

STUDIES ON COKE FORMATION ON DEALUMINATED MORDENITES BY IN-SITU IR AND EPR MEASUREMENTS

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ABSTRACT

Coke formation during dealkylation of ethylbenzene and reaction of ethylene over dealuminated mordenites was followed by simultaneous in-situ IR spectroscopic and conversion measurements as well as by in-situ EPR spectroscopy.

A close correlation emerged between the Si/Al ratio, the number of Brønsted acid sites and the coking tendency of the mordenite catalysts. The rate of deactivation was similar for two catalysts with different Si/Al ratios, in agreement with TPD results according to which these catalysts had sites of similar strength. EPR results suggest that at low reaction temperatures ($T < 373$ K), oligomeric radicals had formed, indicated by a signal at $g=2.0028$ with hyper-fine structure, whereas at higher temperatures a single coke signal appeared. It cannot be excluded that the oligomeric radicals were precursors of the coke; however, no simple relationship between both species was established. Coke formation seemed to proceed via a carbenium ion rather than a radical mechanism.

INTRODUCTION

With most hydrocarbon reactions catalysed by zeolites, deactivation of the catalyst due to coke deposition is a serious problem. More recently, reinforced efforts were made to elucidate the nature of coke as well as the parameters which influence coke formation (1 - 5). A particularly interesting question is that of the mechanism of coke formation. IR studies on coke formation are particularly useful, since they simultaneously may provide information about changes in the properties of the catalyst (e.g. concentration and involvement of surface OH groups), constituents of the deposited coke (e.g. saturated or aromatic hydrocarbons) and the amount of the carbonaceous deposits present on the surface (measured, e.g., through the intensity of the so-called coke band around 1585 cm^{-1} (3,6)). However, there have been not too many of such investigations, and they generally were designed

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for static conditions. Only a very few in-situ experiments have been reported, where the zeolite catalyst was studied under on-stream conditions (4,7 - 9). Similarly, all the EPR experiments which were concerned with deactivation of zeolites via coke deposition seem to be conducted under static conditions. Thus, Kucherov and Slinkin (10-11) recently reported interesting results of olefin adsorption and static interaction with mordenite. Typical EPR signals with remarkable hyper-fine structure (hfs) were observed and their changes with temperature were followed. As is well-known from the literature (12-13), at higher temperatures coking of organic material usually results in the appearance of a typical single EPR line with a g-value close to that of free electrons (2.0023). It seemed worthwhile to investigate both the radicals with hfs, which may or may not be precursors of the coke, and the coke itself in dynamic experiments, i.e. on catalysts under stream. The aim of the current study was to test the in-situ technique and to correlate dynamic IR and EPR results. This paper presents first results of that approach.

EXPERIMENTAL

Materials. Commercial hydrogen mordenite, HM (No.1, Si/Al = 6.8), was purchased from Norton Comp., Mass. Dealuminated hydrogen mordenite was prepared in the laboratory of Professor Fetting, TH Darmstadt, via treatment of sodium mordenite with hydrochloric acid; the sodium mordenite had been supplied by Norton Comp.

Two differently dealuminated HM samples were used (No.2, Si/Al = 12 and No.3, Si/Al = 39). Ethylene (99.95 vol.%) was purchased from Messer-Griesheim, Düsseldorf; ethylbenzene was obtained from Merck, Darmstadt, and carefully purified using a distilling column.

Apparatus and procedure. The IR flow reactor cell, which was integrated into a set-up for catalytic experiments, has been described in detail elsewhere (8). Operation of the cell and experimental procedure were, however, somewhat modified. After activation of the catalyst wafer in high vacuum at 673 K and subsequent cooling to 350 K, a stream of ethylbenzene (0.8 kPa) in He, containing 2 vol-% CH₄ as an internal standard, was passed under normal pressure through the wafer. At such a low temperature, practically no reaction occurred, in particular no coking. When a steady state was reached as shown by the gas chromatograph (constant CH₄ reference peak) the temperature was raised to 550 K within three minutes. Immediately, dealkylation of ethylbenzene started and, as a result of subsequent reaction of ethylene,

deactivation due to coke formation set in. This was followed by GC determination of the conversion of ethylbenzene (and the yield of benzene and diethylbenzenes). The deactivation was also traced via the IR spectra, which were simultaneously scanned in short time intervals by a computerized Perkin-Elmer Model 580B spectrometer.

