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Coke Formation through the Reaction of Olefins over Hydrogen Mordenite

I. EPR Measurements under Static Conditions

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Depending on the reaction temperature, the carbonization of ethylene and propylene over hydrogen mordenite can be separated into two processes. Below 500 K, radicals of a low-temperature coke develop and are subsequently annihilated. Above 500 K, highly unsaturated radicals of high-temperature coke form. The presence of reactive species in the gas phase, which approximates the on-stream situation, may affect the carbonization of the low-temperature coke. However, radicals of the low-temperature coke do not appear to be necessary precursors of the high-temperature coke. Paramagnetic centers which are detectable after dehydration of the zeolite do not interact with the adsorbed olefins to form radicals © 1988 Academic Press, Inc.

INTRODUCTION

In most hydrocarbon reactions catalyzed by zeolites, the deactivation of the catalyst due to coke deposition is a serious problem. Recently, reinforced efforts were made to elucidate the nature of the coke deposits as well as the parameters which influence its formation. Interesting review papers on this subject have appeared (*1, 2*).

For studies on coke formation, EPR spectroscopy has long been an effective technique. Free radicals were observed in thermally carbonized organic materials (*3–5*) as well as in the coke formed on solid catalysts. Interestingly, a linear relationship was found between the number of radicals and the amount of coke deposited on silica–alumina (*6*) and on Y-zeolite (*7*). Densities of about one radical per 1000–10,000 carbon atoms were reported.

As was pointed out in a number of studies, solid catalysts, particularly zeolites, exhibit redox properties (*8, 9*). Therefore, they were expected to generate radicals from adsorbed unsaturated hydrocarbons; this might occur even at room temperature. However, only a few EPR investigations were concerned with the carbonization of such radicals (*10–13*). Hence the role of these radicals with respect to the carbonization process remained to be clarified.

The EPR investigations reported in the literature were generally carried out under static conditions. Results were therefore not necessarily relevant for real on-stream processes. In order to overcome this drawback, the coke formation on-stream of olefins over acidic mordenite zeolites was approximated through a particular design of the static experiments. The results of this approach are described here. In a second step, we have studied the real process, conducting EPR measurements *in situ*, i.e., under on-stream conditions. This is the subject of Part II of the current study (*14*).

EXPERIMENTAL

Materials and Apparatus

A commercial hydrogen mordenite, with a Si/Al ratio of 7, was purchased from

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0021-9517/88 $3.00

Norton Co., Massachusetts. Ethylene (99.95%) and propylene (99.98%) were supplied by Messer Griesheim, Düsseldorf.

The EPR measurements were carried out mainly at *X*-band frequency using a Varian Model V-4502-15 spectrometer. When necessary, the spectrometer could be set at *Q*-band frequency. In order to enhance the accuracy of the intensity measurements, a double-cavity TE_{104} was employed, operating at modulation frequencies of 100 kHz and 400 Hz for the sample and the reference (diphenylpicrylhydrazyl dispersed in alumina), respectively. The EPR signals were stored and integrated by an on-line Digital Equipment PDP-11 computer. They were recorded at a microwave power sufficiently small to avoid saturation effects. Modulation amplitudes were chosen to be as small as possible, i.e., between 0.1 and 0.3 mT for recording the low-temperature coke radicals, and about 0.1 mT for the high-temperature coke radicals. The reference was regularly recalibrated using the strong pitch standard 904450-01 from Varian; hence, the radical number could be determined with a reproducibility of ±10% and an accuracy of ±25%. The *g*-values of free radicals could be measured with a reproducibility of ±0.0002.

The samples were studied in a capillary cell of 6 mm o.d. (Fig. 1) made from high-quality quartz glass (Suprasil). The cell could be connected to an ultrahigh vacuum and gas-dosing system and closed by an all-metal valve prior to dismounting and placing it in the spectrometer (*15*).

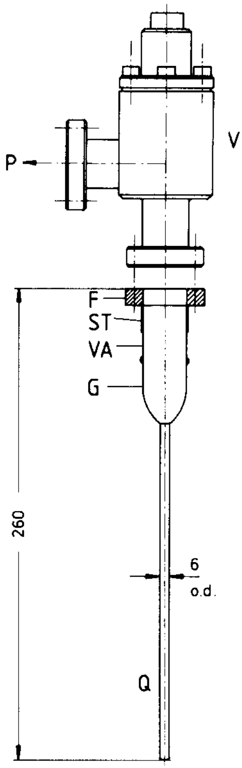

FIG. 1. EPR cell for static measurements: (P) to pump, (V) valve, (F) flange, (ST) stainless steel, (VA) VACON metal, (G) pyrex glass, (Q) quartz glass.

