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"NMR and Computational Studies of Solid Acidity/Fundamental Studies of Catalysis by Solid Acids"

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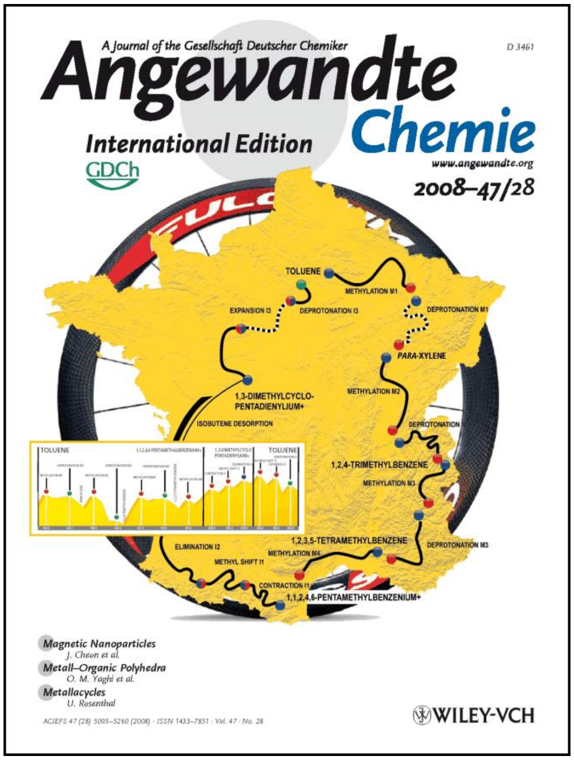


This project focused on catalysis by zeolites and the synergy of spectroscopic characterization and theoretical modeling. In collaboration with the Waroquier group in Belgium we used state-of-the-art quantum chemical simulations on a supramolecular model of both the HZSM-5 zeolite and the co-catalytic hydrocarbon pool species and calculated a full catalytic cycle (including all rate constants) for methanol-to-olefin (MTO) catalysis involving a hydrocarbon pool species. This work not only represents the most robust computational analysis of a successful MTO route to date, but it also succeeds in tying together the many experimental clues. That work was featured on the cover of *Angewandte Chemie*.

More recently we elucidated several unsuspected roles for formaldehyde in methanol to olefin catalysis. Formaldehyde proves to be a key species responsible for both the growth of the catalytically active hydrocarbon pool and its inevitable aging into deactivated polycyclic aromatic species. The apparent inevitability of formaldehyde formation at high temperatures, in particular in contact with active metal or metal oxide surfaces, may put some fundamental limitations on the economic potential of conversion of methanol to olefins. Several papers from the formaldehyde work, abstracted below, are still being written up.

Accelerated MTO Deactivation by Formaldehyde

Industrial-scale MTH catalysis is preformed in stainless steel reactors at temperatures upwards of 723 K. Stainless steel (specifically Type 316) is composed of primarily of iron and carbon but it also contains chromium (16-18%), nickel (10-14%), molybdenum (2-3%) and traces of manganese, silicon, phosphorus, and sulfur. Upon exposure to air, the non-ferrous metals are oxidized and form a thin protective oxide layer on the surface of the iron that prevents rusting. Some metal oxides, such as molybdium oxide, have shown catalytic activity in producing formaldehyde from methanol.

The primary means of producing formaldehyde is the catalytic oxidation of methanol as described by equation (1), which can be accomplished by two different pathways.

$$2\,CH_3OH + O_2 \rightarrow 2\,CH_2O + 2\,H_2O \qquad (1)$$

The first route uses a silver catalyst at temperatures of 870-970 K. A methanol-air-steam feedstock, containing 36-45% methanol, is required for the reaction and both methanol oxidaton and methanol dehydrogenation, as described by equation (2), result in formaldehyde generation. The second route is the formox process that employs an iron-molybdenum oxide catalyst. This process has several advantages over the silver pathway, as it is a lower temperature (570-670 K) process and required a lower concentration methanol, only 10-15% to produce formaldehyde.

$$CH_3OH \rightarrow CH_2O + H_2 \qquad (2)$$

Formaldehyde has been proposed in early indirect mechanisms as a key methylating agent, but it has not been extensively studied under MTO conditions. There are many potential reactions available to formaldehyde in an MTO environment. Formaldehyde is a good electrophile and can react with both olefins and aromatics in electrophilic addition and substitution reactions, respectively, and the product of both of these reactions is an alcohol. One specific example is known as the Prins reaction, where formaldehyde reacts with an alkene to produce a diol or allyic alcohol depending on reaction conditions.

The reaction of formaldehyde with olefinic species was investigated on 200 mg of 50 wt% HSAPO-34 with SiC at 648 K. A flow of formaldehyde was introduced into the system by a syringe pump, and the flow rate was 0.1843 mL/hr (WHSV= 0.74 hr^{-1}). Propene was introduced into the system in a 5% mixture with helium at a rate of 20 sccm, which brought the total flow of helium to approximately 50 sccm. The ratio of propene to formaldehyde was equimolar, and equated to approximately two moles of each per acid site over five minutes. The effluent was sampled at five-minute intervals for 75 minutes.

To generate formaldehyde directly from methanol, additional stainless steel tubing (8 feet) heated to 773 K was added to the reactor system downstream of the methanol introduction but upstream from the catalyst. A 200 mg catalyst bed of 50 wt% HZSM-5 (Si/Al=40) with SiC heated to 648 K with 50 sccm He was used, allowing the diffusion of aromatic species. Methanol was injected into the system via syringe pump at a rate of 0.506 mL/hr (WHSV=4 hr^{-1}) for five minutes. A control experiment was conducted under the same conditions but without the additional tubing.

