} cations. This means that its sorption capacity does not change after the hydration-dehydration cycles. This is not true with the corresponding initial zeolite $NH_4$70-Y whose sorption capacity decreases. Also, the thermal stability of this non-stabilized zeolite NH_4/70/Cr/30/-Y is substantially higher, because the lattice collaps occurs at about 1050°C; thus, it is similar as the lattice collaps of the stabilized zeolites either with H^+ or Cr^{3+} cations (1100°C).

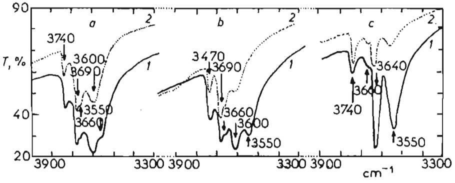


FIG. 2

Infrared Spectra of the Zeolites USE-Cr30, USC-Cr30, and NH_4(70) Cr(30)-Y after Activating at 350°C Overnight *in vacuo* *1* and after Activating at 500°C Overnight *in vacuo* *2*
a USC-Cr30, *b* USE-Cr30, *c* NH_4(70)Cr(30)-Y.

At the same time, it differs substantially from the thermal stability of the initial $NH_4$70-Y zeolite, where the skeleton collapses as early as at about 800°C (ref.[12]). It follows from these facts that even the presence of Cr^{3+} has a stabilizing influence on the zeolite lattice.

The infrared spectra characterizing surface OH groups are shown in Fig. 2. For the sake of clarity, Table IV compares positions of the particular bands of Cr^{3+} stabilized zeolites with those of the initial samples. The bands at 3740, 3690, and 3600 (3610) cm^{-1} were observed both with the chromium-containing zeolites (USC-Cr30 and USE-Cr30) and the initial zeolites (USC, USE). This is in agreement with earlier published results[2-4]. New bands of the stabilized zeolites with Cr^{3+} lie at 3660 and 3550 cm^{-1}. They probably hang together with the presence of Cr^{3+} in the zeolites. Their wavenumbers are close to the wavenumbers of OH groups in the spectra of Y-zeolites with La^{3+} cations[6,13], 3520 and 3640 cm^{-1}. Therefore, we consider it resonable to interpret these new bands in the spectra of our Cr^{3+}-containing zeolites in a similar manner. The wavenumber 3550 cm^{-1} corresponds to the OH-vibration in Cr^{2+}—OH, while 3660 cm^{-1} to the OH vibrations in —Si—(OH)—Al—. The formation of the Cr^{2+}—OH group may be understood as a result of the hydrolysis[14] during the dehydration process at 350°C of the fully hydrated zeolite

$$Cr^{3+}(H_2O) + \text{OSi-zeolite} \rightleftharpoons Cr^{2+}\text{—OH} + \text{H—OSi-zeolite}$$

The band at 3550 cm^{-1} disappears during the evacuation procedure of samples at 500°C (Fig. 2, curve 2). This does not contradict the above suggested interpretation, however, it indicates that the Cr^{2+}—OH group is thermally labile. During the evacuation at higher temperatures the bridge structure of the type Cr—O—Cr accompanied by water release may be formed, too[15]. The shift of the 3550 cm^{-1} band to higher wavenumbers (in comparison with the 3520 cm^{-1} band in the Y-zeolites with La^{3+}) may hang together with a smaller Cr^{3+} radius: according to Ward[16], the smaller the cation radius, the larger the surrounding electrostatic field which causes a strengthening of the OH bond and a shift of ν(OH) to higher wave numbers.

In the infrared spectrum of the non-stabilized NH_4/70/Cr/30/-Y (Fig. 2), in comparison with the initial zeolite $NH_4$70-Y, there are also two new bands, 3660 and 3550 cm^{-1}. The 3550 cm^{-1} band occurs in the initial zeolite $NH_4$70-Y, too (Table IV), contrarily to the stabilized zeolites. We assume that this is the case of a superimposed band, where one contribution comes again from the Cr^{2+}—OH group, according to the above mentioned scheme. This interpretation is supported by the presence of the other new band at 3660 cm^{-1} which was also found in the stabilized zeolites with Cr^{3+}.

The interaction of ethylene with the stabilized zeolites containing Cr^{3+} is characterized by the spectra in Fig. 3*a*,*b*. The bands at 2950, 2920, and 2850 cm^{-1} cor-

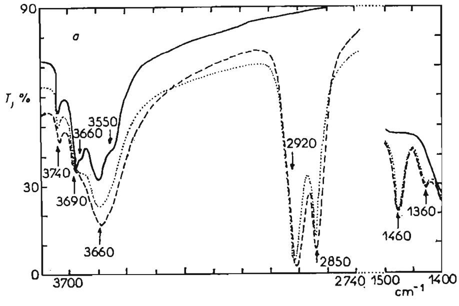
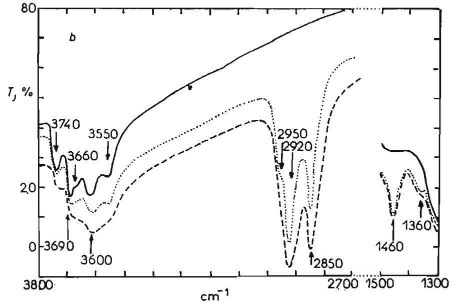