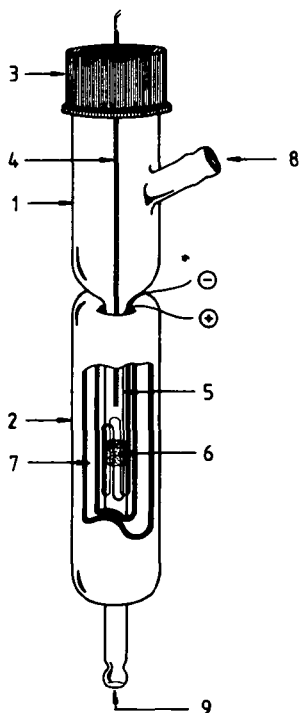


Figure 1.

Flow reactor for EPR in-situ measurements.

(1) reactor tube; (2) Dewar; (3) cap with rubber sealing; (4) thermocouple; (5) heating wire; 0.05 mm diam. Pt; (6) catalyst sample; (7) high vacuum (8) inlet; (9) outlet.

EPR measurements were carried out at X-band frequency with a Varian Model V-4502-15 spectrometer, equipped with a Digital MF-211 computer. A double cavity TE_{104} was employed. Thus, two modulation frequencies (100 kHz and 400 Hz) could be used, which allowed independent measurements of the signal of the sample (e.g. coke, at 100 kHz) and the signal of the reference (e.g. DPPH, at 400 Hz). This arrangement greatly enhanced the accuracy of the measurements of intensities and g-values.

In-situ EPR measurements have been rendered possible by a particularly designed reactor, which could be placed into the resonance cavity of the spectrometer. A schematic drawing of the reactor is presented in Figure 1.

The reactor permitted reactions to be carried out within a temperature range from 300 to 800 K. The zeolite catalyst was activated inside the reactor in a flow of N_2 . The sample (0.01 g) was heated at a rate of 200 K/hour to 673 K and kept at this temperature for two hours. Subsequently, the reactor was cooled to the reaction temperature and a mixture of 8 vol% ethylene in nitrogen was passed under normal pressure through the catalyst bed. EPR spectra were taken at certain time intervals, in order to follow the progress of the reaction.

RESULTS AND DISCUSSION

IR in-situ experiments. Figure 2 demonstrates the time on-stream behaviour of two hydrogen mordenite catalysts with significantly different Si/Al ratios, as measured at 550 K in the IR flow reactor cell.

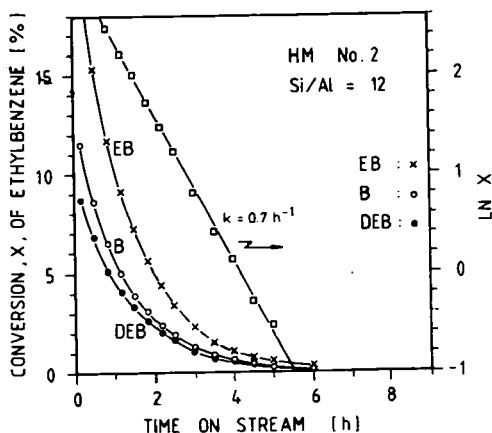


Figure 2A.

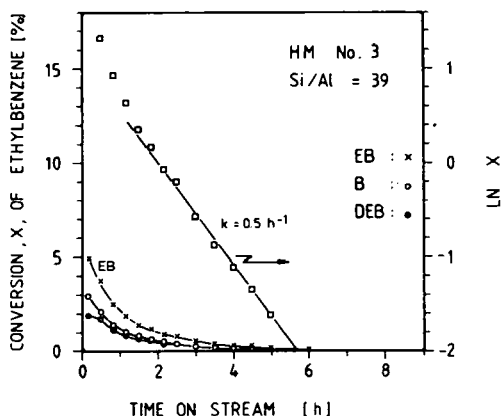


Figure 2B.

Time-on-stream behaviour of two hydrogen mordenite catalysts (HM No. 2 and No.3) upon dealkylation of ethylbenzene at 550 K.

