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Methanol to hydrocarbon catalysis on sulfated zirconia proceeds through a hydrocarbon-pool mechanism

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Aromatic hydrocarbons and other cyclic organic species have recently been identified as the locus of carbon–carbon bond forming and breaking in the conversion of methanol to olefins (MTO) on microporous solid acids such as HZSM-5 and HSAPO-34. In order to ascertain whether or not this hydrocarbon-pool mechanism for MTO catalysis is unique to zeotype solid acids, we studied the stronger solid acid sulfated zirconia. This study establishes a greater generality for the hydrocarbon-pool mechanism.

KEY WORDS: solid acids; methanol conversion; isotope tracing; *in situ* NMR.

1. Introduction

The conversion of methanol to hydrocarbons on zeolite HZSM-5 [1] has long been recognized as showing autocatalysis [2,3]. Also it was recognized by Mole and coworkers [4,5] that co-feeding toluene accelerated methanol conversion. Dahl and Kolboe [6,7] used a variety of evidence to formulate a phenomenological hydrocarbon pool mechanism for methanol conversion on HZSM-5 or the silico-aluminophosphate HSAPO-34. Using pulse-quench *in situ* ^{13}C NMR and isotope tracer methods, we identified specific hydrocarbon-pool species and modeled some of the reactions leading to olefins theoretically [8–11]. We identified cyclic carbenium ions as hydrocarbon-pool species (reaction centers) on HZSM-5 [8,9] and methylbenzenes as reaction centers on HSAPO-34 [10,11]. We also verified the effect of co-fed toluene on the rate of methanol to olefin (MTO) chemistry in HZSM-5. Arstad and Kolboe [12] used acid digestion and *ex situ* analysis to independently establish that methylbenzenes are hydrocarbon-pool species in HSAPO-34. In flow experiments on HZSM-5, the same authors [13] found that methylbenzenes undergo carbon label scrambling into ring positions during MTO reactions.

Thus, early hints about the effects of toluene or other organic adsorbates on methanol conversion catalysis formed the basis for very rapid recent progress towards increasingly specific details of the structure and function of the hydrocarbon pool in microporous solid acid catalysts. Hydrocarbon-pool mechanisms for MTO catalysis are displacing a number of “classical mechanisms” that involve oxonium-ylides, carbenium (CH_3^+) ions, carbenes, free radicals, or other small, energetic intermediates [14,15].

Here we consider whether a hydrocarbon pool can also function in MTO chemistry on a very different solid acid catalyst. While sulfated zirconia [16,17] has no potential as a commercial MTO catalyst, it has several properties that could assist one or more of the classical mechanisms for the direct conversion of methanol (or dimethyl ether) to olefins, eliminating the need for indirect conversion through less-energetic hydrocarbon-pool intermediates. Sulfated zirconia is commonly regarded as having stronger Brønsted acid sites than zeolite HZSM-5. Stronger acid sites would be expected to promote carbenium-type mechanisms. Sulfated zirconia also has a significant number of Lewis acid sites. Several of the classical mechanisms for “formation of the first C–C bond” in MTO chemistry require a fairly strong basic site for deprotonation of an intermediate species [15]. For example, in the long-studied oxonium-ylide mechanism, trimethyloxonium ion must be deprotonated to form the corresponding ylide, setting up either a Stevens rearrangement or a methylation step to form an $-OCH_2CH_3$ group that eliminates ethylene. The conjugate base site of zeolite ZSM-5 is weakly basic, and it is difficult to image ylide formation on the zeolite. Sulfated zirconia, however, has basic sites strong enough to deprotonate nitromethane [18].

We find that methanol conversion on sulfated zirconia proceeds through a hydrocarbon-pool mechanism that uses methylbenzenes as reaction centers for olefin synthesis. At 300 °C a first pulse of methanol onto freshly activated sulfated zirconia is not converted to hydrocarbons, but a sample spiked with toluene shows high conversion. GC-MS analysis of the volatile product stream from conversion of methanol–^{13}C and toluene shows extensive carbon label scrambling including aromatic ring carbons. *In situ* NMR confirms that methylbenzenes form spontaneously on sulfated zirconia during methanol conversion.

