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The Reactivity of Molecules Trapped within the SAPO-34 Cavities in the Methanol-to-Hydrocarbons Reaction

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Since the initial discovery in 1976 that methanol may be converted to hydrocarbons over H-ZSM-5 various aspects of the reaction mechanism have been important issues.[1,2] Despite a very considerable effort no general agreement on the mechanism has been reached. However, during the past few years evidence for a mechanism based on a pool of adsorbed hydrocarbons that is all the time adding methanol and splitting off ethene and propene has been presented.[3−8] This pool mechanism differs markedly from the prevailing views on the methanol-to-hydrocarbons (MTH) reaction during the first 20 years or so after its discovery. The results to be presented here lend further strong support for the hydrocarbon pool mechanism, and suggest that the reaction mainly proceeds via penta- and hexamethylbenzene.

The MTH reaction is also catalyzed by other zeotype catalysts. The product spectrum varies strongly with the pore size of the catalytic material (shape selectivity), and when the small pore SAPO-34 (chabasite structure) is used as catalyst the hydrocarbon products are mostly ethene and propene, the only product molecules small enough to escape with ease through the narrow pores. The reaction is in this case most often referred to as a methanol-to-olefins (MTO) reaction. The fundamental mechanism is likely to be the same over all catalysts based on protonated zeotype materials.

Previous work carried out in our group where ^{13}C-methanol and ordinary toluene were co-reacted over medium and large pore zeolites pointed to arenes adsorbed within the zeolite cavities as being important participants in the MTH reaction.[7] Guided by the results in ref 7 we decided to extend the work by studying the molecules that are retained within the catalyst cavities when SAPO-34 is used as catalyst in the MTO reaction.[9] The rationale for choosing this catalyst being that only small linear hydrocarbons may escape the pores, all other hydrocarbons are retained. Knowledge about which molecules are present inside the working catalyst might give valuable information about the reaction. In addition SAPO-34 is easily dissolved in dilute acids, so detailed analysis of the trapped molecules by gas chromatography may be carried out. The mixture of organic molecules trapped in the cavities is very complex, ranging from the C_3 molecule propane to C_{12}−C_{15} molecules. Polymethylbenzenes are, however, strongly dominating.[9] It was found that if methanol feeding was stopped and the catalyst flushed with carrier gas, hexamethylbenzene (HMB), one of the major retained products, was evidently unstable and disappeared within a couple of minutes. The amount of pentamethylbenzene (PMB) also decreased rapidly, but not so fast. Simultaneously, the content of di-, tri-, and tetramethylbenzenes in the SAPO-34 cavities stayed constant or even appeared to increase. This observation showed that the aromatics are not the rather inert pore-filling and deactivating compounds—not taking part in the main reaction—they are often tacitly supposed to be.[10,11] The observation also suggested that PMB and HMB might split off C_2 and C_3 alkenes (possibly also C_4).

