10726 *J. Am. Chem. Soc.* **2000,** *122,* 10726−10727

Methylbenzenes Are the Organic Reaction Centers for Methanol-to-Olefin Catalysis on HSAPO-34

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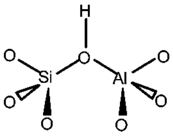
Received June 20, 2000

The catalytic conversion of methanol to olefins[1] is a major emerging chemical technology and the key step in the conversion of natural gas to polyolefins using otherwise mature chemistry. The most promising catalysts for commercial trials are solid acids based on silico-aluminophosphates of the chabazite (CHA) structure, most simply HSAPO-34.[2] The acid function in this material **1** is similar to that in aluminosilicate zeolites, but it is imbedded in an aluminophosphate lattice. The CHA topology features cages of ca. 1.0 nm by 0.67 nm diameter that are interconnected through windows of ca. 0.38 nm diameter. Thus, reactants such as methanol and dimethyl ether and products such as ethylene and propene may freely diffuse through active catalysts, but products with larger kinetic diameters, even isobutylene, are trapped within the cages.



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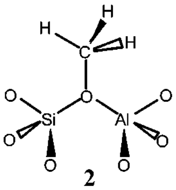

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Figure 1 reports ^{13}C MAS NMR spectra of HSAPO-34 samples[3] that were exposed to identical pulses of methanol-^{13}C for between 2 and 7200 s in a flowing He stream at 673 K prior to a rapid thermal quench.[4] In this experiment, the product gases were also analyzed by GC. At the shortest reaction times, the conversion of methanol and dimethyl ether was low, and the ^{13}C NMR spectra reveal both adsorbed methanol (50 ppm) and a shoulder at 56 ppm that we assign to the chemisorbed methoxy (methoxonium) species **2** in agreement with previous NMR studies of catalysts,[5] and in particular, to account for the time-course of this resonance in Figure 1.

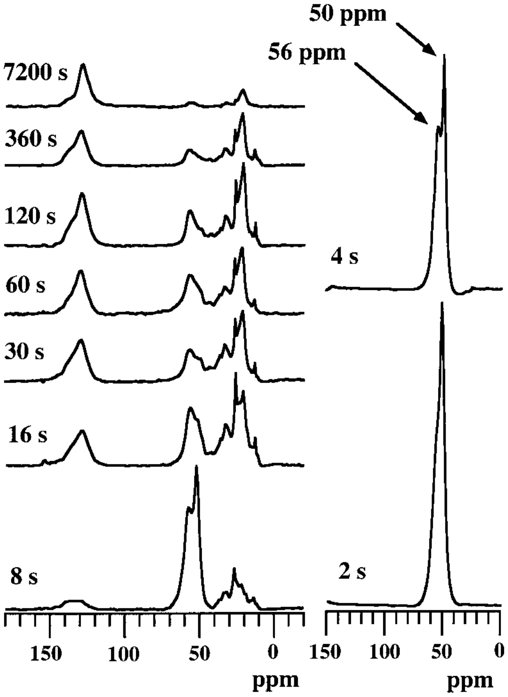

Figure 1. 75 MHz ^{13}C CP/MAS NMR spectra of samples from a pulse-quench study of methanol conversion on HSAPO-34 at 673 K. Each sample was prepared by injecting 20 μL of methanol-^{13}C onto a freshly activated catalyst bed (0.3 g) while He was flowed at 600 mL min^{-1}, and reaction occurred for the times shown followed by a rapid thermal quench. All spectra (4000 scans) were measured at 298 K using a 2-ms contact time.

After 4 s of reaction there is a dramatic reduction in the amount of methanol on the catalyst and methyl-substituted aromatics form as signaled by the aromatic resonance at 129 ppm (with a shoulder at 134 ppm due to substituted ring carbons) and methyl groups at 20 ppm. Other upfield signals are accounted for by alkane products trapped in the cages. The average number of methyl groups per ring reaches a maximum of ca. 4 between 30 and 120 s of reaction, but this decreases to ca. 1.4 after the catalyst ages for 7200 s at 673 K without injection of additional feed. GC analysis confirms that *traces* of olefin products exit the catalyst bed even 7200 s after methanol injection. The 56 ppm resonance persists in catalyst samples for at least several minutes, and a small amount is present after even 2 h at 673 K. This evidence of strong adsorption supports the assignment of this resonance to the framework methoxonium species **2**.

Figure 2 reports GC traces that compare the activity of a completely fresh catalyst exposed to a single pulse of methanol with that of a second catalyst that was first treated with a methanol pulse 360 s prior to a second, identical pulse. With fresh catalyst the conversion was only 14%, but the catalyst pretreated to form methylbenzenes achieved nearly 100% conversion of the second methanol pulse. A control experiment in Figure 2 shows that the products from the second pulse vastly overwhelm those from the first pulse after 360 s of reaction. Experiments such as those in Figures 1 and 2 provided very strong evidence that in order for HSAPO-34 to be active for MTO chemistry, it must have methylbenzenes trapped in some of its cages.

We performed a number of experiments using methanol-^{13}C in a first pulse to synthesize methylbenzenes followed by a smaller pulse of natural abundance methanol. In a typical result, we found that the ethylene sampled 3 s after the second (natural abundance) methanol pulse had the following carbon isotopomer distribu-

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(1) Stöcker, M. *Microporous Mesoporous Mater.* **1999**, *29*, 3−48.

(2) Wilson, S.; Barger, P. *Microporous Mesoporous Mater.* **1999**, *29*, 117−126.

