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Methanol-to-hydrocarbons reaction over SAPO-34. Molecules confined in the catalyst cavities at short time on stream

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In order to obtain more insight into the methanol-to-hydrocarbons (MTH) reaction the organic molecules confined in a working SAPO-34 catalyst have been studied. The reaction was run for varying times, 30 s to 30 min. At a predetermined time the reaction was stopped and the catalyst dissolved in 1 M HCl. The gas phase above the solution as well as a CCl_4 extract were analyzed by gas chromatography (MS detector). The gas phase consists mainly of isoalkanes $C_{4–6}$. The less volatile organic molecules were concentrated in the CCl_4 extract. More than 200 different species are present, but polymethylbenzenes, with one to six methyl groups, are always dominating. They constitute 30–50% of the samples. Penta- and hexamethylbenzene easily split off small hydrocarbons and turn into di- and trimethylbenzenes. It is speculated that methylations of arenes which thereupon split off small alkenes and then are remethylated again may be an essential part of the catalytic activity in the MTH reaction.

KEY WORDS: reaction mechanism; methanol-to-hydrocarbons; SAPO-34; hexamethylbenzene

1. Introduction

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 much discussed [1,2]. It is now well known that there are also other zeotype materials which catalyze the MTH reaction. The product spectrum varies with reaction conditions, in particular the pore size of the catalytic material (shape selectivity), but the fundamental mechanism is likely to be the same over all catalysts.

We have recently investigated co-reaction of ^{13}C-methanol and (^{12}C) toluene over ZSM-5, dealuminated mordenite and beta zeolite [3]. This investigation gave clear evidence that arenes play a very central role in the MTH reaction. SAPO-34, which has a chabazite structure (8-ring channels), is a good methanol-to-olefins (MTO) catalyst. Only small linear hydrocarbons may escape the pores. Any branched or ring molecule is retained within the cavities. In addition, dilute acids easily break down the structure. For this reason we found it worthwhile to carry out the MTH reaction over SAPO-34, stop the reaction after a quite short time on stream (TOS), dissolve the catalyst and analyze it for organic compounds. The mixture of organic molecules thus obtained is very complex, and the composition changes with TOS and temperature. Again organic polymethylarenes point themselves out as being of central importance for the MTH reaction. Only a preliminary account can be given here.

It is often stated that once the MTH reaction has started, ordinary acid-catalyzed alkene interconversion reactions and hydrogen transfer reactions determine the product composition [1]. From such a viewpoint it is to be expected that the hydrocarbon mixture confined within the cavities to a large extent should be independent of the exact nature of the feed. For this reason parallel experiments using propene as feed have been carried out.

2. Experimental

The experiments were carried out using a SAPO-34 synthesized in accordance with standard procedures. The mean crystal size is 2 μm (1–6 μm); elemental composition $\mathrm{Si:Al:P} \approx 1:6:5$. The catalytic experiments were performed using a fixed-bed reactor (Pyrex). Temperature was measured using a thermocouple immerged in the catalyst mass which usually was 30 mg. Partial pressure of methanol was 130 mbar. Nitrogen was used as carrier gas. It was worked with a space velocity, $\mathrm{WHSV} = 10\ \mathrm{h}^{-1}$. Prior to the experiments the reactor temperature was set to the desired level, while flushing with carrier gas. The experiments were started by switching the carrier gas to pass through the methanol saturator. Under the chosen conditions there was a delay of 40 s before the methanol reached the catalyst bed (taken into account). After a predetermined time the reactor was quickly removed from the oven. Cooling to a non-reacting temperature would take a few seconds. Alternatively the methanol feed could be stopped so that the reactor was flushed for a predetermined time before removing and cooling the reactor. Experiments have also been done using propene (100 mbar) as reactant. Experimental conditions were the same in the two cases.