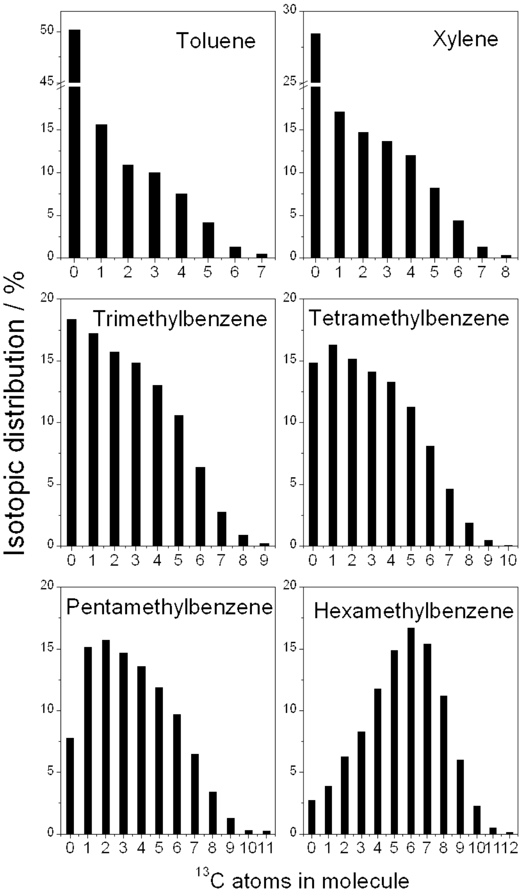

Figure 1. Isotopic analysis of the trapped organic material in SAPO-34. The catalyst was first exposed to ordinary methanol for 6 min, thereafter to ^{13}C-methanol for 60 s. WHSV = 10 h^{-1}. Reaction temperature 325 °C.

We decided that valuable detailed information about the reactions taking place might be obtained by using isotopic labeling and performing the experiments in such a way that at a given time on stream the feed might be switched from ordinary methanol to ^{13}C-methanol. By carrying out a series of experiments with varying times of exposure to ^{13}C-methanol before cutting the experiment, the rate of incorporation of ^{13}C-atoms might possibly be monitored. This knowledge might then give quite detailed information about the processes taking place in the interior of working catalysts, vital information that until now was unavailable for this kind of catalytic chemistry.

We used the same catalyst batch as before and the experiments were carried out largely as described earlier,[9] i.e., at 325 °C, with methanol pressure = 120 mbar and WHSV = 10 h^{-1}. The isotopic compositions of the products were determined by the same procedure as previously outlined for isotopically mixed molecules.[3]

The isotopic compositions of the polymethylbenzenes as obtained in an experiment are displayed in Figure 1. The sum of

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polymethylbenzenes constitutes nearly one-half of the trapped products under the chosen reaction conditions. In this specific experiment the catalyst was exposed to ordinary methanol for 6 min before switching over to ^{13}C-methanol for 60 s. After 60 s the catalyst mass was rapidly transferred to a room-temperature glass vial, thus freezing the reaction. The catalyst and its contents were thereupon dissolved in dilute HCl (1 M) so that the confined organic compounds became available for analysis. The procedure has been described earlier.[9]

The usual temperature for running an MTO reaction is 400−450 °C. Our experiments were performed at 325 °C to slow the reaction enough to allow us to follow the changes in isotopic composition of the confined molecules. Even at the low reaction temperature employed here the rate of incorporation of ^{13}C-atoms in HMB, and consequently also splitting off ^{12}C-atoms, is dramatically fast. After 60 s of exposure to ^{13}C-methanol HMB has changed from being a ^{12}C-atom based compound to containing about 50% ^{13}C. In addition, at least 40% of the HMB molecules contain one or more ^{13}C incorporated in the benzene ring. A corresponding amount of ^{12}C-atoms must have left the HMB pool. Before exposure to ^{13}C-methanol, HMB exhibits the natural carbon isotope distribution where 87% of the molecules contain no ^{13}C. After 60 s of exposure to the labeled methanol only 3% are free from ^{13}C. The isotopic distribution in HMB as given in Figure 1 is essentially random. The other arenes do not display random isotopic distributions. However, after longer exposure to ^{13}C-methanol they gradually approach randomness.

HMB represents a very reactive arene species. The other extreme among arenes is represented by toluene. In the same time only half of the molecules have acquired one or more ^{13}C-atoms. But also toluene is evidently a reactive molecule. If it were unreactive one should observe a distribution where the molecules would be either all-^{12}C or all-^{13}C. It is furthermore seen that at least two-thirds of the toluene molecules that have acquired ^{13}C-atoms have one or more ^{13}C in the ring. The other arenes lay between the two extremes and there is a quite smooth and steady transition toward a more rapid incorporation of ^{13}C-atoms as we proceed from mono- to hexamethylbenzene.

