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Selective Homogeneous and Heterogeneous Catalytic Conversion of Methanol/Dimethyl Ether to Triptane

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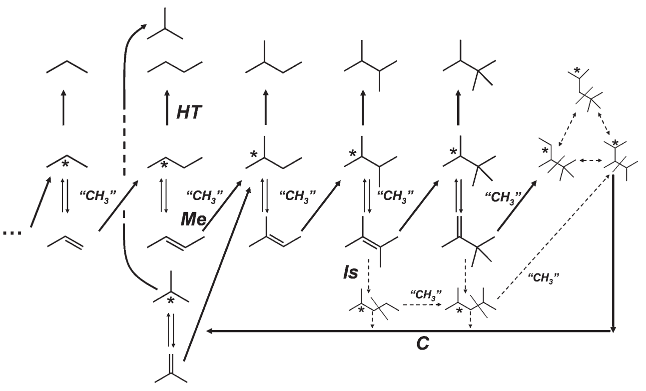
CONSPECTUS



The demand for specific fuels and chemical feedstocks fluctuates, and as a result, logistical mismatches can occur in the supply of their precursor raw materials such as coal, biomass, crude oil, and methane. To overcome these challenges, industry requires a versatile and robust suite of conversion technologies, many of which are mediated by synthesis gas (CO + H$_2$) or methanol/dimethyl ether (DME) intermediates. One such transformation, the conversion of methanol/DME to triptane (2,2,3-trimethylbutane) has spurred particular research interest. Practically, triptane is a high-octane, high-value fuel component, but this transformation also raises fundamental questions: how can such a complex molecule be generated from such a simple precursor with high selectivity?

In this Account, we present studies of this reaction carried out in two modes: homogeneously with soluble metal halide catalysts and heterogeneously over solid microporous acid catalysts. Despite their very different compositions, reaction conditions, provenance, and historical scientific context, both processes lead to remarkably similar products and mechanistic interpretations. In both cases, hydrocarbon chains grow by successive methylation in a carbocation-based mechanism. The relative rates of competitive processes—chain growth by methylation, chain termination by hydrogen transfer, isomerization, and cracking—systematically depend upon the structure of the various hydrocarbons produced, strongly favoring the formation of the maximally branched C$_7$ alkane, triptane.

The two catalysts also show parallels in their dependence on acid strength. Stronger acids exhibit higher methanol/DME conversion but also tend to favor chain termination, isomerization, and cracking relative to chain growth, decreasing the preference for triptane. Hence, in both modes, there will be an optimal range: if the acid strength is too low, activity will be poor, but if it is too high, selectivity will be poor.

A related reaction, the methylative homologation of alkanes, offers the possibility of upgrading low-value refinery byproducts such as isobutane and isopentane to more valuable gasoline components. With the addition of adamantane, a hydride transfer catalyst that promotes activation of alkanes, both systems effectively catalyze the reaction of methanol/DME with lighter alkanes to produce heavier ones. This transformation has the further advantage of providing stoichiometric balance, whereas the stoichiometry for conversion of methanol/DME to alkanes is deficient in hydrogen and requires rejection of excess carbon in the form of carbon-rich arenes, which lowers the overall yield of desired products. Alternatively, other molecules can serve as sacrificial sources of hydrogen atoms: H$_2$ on heterogeneous catalysts modified by cations that activate it, and H$_3$PO$_2$ or H$_3$PO$_3$ on homogeneous catalysts.

We have interpreted most of the features of these potentially useful reactions at a highly detailed level of mechanistic understanding, and we show that this interpretation applies equally to these two widely disparate types of catalysts. Such approaches can play a key role in developing and optimizing the catalysts that are needed to solve our energy problems.

