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Coke Formation through the Reaction of Olefins over Hydrogen Mordenite

II. *In Situ* EPR Measurements under On-Stream Conditions

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Depending on the reaction temperature, the carbonization of ethylene over hydrogen mordenite led to low-temperature coke radicals (below about 500 K) or high-temperature coke radicals (above about 500 K). The formation of low-temperature coke radicals, which are olefinic or allylic oligomeric species, is favored by an increase in the acidity of the zeolite catalyst. In the formation of high-temperature coke radicals, which are highly unsaturated species, homolytic bond splitting of carbonaceous deposits may be involved. The acidity of the zeolite affected the formation of the high-temperature coke radicals in a complex way. A comparison between EPR and thermogravimetric measurements showed a good linear correlation between the number of radicals and the amount of coke formed at high temperature.

INTRODUCTION

EPR studies on coke deposition on solid catalysts are generally conducted by static measurements. Therefore, they do not necessarily provide results that are relevant for the real on-stream processes. In the current study, experiments were designed to overcome this difficulty.

First, it was shown that upon coke formation ethylene yielded the so-called intermediate radicals under an atmosphere of ethylene renewed prior to each heating step but not under autogenous atmosphere. Hence it was suspected that the on-stream conditions have a decisive influence on coke formation. Therefore, subsequent studies were carried out by *in situ* monitoring of the coke formation during the reaction of ethylene. Another interesting problem to be elucidated was the effect of Al content of the zeolite catalyst on the formation of low-temperature and high-temperature coke. Finally, attention was paid to the question of how to distinguish between radicals of the catalytically formed high-temperature coke and those observed in thermally carbonized matter.

EXPERIMENTAL

Materials. Commercial hydrogen mordenite (HM-1, Table 1) and sodium mordenite were purchased from the Norton Company. A series of dealuminated hydrogen mordenites (HM-2 to HM-5) was prepared by treatment of sodium mordenite with hydrochloric acid. Ethylene (99.95%), nitrogen (99.996%), and synthetic air were obtained from Messer Griesheim, Düsseldorf.

Apparatus. The EPR spectrometer and accessories have been described in Part I of this study (*1*). *In situ* EPR measurements were rendered possible by use of a specially

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TABLE 1

Characterization of the Catalysts Used[a]

Zeolite	Al/unit cell	A(OH) (a.u.)	A(LPy) (a.u.)
HM-1	6.1	0.49	0.36
HM-2	3.8	0.35	0.26
HM-3	2.7	0.22	0.24
HM-4	1.6	0.20	0.20
HM-5	1.2	0.25	0.08

[a] A, absorbance; OH, acidic hydroxyls; L, Lewis sites; Py, adsorbed pyridine.

designed EPR fixed-bed flow reactor cell (Fig. 1), which could be placed in the resonance cavity. The Pt heating wire (0.05 mm diam) was wound bifilarly, as shown in Fig. 1, around the reactor tube and fixed with a two-component cement, Thermostix 2000 from Klebchemie GmbH. The temperature inside the reactor was measured with a 0.25-mm-diam thermocouple from Philips. To avoid overheating and subsequent damage of the resonance cavity, the reactor was isolated in a Dewar tube. Reactor and Dewar tube were made from high-quality quartz glass (Suprasil). The fixed-bed reactor allowed reactions to be carried out within the temperature range 300 to 800 K.

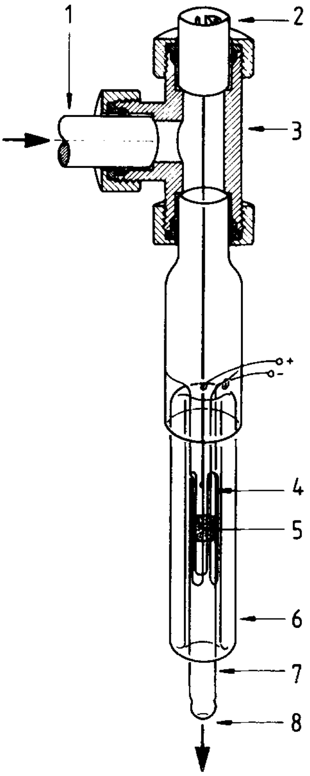


FIG. 1. Flow reactor for *in situ* EPR measurements: (1) gas inlet, (2) thermocouple, (3) Cajon T-connection, (4) Pt heating wire, (5) catalyst, (6) Dewar tube, (7) reactor tube, (8) gas outlet.