After being removed from the cooled reactor the catalyst was dissolved in 1 M HCl. This was done in a closed vessel (9 ml) filled with helium. A gas sample could be withdrawn from the vessel and analyzed. Thereupon the solution was treated with CCl_4 to extract little volatile organic compounds. The CCl_4 solution was then analyzed. The technique of dissolving the zeolite crystals in an acid and recover confined constituents by extraction was introduced by Guisnet and co-workers [4].

The analysis was carried out by GC-MS (Hewlett–Packard HP 6890 with MSD 5973) using a 30 m column, 0.25 mm i.d. HP-5MS (5% diphenyl-, 95% dimethylsiloxane copolymer) with stationary phase thickness 0.25 μm. Temperature programming was applied. The gas phase analysis was run from -40 to 300 °C (no peaks above ca. 200 °C), and the CCl_4 extract analysis from 10 to 300 °C; this temperature was held 5 min. Unless at high reaction temperatures and long time on stream no peaks eluted above 250 °C ($\sim C_{20–21}$).

3. Results

We will here concentrate on results obtained at 325 °C. This temperature is about 100 °C below the optimal temperature for converting methanol to hydrocarbons, and the catalyst deactivates quite fast at this temperature. On the other hand, one may expect that at this low-temperature transformations of the confined molecules may be slow enough that it will be possible to follow at least some processes which may go on.

The gas chromatograms display a very complex mixture. Some 200+ different compounds may be discerned, but nearly 50% area of the total ion chromatograms are caused by 6–10 compounds.

In order to present the results in a meaningful way chromatograms obtained from a few experiments must be given. The chromatograms are truncated; they were actually recorded to 35 min. The cuts shown cover the interesting part. Omitted peaks are all small. Figure 1(a) shows the CCl_4 extract from a sample after 30 s on stream; no flushing before removal from the oven and cooling. Figure 1(b) shows a corresponding experiment after 120 s on stream; again no flushing. Figure 1(c) displays the analysis result after 120 s on stream and 160 s flushing before removal and cooling. Figure 2(a) is for TOS $=$10 min, no flushing. Figure 2(b) was obtained with propene feed, TOS $=$ 10 min, no flushing.

The chromatograms are displayed so that the largest peaks are of similar height. Because the amount of confined molecules increases strongly with TOS the experiments with TOS $=$ 30 and 120 s were performed with double amount of catalyst and less CCl_4 was used for extracting organic molecules. The 30 s sample still gave too small peaks and was further concentrated by evaporating 85–90% of the CCl_4 solvent. The relative concentrations of molecules with more than eight carbon atoms appeared unchanged by this treatment. When the different procedures for making the CCl_4 extracts that were analyzed are taken into account it is clear that the amount of extractable material increased more than linearly with time during the first few minutes on stream. Going from 30 to 120 s appears to increase the amount fifteen to twenty times.

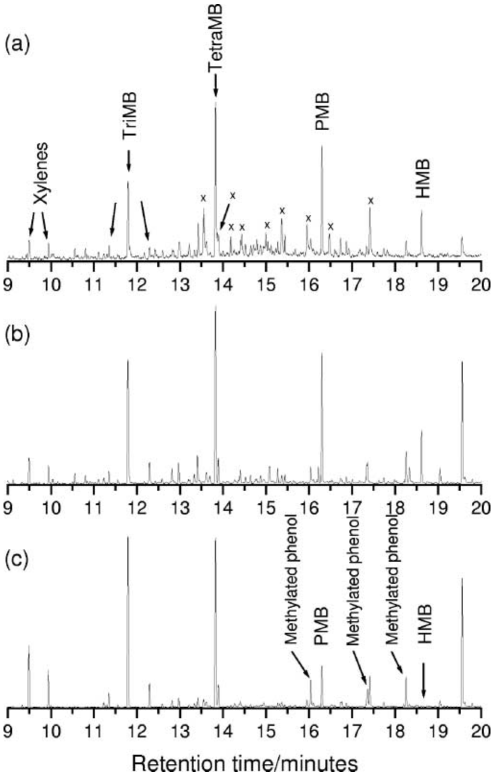

Figure 1. Chromatogram (GC-MS) of the CCl_4 extract of SAPO-34 dissolved in HCl. The MTH reaction was run at 325 °C with methanol feed. (a) 30 and (b) 120 s on stream, no flushing. (c) 120 s on stream, the reactor was flushed for 2 min 40 s before being removed from the oven and cooled to a non-reaction temperature.