In the case of the higher Si/Al ratio (39, HM No.3) the conversion-versus-time curve dwells at a substantially lower conversion level than with Si/Al = 12 (HM No.2). The drop of the conversion, x , with time on stream, however, proceeds with roughly the same rate, as in both cases plots of $\ln x$ vs. time on stream provide straight lines with slope $k = 0.5 \pm 0.2 \text{ h}^{-1}$ (see Figure 2A and 2B). These results suggest that (i) the conversion of ethylbenzene over acidic mordenites is proportional to the number of active sites, $N(t)$, in agreement with earlier observations (14) and (ii) the deactivation reaction is first order w.r.t. $N(t)$ according to

$$N(t) = N(t=0) \cdot e^{-k \cdot t} \quad (1)$$

Since the rate constant k is almost equal for both catalysts, one has to conclude that the rate of deactivation is not affected by the Si/Al ratio. The difference in time-on-stream behaviour is merely due to the fact that the initial numbers of active sites of both catalysts differ; they do not differ, however, in strength.

This conclusion is confirmed not only on the simultaneous in-situ IR measurements (see Figure 3), but also by the IR determination of the number of sites and by the TPD experiments evaluating the strength of the Brønsted centers. To start with the latter, TPD of ammonia from both mordenite samples (HM No.2 and No.3), activated at 673 K, produced the TPD peaks due to NH_3 desorption from Brønsted sites (15) at the same desorption temperature, viz. 680 ± 5 K. This indicated similar strength of the sites of both catalysts. Static IR experiments, which were carried out as described elsewhere (16-17), showed that hydrogen mordenite No.2 exhibited a markedly higher number of Brønsted sites than sample No. 3, as could be expected as a consequence of the lower Si/Al ratio of HM No.2. The maximum absorbances of the OH bands at 3610 cm^{-1} (acidic OH groups (16)), were $A_{\text{max}}(\text{OH}) = 0.40$ and $A_{\text{max}}(\text{OH}) = 0.25$ for sample No.2 and No.3, respectively. Correspondingly, the absorbances of the pyridinium ion band at 1542 cm^{-1} , being indicative of acidic Brønsted sites (16) were $A_{\text{max}}(\text{HPy}^+) = 0.20$ and $A_{\text{max}}(\text{HPy}^+) = 0.10$

Figure 3 shows the absorbance of the coke band, $A(1585 \text{ cm}^{-1})$, as a function of time on stream. Figure 4 relates the conversion to the amount of deposited coke. These plots again demonstrate that on the catalyst with the higher number of sites (HM No. 2, Si/Al = 12) the amount of coke deposited during dealkylation of ethylbenzene is significantly higher than with the much shorter-lived catalyst HM No.3. This result is supported by the observation that, after almost complete dehydroxylation at 973 K in high vacuum, i.e. after removal of acidic Brønsted sites, hydrogen mordenite exhibited only a very low activity towards coke formation.

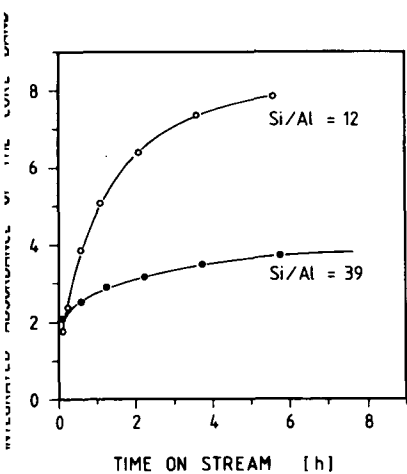
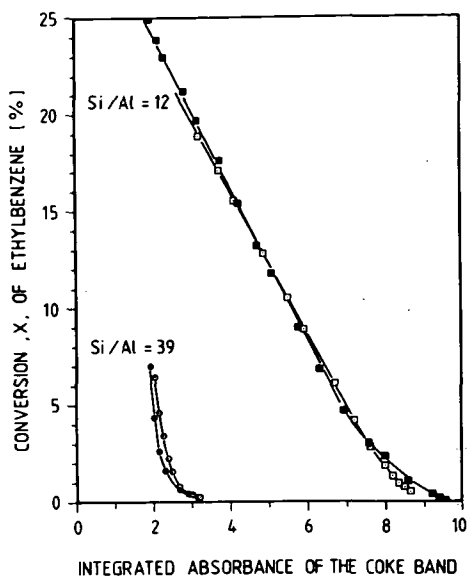


Figure 3.