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Introduction

Methanol and dimethyl ether (DME) are potential fuels and important petrochemical precursors.[1,2] They are key intermediates in the conversion of synthesis gas derived from methane, coal, or biomass to chemicals (e.g., acetic acid, formaldehyde) and fuels. The dehydrative conversion of methanol/DME to hydrocarbons was first reported more than a century ago; acid catalysts, both liquids and solids, mediate these transformations, leading to different products depending on the catalyst and the reaction temperature.[3] Two processes have been developed, methanol-to-gasoline (MTG) and methanol-to-olefins (MTO); they use aluminosilicate and aluminophosphate microporous catalysts at temperatures above 600 K to produce streams rich in arenes and alkenes, respectively.[4] MTG was operated commercially in New Zealand during the 1980s (when high aromatic contents were less of a concern),[5] and MTO appears to be approaching commercial implementation.[6]

Other reports include methanol conversion to methane-rich mixtures of light hydrocarbons on $WO_3-Al_2O_3$ at 573−673 K,[7] alkane and arene formation from methanol using polyphosphoric acid at 453 K,[8] and reactions of methanol with ZnI_2 at 453 K to give highly branched alkanes and methylated arenes.[9] The last process was notable for its selectivity for one alkane, 2,2,3-trimethylbutane (triptane), obtained in yields as high as 20% (carbon basis) and accounting for $\sim$50% of all molecules in the gasoline range. More recently, large-pore zeolites were shown to catalyze analogous transformations.[10]

These reactions offer possible routes to high value-added fuels (triptane; 112 research octane) but also raise mechanistic questions about the basis for such remarkable selectivity. Many mechanistic studies of MTG/MTO processes have addressed how C_1 fragments form the first C−C bond (or whether impurities are instead responsible for the first C−C bond) and the species involved in subsequent C−C bond formation via methylation of "hydrocarbon pools".[11−13] Much less is known about other catalytic systems; the products observed on WO_3/Al_2O_3 were attributed to reactions of surface-bound radical-like intermediates,[7] while CO and ketene were proposed as intermediates for the first C−C bond formation on polyphosphoric acid catalysts.[14] The initial report of the ZnI_2 system[9] proposed that carbenoid organozinc intermediates were responsible for remarkable triptane selectivity, without specific mechanistic explanations or experimental evidence.

We have recently reported parallel studies of homogeneously[15−18] and heterogeneously[10,19] catalyzed methanol/DME conversion to triptane (henceforth denoted MTT). Kinetic and isotopic studies suggest that these transformations are mediated by carbocationic transition states in both systems. These carbenium ions account for all experimental observations, including the high triptane selectivity, which reflects the relative rates of methylative growth and chain termination by hydride transfer. This is perhaps the most noteworthy aspect of this work: although there are many examples of transformations mediated by both homogeneous and heterogeneous catalysts, we are unaware of precedents in which mechanisms have been so clearly elucidated and shown to be so similar. We have also been able to exploit our mechanistic insights to improve rates and selectivities and to accomplish a previously unrecognized transformation, the methylative homologation of alkanes.[20,21] In this Account, we describe and compare these homogeneous and heterogeneous systems in terms of their performance and underlying mechanistic details.

Conversion of Methanol/DME to Triptane: Phenomenological Observations

Homogeneous Catalysts. As originally reported,[9] methanol forms a complex mixture of hydrocarbons upon contact with ZnI_2 at 473 K; the most abundant products are highly branched alkanes and methylated benzenes, with triptane and hexamethylbenzene (HMB) as the predominant species. There are several requirements for a successful reaction. When methanol to ZnI_2 molar ratios were much larger than 4:1 (remarkably, ZnI_2 can be fully dissolved in methanol at >5:1 mass ratio), hydrocarbons were not detected and methanol formed only DME. Also, unexpectedly, the complete predissolution of ZnI_2 or stirring during heating to reaction temperature suppressed hydrocarbon formation. In contrast, small amounts of alkenes or C_{2+} alkanols added to methanol led to hydrocarbon formation irrespective of stirring or the presence of solids.[15]

The constraints on methanol/ZnI_2 stoichiometry suggest that fully hydrated $[Zn(OH_2)_4]^{2+}$ ions do not catalyze MTT. Indeed, successive additions of smaller amounts of either methanol or DME to the reaction mixture led to the conversion of each additional aliquot to hydrocarbons, but only to the point that the 4:1 O/Zn stoichiometry was reached. Conversely, if all volatiles (including water) were removed by evacuation after each experiment before adding fresh reactants, MTT continued indefinitely during consecutive batch experiments.[15] These stirring/predissolution effects, which can be overcome by adding a suitable C_{2+} promoter, suggest that initiation (in the absence of such promoters) involves the formation of species with a C−C bond directly

