

Communications to the Editor

Pulse-Quench Catalytic Reactor Studies Reveal a Carbon-Pool Mechanism in Methanol-to-Gasoline Chemistry on Zeolite HZSM-5

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The mechanism of methanol-to-gasoline (MTG) chemistry¹ catalyzed by zeolite HZSM-5 is one of the most intensively studied problems in heterogeneous catalysis. In situ NMR methods using sealed samples have been applied by several groups in an effort to better understand MTG chemistry.^{2–5} Recent theoretical investigations have focused on the structure of adsorbed species⁶ and reaction pathways leading to the first carbon–carbon bond.^{7–9} Two features of the reaction are clear: methanol equilibrates with dimethyl ether and water and there is an induction period before the onset of extensive hydrocarbon synthesis.

We have used our recently developed pulse-quench catalytic reactor¹⁰ in the first NMR study of MTG chemistry under conditions identical to conventional flow reactors. The organic species on the catalyst bed were characterized by NMR at room temperature following a rapid (200 ms) quench from reaction temperature. In addition, the volatile products which exited the reactor at high temperature were analyzed by gas chromatography or GC-MS. Figure 1 reports ¹³C MAS NMR spectra of the catalyst beds from pulse-quench experiments in which [¹³C]-methanol was injected onto the bed¹¹ at 643 K and allowed to react with continuous He carrier gas flow for between 200 ms and 16 s prior to quench. The induction period was obvious in the first 2 s of the reaction: methanol was partially converted to dimethyl ether, but the only hydrocarbons detected were traces of ethylene seen in the GC traces at 1 s and later and sometimes traces of isobutane seen in the NMR spectra of the catalyst. Four

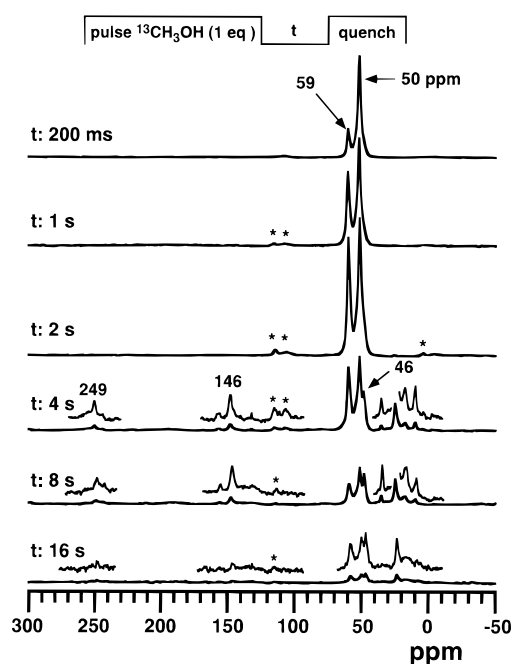
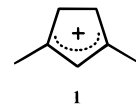


Figure 1. ¹³C MAS NMR (90.5 MHz) spectra from pulse-quench in situ studies of MTG chemistry on zeolite HZSM-5 at 643 K with He carrier gas flow; reaction times from 200 ms to 16 s are shown. ¹³C NMR signals of methanol (50 ppm), dimethyl ether (59 ppm), and cations similar to **1** (249, 146 and 46 ppm) are indicated. Signals in the upfield region (10–35 ppm) are due to hydrocarbons. Spectra were measured at 298 K after a rapid thermal quench. An asterisk denotes spinning sideband.

seconds of reaction reproducibly formed abundant hydrocarbons; propene and smaller amounts of ethylene and C₄ olefins then dominated the GC trace, and the NMR spectrum showed alkanes and alkyl substituted cyclopentenyl carbenium ions similar to **1**.

Species **1** is a very stable carbenium ion that has been shown to form readily on zeolites from the reactions of olefins,^{12,13} including ethylene,¹⁴ and we observed ethylene during the induction period. Cyclopentenyl cations readily undergo extensive skeletal rearrangements that include equilibration with six-membered rings and open-chain species.



We investigated the possible mechanistic consequences of olefin oligomerization products in MTG chemistry by a series of “double-pulse” experiments in which we introduced various reagents in a first pulse and then interrogated the MTG reaction at times shorter than the normal induction period with [¹³C]-methanol delivered in a second pulse (Figure 2). When the first pulse delivered N₂, *p*-difluorobenzene, or *n*-heptane, there was no effect on the induction period following the [¹³C]methanol pulse, and the only ¹³C-labeled hydrocarbon product seen in Figure

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
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(11) For each experiment, 0.25 g of catalyst was used. This was prepared from zeolite (Si/Al = 19) powder mixed with a minimal amount of alumina binder and extruded into 1-mm diameter pellets. The catalyst bed was isolated immediately following the quench, and it was transferred to an MAS rotor and sealed in a glovebox. The sample was at no time exposed to the atmosphere.