Errors in intensity measurements, which occurred because of the variation in length of the sample and the so-called sucking-in effect, were corrected. The sucking-in effect is caused by concentration of the electromagnetic field at the locus of the sample due to the dielectric constant of the surrounding quartz glass of the reactor. A correction factor was evaluated via comparative measurements of a standard with and without the quartz glass reactor. Numbers of radicals could be determined with a reproducibility of ±10% and precision of ±25%. The spectra were recorded at a microwave power small enough to avoid any saturation effects. The modulation amplitudes were chosen to be as small as possible, usually about 0.2 mT.

Conversion measurements could be conducted by using gas chromatograph F20 from Perkin–Elmer, on line with the EPR reactor cell. The density of radicals in the coke deposits was determined using complementary thermogravimetric data which were obtained with a thermobalance TGS-2 from Perkin–Elmer.

Procedure. Samples of 0.2 g were used to investigate the carbonaceous deposits formed below 500 K, since experiments carried out under static conditions have shown that only a small number of radicals could be expected. For experiments above 500 K, only 0.01 g of the zeolites was employed. The small grains of pressed zeolite powder were heated at the rate of 200 K/h to 700 K in a stream of air flowing at 15 ml min^{-1}. After 1 h of calcination at this temperature the flow of air was replaced by a flow of nitrogen for one more hour. Thereafter, the sample was cooled to the reaction temperature, and a flow of a mixture of 8 vol% ethylene in nitrogen was admitted through the reactor at a flow rate of 16 ml min^{-1}.

For complementary measurements at Q-band frequency or at low temperature, the zeolite sample was pretreated under stream conditions, subsequently exposed to air, and transferred to a capillary tube which was connected to a high vacuum and gas-dosing system.

Pretreatment for the thermogravimetric measurements was as follows. The sample was first maintained at room temperature under a nitrogen flow of 200 ml min^{-1}. Thereafter it was heated to 700 K within 20 min and calcined at this temperature for 2 h. The cell was subsequently cooled to the reaction temperature and purged for 4 min with the reactant mixture, i.e., 5 vol% ethylene in nitrogen, at a flow rate of 200 ml min^{-1}. After 4 min the rate was decreased to 16 ml min^{-1} and recording of the weight gain was started.

RESULTS AND DISCUSSION

Low-Temperature Coke

When the flow of ethylene in nitrogen was passed through the HM-1 zeolite at increased temperatures (380–470 K), a spectrum composed of seven hyperfine lines appeared (Fig. 2). Its hyperfine splitting constant was approximately 1.6 mT and the *g* value, 2.0025. The corresponding radicals have been referred to as intermediate radicals (Part I (*1*)). During a further increase in the temperature up to about 500 K, the hyperfine structure vanished, and there remained a single line which is typical of the high-temperature coke.

This two-stage process of coke formation is very similar to that observed in the series B of the static experiments (Part I). Obviously, the static process with renewal of the reactant atmosphere prior to each heating step was a good approximation to the real on-stream situation.

