JOURNAL OF CATALYSIS **113**, 525–528 (1988)

NOTES

Carbonization of Polyethylene over Acidic Zeolites

When ethylene reacts over acidic mordenites at low temperatures, e.g., at 300 K, an IR spectrum similar to that of polyethylene is observed. Thus, acidic mordenites strongly catalyze polymerization of olefins, as has been reported in earlier papers (*1*, *2*). Moreover, it is also known from IR measurements that carbonization of polymerized olefins over acidic zeolites is responsible for the deactivation of the zeolite catalysts in many hydrocarbon reactions (*3*). However, the question arises whether further transformations of the polymers, having formed over acidic zeolites, e.g., mordenites, are influenced by the catalytic properties of the zeolite as well or whether the polymers rather behave like common polyethylene. Therefore, coke formation during the carbonization of polyethylene formed over hydrogen mordenite has been studied using ESR and ^{13}C NMR. To distinguish the roles of ethylene and polyethylene on zeolite in this process, similar experiments were conducted for the carbonization of solid polyethylene. ESR measurements were performed using a Varian Model V-4502-15 *X*-band spectrometer equipped with a Digital PDP-11 computer. A double-cavity TE_{104} was employed, operating at two modulation frequencies, 100 kHz for the sample and 400 Hz for the reference, DPPH dispersed in alumina. An appropriately designed ESR variable-temperature flow reactor allowed *in situ* monitoring of the carbonization process (*4*). ^{13}C NMR/CP/MAS spectra were obtained using a Bruker CXP-300 spectrometer.

Within the flow reactor in the ESR cavity commercial hydrogen mordenite (Si/Al = 6.8) was pretreated in a nitrogen stream at 670 K and then cooled to room temperature. Subsequently, it was exposed to a stream of 8% (v/v) ethylene in nitrogen at the specific temperatures at which ESR experiments were also conducted. For NMR studies, at each temperature the activated catalyst was exposed to the ethylene/nitrogen stream for 16 h and then placed in the Andrew-type rotor.

For ESR experiments using solid polyethylene, the sample was preheated (temperature range 300–700 K) under vacuum for 30 min and then cooled to room temperature, after which the ESR spectra were obtained. For NMR experiments the sample was sequentially preheated, cooled, ground to powder, and placed in the NMR rotor.

The ESR signal observed after the ethylene/nitrogen stream had been passed over the catalyst at room temperature was very weak. When the experiment was repeated at 420 K, an isotropic seven-line spectrum developed, with a g factor of 2.0025 and a hyperfine splitting constant of $a = 1.4–1.6$ mT (Fig. 1). For experiments performed above 470 K the seven-line spectrum was not detected, but instead a single-line coke spectrum ($g = 2.0024$) was observed (*5*), the intensity of which increased with increasing temperature.

Since the spectrum at 420 K comprises more than five lines, it cannot be due to ethylene radicals. Thus the spectrum is indicative of oligomeric radicals. The value of the splitting constant for the low-temperature spectrum indicates that the signal arises from radicals which have an olefinic or allylic nature (*6*, *7*). Ayscough and Evans (*6*) observed, after γ-irradiation of vit-

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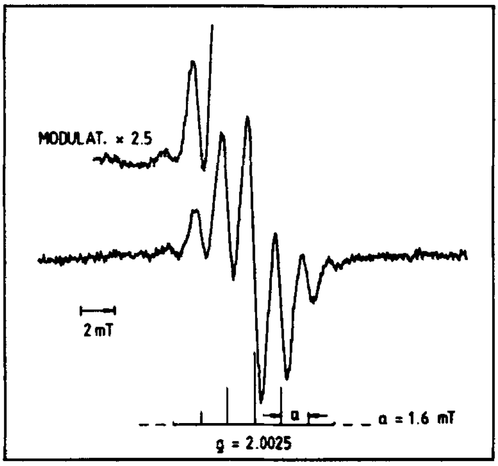