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2. Experimental

2.1. Materials and reagents

Methanol was supplied by Mallinckrodt, methanol–^{13}C (99%) was obtained from Cambridge Isotope Laboratories, while toluene (99.8%), benzene (99.8%) and zirconyl chloride octahydrate (98%) were purchased from Aldrich. Sulfated zirconia samples were prepared using the standard, two-step method [19,20]. Zirconium hydroxide was prepared by hydrolysis of zirconyl chloride ($ZrOCl_2 \cdot H_2O$) with aqueous ammonia (29.8%). Ammonia was slowly added to an aqueous solution of zirconyl chloride at room temperature. After stirring for 1 h, the precipitated gel (zirconium hydroxide) was washed with deionized water and filtered and dried at 673 K for 24 h. Zirconium hydroxide was soaked with 1 N sulfuric acid solution (12 ml per 4 g of zirconium hydroxide) with stirring for 1 h at room temperature. The H_2SO_4-impregnated zirconium hydroxide samples were dried at 673 K in air for 24 h.

2.2. Catalysis

We used a pulse-quench reactor [8–11,21] to study hydrocarbon synthesis reactions. For each experiment we loaded the reactor with a cylindrical bed (0.350 g) of fresh sulfated zirconia. In every case, the catalyst bed was activated in place immediately prior to use by heating at 500 °C for 1 h in flowing air. The pulse-quench reactor is essentially a fixed-bed microflow reactor. Helium (600 sccm) was used as the carrier gas, and reactants were introduced in pulses using injection valves.

2.3. NMR spectroscopy

^{13}C solid-state NMR experiments [8–11] were performed with magic angle spinning (MAS) on a modified Chemagnetics CMX 300 MHz spectrometer operating at 75.4 MHz for ^{13}C. Hexamethylbenzene (17.4 ppm) was used as an external chemical shift standard, and all ^{13}C chemical shifts are reported relative to TMS. Chemagnetics-style pencil probes spun 7.5 mm zirconia rotors at typically 6.5 kHz with active spin speed control (±3 Hz). Typical ^{13}C experiments included the following cross polarization (CP, 2 ms contact time, 1 s pulse delay, 4000 transients). All the spectra shown were obtained with cross polarization.

2.4. GC-MS

Reaction products were separated by gas chromatography (Agilent 6890 Series GC system) equipped with a Petrocol DH 150 capillary column (fused silica capillary column, 150 m long, 0.25 mm diameter, 1.0 μm film thickness). The products were analyzed by mass spectrometry (Agilent 5973 mass selective detector) with an ionization voltage of 69.9 eV and a source temperature of 240 °C.

3. Results

3.1. Methanol conversion on sulfated zirconia at 400 °C

Figure 1 reports a GC-MS total ion chromatogram of the product stream sampled 2 s after injection of methanol