Coke deposition as measured by the integrated absorbance of the coke band at 1585 cm^{-1} , as a function of time on stream.

It is interesting to note from Figure 4 that over a wide range of coke deposition, the decrease in conversion is directly proportional to the amount of deposited coke. This holds for both catalysts irrespective of the Si/Al ratio. However, a significant and repro-



ducible difference in the slopes of the straight lines was observed, i.e. the activity is much more affected in the case of the catalyst with higher Si/Al ratio.

Figure 4.

Conversion of ethylbenzene related to coke deposition, as measured by the integrated absorbance of the band at 1585 cm^{-1} ; different experiments are represented by different symbols.

In-situ EPR experiments. EPR spectroscopy provided three contributions to the current investigations into the coke problem, viz. the study of (i) formation of oligomeric radicals upon ethylene interaction with the catalyst at low temperatures (373-423 K), (ii) formation of coke radicals at higher temperatures ($T > 423\text{ K}$), and (iii) annihilation and generation of radicals during oxidative regeneration of coked catalysts.

Oligomeric radicals. When a flow of nitrogen and ethylene was passed through the catalyst sample at room temperature, no EPR signal was observed. At 373 K, however, a weak signal with hyper-fine structure (hfs) appeared. When the reaction temperature was raised to 423 K the signal intensified and exhibited a well-resolved hfs with several lines, the parameters of the spectrum being $g = 2.0028$ and $a = 1.4\text{-}1.6\text{ mT}$ (hyper-fine splitting constant). This spectrum differs significantly from the spectrum obtained by Kucherov and Slinkin (10-11) in that the hyper-fine splitting constant is about twice as large as the constant reported by these authors.

Since the spectrum comprises more than five lines, it cannot be due to an ethylene radical. However, ethylene polymerizes on acid mordenites, even at room temperature (2). At higher temperatures subsequent cracking may occur. Thus, the signal is probably indicative of an oligomeric radical generated via polymerization and subsequent homolytic splitting.

In view of the value of the hfs constant, the signal could be ascribed to alkenic or allylic radicals; alkyl radicals appear to be much less likely. A detailed study upon formation of oligomeric radicals due to olefin reaction on zeolites will be published elsewhere (18).

Coke radicals. When the temperature was increased to 453 K, the hfs started to vanish, and in a slow process a symmetrical single line at $g = 2.0024$ emerged, which is generally ascribed to species generated upon coking of organic material (12-13). Thus, the appearance of this line indicated the onset of coke formation. With increasing temperature, the intensity of the coke signal was markedly enhanced. At 473 K, the hfs had completely disappeared, the intensity of the single line corresponded to ca. 10^{17} spins·(g catalyst)⁻¹, the line width was $\Delta H = 1.0$ - 1.5 mT, and the g -factor still equalled 2.0024. This coke signal with $g = 2.0024$ immediately developed, i.e. without a preceding oligomeric signal when freshly activated hydrogen mordenite was contacted with ethylene at 473 K. Hence, it seems to be rather unlikely that those oligomers are inevitable precursors of the coke.

The intensity of the coke signal steadily increased, but finally (after 15 hours on stream) approached a constant value, viz. 1.2×10^{19} spins·g⁻¹. The line width was nearly constant, and the g -value remained 2.0024.

The initial rate of coking strongly depended on the reaction temperature. This is demonstrated by Figure 5, where the intensities of the coke signal were plotted versus time on stream for three different reaction temperatures. It is evident from this figure that the initial increase of the intensity of the coke signal is steeper the higher the reaction temperature.