The FID chromatograms from the reaction of formaldehyde with propene are shown in Figure 1, and Figure 2 depicts the evolution of product selectivities with increasing time on stream. Butenes were the dominant product after five minutes time on stream, with nearly an 80% product selectivity. Small amounts of ethylene and pentenes were also observed; however, no alcohols or other unusual MTO products were seen. After 10 minutes of flowing propene and formaldehyde, ethylene became the main product, increasing selectivity from 11% at five minutes to almost 50% at 10 minutes. Butene selectivity was still high at this time but pentene selectivity decreased by half with less than 5% selectivity at 10 minutes. A new product, butadiene, was also observed but the selectivity was low, similar to that of the pentenes. From 15 to 25 minutes time on stream, the ethylene selectivity increased to approximately 60%. Butene selectivity continued to decrease over these times, as did pentene selectivity. More butadiene was observed, doubling from 10 to 15 minutes and increasing slightly at 20 and 25 minutes. At 20 minutes, small amounts of methanol and dimethyl ether (DME) were observed, and increased consistently with additional time on stream. At 75 minutes, only small amounts of ethylene, butanes, and pentenes were observed. Butadiene was still observed in the product stream, but the selectivity decreased significantly compared to the maximum selectivity seen at 25 minutes. Methanol and DME were the main products after 75 minutes on steam.

At 20 minutes time on stream, methanol and DME were observed in the reactor effluent and increased in selectivity throughout the remainder of the experiment. The formaldehyde used in this study contained methanol as a stabilizing agent to prevent polymerization thus methanol and DME were not actual products of the reaction between propene and formaldehyde. They were more like impurities in this case, but were included in the product selectivity to represent catalyst activity: the more methanol and DME in the reactor effluent, the more deactivated the catalyst. The flow rate of the methanol was 0.025-0.038 mL/hr, which corresponded to $WHSV_{MeOH}$= 0.20-0.30 hr^{-1}. In a standard MTO experiment, the methanol flow rate was between WHSV= 4 and WHSV= 8 hr^{-1} thus the contribution of methanol conversion to the overall product selectivity would be small but not negligible.

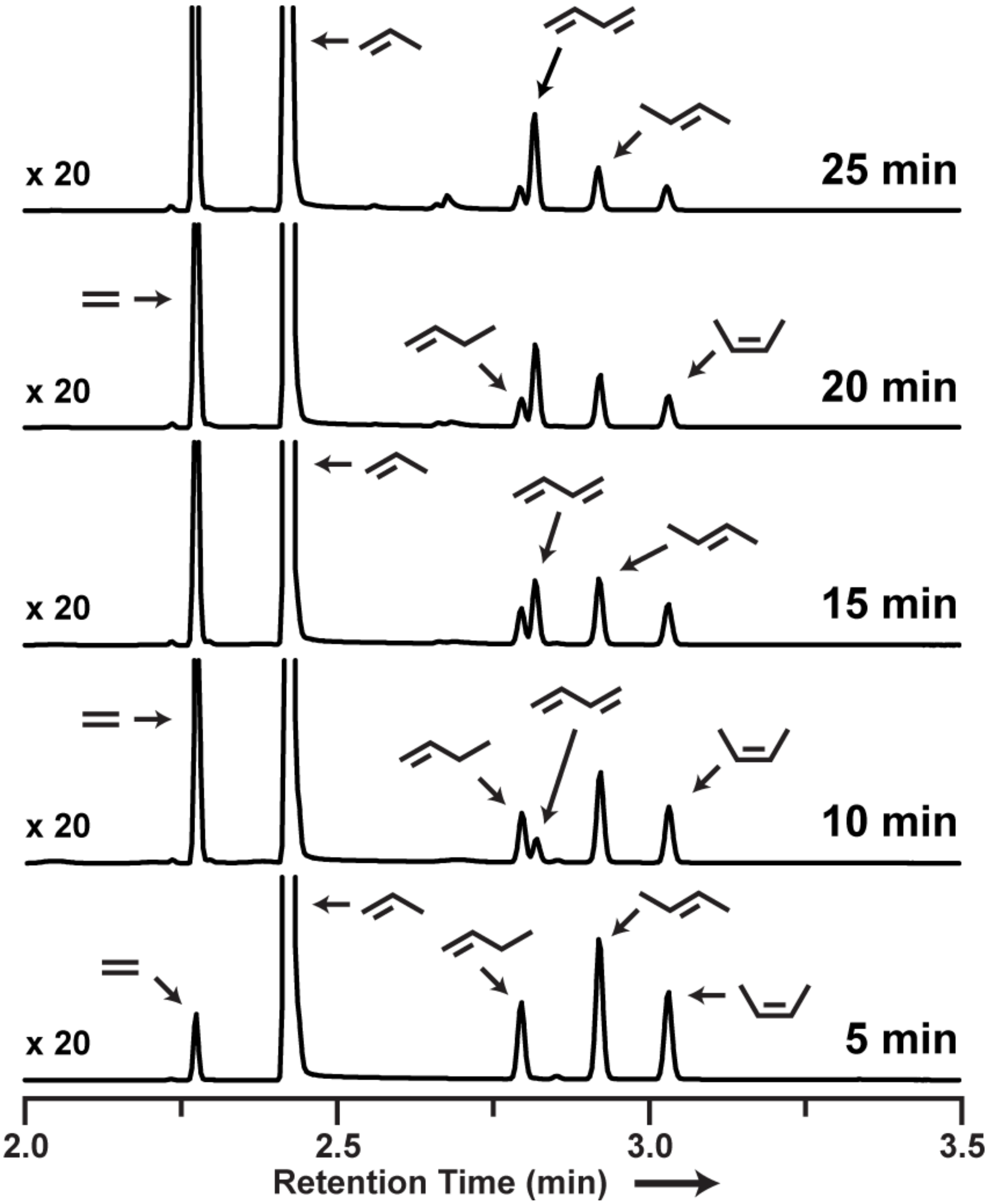


Figure 1. In-situ butadiene generation from propene and formaldehyde. The Prins reaction of propene and formaldehyde on HSAPO-34 resulted in butadiene formation instead of an alcohol. Acid-catalyzed dehydration of the alcohol product would explain the diene product. High ethylene selectivity was also observed, suggesting potential butadiene involvement in ethylene production.