Procedure

The cell was filled with small grains of pressed zeolite powder (130 mg) and heated in air at a rate of 200 K/h up to 700 K. After several hours of calcination, the cell was evacuated to 10^{-6} Pa for one more hour at the same temperature and subsequently cooled to room temperature. In order to remove any traces of oxygen from the olefins, they were repeatedly frozen at 77 K and submitted to a vacuum of 10^{-6} Pa prior to the adsorption (freeze-and-thaw cycles).

Two series of experiments were carried out. In series A, the olefin was adsorbed for 5 min at 300 K under a pressure of 1 kPa. Subsequently, the residual gas phase was pumped off, the cell closed, and the sample heated stepwise under autogenous atmosphere up to 700 K and kept at each temperature for 30 min. After each heating step the cell was cooled to room temperature, and the EPR spectra were obtained.

In series B the olefin was adsorbed at room temperature under pressures between 1 and 20 kPa. The sample was also heated stepwise up to 700 K. At variance with series A, the residual gas phase was replaced by a fresh olefin atmosphere before each subsequent heating step. Thus, in series B the on-stream situation was approached.

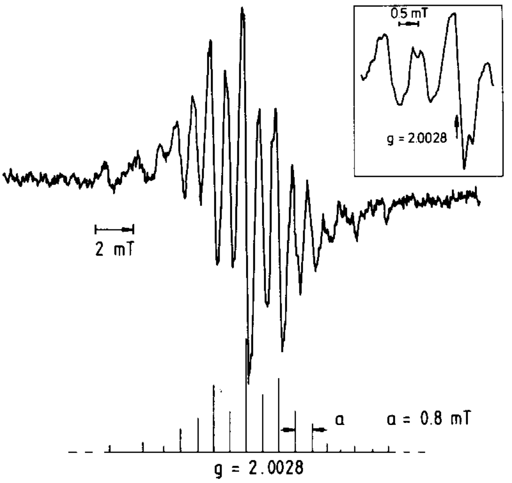

FIG. 2. EPR spectrum of the oligomeric radicals formed after adsorption of propylene on hydrogen mordenite at 300 K. Section around the central line (insert) reveals the asymmetry of the 15-line spectrum.

RESULTS AND DISCUSSION

Oligomeric Radicals

In agreement with earlier results reported in the literature (*10, 11*), the adsorption of light olefins, e.g., ethylene or propylene, on hydrogen mordenite gave rise to the appearance of an EPR spectrum composed of 15 hyperfine lines (Fig. 2). The hyperfine splitting constant of the EPR spectrum presented in Fig. 2 was 0.8 mT and the *g*-value was 2.0028. This spectrum can be ascribed to allylic or olefinic radicals of oligomeric species (*10, 11*).

It is well known that the Brønsted acidity of hydrogen forms of zeolites efficiently catalyze oligomerization and polymerization of olefins. Indeed, ethylene polymerizes on acidic mordenite already at room temperature (*16, 17*). A fraction of the so-formed oligomeric or polymeric species subsequently transforms into radicals through a transfer of either electrons or hydrogen atoms between these species and suitable acceptor (or donor) sites of the zeolite. As a result EPR signals can be detected.

As will be shown later (Fig. 9), the oligomeric radicals were not stable (*11*) but disappeared, e.g., when they were kept for some hours at 300 K. It should be mentioned that the number of oligomeric radicals is indeed very small, viz. approximately 2 × 10^{17} per gram catalyst. This figure corresponds roughly to one radical per 1000 adsorbed olefin molecules, or one radical per 1000 unit cells of the zeolite, or one radical per 6000 Al atoms. Nevertheless, there are good reasons to assume that coke radicals are representative of the overall coke, for both its nature and its amount. Thus, the formation of radicals enables us to discriminate between low-temperature and high-temperature coke (vide infra), in agreement with IR results, and to estimate the total amount of coke deposited (compare Part II (*14*)).