(3) HSAPO-34 was prepared according to the following: Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. U.S. Patent 4,440,871, 1984. XRD showed a pure crystalline phase with the CHA structure. The product was calcined at 873 K for 10 h to remove the template agent and pressed into 10−20 mesh pellets. The Brønsted site concentration was determined to be 1.1 mmol/g. In typical experiments 0.3 g of catalyst was activated at 673 K under 600 sccm He flow for 2 h immediately prior to use in a pulse-quench reactor.

(4) For discussion of the pulse-quench in situ NMR experiment see: (a) Haw, J. F.; Goguen, P. W.; Xu, T.; Skloss, T. W.; Song, W.; Wang, Z. *Angew. Chem.* **1998**, *37*, 948−949. (b) Goguen, P. W.; Xu, T.; Barich, D. H.; Skloss, T. W.; Song, W.; Wang, Z.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 2651−2652. (c) Xu, T.; Barich, D. H.; Goguen, P. W.; Song, W.; Wang, Z.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 4025−4026.

(5) Anderson, M. W.; Sulikowski, B.; Barrie, P. J.; Klinowski. *J. Phys. Chem.* **1990**, *94*, 2730−2734.

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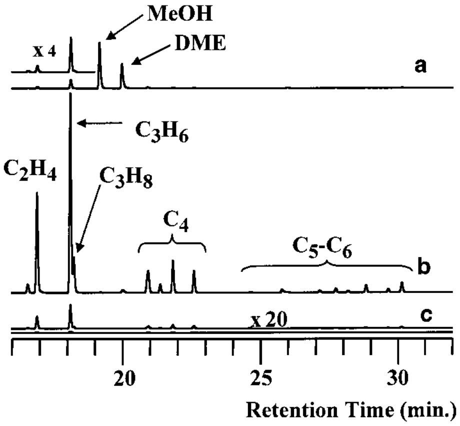

Figure 2. GC (flame ionization) analyses of the gases exiting the HSAPO-34 catalyst bed operated as in the previous figure, except as a "double-pulse" experiment. Identical, 20 μL methanol pulses were applied at 0 and 360 s: (a) 4 s after the first pulse the total conversion of methanol and dimethyl ether (DME) to hydrocarbons was only ca. 14%. (b) 364 s after the first pulse and 4 s after the second pulse, the conversion was essentially 100%. (c) This control experiment shows that only traces of products exit the reactor 358 s after the first methanol pulse; hence, the products observed at 364 s reflect conversion of the second methanol pulse.

tion: 43% $^{13}C_0$, 47% $^{13}C_1$, and 10% $^{13}C_2$. The formation of ethylene-$^{13}C_1$ is consistent with side-chain alkylation followed by elimination. Competing reactions including ring methylation and de-methylation and exchange of methoxonium species **2** account for the formation of other isotopomers. Propene was also synthesized using carbon from both the labeled methylbenzenes and unlabeled methanol.

Figures 1 and 2 show that MTO chemistry on HSAPO-34 exhibits a kinetic induction period and that the ship-in-a-bottle synthesis of methylbenzenes in the cages produces a working catalyst. These aromatic rings are trapped by the catalyst's topology, but the methyl groups are free to exchange or react with methanol. In recent pulse-quench NMR and theoretical studies of hydrocarbon synthesis on the aluminosilicate zeolite HZSM-5, we found that methyl-substituted cyclopentenyl carbenium ions, in equilibrium with neutral cyclic dienes, served as organic reaction centers for MTO chemistry.[6] Theoretical calculations outlined a catalytic cycle that led to elimination of ethyl and propyl groups to form the primary olefinic products.[6] HSAPO-34 is a weaker acid than HZSM-5 and it is used at a higher temperature. Also, the topology of HZSM-5 permits methylbenzenes, which are synthesized through cyclopentenyl cation intermediates,[6] to readily desorb from the catalyst and enter the product stream. Indirect evidence of the "cocatalytic" role of toluene in methanol conversion on HZSM-5 includes the work of Mole.[7] Dahl and Kolboe have previously suggested that methanol conversion on solid acids passes through a phenomenological "carbon-pool" mechanism.[8]

We also discovered that the deactivation of HSAPO-34 is the result of the conversion of methylbenzenes to polycyclic aromatics. For example, with continuous injection of methanol at a WHSV of 33 h^{-1}, catalyst deactivation occurred after ca. 40 min, at which time the catalyst was 16.2% C by weight. This deactivated catalyst had negligible methanol uptake at 298 K. ^{13}C solid-state NMR shows that as the catalyst deactivates, there is not only an increase in carbon content, but also a structural change in the organic component to polycyclic aromatics typified by methylnaphthalene. Indeed, the observed carbon content of the deactivated catalyst is consistent with, on average, a C_{10} species in every cage.

In conclusion, the active site for olefin synthesis on HSAPO-34 is a composite of a well-defined organic species and one or more inorganic acid sites, which can activate methanol and hold methyl cation equivalents. All of this takes place in a nanocage that preserves the organic component and regulates selectivity through steric constraints. The HSAPO-34 active site then is no less elegant than those praised in enzyme chemistry, and if it operates at far higher temperatures it also self-assembles with little to work with. The detailed mechanism by which this site operates is under intensive investigation.

Acknowledgment. J.F.H. is supported by the National Science Foundation (CHE-9996109) and the U.S. Department of Energy (DOE) Office of Basic Energy Sciences (BES) (Grant No. DE-FG03-93ER14354). J.B.N. is funded by the Department of Energy (DOE) Office of Science. Pacific Northwest National Laboratory is a multipurpose national laboratory operated by Battelle Memorial Institute for the U.S. DOE.

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