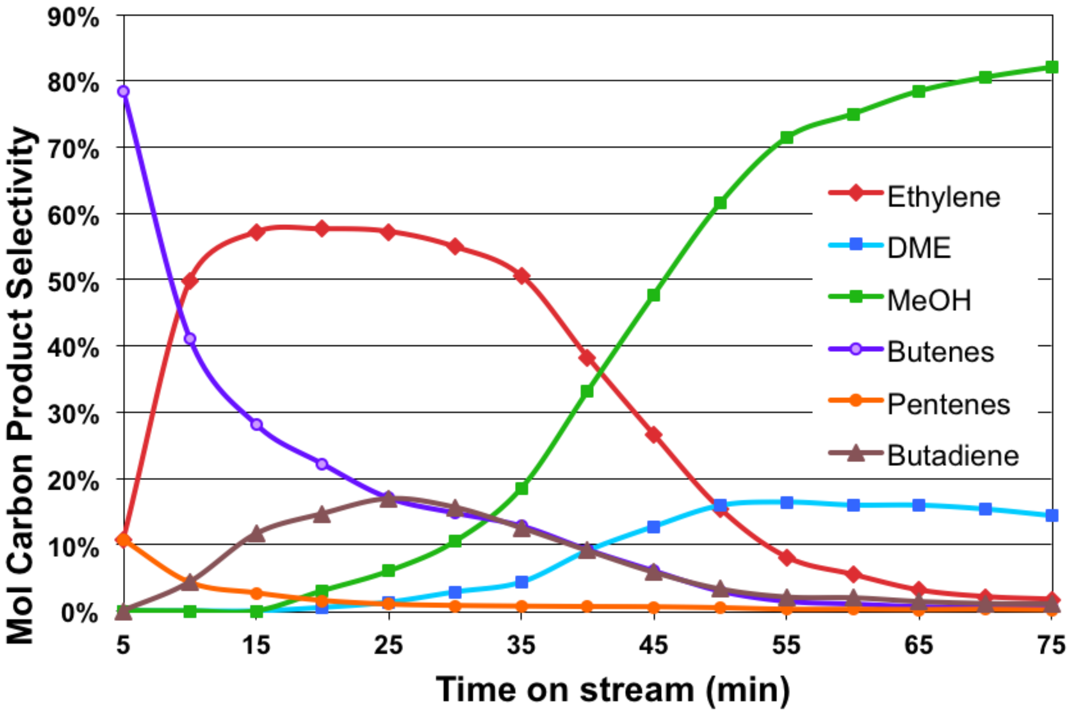
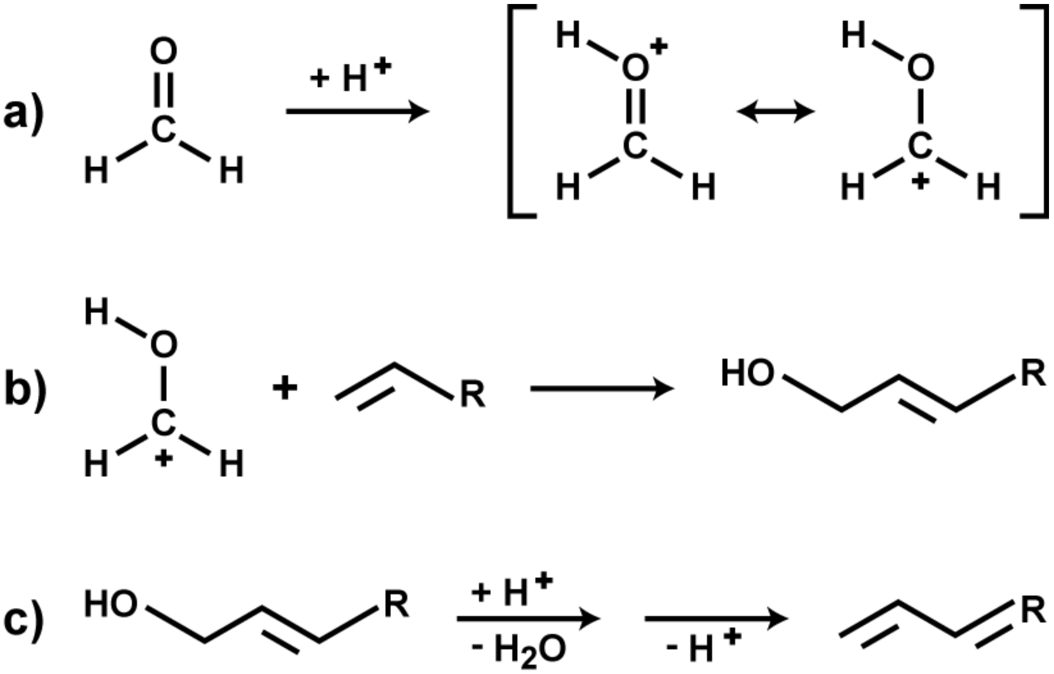


Figure 2. Evolution of product selectivities for in-situ butadiene generation. Mole carbon product selectivities for the products of the Prins reaction between propene and formaldehyde are presented versus time on stream.

As previously mentioned, the typical products of a Prins reaction were alcohols, specifically diols or allylic alcohols. No alcohol other than methanol was observed in the products from the reaction of propene and formaldehyde on HSAPO-34; instead, butadiene was observed. If the diol or allylic alcohol were then dehydrated, the product would be a diene. Butadiene formation was determined to occur through acid-catalyzed dehydration as it would be facile in the acidic zeolite environment.

Scheme 1 illustrates the mechanism of diene generation via the Prins reaction. The first step (a) of this reaction was the protonation of formaldehyde, which was followed by nuecloephilic addition to the carbonyl carbon by the olefinic species to produce an allylic alcohol (b). The final step was the dehydration of the allylic alcohol to a diene species (c).

As shown in Figure 2, ethylene selectivity was small at five minutes time on stream, and increased considerably by 10 minutes. It reached maximum selectivity at 20 minutes then decreased with time on stream. Butadiene emerged in the reactor effluent at 10 minutes time on stream and increased to a maximum selectivity at 25 minutes. The similarities in the selectivity trends of these species indicated butadiene was specifically active in forming ethylene, but the mechanism of this reaction remain unclear. In addition, the maximum butene selectivity was at five minutes and decreased with time on stream. Methylation of propene by the methanol could account for some of the butene selectivity, but not for the high initial selectivity.