It had been generally assumed that the 15-line spectrum is symmetric. However, the spectrum of Fig. 2 showed a weak asymmetry which was particularly visible in the central hyperfine line. This asymmetry became more evident when the spectrum was recorded at *Q*-band frequency. The right part of the hyperfine structure was then more distinctly resolved than the left part (Fig. 3). Therefore, the 15-line spectrum should be characterized by more than one *g*-value. This could be due to different overlapping spectra, but could also originate from an anisotropy of the *a*- and *g*-values, which would occur in the

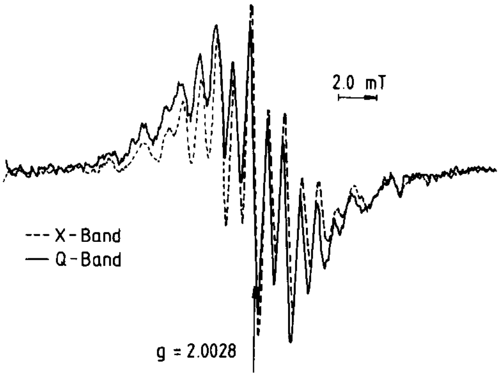

FIG. 3. EPR spectra of the oligomeric radicals recorded at *X*-band and *Q*-band frequencies.

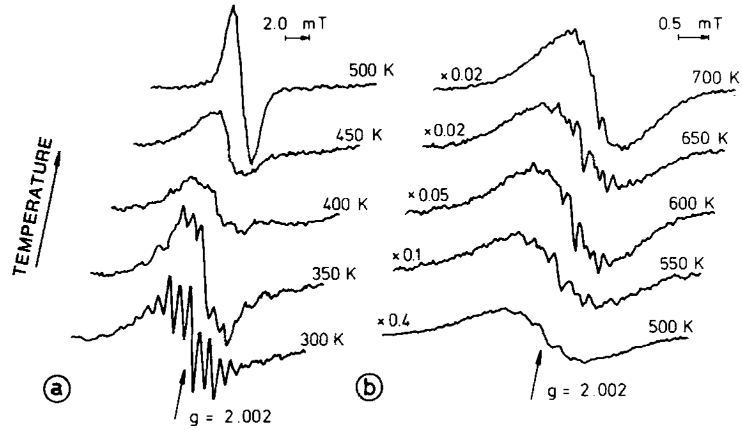

FIG. 4. EPR spectra recorded after carbonization of ethylene on hydrogen mordenite under autogenous atmosphere (series A). (a) Low-temperature coke; (b) high-temperature coke.

case of insufficient tumbling of the radicals. Therefore, at present no definite interpretation of the 15-line spectrum can be proposed. However, it seems reasonable to assume tentatively that a mixture of variously substituted olefinic or allylic radicals, $[{>}C{=}C{<}]^{\cdot +}$ or $[{>}C{=}C{=}C{<}]^{\cdot}$, are involved. The 15-line spectrum would then result from overlapping of several spectra characterized by a = 1.6 mT, some of them exhibiting an odd number of hyperfine lines and others an even number.

Carbonization Processes

Under autogenous atmosphere (series A), adsorbed ethylene and propylene yielded coke in a similar manner. The hyperfine structure of the 15-line spectrum vanished completely upon heating to 500 K (Fig. 4), in agreement with the observation of earlier authors (*10, 11*). However, the number of radicals decreased (Fig. 5). Obviously, the oligomeric radicals were annihilated by reactions such as recombination or disproportionation. Deposits formed up to about 500 K were referred to as "low-temperature coke" and thereby distinguished from those formed at higher temperatures. Above 500 K, the EPR line of the "high-temperature coke" appeared with g = 2.0024. It exhibited a hyperfine structure with a = 0.18 mT, which has been attributed to 1,2-dialkylphenylene radicals (*11*). With a further increase in the temperature the line of the high-temperature coke