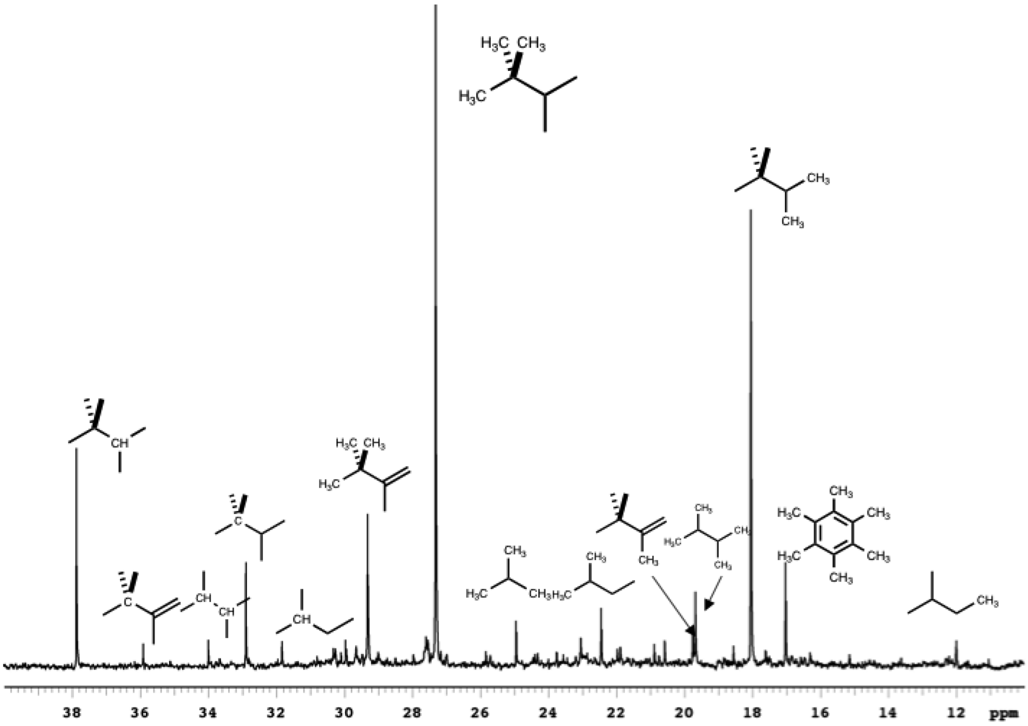


FIGURE 1. ^{13}C NMR spectrum of a typical product mixture, showing the sp^3 carbon signals for triptane, triptene, HMB, and several minor components. Reproduced from ref 15. Copyright 2006 American Chemical Society.

from a C_1 species at surfaces, such as those provided by undissolved ZnI_2 solids.[22]

A number of iodide salts of late transition and early p-block metals were evaluated for MTT rates and selectivities. Among these, only InI_3 gave rates comparable to ZnI_2; bromides gave much lower conversions to hydrocarbons, while chlorides showed no detectable reactivity at similar conditions. The ^{13}C NMR spectrum of the hydrocarbons formed from ZnI_2-catalyzed reactions is shown in Figure 1; the major products are triptane and triptene (2,4,4-trimethylbut-1-ene), smaller branched alkanes, and hexamethylbenzene. Product distributions (by class and for selected products) are compared in Table 1 for InI_3 and ZnI_2 catalysts; the former gives somewhat lower triptane yields, much lower alkene yields, and higher arene yields.[16]

Heterogeneous Catalysts. In contrast to most previous studies (above 573 K), which led to a broad distribution of products (MTG) or light alkenes (MTO), DME reactions on large-pore acidic zeolites at lower temperatures (453−493 K) and higher pressures (60−250 kPa DME) give high selectivities to branched hydrocarbons, specifically triptane and isobutane. The use of methanol instead of DME leads to much lower MTT rates and selectivities, because of inhibition by water (which forms in larger amounts from methanol). Also, the lower volatility of methanol makes it more difficult to operate at the high reactant pressures that favor formation of larger alkanes.[10]

TABLE 1. Product Distribution for Standard Reactions[a] by Refinery GC Analytical Protocol ("PIANO")[18]

compound or class	InI_3[b] (wt %)	ZnI_2[b] (wt %)
n-alkanes	1	1
isoalkanes	60	45
arenes	23	11
naphthenes	5	5
alkenes	0.4	14
isobutane	3	3
triptane	27	25
triptene		6
total C_7	31	36
hexamethylbenzene	6	3

[a] Methanol and metal iodide (3.3:1 molar ratio) in sealed glass tube for 2 h at 473 K. [b] Fraction of product in organic layer.