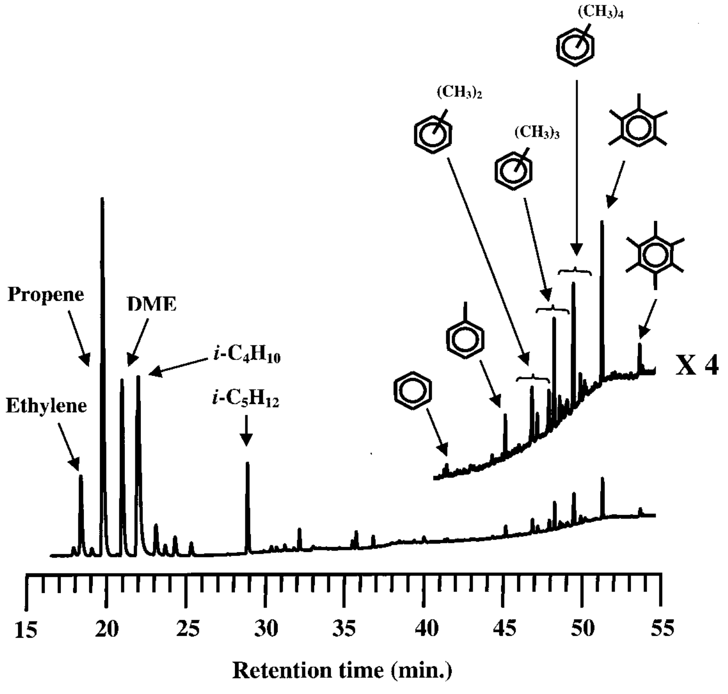

Figure 1. GC/S total ion chromatogram of the product stream from a sulfated zirconia catalyst bed sampled 2 s following injection of 20 μl of methanol onto a 350 mg bed of sulfated zirconia operated at 400 °C.

onto a sulfated zirconia catalyst bed operated at 400 °C. Conversion of methanol and dimethyl ether to hydrocarbons was over 85%. The products included some olefins, notably ethylene and propene, but the yields of methylbenzenes and alkanes were high as well, reflecting secondary reactions.

3.2. In situ NMR

We made several injections of methanol–^{13}C onto sulfated zirconia catalyst beds at 400 °C in a flow reactor and several seconds later rapidly quenched the reactor temperature to ambient. Entire catalyst beds were loaded into MAS NMR rotors and ^{13}C CP/MAS NMR spectra of the catalysts were measured at room temperature. Figure 2 reports spectra measured for samples that reacted at 400 °C for 2 s (a) and 4 s (b), after methanol injection but prior to thermal quench. Both spectra show methylbenzenes (19 and 135 ppm) and surface-bound methoxy (methoxonium) species (53 ppm). This is reminiscent of an analogous study on HSAPO-34 [9] with the exception of the more rapid formation of aromatic hydrocarbons on sulfated zirconia. A small amount of isobutane is seen at 27 ppm. Aromatics are trapped in the cages of HSAPO-34, and their number does not decrease with time. In contrast, they may freely desorb from sulfated zirconia, and the spectrum acquired after 4 s of reaction shows about half the intensity of the one after 2 s.

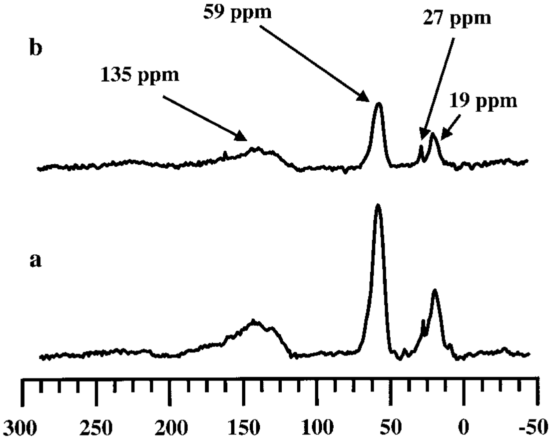

Figure 2. 75.4 MHz ^{13}C CP/MAS NMR spectra of the reaction products formed on sulfated zirconia catalyst beds from the reactions of methanol–^{13}C at 400 °C using conditions very similar to those for the experiment in figure 1. Samples were prepared using a pulse-quench reactor and the catalyst bed was quenched after 2 s (lower spectrum) or 4 s (upper spectrum) of reaction. Signals due to methylbenzenes on the catalyst surface and surface-bound methoxy (methoxonium) species (59 ppm) are indicated.