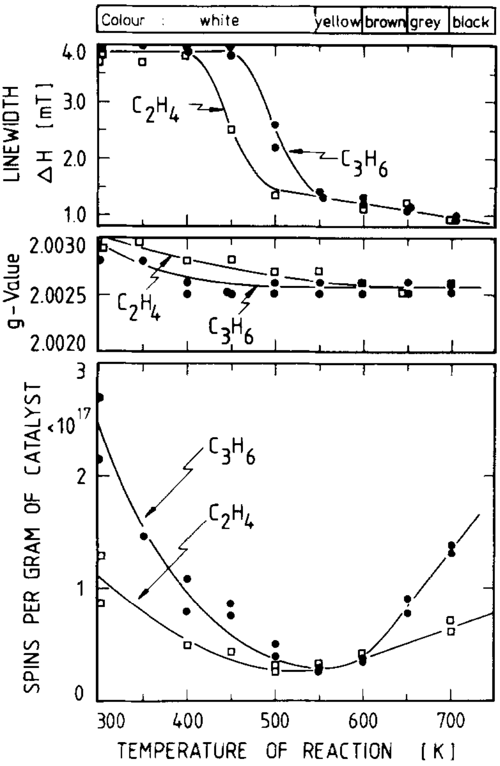

FIG. 5. Intensity, g-value, and linewidth of the EPR spectra recorded after carbonization of ethylene and propylene on hydrogen mordenite under autogenous atmosphere (series A).

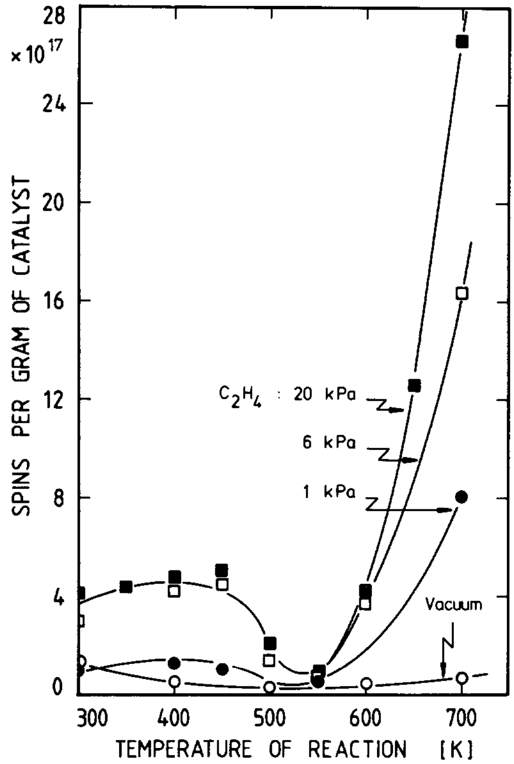

FIG. 6. Intensity of the EPR spectra recorded after carbonization of ethylene over hydrogen mordenite under ethylene atmosphere of varying pressures, renewed after each heating step (series B).

continued to grow. Concomitantly, the splitting constant decreased to 0.1 mT and below, and the hyperfine structure finally disappeared. Hence, the structure of 1,2-dialkylphenylene might represent only an intermediate form of the high-temperature coke. Further characterization of low- and high-temperature coke is given in Part II (*14*) where the results are summarized.

In the case of propylene, the presence of a renewed atmosphere of reactive gas (series B) did not essentially affect the coke formation. As could be expected, the number of high-temperature coke radicals increased more steeply the higher the pressure of propylene.

Ethylene, however, formed coke under a stepwise renewed atmosphere of ethylene (series B) in a way different from that under autogenous atmosphere (series A). Here, when the temperature was raised to 450 K, the number of radicals did not decrease but intermittently increased (Fig. 6). Simultaneously a new EPR spectrum developed with seven hyperfine lines, a hyperfine splitting constant of a = 1.6 mT (Fig. 7), and a g-value of 2.0025. The corresponding radicals will be referred to as intermediate radicals. They are ascribed to olefinic or allylic radicals, which are almost frozen in the zeolite channels (compare Part II and Ref. (*18*)) and similar to those of Fig. 1. In contrast to the spectrum of Fig. 1 (with a = 0.8 mT) the EPR spectrum of the intermediate radicals (a = 1.6 mT) is not composed

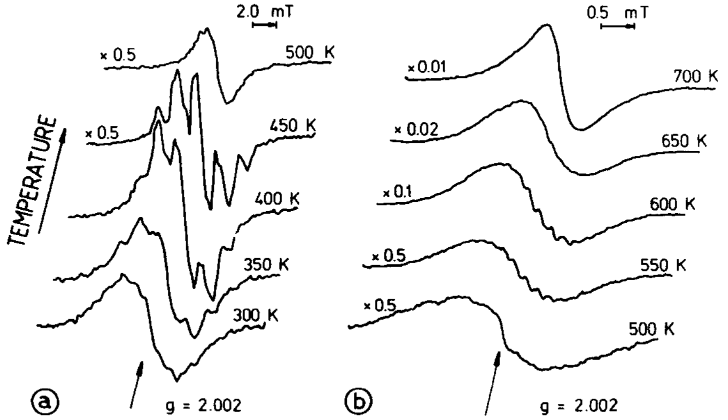

FIG. 7. EPR spectra recorded after carbonization of ethylene over hydrogen mordenite under an atmosphere of 20 kPa ethylene, renewed after each heating step (series B). (a) Low-temperature coke; (b) high-temperature coke.

of a superimposition of several spectra. Thus, the intermediate radicals appear to be more uniform.