Zeolite Beta (H-BEA) showed the highest turnover rates (per proton), triptane and isobutane selectivities, and resistance to deactivation. A typical product distribution is shown in Figure 2. H-ZSM-5 and H-FAU showed similar turnover rates for conversion of DME to hydrocarbons but lower triptane selectivities than H-BEA, while H-MOR and H-FER gave much lower rates and selectivities.[10] All solid acids deactivate over several hours, apparently because alkylarene coproducts (required for hydrogen balance) are retained within their pore structures and inhibit access to acid sites.[10]

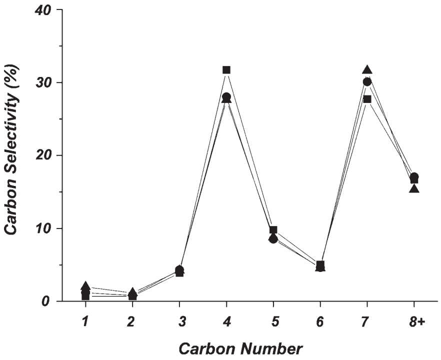


FIGURE 2. Hydrocarbon chain size distribution for the conversion of DME (60 kPa (■), 125 kPa (●), and 250 kPa (▲)) on H-BEA (Si/Al = 12.5) at 473 K. Reprinted with permission of ref 10. Copyright 2009 John Wiley and Sons.

TABLE 2. Comparison of H-BEA and ZnI$_2$ as MTT Catalysts

catalyst	H-BEA[a]	ZnI$_2$[b]
triptyl formation rate (μmol s^{-1} mol^{-1})[c]	16	11
triptyl selectivity in C$_7$ fraction (%)	72	86
triptyl selectivity in all aliphatics[d] (%, carbon basis)	15	50
triptyl selectivity in all products (%, carbon basis)	10[e]	20

[a] Reaction of 60 kPa DME at 473 K after 4.8 ks on stream. [b] Reaction of 3.3:1 (molar ratio) MeOH/ZnI$_2$ in sealed tube for 7.2 ks at 473 K. [c] Units refer to the number of Al or Zn sites, respectively. For the latter, the rate is an average value assuming the full reaction period is required for completion. [d] Includes all measured products for H-BEA and only measured alkanes and alkenes (see Table 1) for ZnI$_2$. [e] Amount of C retained on the catalyst was estimated from gas-phase C balance.

Comparison of Homogeneous and Heterogeneous Catalysts. Quantitative comparisons of rates and selectivity between homogeneous and heterogeneous systems are difficult, because their respective protocols complicate acquisition of comparative data. Homogeneous reactions are carried out in batch reactors that make continuous sampling inconvenient, thus preventing quantitative assessments of product evolution with reaction time. Most importantly, methanol/DME concentrations decrease with reaction time (most experiments were performed at complete conversion) and determining the nature and length of induction periods or the extent of catalyst deactivation is not feasible. In heterogeneous systems, retention of large hydrocarbons (C$_{10+}$) within the pores of the catalyst complicates measurements of the amounts of alkylarenes formed and, in turn, the determination of selectivities based on *all* reactants converted. Furthermore, there is no straightforward way to compare reactant pressures in these two systems. Despite these complicating factors, the nominal performances of the two catalytic systems are remarkably similar (Table 2), consistent with a common mechanistic basis. The most pronounced difference is the ratio of isobutane to triptyl (i.e., triptane plus triptene) selectivities (~1:1 for H-BEA (Figure 2), 1:10 for ZnI$_2$ (Table 1)), a difference that may account for their different triptyl selectivities among aliphatics (Table 1). In light of the above disclaimers and the different catalysts used, the resemblance in rates seems coincidental.