Table 1. ^{13}C Isotopic Distributions for Propene Samples Synthesized on Zeolite HZSM-5 in Double-Pulse Experiments Similar to Those Reported in Figure 2^a

injection 1		injection 2		isotopic distribution (%)			
loading ^b (equiv)	reagent	loading ^b (equiv)	reagent	$^{13}\text{C}_0$	$^{13}\text{C}_1$	$^{13}\text{C}_2$	$^{13}\text{C}_3$
0.5	$^{13}\text{CH}_3\text{OH}$	0.5	$^{13}\text{CH}_3\text{OH}$				100.0
0.5	$^{13}\text{CH}_3\text{OH}$	0.5	$^{12}\text{CH}_3\text{OH}$	39.4	19.4	11.4	29.8
0.5	$^{12}\text{CH}_3\text{OH}$	0.5	$^{13}\text{CH}_3\text{OH}$	41.4	11.9	21.4	25.3
0.4	$\text{CH}_3^{13}\text{C}(\text{OH})\text{CH}_3$	1.0	$^{12}\text{CH}_3\text{OH}$	15.4	81.4	3.2	
0.6		0.4	$^{13}\text{CH}_3\text{OH}$	51.9	34.9	13.2	

^a The distribution of the isotopomers was determined by a nonlinear least-squares fit for m/e peaks 37–45. ^b Loadings are reported in units of molecules injected per acid site in the catalyst bed.

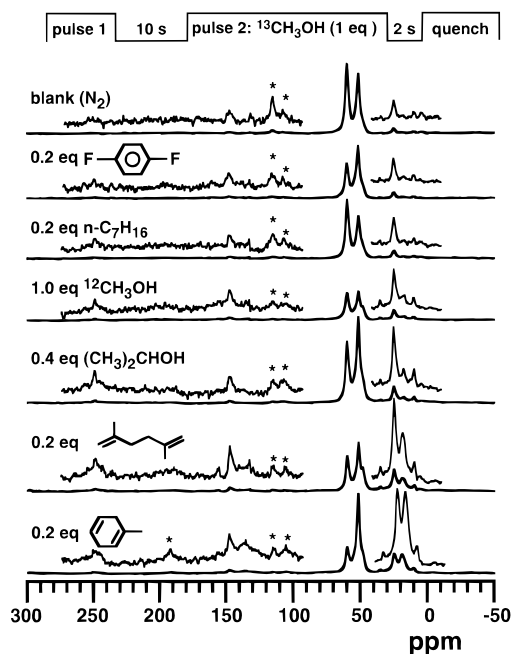


Figure 2. ^{13}C MAS NMR (90.5 MHz) spectra from double-pulse experiments probing the effects of injecting various reagents in a first pulse 10 s before a second pulse of ^{13}C methanol. Signals in the upfield region (10–35 ppm) are due to hydrocarbons. Spectra were measured at 298 K after a rapid thermal quench from the reaction temperature, which was 643 K. An asterisk denotes spinning sideband.

2 is a small quantity of isobutane. When ^{12}C methanol (99.95% ^{12}C) was injected in the first pulse, some hydrocarbons were synthesized from the ^{13}C methanol delivered in the second pulse. Injection of olefins or olefin precursors in the first pulse had a dramatic effect on hydrocarbon synthesis from ^{13}C methanol delivered in the second pulse. Furthermore, the effect increased with the degree of unsaturation of hydrocarbon delivered in the first pulse.

Of the many and varied mechanisms previously proposed for MTG chemistry, only the “carbon-pool” idea of Kolboe^{15–17} explains our observations. Kolboe proposed that olefin synthesis in MTG chemistry occurs through a carbonaceous species of unknown stoichiometry, possibly a carbenium ion.¹⁸ This species is assumed to be alkylated by methanol or dimethyl ether until it eliminates an olefin and restarts the catalytic cycle. We trapped the volatile gases from several double-pulse experiments (suggested by Figure 2) and measured the isotope distributions in propene by GC-MS. Table 1 shows that the propene contained carbon atoms from both reagent pulses, and this strongly supports a carbon-pool mechanism.

On the basis of Figures 1 and 2, it is tempting to identify cyclopentenyl cations as the active carbon species. However, ab initio calculations predict that dimethyl ether does not bind to cation **1**, and more reactive species must be considered. We conclude that the cyclopentenyl cations are in equilibrium with the active carbon species at high temperature. These species would include polyenes, and the moderately stable carbenium ions formed from polyenes are also plausible candidates for reaction intermediates.

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