FIG. 1. *In situ* ESR spectrum of C_2H_4 over H mordenite; olefinic or allylic radicals formed at 420 K.

reous allyl chloride, a similar spectrum, viz. with $a = 1.6 \pm 0.2$ mT. From the hfs constant and the number of lines, however, it is not possible to derive unambiguously the structure of the respective radical species. The observed EPR spectrum could originate from allylic species like $[H_3C{-}CH{=}CH{=}CH_2]^{\cdot}$ or $[H_3C{-}CH{=}CH{=}CH{-}CH_3]^{\cdot}$, etc., but could be indicative of olefinic radicals like $[H_3C{-}CH{=}CH_2]^{\cdot +}$ or $[CH_3{-}CH{=}CH{-}CH_3]^{\cdot +}$, etc., as well. Without extensive computer simulation one is unable to decide which of the possible structures is definitely responsible for the spectrum observed even though assumption of a π-allylic structure seems to be more likely. However, in the present context it is sufficient to state that the seven-line spectrum with $a = 1.6$ mT indicates oligomerization of the olefin on the zeolite catalyst prior to or during heat treatment since more than the four hydrogen atoms of ethylene are required to give seven hf lines. Moreover, the spectrum is typical of so-called low-temperature coke and can be used for discriminating that type of carbonaceous deposit from high-temperature coke formed above 450 K.

The ^{13}C NMR/CP/MAS spectrum of ethylene adsorbed at 300 K (Fig. 2) is consistent with oligomerization of ethylene to linear and branched paraffins (several lines between 18 and 40 ppm). Components which may give rise to signals within this range include (*8*, *9*)

$CH_3{-}CH_2{-}CH_2{-}$ with lines at 18, 24, and 33 ppm, respectively,

$(CH_3)_2{-}CH{-}CH_2{-}$ with lines at 24, 30, and 41 ppm, and

$CH_3{-}CH{=}CH{-}CH_2{-}$ with lines at 18, 124, and 33 ppm.

For the spectrum of ethylene adsorbed at room temperature, the weak line at 124 ppm may include some intensity due to ethylene. Above 420 K the olefin line at 124 ppm is not observed, and the lines at 23–26 ppm are more intense. An explanation for these data is that olefinic components and linear paraffins are partially isomerized to branched species.

Cycloparaffins may have also been formed. A weak signal which appeared at

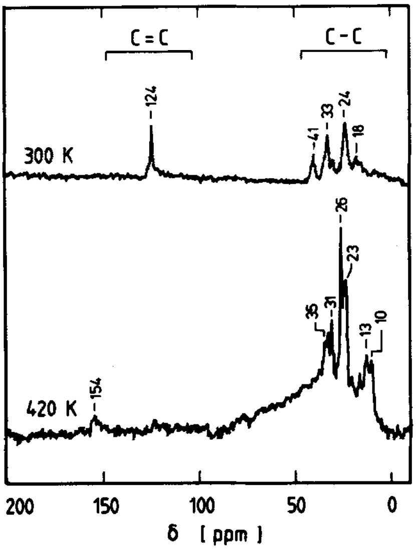

FIG. 2. ^{13}C NMR/CP/MAS spectrum of C_2H_4 over H mordenite; oligomerization at 300 K, and isomerization at 420 K (experimental conditions: acquisition time, 0.041 s; repetition time, 4 s; number of scans, 900 at 300 K, 2000 at 420 K; rotation frequency, 4.5 kHz; contact time, 5 ms; standard, TMS).

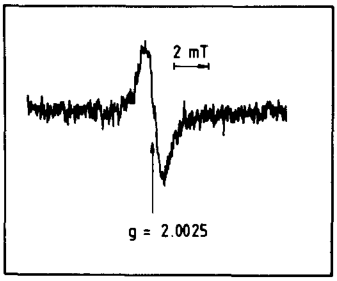

FIG. 3. ESR spectrum of solid polyethylene heated to 700 K.

154 ppm has not been identified, but could arise from linear and branched olefins or carbocations (*9*, *10*).