Scheme 1. Prins Reaction in the Acidic Zeolite Environment

Several pulses of butadiene were introduced to HSAPO-34, two of which are shown in Figure 3.3, with corresponding product selectivity data shown in Table 3.1. Several olefinic products were observed exiting the catalyst following each butadiene pulse. Butadiene conversion was 95% after 4.0 mL of butadiene (0.5 eq) and decreased with subsequent pulses. Propene selectivity was highest of the olefins, hovering around 40%, and then decreasing after 14 mL of butadiene (1.75 eq). Butanes had the next highest selectivity, followed by ethylene then pentenes. The molar ethylene to propene ratio started around 0.5 and decreased with increasing amounts of butadiene.

Acid digestions were performed on two HSAPO-34 catalyst beds exposed to different amounts of butadiene. Figure 3.4 depicts GC-FID chromatograms from the extractions of acid digestions exposed to 8.0 mL of butadiene (1 eq) and 30.0 mL of butadiene (3.75 eq). For comparison, an HSAPO-34 catalyst bed deactivated with methanol under similar conditions was included also. A high degree of aromatic formation, especially naphthalene and methylnaphthalenes, was observed from the reaction of butadiene on HSAPO-34. The aromatic content trapped in the HSAPO-34 cages formed quickly and increased with more butadiene. In general, the aromatic species were the same as found in the catalyst deactivated with methanol, except for small amounts of vinyl methylbenzene. Unlike the methanol-deactivated catalyst, larger polycyclic aromatic hydrocarbons like phenanthrene and pyrene were not observed in significant amounts. Dimerization of butadiene through a Diels-Alder cycloaddition followed by subsequent dehydrogenation would account for the presence of vinyl methylbenzene.

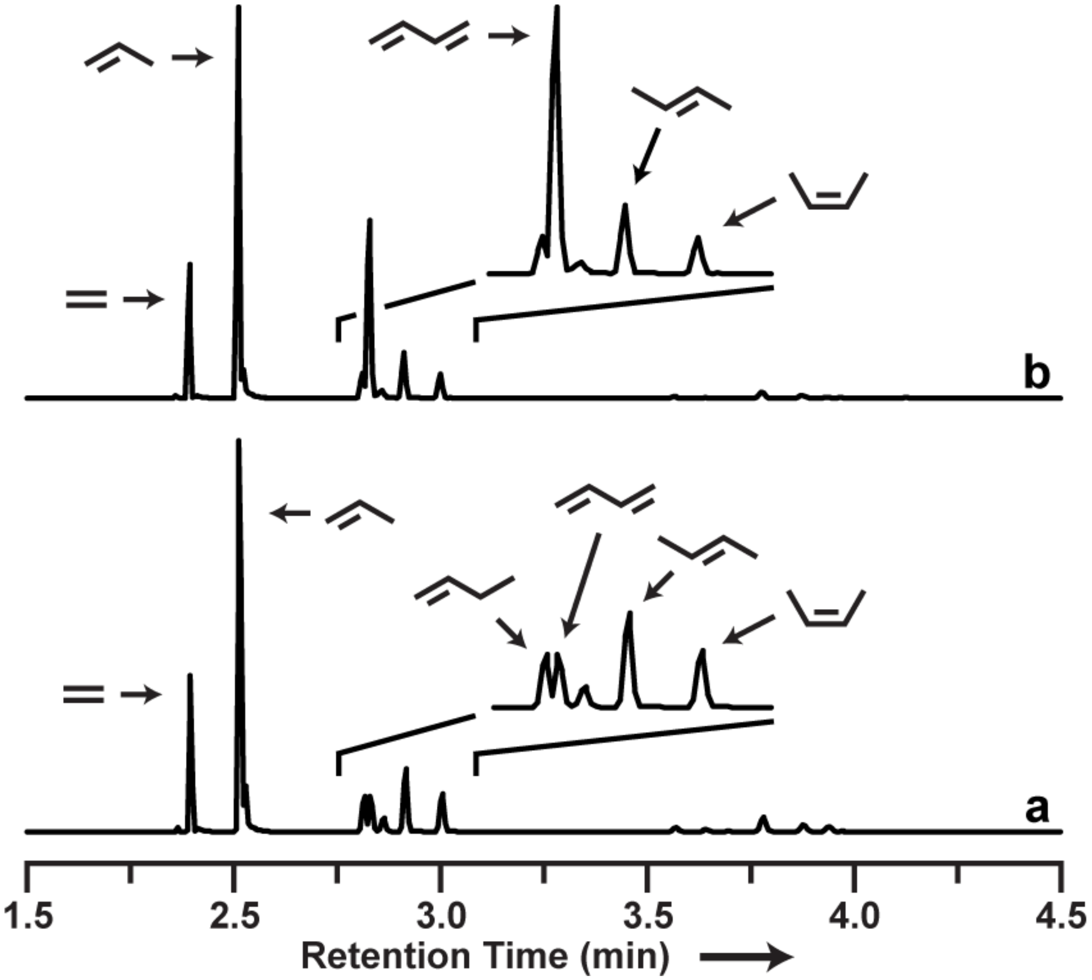


Figure 3. Reaction of Butadiene on HSAPO-34. GC-FID chromatograms from pulses of butadiene on HSAPO-34, **a)** 4.0 mL (0.5 eq) and **b)** 14.0 mL (1.75 eq), show extensive olefin production. The reaction was stopped after 30.0 mL of butadiene when butadiene conversion dropped below 30% (chromatogram not shown) and the catalyst was essentially deactivated.

Table 1. Mole carbon product selectivities for Figure 3.