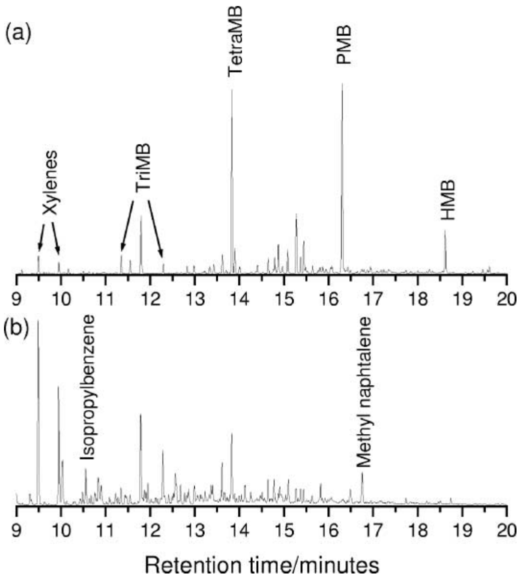

Figure 2. Chromatogram (GC-MS) of the CCl_4 extract of SAPO-34, dissolved in HCl after 10 min on stream at 325 °C. No flushing. (a) Methanol feed and (b) propene feed.

No gas phase chromatograms are displayed here. They were dominated by small isoalkanes (C_4–C_6). Only approximate estimates for the relative amounts of gas phase constituents and CCl_4 extract constituents can be given. At

325 °C and TOS = 10 min we found that the extract contained about 80% (by mass) of the confined molecules.

At a first glance the chromatograms in figures 1 (a)–(c) and 2(a) are rather similar. The (usually) dominating peaks at 11.80, 13.83, 16.30 and 18.62 min are marked in figure 1(a) as being a trimethylbenzene (TriMB), a tetramethylbenzene (TetraMB) (co-eluted with a smaller amount of a methyladamantane), pentamethylbenzene (PMB) and hexamethylbenzene (HMB). The somewhat smaller peaks at 9.48 and 9.95 min are caused by the xylenes. In addition to the above major peaks there is a peak at 19.57 min. For TOS = 2 min this is a major peak. It is not yet identified, and it is not recognized by the NIST98 MS-library. In figure 1(b) the polymethylbenzenes constitute 35% area; other alkylbenzenes may contribute another 5% area. The unidentified peak at 19.57 min constitutes 6.9%. The remaining 200+ compounds contribute the remaining 50+% area.

In spite of the similar traits seen in figures 1 (a)–(c) and 2(a) there are also differences we believe are important. The medium large peaks marked by X are much more prominent in figure 1(a) than in figure 1(b), where they have essentially disappeared. These peaks are not yet definitely identified. They do not appear to be recorded in the NIST98 library. Their mass spectra indicate similar building blocks not found in other peaks in many of them (they are likely to be oxygen-containing species).

Also when going from figure 1 (b) to (c) (flushed for 2 min 40 s) some noteworthy changes are taking place. HMB disappears completely and PMB is strongly reduced. On the other hand, xylenes and TriMB increase. TetraMB stays relatively unchanged.

Some medium peaks (e.g., at 16.05, 17.37 and 18.25 min) are indicated by NIST98 to be di- or trimethylphenols. Phenols are weakly acidic; it was therefore reasoned that by agitating the CCl_4 extract with 1 M NaOH phenols should be transferred to the aqueous phase. This was indeed the case. Neighboring peaks, expected to be hydrocarbons, remained unchanged.