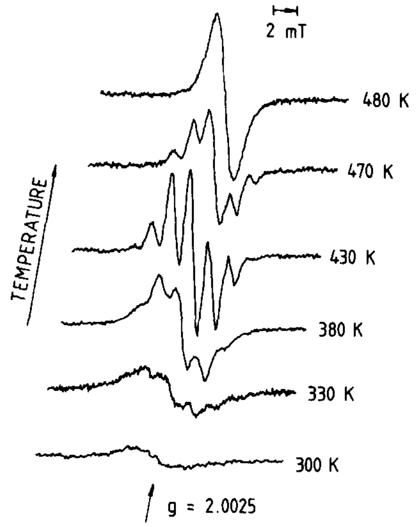


FIG. 2. EPR spectra of intermediate radicals (430 K) and high-temperature coke (480 K) during coke formation upon ethylene reaction over hydrogen mordenite, HM-1.

The static experiments mentioned above indicated that formation of the intermediate radicals requires the presence of gaseous ethylene and low-temperature coke. It was suggested that the intermediate radicals are probably formed via a reaction between gaseous ethylene and the coke deposited on the zeolite rather than by oxidation or homolytic cracking of the deposited low-temperature coke. This is supported by the results presented in Fig. 3. Here, the conversion of ethylene was monitored by gas chromatography. Significant consumption of ethylene was observed concomitant to the formation of the intermediate radicals.

The number of intermediate radicals was shown to decrease strongly with decreasing Al content of the zeolite (Fig. 4). This can be attributed to a decreasing number of acidic sites, which are required for (i) oligomerization and (ii) radical formation. The protonating capability (Brønsted acidity), which is required for olefin oligomerization, polymerization, and formation of low-temperature coke (*2*), corresponds to the number of tetrahedrally coordinated Al, whereas the electron acceptor capacity

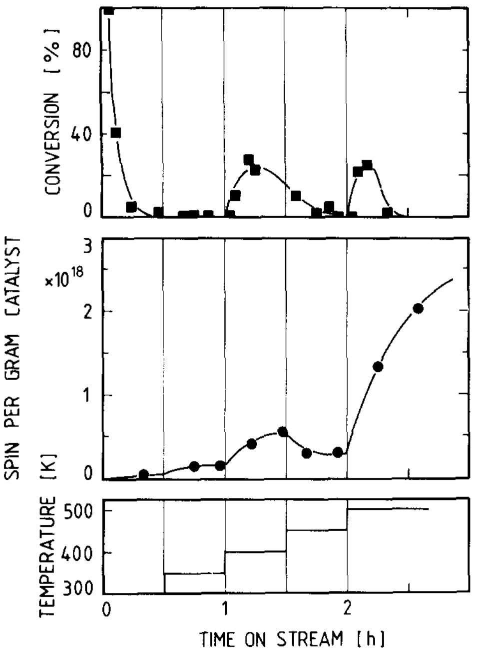


FIG. 3. Conversion and number of radicals as a function of the temperature during the reaction of ethylene over hydrogen mordenite, HM-1.

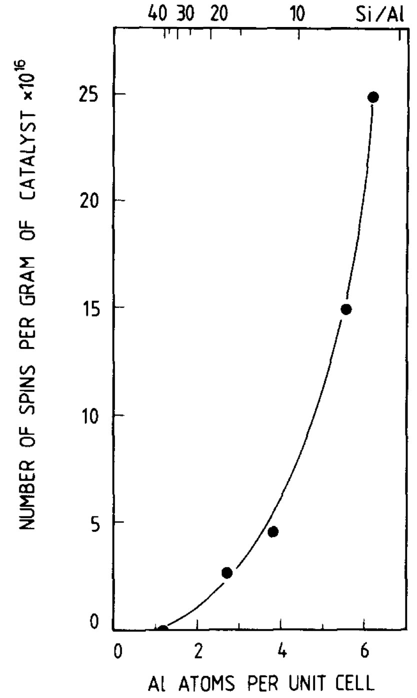


FIG. 4. Number of intermediate radicals as a function of the Al content of hydrogen mordenite, after 14 h of ethylene stream at 430 K.

should be related to the extra-framework aluminum, i.e., possibly to certain types of Lewis sites [compare Ref. (*1*)]. As was pointed out in Part I of this study, Lewis sites might be responsible for the second step, i.e., generation of radicals from oligomeric hydrocarbon species deposited onto the zeolite and subsequent radical stabilization. Both types of site obviously decrease with decreasing overall Al content (compare Table 1). This accounts for the observed decrease in the number of radicals as a function of decreasing Al content as demonstrated in Fig. 4.