	4.0 mL Butadiene (0.5 eq)	14.0 mL Butadiene (1.75 eq)	30.0 mL Butadiene (3.75 eq)
Butadiene conversion[a]	95.0%	75.2%	30.8%
Ethylene to propene[b]	0.54	0.46	0.33
Mole Carbon Selectivities			
Ethylene	14.7%	12.2%	4.0%
Propene	41.1%	39.9%	18.4%
Butenes	21.5%	14.7%	4.1%
Pentenes	8.5%	3.3%	0.6%
Alkanes[c]	9.2%	5.1%	3.7%
Butadiene	4.9%	24.8%	69.2%

[a] Mole carbon conversion. [b] Molar ratio. [c] Includes C_1-C_4 alkanes.

One observation from Figure 2 was a trend similarity between ethylene and butadiene selectivities: increased ethylene selectivity was observed with an increase in butadiene selectivity. Since butadiene was shown to generate aromatics in the zeolite, it was concluded that ethylene selectivity increases with increasing entrained aromatic content. These findings were in agreement with previous research that demonstrated an aromatic hydrocarbon pool was mainly responsible for ethylene production.

The reaction of formaldehyde with the olefins generated during the MTO process has been shown to produce diene species that appear to result in aromatic formation. A ^{13}C study was preformed using ^{13}C-enriched formaldehyde to examine the extent of aldehyde incorporation into the volatile products as well as aromatic species. Mole carbon product selectivities for the volatile products are shown in Table 3.2, and ^{13}C percentages are included for some of these products. A flow of ^{13}C-formaldehyde in methanol was sampled every ten minutes for starting at one minute time on stream.

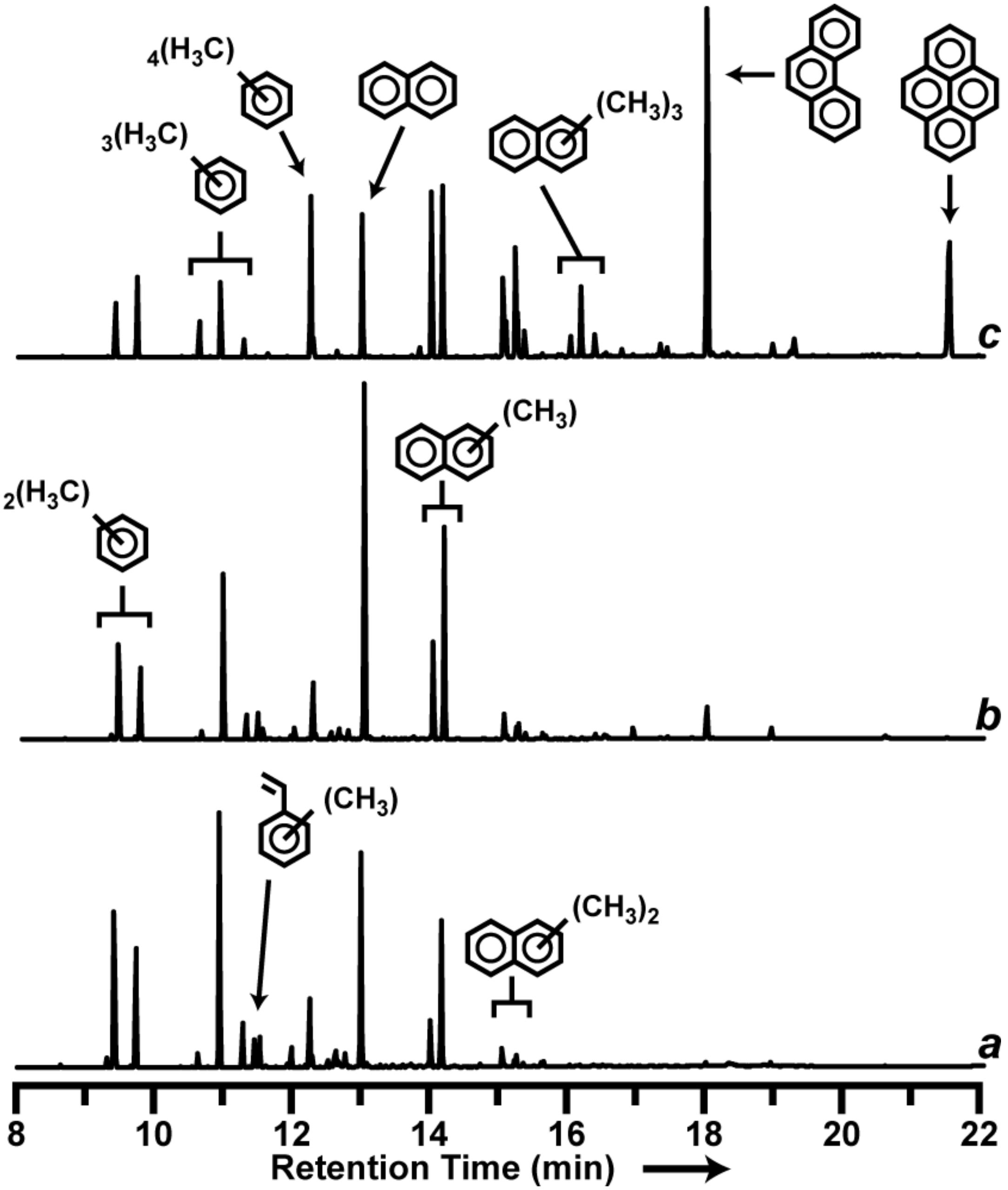


Figure 4. Acid digestion analysis shows significant aromatic formation from butadiene on HSAPO-34. GC-FID chromatograms from acid digestion extractions of HSAPO-34 catalyst beds exposed to a) 8.0 mL of butadiene (1 eq), b) 30.0 mL of butadiene (3.75 eq), and c) 15 mL of methanol (1120 eq). Butadiene was found to be highly deactivating, producing many methylbenzenes and methylnaphthalenes. Comparing to a catalyst deactivated with butadiene to one deactivated with methanol, the only differences were the presence of a small amount of a vinyl methylbenzene and fewer large polycyclic aromatics such as phenanthrene and pyrene in the butadiene catalyst.