Isobutane is the most common alkane trapped in the catalyst. The rate of ^{13}C incorporation appears to be lower than was found for toluene. Branched C_5 and C_6 alkanes were also observed. The corresponding alkenes were absent. Linear alkenes can leave the cavities fairly easily, and were only observed in minute quantities among the retained products. They appear as products in the effluent.

Analysis of the gaseous products formed in the MTO reaction, ethene, propene, and linear butenes, have also been carried out. Analysis results for samples taken 25 and 50 s after replacing ^{12}C- by ^{13}C-methanol are seen in Figure 2. In the same figure the isotopic composition of unconverted C_1 (as dimethyl ether) is also shown. All three hydrocarbon product molecules show about 50% ^{13}C content 25 s after the switch and are strongly dominated by ^{13}C-atoms after 50 s. It should, however, be noticed that the isotopic composition of the feed molecules (represented by dimethyl ether) changes much faster than the product isotopic composition. Even though the isotopic composition of the products changes rapidly there is a considerable time delay relative to the feed composition. The alkene products are, however, richer in ^{13}C than is, e.g., HMB. The isotopic distribution in the alkene products is in all three cases fully random.

Contrary to what might be expected there is evidently a rapid incorporation of ^{13}C atoms in the trapped arenes. If the aromatics were inert and nonreactive after being formed we would get an isotopic distribution dominated by either all-^{12}C or all-^{13}C, and insignificant amounts of isotopically mixed molecules. Combining the earlier finding that PMB and HMB are unstable and loose methyl groups (without producing methane) with the results obtained here, which show rapid incorporation of methyl groups, we have a virtual proof that polymethylbenzenes are the "catalytic engine" in the MTO reaction, and probably also in the MTH reaction in general. HMB and PMB appear to be particularly active. A cycle where HMB and PMB split off ethene or propene and are turned into di-, tri-, or tetramethylbenzene that may again be methylated is appealing. Very recently Song et al. have also obtained clear indications that polymethylbenzenes are of vital importance for the MTH reaction.[12,13] By combining NMR spectroscopy and gas chromatographic analysis they obtained a high level of integration of volatile product analysis and NMR characterization of products confined within the solid catalyst. The NMR/GC integration showed that the highly methylated benzenes lost methyl groups fairly easily, and that formation of ethene and propene took place simultaneously. Rønning et al. in 1998 pointed out a remarkable similarity between the isotopic composition of ethene and the arenes xylene(s) and trimethylbenzene(s) when ^{13}C-methanol and ordinary propene were coreacted over an H-ZSM-5 catalyst.[14] Further work on mechanistic details and a more detailed mapping of the kinetics of the various reactions taking place inside the catalyst cavities are in progress.

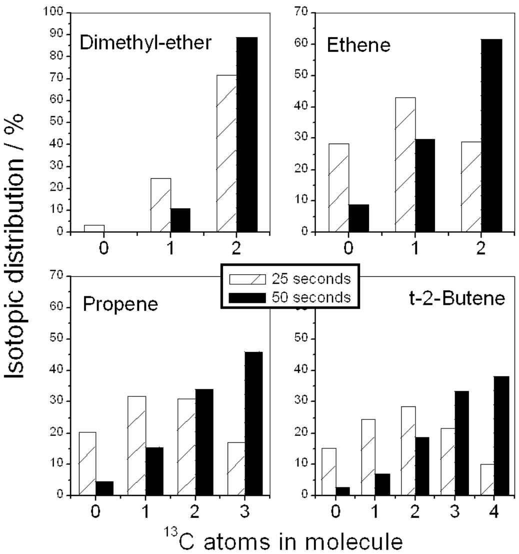

Figure 2. Isotopic composition of dimethyl ether and the three main hydrocarbon products in gaseous effluent samples taken 25 and 50 s after replacing ordinary methanol feed by ^{13}C-methanol. Same conditions as in Figure 1.

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