The seven-line spectrum showed a weak asymmetry, which was even more pronounced in the spectrum recorded at Q-band frequency (Fig. 5). This finding suggested that the *a* and *g* values are anisotropic; i.e., the radicals do not undergo rapid random tumbling inside the zeolite channels. Since freezing of the radicals at 10 K did not result in any change of their hyperfine spectrum (Fig. 6), the assumption is strongly supported that the motion of the radicals is restricted already at the higher temperatures where they had formed. The main fraction of the radicals was stable over a period of months, even after having been brought into contact with oxygen. However, it could not be decided whether the radicals were inherently stable or, rather, were stabilized or protected by the zeolite matrix.

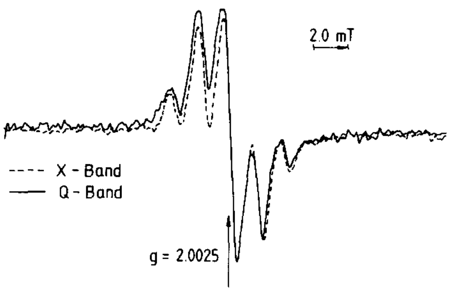


FIG. 5. EPR spectra of intermediate radicals at X- and Q-band frequencies.

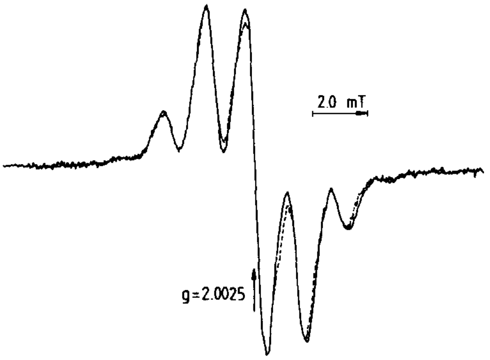


FIG. 6. EPR spectra of the intermediate radicals at 300 K (dash line) and 9.5 K (solid line).

Ayscough *et al.* (*3*) reported that irradiation of allyl-chloride glasses, yielding most probably allyl radicals, gave rise to a weakly asymmetric spectrum very similar to the seven-line spectrum of Fig. 2. Therefore, the seven-line spectrum is very probably due to olefinic or allylic radicals, i.e., to $[{>}C{=}C{<}]^{\cdot+}$ or $[{>}C{=}C{=}C{<}]^{\cdot}$. Since the spectrum comprises more than five lines, it cannot be ascribed to ethylene radicals but must be generated from an oligomeric product. A more precise interpretation seems possible only by computer simulation of the seven-line spectrum using anisotropic a and g parameters.

High-Temperature Coke

When heated to temperatures higher than about 500 K, the adsorbate showed only the single EPR line of high-temperature coke. This line developed instantaneously when ethylene was conducted above 480 K through a freshly activated HM-1 zeolite, without intermittent appearance of the seven-line spectrum. Indeed, this finding does not completely exclude that the intermediate radicals are indicative of inevitable precursors of the high-temperature coke since their steady-state concentration may be below the limit of detection. However, in view of the high sensitivity of EPR spectroscopy one can conclude that the lack of spectroscopic evidence renders it unlikely that the intermediate radicals are precursors of high-temperature coke species (compare Ref. (*1*)). Only after short contact times, the single line exhibited traces of the hyperfine structure with a = 0.18 mT, as was reported by Kucherov and Slinkin (*4*, *5*) and in Part I (*1*) of this study; this hyperfine structure was attributed to 1,2-dialkylphenylene radicals.