Table 2. Volatile product selectivities and percent ^{13}C incorporation from a flow of ^{13}C-formaldehyde in methanol on HSAPO-34

	1 min TOS[a]		11 min TOS		21 min TOS	
Methanol Conversion[b]	98.4		98.7		93.8	
Ethylene to Propene[c]	1.6		2.3		2.5	
	Mol C Selectivities	**% ^{13}C**	**Mol C Selectivities**	**% ^{13}C**	**Mol C Selectivities**	**% ^{13}C**
Methane	0.4%	--[d]	0.4	--	0.5	--
Ethylene	42.0%	12.3%	53.2%	14.3%	52.5%	16.1%
Propene	40.3%	10.0%	34.9%	12.4%	31.7%	13.9%
Butenes	9.9%	10.6%	7.3%	12.5%	6.3%	14.0%
Butadiene	0.4%	--	0.6%	--	0.9%	--
Pentenes	5.6%	9.4%	2.3%	10.8%	2.0%	12.5%
DME	0.2%	--	0.3%	--	2.3%	X%
Methanol	1.4%	X%	1.1%	X%	3.9%	X%

[a] Time on stream. [b] Mole carbon conversion. [c] Molar ratio. [d] ^{13}C percentage not available as MS signal was too low for accurate measurement.

Conversion of methanol was above 90% for each of the three sample times, but the catalyst began to show signs of deactivation as evidenced by the increasing dimethyl ether (DME) and methanol selectivities. The molar ethylene to propene ratio increased with time on stream, consistent with expected results with the increase in aromatic species. Olefin selectivities decreased with time on stream with the exception of ethylene, which increased after one minute to level off around 50% selectivity.

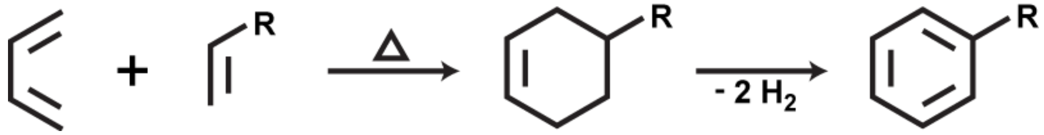
The ^{13}C-incorperation in the olefins was around 10% after one minute time on stream and increased approximately 2% with each additional ten minutes time on stream. Kolboe et al have demonstrated a mechanistic separation in the generation of ethylene and other olefins, which lead to the proposed secondary hydrocarbon pool. The results shown in this study also show a mechanistic separation between ethylene and the other olefins based on ^{13}C-incorporation. Ethylene exhibited increased amounts of ^{13}C throughout the course of the experiment, indicating formaldehyde impacted ethylene production more than the other olefins.

Previous work by Guenther et al. showed the aromatic pool species were primarily responsible for ethylene production thus formaldehyde must be incorporated into the aromatic hydrocarbon pool. An acid digestion was preformed on the HSAPO-34 catalyst and the mass spectra of some of the aromatics were analyzed, the results of which are presented in Table 3. The aromatic species all were found to contain at least 18% ^{13}C compared a maximum of 16% observed in ethylene at 21 minutes, in agreement with results previously discussed regarding the reaction of butadiene in the MTO environment. Interestingly, the larger polycyclic aromatic hydrocarbons actually have the highest amounts of ^{13}C incorporation, with pyrene displaying over 40% incorporation. This result indicated formaldehyde was directly involved in the formation of aromatic species.

Table 3. ^{13}C-Incorporation into the entrained aromatic species from a flow of ^{13}C-formaldehyde in methanol on HSAPO-34.

Aromatic Species	**Percent ^{13}C Incorporation**
Methylbenzene (Toluene)	23.2%
Dimethylbenzene (Xylene)	17.7%
Trimethylbenzene	23.0%
Tetramethylbenzene	23.0%
Naphthalene	21.1%
Methylnaphthalene	21.8%
Dimethylnaphthalene	29.1%
Trimethylnaphthalene	31.4%
Phenanthrene	34.7%
Pyrene	42.6%

A potential mechanism for aromatic formation is presented in Scheme 2. In this mechanism, butadiene, formed from the reaction of propene and formaldehyde, reacts with an olefin via a thermally-allowed [4 + 2] Diels-Alder cycloaddition. This is the same mechanism suggested for the dimerization reaction of butadiene presented in Section 3.4.2. The product of the Diels-Alder reaction is a cyclohexene species, which can be converted to an aromatic species by dehydrogenation.



Scheme 2. Proposed mechanism for aromatic formation via a Diels-Alder cycloaddition of butadiene with MTO olefins.

Methanol was used to create an active hydrocarbon pool and acted as a baseline for aromatic formation. Potential deactivating species (1 eq) were pulsed onto separate catalyst beds and acid digestions were conducted to release the entrained organic species, the results of which are shown in Figure 5. Methylbenzenes were the main aromatics were present in the methanol baseline acid digestion but some methylnaphthalenes were also seen. Further reaction of this baseline hydrocarbon pool with formaldehyde resulted in an increase in methylnaphthalenes, but also in tetramethylbenzene. Similar results were obtained for dimethoxymethane the dimethyl acetyl of formaldehyde, except not as much tetramethylbenzene was seen. When the hydrocarbon pool was exposed to an equivalent of butadiene, the effect was increased overall aromatic formation, especially naphthalene and methylnaphthalenes, consistent with the results observed from the reaction of butadiene alone.

The hydrocarbon pool was generated with 0.5 mL of methanol, which is approximately 40 equivalents on a 300 mg HSAPO-34 catalyst bed. In Figure 4, the same size catalyst bed under similar conditions was deactivated with 1120 equivalents of methanol thus the 40 equivalents used to create the hydrocarbon pool was only a fraction of the methanol conversion capacity. The addition of one equivalent of each of formaldehyde, dimethoxymethane, and butadiene is an increase in carbon of one equivalent, three equivalents, and four equivalents respectively. Compared to the methanol carbon equivalents necessary for deactivation, one equivalent of each of these molecules do not represent a significant increase in carbon equivalents. However, a small amount of each of these species does significantly impact the entrained organics in the catalyst.

More aromatic species were present after an additional equivalent of each of the potential deactivating species compared to the methanol baseline, and in general there was an increase in the methylation of these aromatic species. For example, tetramethylnaphthalenes were observed in the catalysts treated with formaldehyde and dimethoxymethane but were not seen in the methanol baseline. These results indicate these species, as well as butadiene, accelerate aromatic formation which speeds deactivation.