The higher the ethylene pressure, the greater the number of radicals (Fig. 6). By a further increase in the temperature, the seven-line spectrum started to collapse into the single line of high-temperature coke (Fig. 7), and the number of radicals decreased. When, finally, temperatures higher than 500 K were reached, the formation of coke proceeded similarly to its formation under autogenous atmosphere (compare Figs. 4b and 7b). Again, the higher the pressure of reactive gas, i.e., ethylene, the steeper the increase in the radical numbers of the high-temperature coke. In any case, it is evident from Figs. 6 and 7 that EPR spectrometry provides a means to discriminate unambiguously between the temperature regions where low-temperature and high-temperature coke is formed upon olefin reaction over hydrogen mordenite catalysts.

Interestingly, this carbonization process was also observed under on-stream conditions (Part II). Obviously, a stepwise renewed gas phase provided a relatively good approximation to the on-stream situation.

The presence of gaseous ethylene seems to be necessary for the formation of the intermediate radicals. Hence, the intermediate radicals are unlikely to form by the transformation of an oligomeric adsorbate, e.g., by homolytic cracking. They are more probably generated by a reaction between the gaseous ethylene and the adsorbate held by the zeolite. It is demonstrated in Fig. 4 that the radicals related to the 15-line spectrum have largely disappeared at temperatures lower than those at which the "intermediate" radicals form. Therefore, it is unlikely that ethylene reacts with the 15-line species to give the intermediate radicals. However, from the EPR data the exact nature of the adsorbate held by the zeolite is not known. Concomitant IR, ^{13}C NMR, and UV–Vis spectroscopic investigations suggest that the original oligomers held on the catalysts (i) were isomerized to more branched molecules (*19*), (ii) have already lost a significant amount of hydrogen, and (iii) were to some extent transformed to polyenes (*20*) when the intermediate radicals appeared.

The reason why the intermediate radicals do not form under a gas phase of propylene is not yet completely clear. It seems possible that the low-temperature coke generated from propylene is more bulky than that deposited from ethylene. Consequently, further sorption of the olefin might be hindered and, hence, the formation of the intermediate radicals impeded.

The present results further indicate that the intermediate radicals are probably not a necessary precursor of the high-temperature coke. After adsorption onto mordenite, both ethylene and propylene carbonize to high-temperature coke in a similar way, although only ethylene is able to form intermediate radicals.

Paramagnetic Centers of the Zeolite

In an attempt to obtain more insight into the nature of possible redox centers of the zeolite catalysts and their role in coke formation, we have monitored the behavior of the observable paramagnetic centers during the reaction of olefins.

First, particular attention was paid to the EPR lines of iron cations. The dehydrated hydrogen mordenite showed two lines, a sharp one with a g-value of 4.34 and a broad one with a = 30 mT and g = 2.05 (Fig. 8). They have been ascribed to tetrahedrally and octahedrally coordinated Fe^{3+} ions, respectively (*21*, *22*). After adsorption of ethylene both lines remained practically unchanged. Obviously, these paramagnetic centers were not responsible for the formation of the oligomeric radicals. During the reaction of olefins above 500 K, however, both iron lines vanished, to be replaced by a broad line with approximately g = 3.0 which could be attributed to amorphous iron oxide (*21*, *22*). The high-temperature

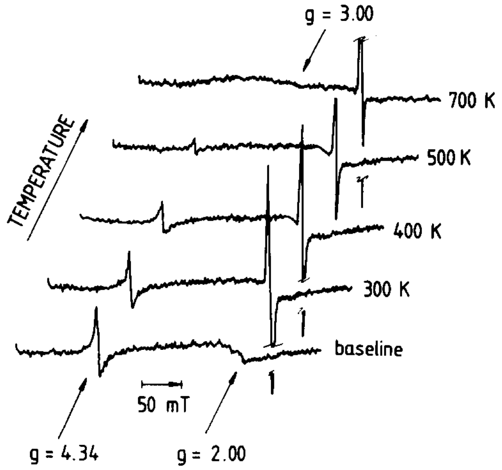

FIG. 8. EPR spectra of iron impurities in hydrogen mordenite before (base line) and after adsorption of ethylene at 300 K and subsequent heating under autogenous atmosphere to increasing temperatures.

coke probably distorted the coordination sphere of the iron cations.