With time on stream the intensity of the single line steadily increased, but finally approached a constant value (Fig. 7). The initial rate of coke formation was higher at higher reaction temperatures. The growth of the signal intensity did not follow the empirical equation proposed by Voorhies (*6*). Instead, a first-order relationship was observed between the number of radicals, n, and the time on stream, t,

$$n(t) = n(\infty)[1 - \exp(-kt)], \tag{1}$$

as shown by the fitting of the solid lines of Fig. 7a, which were calculated according to Eq. (1), to the experimental data.

The linewidth first increased to a maximum of around 1.3 mT and subsequently

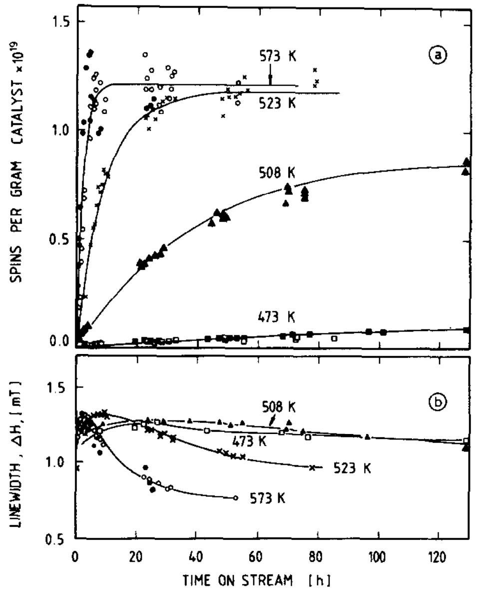
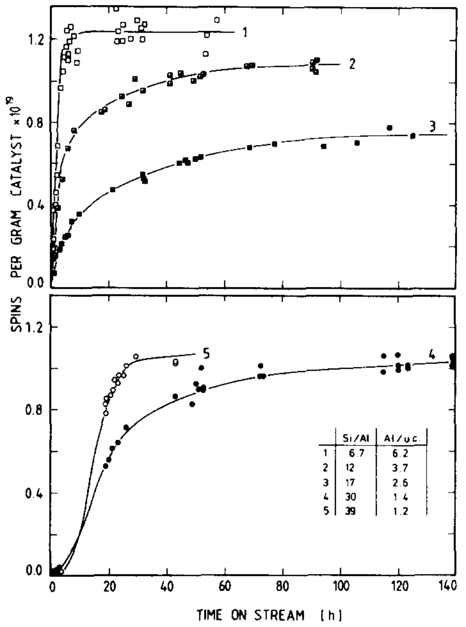


FIG. 7. (a) Intensity and (b) width of the high-temperature coke signal as a function of time on stream, during reaction of ethylene over hydrogen mordenite, HM-1, at various temperatures.



	Si/Al	Al/u.c.
1	6.7	6.2
2	12	3.7
3	17	2.6
4	30	1.4
5	39	1.2

FIG. 8. Intensity of the high-temperature coke signal as a function of time on stream, during reaction of ethylene over hydrogen mordenites of various Al content.

decreased, more pronouncedly at higher reaction temperatures (Fig. 7b). Similar to the results obtained with carbonized materials (*7–9*), the narrowing of the single line could be attributed to a decrease in hyperfine splitting. This is supported by the experiments under static conditions (see Part I) where a decrease of the hyperfine splitting constant a from $a = 0.18$ mT to 0.1 mT and below was observed. However, a contribution from the exchange narrowing effect to the narrowing of the linewidth cannot be excluded here. The g value of the single line, however, remained at 2.0024 during the entire carbonization process.

The rate of formation of high-temperature coke radicals also proved to be dependent on the acidity of the zeolite (Fig. 8). When the Al content of the mordenite decreased, the initial rate first decreased as well. In fact, below approximately 2 Al atoms per unit cell, i.e., above a Si/Al ratio of 20, a pronounced induction period of 5 to 10 h occurred, but thereafter the rate of coke formation increased very sharply. The lower the Al content, the higher was the rate of coking subsequent to the induction period. The very same feature was observed when the total deposition of coke was monitored by *in situ* TGA. This complex behavior is not yet understood. Nevertheless, it seems to indicate that the electron acceptor properties of the zeolite, which may be determined by the Al content, are insufficient to explain the formation of high-temperature coke. However, detailed analysis of the distribution of Al on tetrahedrally coordinated (framework) and octahedrally coordinated (extra-framework) sites by means of ^{27}Al MAS NMR seems to be necessary to clarify this problem further.