Formaldehyde has been shown to be deactivating but its formation under MTO conditions has not been observed. Figure 6 depicts the formation of formaldehyde in an MTO study by inclusion of additional stainless steel tubing to the regular bench-top reactor. Methanol conversion data and product selectivities are presented in Table 4.

The most notable result of this experiment was the increase in aromatic species observed upon the addition of stainless steel tubing. The overall aromatic selectivity nearly tripled with the added tubing, increasing from 10% on the unmodified reactor to 27% on the modified reactor. In addition, ethylene selectivity doubled on the modified reactor and the ethylene to propene ratio increased from 0.3 to 0.7. Collectively, the selectivity of the C_4 to C_6 alkenes roughly decreased by half on the modified reactor, from 38% to 24%. Alkane selectivity also decreased on the modified reactor but only slightly.

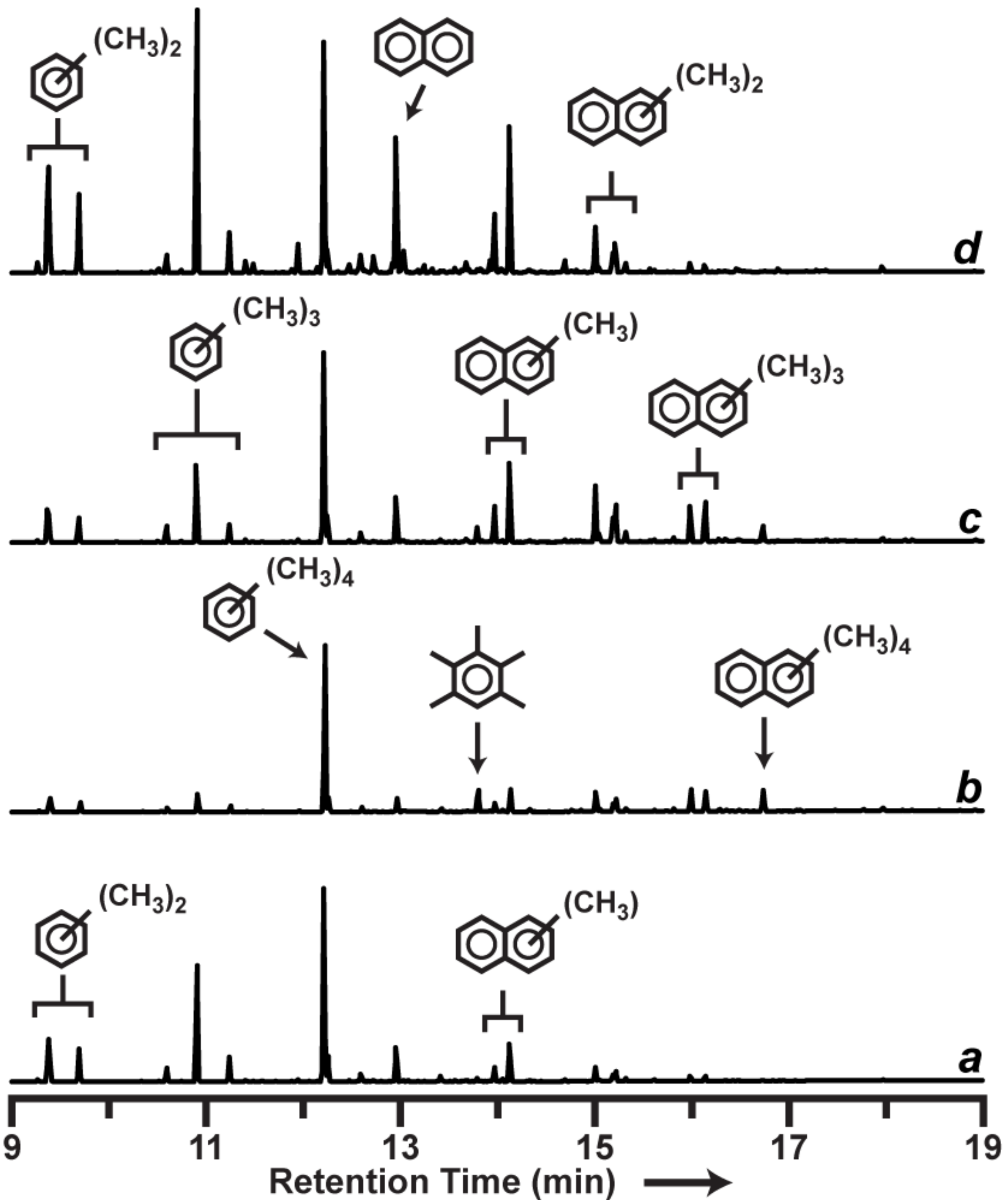


Figure 5. Acid digestion analyses showing the effect of potential deactivating species on the MTO hydrocarbon pool. GC-FID chromatograms of HSAPO-34 acid digestion extractions from a) 0.5 mL methanol, and 0.5 mL methanol followed by one equivalent of b) formaldehyde, c) dimethoxymethane, and d) butadiene. All potential species were found to be deactivating by accelerating aromatic formation in the HSAPO-34 cages.