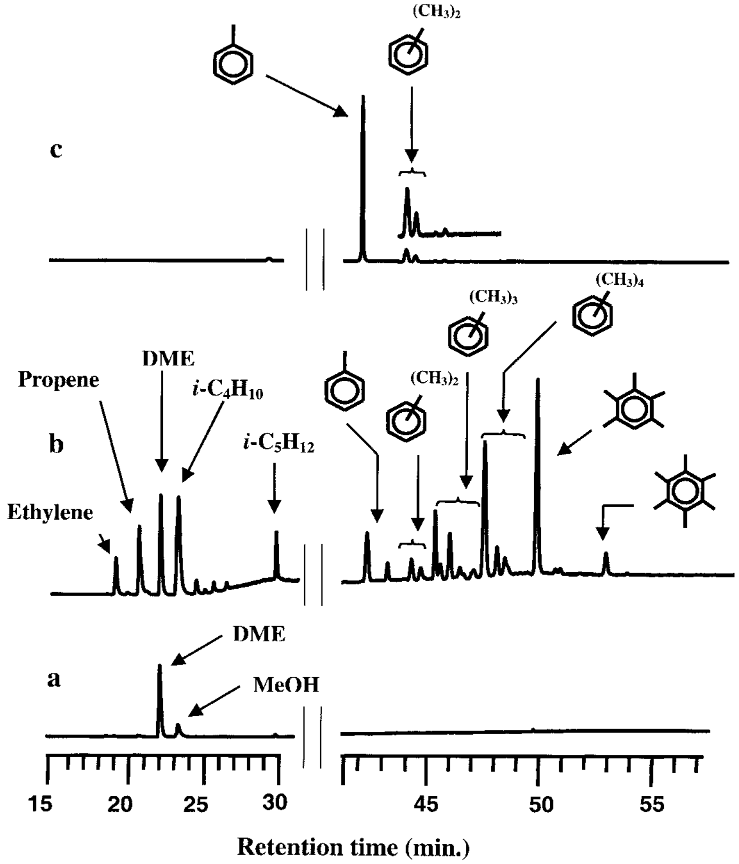

Figure 3. GC/MS total ion chromatograms from experiments testing whether or not MTO chemistry proceeds through a hydrocarbon-pool mechanism on sulfated zirconia catalyst at 300 °C. (a) No conversion to hydrocarbons was observed following injection of 20 μl of methanol alone onto a fresh catalyst bed. (b) High conversion was obtained after injection of 25 μl of a solution of toluene in methanol–^{13}C (1 : 10 mol : mol). (c) Control experiment showing that toluene alone (5 μl) is nearly unreactive on sulfated zirconia. A small amount of disproportionation was observed, but no olefin formation.

3.3. Methanol conversion on sulfated zirconia at 300 °C

Hydrocarbon-pool mechanisms are more easily detected at lower temperatures where the catalyst does not so readily synthesize reaction centers from impurities in the feed or minority reaction pathways. The total ion chromatogram in figure 3(a) shows that 2 s after the injection of methanol onto sulfated zirconia at 300 °C there was no conversion to hydrocarbons.

For the experiment in figure 3(b) we injected a solution of methanol–^{13}C and toluene (10 : 1 mol : mol) onto a freshly activated sulfated zirconia catalyst bed at 300 °C and sampled the product stream 2 s later for GC-MS analysis. As Mole and co-workers [4,5] originally observed on HZSM-5, co-injected toluene has a dramatic effect on methanol conversion on sulfated zirconia. The light products included ethylene, propene, isobutane and isopentane, while the aromatics included essentially all methylbenzenes including penta- and hexamethylbenzene. Figure 3(c) is a control experiment that shows that toluene alone was unreactive on sulfated zirconia except that a trivial amount of disproportionation benzene and xylenes occurred.

Quantitative analysis of the mass spectra showed that the carbon-isotope distribution of the ethylene in figure 2(b) was 22.4% $^{13}C_0$, 32.4% $^{13}C_1$ and 45.3% $^{13}C_2$. Propene also showed extensive scrambling: 15.6% $^{13}C_0$, 15.0% $^{13}C_1$, 29.4% $^{13}C_2$ and 40.0% $^{13}C_3$. Figure 4 reports ion mass distributions in the vicinity of the molecular ions for selected methylbenzene products from the experiment in figure 3(b). Toluene incorporated only a trivial amount of ^{13}C label from methanol, suggesting that the toluene seen in figure 3(b) for the most part passed through the reactor without undergoing methylation. The xylenes (*o*-xylene shown) all picked up one ^{13}C from methanol, and most of them also scrambled one or more ^{13}C into the ring. With three or more methyl groups extensive ring methylation was the rule.