The further evolution on going to the 10 min sample displayed in figure 2(a) may appear modest, but may still be of importance. The amount of adamantanes in the 14.5–15.5 region clearly increases, while the di- and trimethylphenols mentioned above disappear. Likewise the previously prominent peak at 19.57 min is no more visible.

When going from figure 2 (a) (methanol feed) to (b), where the feed is propene (both at TOS = 10 min) it is quite clear that the two product spectra display disparity, in particular with regard to quantitative aspects. There are also many peaks that are only found in one of the chromatograms. The polymethylbenzenes which are so prominent in figures 1 (a)–(c) and 2(a) display a rather different distribution in figure 2(b). Toluene (not shown in the chromatogram cuts) and xylenes are dominating products when the feed is propene. Benzene rings with isopropyl substituent(s) also appear. When methanol is feed, toluene is hardly present and xylenes are mostly minor products. A good part of the peaks with retention time between 14 and 16 min appear, however, to be present in both cases, and in similar amounts. Many of these peaks are caused by various adamantanes.

4. Discussion

The observation that arenes are dominant confined molecules, formed in parallel with the MTH reaction suggests that they may be intimately connected to the MTH reaction. One might argue that they might just be stable spectator molecules, which eventually fill up the cages and thus deactivate the catalyst. Figure 1 (b) and (c) shows that this is not the case. After a short flushing with carrier gas, PMB and HMB are strongly reduced or fully disappeared, while at the same time xylenes and TriMB increase correspondingly. Ignoring mechanism issues one may describe the observations by equations like:

$$\varphi(CH_3)_6 \rightarrow \varphi(CH_3)_3 + C_3H_6$$

or

$$\varphi(CH_3)_5 \rightarrow \varphi(CH_3)_3 + C_2H_4$$

Arene methylation is known to be rather fast. The arenes formed by the above reactions are therefore quickly remethylated. Figure 1 (b) and (c) shows that there are also other quite unstable molecules present that conceivably might take part in similar cycles.

Figure 1(a) shows that in addition to the polymethylbenzenes there are many other species formed after a very short time on stream. Figure 1(b) shows that many of these species constitute only a negligible fraction after 2 min on stream. At present we do not know if they actually disappear, or if the amount stays essentially constant and does not increase like the other compounds, thereby becoming insignificant. They might possibly be connected to the initial C–C bond forming activity of the catalyst. The reason for the presence of non-negligible amounts of phenols is not entirely clear, but they may point to carbocations within the cavities which react with water during the dissolution process.

It may not be superfluous to emphasize the great similarity in reaction conditions within the SAPO-34 cavities and the reaction conditions which prevailed during the ^{13}C-methanol/^{12}C-toluene experiments recently published [3]. In the co-reaction experiments it was worked with a molar feed ratio methanol/toluene ranging roughly from 5 : 1 to 1 : 1. These experiments strongly indicated that arenes or arene precursors play a vital role in the MTH reaction. There were no signs that C–C bond formation by reactions directly between C_1-entities was of any importance for forming ethene or propene. An objection that might be raised to the previous experiments and the conclusions drawn is that the arene content in the feed was unrealistically high for ordinary MTH reaction conditions.

The results obtained here, with methanol as the only feed, eliminate such an objection. After even a short time on stream there are evidently far more aromatic molecules than methanol/dimethyl ether within the SAPO-34 cavities. The results obtained here are in full accord with the previous co-reaction experiments.

An obvious extension of the work reported here would be to employ isotopic labeling. By switching between ^{12}C- and ^{13}C-methanol information about how, and through which molecules, methanol is incorporated in the confined molecules. Simultaneous isotopic analysis of the gas phase products in the MTH reaction is likely to be highly illuminating. Such work is in the initial phase – results are not yet available.

Note added in proof

Very recently Haw and his co-workers have, using NMR spectroscopy, arrived at essentially identical viewpoints on the MTH reaction taking place in SAPO-34 [5].

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