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NOTE

In Situ Solid-State NMR Investigation of Cracking Reactions on Zeolite HY

In situ ^{13}C solid-state NMR spectroscopy was used to monitor the cracking of propene oligomers on zeolite HY at elevated temperatures. Experiments were performed in sealed magic-angle spinning rotors, the temperatures of which were cycled between ambient and 503 K. At the upper temperature, the oligomers cracked to form branched butanes, pentanes, and other alkanes. The driving force for this reaction was the formation of highly aromatic coke. These products remained after the catalyst temperature was reduced to ambient. Although olefins are observed in the product stream from cracking in flow reactors, they did not accumulate in detectable quantities in the *in situ* NMR experiment. We conclude that olefins are unstable with respect to conjunct polymerization for long reaction times on zeolite HY at 503 K. The results of this study are consistent with the view that coke formation can be important in hydrogen-transfer reactions during cracking.

INTRODUCTION

Catalytic cracking is used to convert a significant fraction of the world's petroleum production into mixtures of smaller hydrocarbons such as gasoline. Mechanistic investigations probing cracking and related zeolite-catalyzed reactions are generally based on gas chromatographic and/or mass spectrometric analysis of the volatile product distributions obtained from fixed-bed, continuous-flow microreactors (*1*, *2*). Such an analysis is limited in that only those products sufficiently volatile and/or having dimensions small enough to escape the zeolitic pores are detected. An alternative approach is to use an *in situ* spectroscopic method to probe the product distribution on the catalyst while the reaction is in progress. Recently, our laboratory has begun the development of high-resolution solid-state NMR techniques for the *in situ* study of catalytic reactions. In the first application of such techniques, several of us reported a low temperature *in situ* NMR study of the oligomerization reactions of propene on zeolite HY (*3*). In the present communication, we describe the use of high temperature *in situ* NMR to study the cracking reactions of oligomers formed by adsorbing ^{13}C-labeled propene samples on HY catalyst at room temperature. These oligomers were observed to crack to branched alkanes at 503 K. A key aspect of the cracking reactions was the formation of coke deposits, a process which provided the necessary hydrogen.

METHODS

Propene-1-^{13}C (99.3% ^{13}C) and propene-2-^{13}C (99.2% ^{13}C) were obtained from MSD isotopes. HY zeolite (Si/Al = 2.3) was used in this study. Active catalyst samples were prepared from the NH_4Y form via a multistep activation procedure described previously (*3*). In a typical adsorption, 0.2 g of active catalyst was exposed to 65 Torr of labeled propene at room temperature, and a loading of 1.7 mmol/g was achieved. Following adsorption, the samples were sealed in zirconia magic-angle spinning rotors using grooved Kel-F caps similar to those described elsewhere (*3*). Variable-temperature ^{13}C solid-state NMR experiments were performed at 75.37 MHz using a Chemagnetics CMX-300 spectrometer. Both single-pulse excitation (Bloch decay) and cross-polarization experiments were performed. Cross-polarization spectra were typically obtained with a contact time of 2

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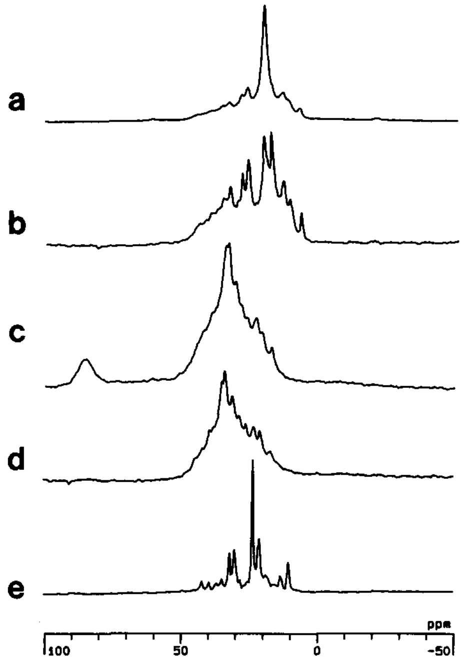

FIG. 1. ^{13}C solid-state NMR spectra of oligomers formed from labeled propene on zeolite catalyst HY. (a) Cross polarization spectrum of the oligomers of propene-1-^{13}C at 298 K prior to heating. (b) Bloch decay spectrum of the sample in a. (c) Cross-polarization spectrum of the oligomers of propene-2-^{13}C at 298 K prior to heating. (d) Bloch decay spectrum of the sample in c. (e) Bloch decay spectrum of the sample in c and d at 298 K after 3 h at 503 K. Magic-angle spinning was used for all spectra.

ms, pulse delay of 1 s, and 400 scans. Bloch decay spectra were typically obtained with a 90° flip of 4.2 μs, pulse delay of 2 s or greater, and 100 scans. All spectra were acquired with magic-angle spinning at rotation rates of 3.5 to 4 kHz.

RESULTS AND DISCUSSION

Figures 1a and 1c show ^{13}C solid-state NMR spectra obtained with cross polarization and magic-angle spinning (CP/MAS) of HY samples at 298 K immediately following exposure to propene-1-^{13}C or propene-2-^{13}C, respectively. Cross-polarization spectra emphasize relatively immobile adsorbates. Bloch decay spectra (which emphasize more mobile sample components) of the samples prior to heating are reported in Figs. 1b (propene-1-^{13}C) and 1d (propene-2-^{13}C). The overall appearance of these spectra is consistent with the oligomerization mechanism of propene on zeolite HY which we advanced previously (*3*). Propene oligomerizes at room temperature with label retention to form highly branched products. The proposed mechanism involves an alkoxy intermediate which functions as an incipient secondary carbocation and which is manifest as a resonance at 87 ppm in Fig. 1c.