Interestingly, the radicals of low-temperature coke and high-temperature coke behave differently upon a change in the Al content in the zeolite (compare Figs. 4 and 8). This is in agreement with the assumption that there is no simple relationship between both types of coke and that the intermediate radicals are probably not necessary precursors of the high-temperature coke (see above).

Characterization of High-Temperature Coke Radicals

In these experiments the paramagnetic behavior attributed to free radicals was studied in more detail. The experiments were expected to provide further insight into the nature of high-temperature coke.

As is demonstrated in Fig. 9, the reciprocal intensity of the EPR signal of high-temperature coke increased linearly with the temperature of measurement, thus following the Curie law. Hence, the paramagnetism is indeed due to free radicals in a doublet state, $S = \frac{1}{2}$.

To determine the relation between the total amount of high-temperature coke deposited and the number of radicals it contains, parallel EPR and thermogravimetric measurements of coke formation upon ethylene reaction over HM-1 mordenite at 573 K

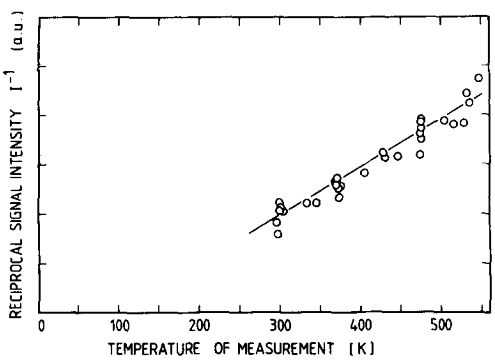


FIG. 9. Effect of temperature on the signal intensity of the high-temperature coke formed upon reaction of ethylene over hydrogen mordenite, HM-1, at 573 K.

were carried out. A linear correlation was found between the number of radicals and the total amount of high-temperature coke, expressed as a weight percentages (Fig. 10). The radical density of the high-temperature coke was constant up to the complete deactivation of the zeolite. It corresponds approximately to one radical per 500 carbon atoms. This density is much higher than that found in coke formed above 700 K on silica–alumina (*10*) and on Y-zeolite (*11*), where only one radical per 1000–10,000 carbon atoms was determined. Interestingly, the final amount of high-temperature coke deposited was almost the same, viz., 12 wt%, for all the samples under investigation, but the final numbers of spins were obviously not the same (compare Fig. 8). Thus, the spin density of the coke varied with the Si/Al ratio which might indicate that the nature of the high-temperature coke depends to some extent on the acidity of the zeolite catalyst.

The radicals of high-temperature coke were very stable; the intensity of their EPR line remained constant for months. The saturation behavior of the single line revealed that weak inhomogeneous line broadening was operative. After exposure of the sample to air, the EPR line suffered a reduction of 10 to 15% in its intensity, indicating efficient relaxation of a portion of the high-temperature coke radicals by oxygen molecules (*9*).

It has been well established that organic materials carbonized at 600 to 800 K contain stable free radicals giving rise to EPR lines similar to those observed in the current study (*7–9*). They have been interpreted as being due to highly unsaturated, most probably polyaromatic, π radicals generated by homolytic bond splitting and subsequent rearrangement reactions. These species were assumed to be not catalytically active in the carbonization process. Interestingly, such radicals exhibited properties (e.g., paramagnetic behavior) similar to those observed here for high-tempera-