FIG. 3

Infrared Spectra

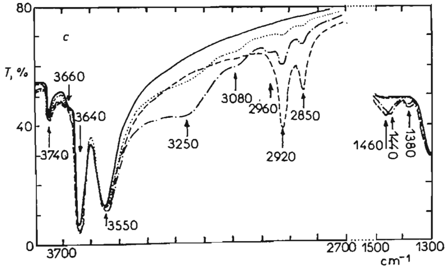
a) of USE-Cr30 with ethylene. ——— Activation of zeolite at 350°C overnight *in vacuo*, ······ sorption of C_2H_4 at the spectrophotometer beam temperature and 7·98 . 10^2 Pa, ----- after desorption of ethylene at the spectrophotometer beam temperature into vacuum.



b) of USC-Cr30 with ethylene. ——— Activation of zeolite at 350°C overnight *in vacuo*, ······ sorption of ethylene at the spectrophotometer beam temperature and 7·98 . 10^2 Pa, ----- after desorption of ethylene at the spectrophotometer beam temperature into vacuum.

respond to the stretching vibrations of CH_3 and CH_2 in saturated hydrocarbons, and the band at 1460 cm^{-1} to the bending vibration δ_{as} of CH_3 (ref.[10,11]). The band 3080 cm^{-1} of the ν(C—H) vibration in $=CH_2$ was not found. This indicates that in the interaction zeolite-C_2H_4 a complete polymerization of the latter occurs. Both new bands in the region of the stretching vibrations of OH groups, 3660 and 3550 cm^{-1}, are visible, though little can be said about their eventual change due to their decreased clarity; in particular, this is true for the 3550 cm^{-1} band. After the gaseous phase was pumped away, the polymer formed – consisting of CH_3 and CH_2 groups – influences the OH vibrations represented by the bands at 3740 and 3690 cm^{-1}. This interaction manifests itself both by a decrease of intensity of these bands and by an increase of the broad band at about 3600 cm^{-1}. The envelope curve with the maximum at 3600 cm^{-1} arises from a superposition of the original bands in this region with the shifted band due to the polymer–OH group interaction[17,18].

A somewhat different is the behaviour of the non-stabilized zeolite with Cr^{3+} in the interaction with ethylene (Fig. 3*c*). Ethylene adsorbs over the zeolite partly physically; this results in a broad band in the vicinity of 3250 cm^{-1} (corresponding to the stretching vibration of OH groups interacting with ethylene), and in the bands 3080 and 1440 cm^{-1}, corresponding to the stretching and bending vibrations ν,δ(C—H) in $=CH_2$. All these bands disappear after pumping away of the gaseous phase, which shows the reversibility of the physical adsorption of ethylene. Besides it, the polymer is formed as well, as show the bands at 2960, 2920, and 2850 cm^{-1}, discussed above. The rate of polymerization of ethylene on the studied zeolites



c) of $NH_4(70)Cr(30)$-Y with ethylene. ——— Activation of zeolite at 350°C overnight *in vacuo*, ······ sorption of ethylene at the spectrophotometer beam temperature and $5{\cdot}586 \cdot 10^3$ Pa, ----- after desorption of ethylene at the spectrophotometer beam temperature into vacuum.

and a quantitative estimation follow more clearly from the kinetic measurements.

Fig. 1 shows the corresponding kinetic curves characterizing the interaction of ethylene with Cr^{3+} zeolites. The shapes of these curves reflect again the different behaviour of the non-stabilized and stabilized zeolites with Cr^{3+} which followed from the infrared spectra. The initial interaction rates are with the stabilized Cr^{3+} zeolites practically by two orders of magnitude higher than with the non-stabilized zeolite. This increased catalytic activity of the stabilized zeolites with Cr^{3+} can also be seen from the relative filling of cavities (Table III) which in fact shows the relative polymer yield in the time intervals listed. In Table III the values of filling are compared under the assumption that the density of the adsorbed ethylene is the same as that one of liquid ethylene or solid polyethylene. The data indicate that the product is the solid substance rather than liquid ethylene, for which as early as in the initial reaction stage (5 min) the filling of cavities is higher than 1·0.

A considerable difference in the activities of the stabilized and non-stabilized zeolites with Cr^{3+} cations follows from the above reported experimental results. From the data on the kinetics of ethylene polymerization reported in the literature one cannot determine unambiguously which valence state of chromium is the active center[19-25]. According to our opinion (see above) the absorption band 3550 cm^{-1} might hang together with the vibration of the hydroxocomplex Cr^{2+}—OH. However, because of contradictions in the published papers, where some authors assume that Cr^{2+} is the active center of the ethylene polymerization[19-21], while others[22-25] assert that Cr^{2+} is absolutely inactive, an independent method has to be used to prove the existence of this complex and to investigate its influence on the polymerization initiation. In view of the fact that in all studied zeolites the chromium content is practically the same, while the activity varies, we think that the reasons may be in a different number of active centers (which may also be formed only during the very reaction – see the autocatalytic character of the polymerization course with NH_4/70/Cr/30/-Y) or in a difference in the activation energy of the process of formation of the activated complex adsorption center–ethylene. No definite conclusions about these problems can be made from the results of this study and, therefore, further investigation along these lines is being prepared.

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