Propene oligomers on zeolite HY provide excellent samples for the initial *in situ* NMR studies of catalytic cracking. Following acquisition of the spectra in Figs. 1a–1d, cracking reactions were initiated by raising the temperature of the samples to 500 K or above while continuing magic-angle spinning and spectral acquisition. These experiments differ from the mode in which standard catalytic reactors are run in two important ways: Since these reactions are carried out in a closed system, the residence time of the hydrocarbons is much longer than normal, and the total mass balance in the catalyst is conserved. Nevertheless, cracking reactions were observed to commence upon temperature equilibration at 503 K, and these reactions were complete after approximately 2 h. Extensive changes in the hydrocarbon adsorbates occurred during high-temperature treatment. This can be appreciated by comparison of Fig. 1d with Fig. 1e, which shows the high-field region of the Bloch decay spectrum of the same sample as that in Fig. 1d at 298 K following 3 h at 503 K.

The ^{13}C signals in Fig. 1e are, in every way, characteristic of highly mobile, low-molecular-weight alkanes. They cross polarized very weakly, if at all, and it was possible to observe scalar coupling to directly bound protons by acquiring a spectrum without decoupling (not shown). From the chemical shifts and scalar multiplet patterns, it was possible to assign the spectrum in Fig. 1e to primarily isopentane, isobutane, 2, 3-dimethylbutane, and pro-

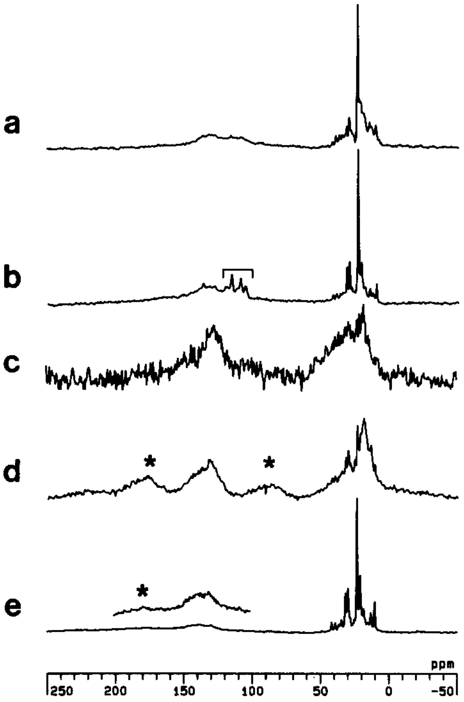

FIG. 2. ^{13}C solid-state NMR spectra showing the results of heating propene oligomers on HY for 3 hr at temperatures above 500 K. (a) Bloch decay spectrum at 523 K of the sample derived from propene-1-^{13}C. (b) Bloch decay spectrum at 503 K of the sample derived from propene-2-^{13}C. (c) Cross-polarization spectrum of the sample in b. (d) Cross-polarization spectrum at 298 K of the sample in b and c after cooling. (e) Bloch decay spectrum of the sample in d. All spectra were obtained with magic-angle spinning. * denotes spinning sideband. The bracketed area in b denotes background signals from a Kel-F plug in the rotor.

pane. These compounds are commonly observed in the product stream of conventional cracking reactions. Neither cyloalkanes nor olefins were observed in this study, whereas the latter are commonly observed in flow reactor studies.

Since one hydrogen molecule is (at least formally) required for each carbon–carbon bond that is cracked to form two noncyclic alkane molecules, the source of hydrogen must be identified. Figures 2a and 2b show high-temperature Bloch decay spectra of the cracked products of oligomers derived fron propene-1-^{13}C and propene-2-^{13}C, respectively, after 3 h above 500 K. Comparison of these spectra suggests that complete scrambling of the ^{13}C labels occurs in HY at high temperature. That result is consistent with the carbocation mechanisms proposed for cracking reactions at high temperatures (*4*, *5*) and differs from the low-temperature oligomerization reactions of propene, in which label retention was observed. More importantly, these spectra show small aromatic carbon signals at chemical shifts between 120 and 140 ppm. These aromatic carbon signals are emphasized when the ^{13}C magnetization is generated by cross polarization at either high temperature (e.g., Fig. 2c) or after the samples were returned to ambient (Fig. 2d). Since cross-polarization spectra emphasize relatively immobile constituents, the aromatic compounds or polymers in Figs. 2c and 2d must be incapable of rapidly diffusing through the catalyst pores, which have a diameter of 7.4 Å for zeolite Y.

The reactions of hydrocarbons on acidic zeolites are frequently accompanied by the formation of highly aromatic or graphitic coke, which can eventually deactivate the catalyst through pore blockage. Two of us have recently published a detailed ^{13}C solid-state NMR study of coke formed on zeolite HY from butadiene (*6*). The spectra in Figs. 2c and 2d resemble the spectra of coked HY samples obtained in that previous study. A Bloch decay spectrum at room temperature (Fig. 2e) more closely represents the relative amounts of cracked products and coke. We conclude that coke formed in the HY catalyst during cracking and that coking was the source of hydrogen for the cracking reactions. This conclusion is supported by an FT–IR study by Ghosh and Kydd, who concluded that propene oligomers were converted directly to coke without passing through simple aromatic compounds at temperatures greater than 473 K (*7*).

This contribution has demonstrated that high-temperature cracking reactions can be monitored *in situ* using solid-state NMR techniques. Coke formation occurs when propene oligomers in zeolite HY are cracked at temperatures above 500 K. Coking plays an essential role in this process in that it provides the source of hydrogen required to form noncyclic alkane products. Neither olefins nor simple aromatics were observed in this study. Since olefins are major products in conventional cracking reactors, these compounds must be unstable with respect to coke formation at the longer residence times used in this study.

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