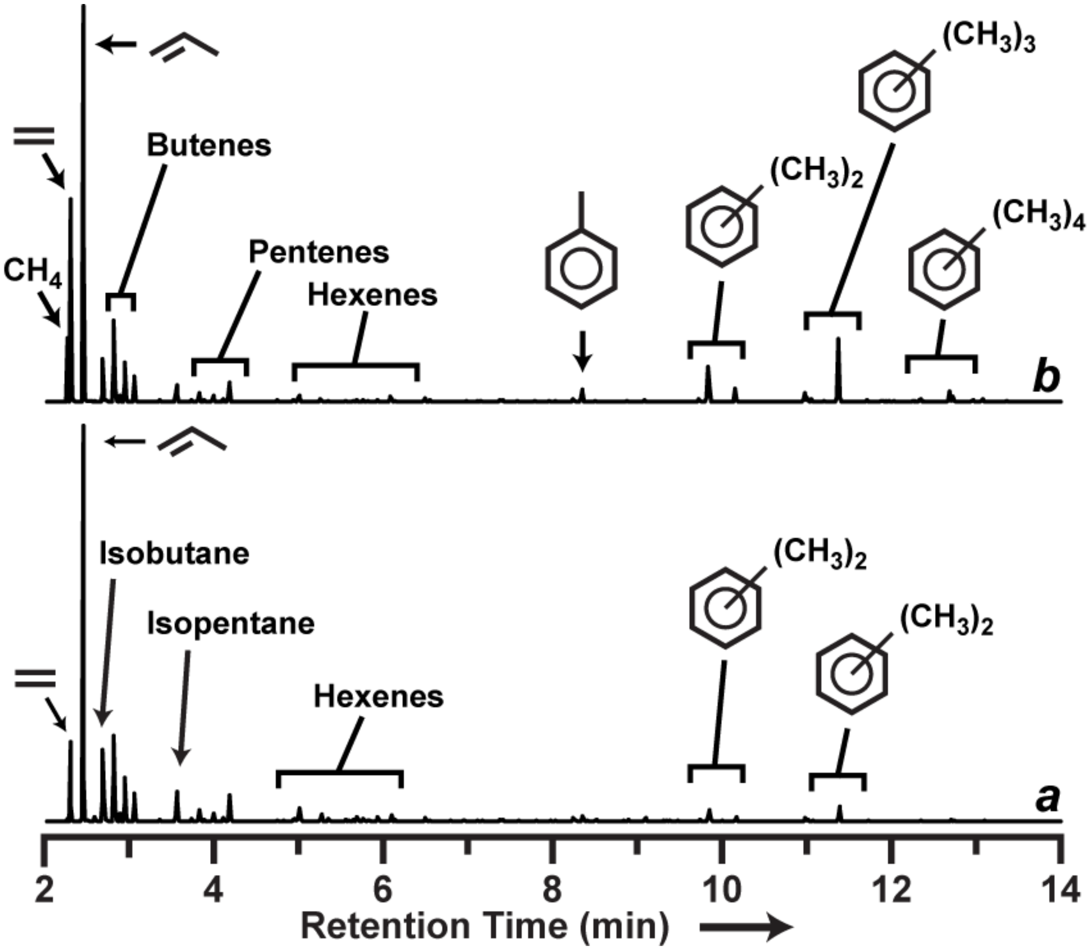


Figure 6. In-situ generation of formaldehyde from methanol using additional stainless steel tubing. GC-FID chromatograms of methanol conversion over HZSM-5 (Si/Al = 40) a) under typical conditions on an unmodified reactor and b) on a reactor modified by addition of 8 feet of 1/8 inch stainless steel tubing heated to 773 K. Overall selectivity for ethylene and aromatic hydrocarbons increased with the additional stainless steel surface area. Yield of alkanes and C_4-C_6 alkenes decreased with the added surface area.

As mentioned previously, stainless steel tubing contains a metal oxide coating to prevent rusting, some of which could catalyze formaldehyde generation under the right conditions. Once formaldehyde is made, it can react with an olefin (except ethylene) and produce a diene. In the acidic zeolite environment, these dienes are highly reactive, reacting with olefins or other dienes resulting in aromatic formation.

Table 4. Product selectivities from Figure 6

	Methanol on unmodified reactor	Methanol on reactor with 8’ S.S. coil

Methanol conversion[a]	100%	100%
Ethylene to propene[b]	0.28	0.72
Mole Carbon Selectivities		
Ethylene	5.9%	12.6%
Propene	31.7%	26.3%
Butenes	19.2%	14.7%
Pentenes	8.7%	5.4%
Hexenes	9.7%	4.1%
Alkanes[c]	13.6%	9.2%
Toluene	0.9%	1.7%
Dimethylbenzenes	4.0%	9.3%
Trimethylbenzenes	4.0%	12.0%
Tetramethylbenzenes	1.0%	3.9%

[a] Mole carbon conversion. [b] Molar ratio. [c] Includes methane, isobutene, and isopentane.

In the MTO environment, there are many potential reactions of formaldehyde, but specifically it will react with olefins to produce dienes through a Prins reaction. Dienes also have a variety of potential reactions with olefins or other unsaturates, and the products of these reactions lead to the formation of aromatic species. There is both a drawback and an advantage to accelerating aromatic formation: the catalyst lifetime will decrease but ethylene selectivity increases with increase aromatic content. Most notably though, formaldehyde can be generated directly from methanol in the reactor system simply by inclusion of heated stainless steel tubing; thus, any industrial-scale methanol catalysis will generate small amounts formaldehyde.

Thus, we conclude that essentially every previous mechanistic study of MTO chemistry has overlooked a key reaction – decomposition of methanol to formaldehyde, and the formaldehyde so formed both accelerates carbon pool formation and ultimately drives catalyst deactivation.

Ph.D. Dissertations Supported by this research

David M. McCann, "Chemical Applications of Density Functional Theory as an Analytical Tool", University of Southern California, 2007.

Darryl R. Guenther, "Investigation of the Hydrocarbon Pool Species Responsible for Methanol to Olefin Catalysis on Acidic Zeolite and Zeotype Catalysts", University of Southern California, 2010.

Miranda Hayman, "Modication of Methanol-to-Olefin Hydrocarbon Pool Species by Oxygenates on Acidic Zeolites", University of Southern California, 2011.

Publication from this project (Sole US funding by DOE-BES and this particular grant)
" A Complete Catalytic Cycle for Supramolecular MTO Conversion by Linking Theory with Experiment," David M. McCann, David Lesthaeghe, Philip W. Kletnieks, Darryl R. Guenther, Miranda J. Hayman, Veronique Van Speybroeck, Michel Waroquier, and James F. Haw, *Angew. Chemie Int. Ed.* **2008**, *47*, 5179-5182.

Additional manuscripts from the latter two Ph.D. Dissertations are in progress.

Inventions. There were no inventions to report.