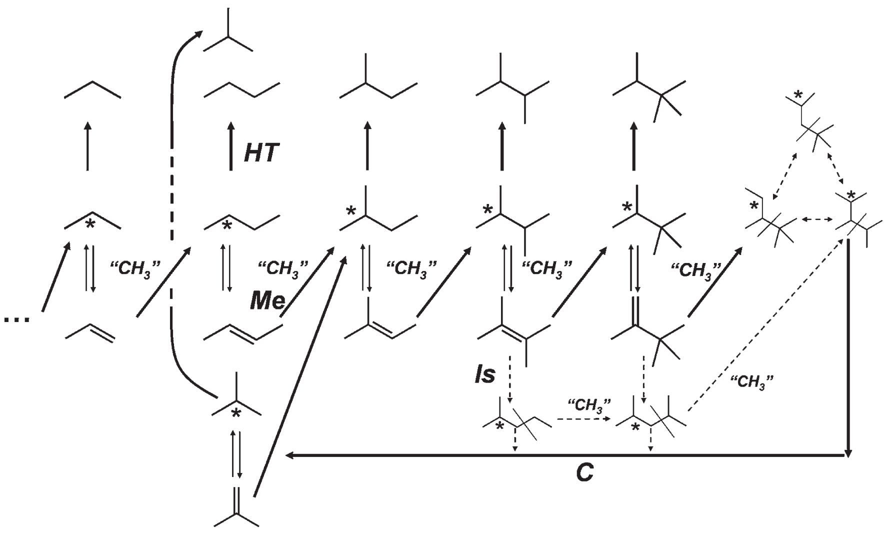
As noted above, up to 4−8 total turnovers (depending on whether methanol or DME was the reactant) could be achieved in homogeneous reactions before deactivation by water; recycling can be accomplished by removing all volatiles. On H-BEA, >10 turnovers of DME were achieved before deactivation via deposition of residues within porous solids, a process that was reversed by oxidative thermal treatments. Both catalyst systems are inhibited by water and hence operate more effectively with DME than methanol.[23]

Conversion of Methanol/DME to Triptane: Mechanistic Studies

Evidence for Pathways Mediated by Carbenium Ions. MTT, which converts C$_1$ precursors to products rich in C$_7$, must involve a complex network of elementary reaction steps, which is best untangled on solid catalysts (H-BEA) because of the convenience of detailed kinetic and isotopic experiments under differential conditions and online assessment of chemical and isotopic compositions by gas chromatography and mass spectrometry. Reactions of ^{13}C-labeled DME with unlabeled alkenes were used to determine relative rates of methylation and hydrogen transfer from the rate of formation and the isotopologue composition of the products formed. The main *primary* products (indicated by their predominance as singly labeled isotopologues) were *n*-butyls (and much smaller amounts of isobutane) from propene methylation, isopentyls from 1-butene or *trans*-2-butene, 2,3-dimethylbutane from 2-methyl-2-butene, and triptane from 2,3-dimethyl-2-butene.[19] These results are consistent with elementary steps mediated by cationic transition states. A "methyl cation" adds to an alkene at the position that forms the most highly substituted, and hence the most stable, "carbenium ion" transition state. Of course, both methylating species and methylated alkenes are adsorbed, the latter presumably as alkoxides, but the reactivity and stability patterns for methylation follow the trends expected for carbenium ions.[24]

In this mechanism (Scheme 1), alkanes form from alkoxides via hydride transfer from gaseous donors. Alkenes with allylic hydrogens are especially reactive as hydride donors, because they form stable allylic cations. These cations deprotonate to give dienes, which are even better hydride donors as a result of conjugation, and ultimately form the arenes required by the MTT stoichiometry.

SCHEME 1. Proposed Mechanism for MTT (Starting with Propene for Simplicity)[a]



[a] The species labeled with asterisks are the "carbenium ion equivalents", presumably surface alkoxides for H-BEA, most likely metal alkoxides or protonated alcohols for homogeneous catalysts, with the asterisk indicating the position of the reactive C–O bond. Methylation, hydrogen transfer, isomerization, and cracking pathways are labeled Me, HT, Is, and C, respectively; "CH_3" represents the reactive (surface or solution) methylating agent.[10,19]

Alkoxides also undergo deprotonation to alkenes and subsequent methylative growth, isomerization to less-branched structures, and β-scission to smaller chains. Isobutane forms in high yields (Figure 2) but is *not* a primary growth product; rather, it forms via β-scission of larger chains.[19]