To test whether or not the seven-line spectrum arises from a product of homolytic cracking of the oligomer, the thermal cracking of solid polyethylene has also been studied. At temperatures at or above 500 K, evolution of gas from polyethylene was observed, which is due to thermal cracking of the polymer. However, the signal of so-called high-temperature coke with $g \approx 2.00$ was first observed for a preheating temperature of 700 K (Fig. 3). No hyperfine splitting was resolved for this line. For each experiment up to 700 K the NMR spectrum consists of a single line close to 31 ppm, attributed to the CH_2 groups of the polymer (Fig. 4).

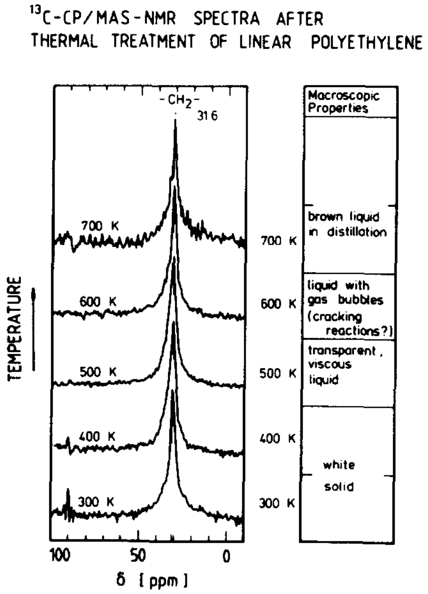

FIG. 4. ^{13}C NMR/CP/MAS spectrum of heated solid polyethylene; the spectrum does not change in the temperature range 300–700 K (experimental conditions: acquisition time, 0.010 s; repetition time, 5 s, number of scans, 100; rotation frequency, 4.5 kHz; contact time, 5 ms; standard, TMS).

The experiments with common polyethylene show that the polymer, which is not supported by the acidic zeolite, starts to crack around 500 K. Nevertheless, the main structure remains that of a linear paraffin up to 700 K. The results are in agreement with a thermal cracking mechanism, i.e., homolytic bond cleavage (*11*). No spectrum with hyperfine splitting was obtained during the thermal cracking of commercial polyethylene, the carbonization process (i.e., the first occurrence of the ESR signal of high-temperature coke) was observed at 700 K (vide supra).

Both ^{13}C NMR and ESR spectra of ethylene adsorbed onto acidic mordenite below 420 K confirm that polymers are formed, in agreement with earlier IR results (*1*, *2*). At variance with the experiment with commercial polyethylene, the ESR spectrum of polyethylene formed on hydrogen mordenite showed up to 470 K a hyperfine structure ascribable to olefinic or π-allylic species. Comparison of the two experiments suggests that the appearance of the olefinic or allylic species during ethylene reaction over hydrogen mordenite is due not to a homolytic cracking of previously formed oligomers but to an interaction with the zeolite.

In contrast to common polyethylene, which is not supported by acidic zeolites, the polymers formed on acidic mordenite are transformed into so-called high-temperature coke and indicated by a single ESR line with $g \approx 2.00$ at temperatures as low as 470 K. This result provides evidence that the mordenite catalyst not only is responsible for the polymerization of ethylene but also is involved in subsequent coke formation from the supported polyethylene.

ACKNOWLEDGMENTS

The authors thank Dr. Alan Sanger (Alberta Research Council, Edmonton, Canada) for helpful discussions. Financial support of the Bundesminister für Forschung und Technologie (Forschungsvorhaben 03C 231 1) is gratefully acknowledged.

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A. GUTSZE[1]
J.-P. LANGE
H. G. KARGE[2]
J. ALLGEIER[3]

Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, 1000 Berlin (West) 33,
Germany (FRG)

Received May 15, 1987; revised March 17, 1988

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[1] On leave from the Department of Biophysics, Medical Academy Bydgoszczy, Poland.

[2] To whom correspondence should be addressed.

[3] Present address: Freie Universität, Fachbereich Physik, Berlin (West), Germany (FRG).