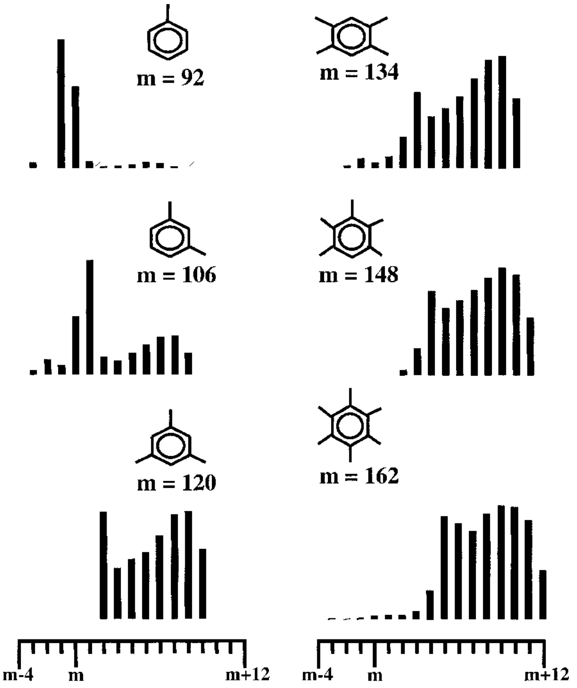

Figure 4. Bar graphs showing ion mass distributions in the vicinities of molecular ions for methylbenzenes formed in the experiment reported in figure 3(b). Some of the hexamethylbenzene molecules had ^{13}C label exchange into all 12 positions, indicating extensive scrambling between ring and methyl positions.

4. Discussion

This contribution demonstrates that methanol is converted to hydrocarbons on sulfated zirconia through a hydrocarbon-pool mechanism with methylbenzenes as reaction centers. Given the diversity and strength of acid–base properties of sulfated zirconia one might have expected that any of several classical mechanisms for the direct conversion of methanol to hydrocarbons would be more facile on this catalyst than on zeolite HZSM-5. On the contrary, at 300 °C in the absence of a hydrocarbon pool there is no conversion of methanol/DME to hydrocarbons on sulfated zirconia. Our findings here tend to generalize the importance of hydrocarbon-pool mechanisms beyond microporous solid acids.

In situ NMR showed the formation of methylbenzenes on the surface during MTO catalysis, as has been observed by analogous studies on HSAPO-34 and HZSM-5, and indeed methylbenzenes are volatile products as on HZSM-5 but not HSAPO-34 (from which they may not exit). The formation of surface methoxy groups on sulfated zirconia was observed in another recent *in situ* study of that catalyst [18].

The mechanistic significance of carbon label scrambling into the aromatic rings of reaction centers during MTO catalysis is not certain, although it has previously been observed by Kolboe and cited as evidence of MTO reactivity [13]. Chang [15] has reviewed some of the possible mechanisms by which methylbenzenes could function as reaction centers in MTO catalysis. He considered both ring contraction followed by expansion (6 △ 5) and expansion followed by contraction (6 △ 7). Either process could in principle extend an alkyl chain for elimination as an olefin and either would necessarily exchange carbon labels between methyl and ring positions. A (6 △ 5) mechanism was proposed in 1961 to account for the elimination of C_4 products from hexamethylbenzene on a bifunctional catalyst [22]. While the carbon label scrambling observed here does not necessarily support any given mechanism for the elimination of olefins from methylbenzenes, the evidence of carbon label exchange is suggestive of ring expansion–contraction routes, but other explanations are also possible.

Acknowledgments

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