Another type of paramagnetic center was also observed. When mordenite was dehydrated in air, a very weak EPR line appeared with a *g*-value of 1.977 and a linewidth of 5 mT (Fig. 9a). This line did not tend to saturate even at the highest available microwave power. The corresponding centers are most probably impurities of transition metals, e.g., titanium or vanadium (*23, 24*), although adsorbed species like CO_2^- cannot be ruled out (*25*).

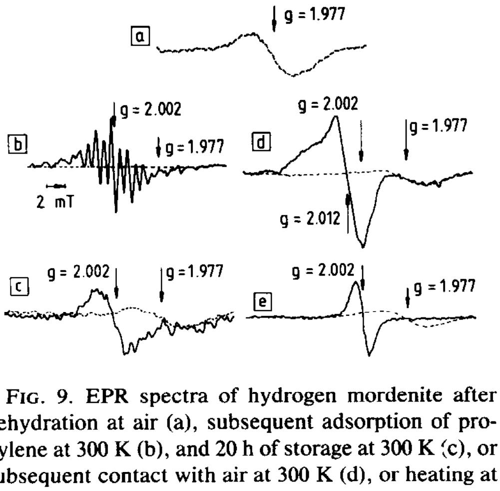

FIG. 9. EPR spectra of hydrogen mordenite after dehydration at air (a), subsequent adsorption of propylene at 300 K (b), and 20 h of storage at 300 K (c), or subsequent contact with air at 300 K (d), or heating at 550 K (e).

Because of the overlapping of the 15-line spectrum (Fig. 9b), it could not be stated whether those paramagnetic centers at $g = 1.977$ were still present and unchanged after the adsorption of the olefin. However, the centers could be observed again after the 15-line spectrum had disappeared due to a slow annihilation of the oligomeric radicals at room temperature (Fig. 9c) or after reaction of the oligomeric radical with oxygen (Fig. 9d) which resulted in a spectrum with $g_{\parallel} = 2.040$ and $g_{\perp} = 2.012$ ascribable to hydrocarbon peroxide radicals. It seems that the paramagnetic centers do not react with the olefins to form oligomeric radicals. Similarly to the iron lines, the line with $g = 1.977$ disappeared completely after formation of the high-temperature coke radicals (Fig. 9e). Again, formation of high-temperature coke probably distorted the coordination sphere of the paramagnetic centers.

In conclusion, the paramagnetic centers existing in the hydrogen mordenite are not responsible for the formation of coke radicals. However, by a large number of IR investigations it has been well established that mordenites nearly always possess so-called Lewis acid sites (e.g., only threefold coordinated Al, Al—). This has also been shown for the samples used in the present study. Such Lewis sites may well function as electron acceptor sites. Some evidence was obtained that these sites indeed accommodate hydrogen radicals (*26*). Similarly, they might be involved in formation and/or stabilization of radicals during coke formation.

CONCLUSIONS

1. The carbonization of ethylene and propylene over hydrogen mordenite could be separated into two processes yielding low-temperature coke or high-temperature coke.
2. Heating of the low-temperature coke resulted in the formation and subsequent

annihilation of oligomeric radicals, indicated by a 15-line spectrum with $a = 0.8$ mT.

3. Through reaction with gaseous ethylene, the low-temperature coke formed intermediate radicals, indicated by a 7-line spectrum with $a = 1.6$ mT.

4. Neither the oligomeric radicals (15-line species) nor the intermediate radicals (7-line species) seemed to be necessary precursors of the high-temperature coke (see also Part II).

5. The number of radicals due to high-temperature coke increased with the partial pressure of olefin in the gas phase contacting the zeolite catalyst.

6. The presence of a stepwise renewed gas phase of reactive olefin proved to be a good approximation of the on-stream situation.

7. Mordenite contained various observable paramagnetic impurities, including iron cations. None of the paramagnetic centers were observed to react with the olefins and to be involved in formation of the oligomeric radicals.

ACKNOWLEDGMENT

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