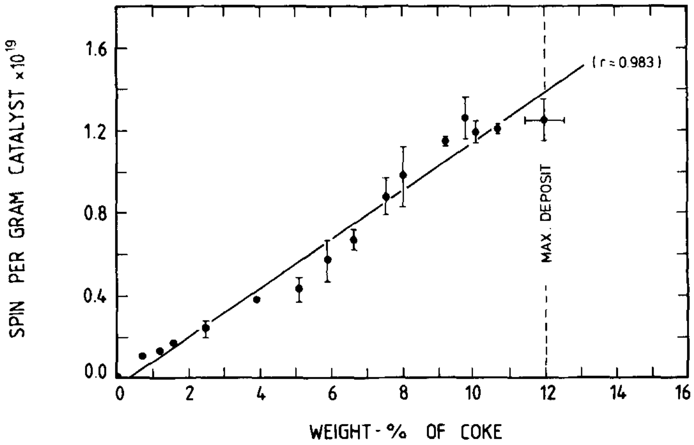


FIG. 10. Correlation between the number of radicals and the amount of high-temperature coke deposited during the reaction of ethylene over hydrogen mordenite, HM-1, at 573 K.

ture coke radicals. Completely different, however, are the properties of graphite compounds (7), which usually form at temperatures above 1000–1500 K.

Therefore, it is proposed that the radicals of high-temperature coke have a nature similar to that of radicals in organic material carbonized at 600–800 K; i.e., they are highly unsaturated, possibly polyaromatic π radicals. Their formation might involve thermal blood splitting in the deposits and be affected in a complex manner by the acidic sites related to the Al content of the zeolite. The radicals represent a final product of the carbonization rather than an active species. It can be excluded that the main part of the high-temperature coke in mordenite has a multilayer graphite-like structure.

In summary, one can state that the investigation of radicals accompanying the formation of coke on zeolite catalysts is a useful means of contributing to a better understanding of this phenomenon. In many aspects the coke radicals seem to be reliable representatives of the coke species from which they are derived by an electron transfer to (or from) the zeolite or a hydrogen abstraction. Thus, EPR spectroscopic studies of the radicals related to coke provide information about the nature of the coke species, render possible the discrimination between low-temperature and high temperature coke, and allow one to estimate, based on the measured spin density, the total amount of coke deposited onto the zeolite catalyst.

Particularly, the EPR results lead to the following characterization of the two types of coke formed upon olefin reaction over hydrogen mordenite catalyst:

(i) "Low-temperature coke," i.e., oligomers of polymers, almost paraffinic or olefinic in character, indicated by olefinic or Π-allylic radicals exhibiting multiple-line EPR spectra.

(ii) "High-temperature coke," i.e., highly unsaturated species, polyenic or aromatic in character, indicated by stable, free, and most probably polyaromatic radicals, exhibiting a single-line EPR spectrum.

CONCLUSIONS

1. Depending on the reaction temperature, the carbonization of ethylene over hydrogen mordenite can be divided into two processes, forming a low-temperature coke below 500 K and a high-temperature coke above 500 K.
2. The low-temperature coke exhibits olefinic or allylic radicals of oligometric species, particularly the so-called intermediate radicals.
3. The number of intermediate radicals decreases with decreasing Al content of the zeolite, i.e., decreasing number of acidic sites which are required for formation of oligomeric species.
4. The paramagnetism of the high-temperature coke is due to the presence of highly unsaturated, possibly polyaromatic, radicals. Those radicals do not belong to graphite-like structures.
5. The number of high-temperature coke radicals increases linearly with the amount of the carbonaceous deposits. From this correlation a density of one radical per 500 carbon atoms could be derived.
6. The reaction temperature strongly affects the rate of formation of the high-temperature coke radicals.
7. The global rate of formation of high-temperature coke radicals passes through a minimum as a function of the Al content of the zeolite. At present, there is no simple explanation for this finding.
8. No simple relationship exists between the intermediate radicals and the radicals of the high-temperature coke. It seems rather unlikely that the intermediate radicals are inevitable precursors of the high-temperature coke.

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