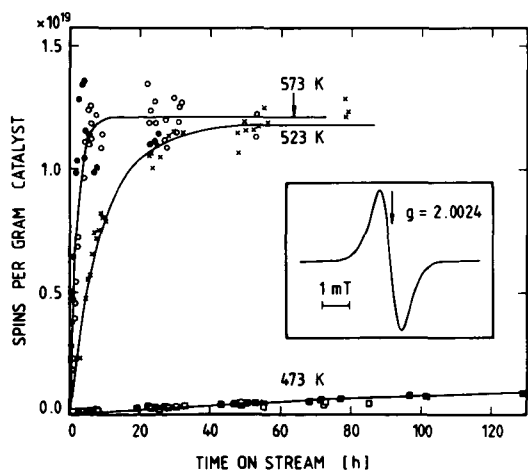


Figure 5.

The intensity of the EPR coke signal at three different reaction temperatures as a function of time on stream (solid lines are calculated curves, eq.3)

After some time, the intensities seem to approach a final level, and the data of Figure 5 may be represented by a first order relationship

$$n(t) = n(t=\infty) (1 - e^{-k \cdot t}) \quad (3)$$

For the experiments at higher temperatures ($T_{\text{react.}} = 523, 573 \text{ K}$) the final levels coincide (see Table 1)

Table 1 Final intensities of the coke signal at various reaction temperatures (eq.3)

T (K)	$n(t = \infty)$ (spins.g ⁻¹)	k (h ⁻¹)
473	0.20×10^{-19}	0.005
523	1.18×10^{-19}	0.11
573	1.20×10^{-19}	0.50

The results in Figures 3 and 5 indicated that after deposition of a certain amount of coke, which depended on the temperature, all the active sites (acidic Brønsted centers) were poisoned or blocked, and coke formation stopped. Indeed, the IR experiments confirmed that the OH bands at 3610 cm^{-1} had not completely disappeared when the conversion (dealkylation of ethylbenzene) dropped to zero and the coke band at 1585 cm^{-1} had virtually ceased to grow. Therefore, deactivation is not solely caused by poisoning or consumption of acidic OH groups, but also to some extent by pore blocking. Nevertheless, from the IR and EPR results it had become evident that a higher number of acidic OH groups corresponded to a greater amount of coke deposit (vide supra). Hence one would conclude that coke formation requires Brønsted acid sites and proceeds via a carbenium ion mechanism. Coke formation through a radical mechanism, involving the radicals indicated by $g=2.0024$, is less likely for the following reason.

A high number of radicals due to coke were present on the catalyst at 573 K (see Figure 5) and a fraction of them must have formed on the external surface of the zeolite crystals, where coke species block the openings of the pores. However, in spite of presence and accessibility of these radicals, coke formation levelled off, which was also indicated by the IR and conversion measurements in the IR flow reactor cell.

Coke_oxidation_and_catalyst_regeneration. When a stream of oxygen was passed through the catalyst, which had been coked upon ethylene reaction at 573 K, oxidation of the coke at 673 K seemed to occur very rapidly. After about one hour, 90% of the initial intensity of the coke signal was gone. Simultaneously, the g-value shifted from 2.0024 to 2.0035 and the line width decreased from 0.8 to 0.6 mT. After 40 hours of oxidation a very small signal (about 2×10^{17} spins.g⁻¹) was left. The g-value of 2.0035 is similar to that of semiquinones of polyaromatics (19-20). Thus, it may indicate that oxidation of coke results in formation not only of CO₂ but also of oxygen containing molecules with high delocalisation of electrons. However, the present results do not permit an unambiguous identification of the species formed upon coke oxidation.

CONCLUSIONS

- (1) Coke formation upon reaction of olefins on acidic mordenites is strongly influenced by the number of Brønsted sites in that a higher density of sites corresponds to a higher yield of coke.
- (2) Over a wide range of coke deposition, the decrease in conversion of ethylbenzene on acidic mordenites is directly proportional to the amount of deposited coke.
- (3) Coke formation proceeds through a carbenium ion mechanism rather than via radicals.
- (4) It is unlikely that oligomeric radicals are necessary precursors of coke. No simple relationship exists between the concentration of such radicals formed at low temperatures and the concentration of coke radicals generated by heating oligomeric radicals at higher temperatures.
- (5) As in-situ IR measurements show, deactivation of hydrogen mordenite catalysts due to coke formation upon olefin reaction proceeds not solely through poisoning or consumption of acidic OH groups, but also to a marked extent by pore blocking.

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