Isotopic methods can be used to measure rates for all processes in Scheme 1. Rates of formation of singly labeled C_{n+1} products from $^{12}C_n$ alkenes give methylation rates, while formation rates of unlabeled C_n alkanes from $^{12}C_n$ alkenes give hydrogen transfer rates. The dependence of these rates on the structure of the specific intermediate accounts for the unique selectivity of MTT reactions. The details are discussed below, but we note two general points here: (i) backbone isomerization is much slower than methylation and hydride transfer for all species, and (ii) β-scission rates are negligible for all species along the chain growth sequence leading up to triptyls but become fast for C_{8+} molecules and for smaller molecules without the four-carbon backbone structure of chains along the path to triptyls (as indicated in Scheme 1).

Similar tracing experiments were carried out for homogeneous catalysts. Kinetic parameters cannot be determined with such detail, but all observations strongly support a similar reaction network. The distribution of triptane isotopologues formed from $^{12}CH_3OH-^{13}C_2H_5OH$ mixtures (the latter forms $^{13}C_2H_4$ during MTT) is consistent with the reactions in Scheme 1, but *not* with proposed routes[9] involving carbenoid intermediates.[25] The addition of both triptene and 1,4-cyclohexadiene (CHD) to methanol–ZnI_2 reactions resulted in fast hydrogenation of triptene to triptane, even at temperatures much lower than required for MTT, consistent with alkane formation via hydride transfer;[15] furthermore, the addition of C_8 alkenes (or C_7 alkene isomers that methylate faster than triptene) to ZnI_2-catalyzed MTT reactions increased isobutane yields, while triptene addition did not, consistent with the low chain growth probability of triptyls and with the facile scission of chains larger than triptyls.[18]

Mechanistic Interpretation of High Triptane (and Isobutane) Selectivities. The mechanism depicted in Scheme 1 accounts for the preferential formation of highly branched hydrocarbons but (by itself) is silent about the remarkably high selectivity for C_7 (and, in the case of solid acids, also for C_4). Rate and isotopic data on H-BEA (and other solid acids) provide a quantitative basis for this interpretation, which agrees with the (somewhat less quantitative) data for homogeneous MTT systems. High triptane selectivities reflect the ratio of methylation and hydride transfer rates at each chain growth stage. That ratio (henceforth denoted as γ) depends on the relative stability of the respective carbenium ion transition states for these two reactions. For example, methylation of disubstituted primary–tertiary double bonds in triptene and isobutene leads to less stable cations than methylation of tetrasubstituted tertiary–tertiary double bonds in 2,3-dimethyl-2-butene; hence, growth from C_6 to C_7 is much faster than from C_7 to C_8 for backbone structures formed in this preferred methylation path. Transition states leading to isomerization and β-scission are disfavored,

TABLE 3. Rates (μmol [mol Al s]$^{-1}$) for Methylation, Hydride Transfer, Skeletal Isomerization, and Cracking of Various Alkenes under MTT Conditions with H-BEA at 473 K, Relative Rates of Methylation–Hydride Transfer (γ) under the Same Conditions,[21] and Estimated Relative γ Values for Selected Alkenes under MTT Conditions with ZnI_2 at 423 K[20]

alkene	isobutene	2-methyl-2-butene	2,3-dimethyl-2-butene	triptene	2,4-dimethyl-2-pentene	3,4,4-trimethyl-2-pentene
methylation rate	33	56	70	33	91	25
hydride transfer rate	38	21	7.4	48	17	0.02
isomerization rate	0.4	0.16	0.73	0.91	2.0	
cracking rate	3.5	0.22	1.0	0.77	1.9	46
γ	0.9	2.7	9.5	0.7	5.4	1250
relative γ, H-BEA (2-methyl-2-butene = 1)	0.33	1	3.5	0.26	2.0	460
relative γ, ZnI_2 (2-methyl-2-butene = 1)		1	2.8	0.05	0.4	

relative to methylation and hydride transfer, for these backbone structures. In contrast, isomers with different backbone structures have a greater tendency to grow beyond C_7 chains and undergo β-scission, leading to the essential absence of C_{8+} aliphatic molecules. These preferences are represented quantitatively in Table 3, in which γ values for lighter and heavier alkenes (and for other C_7 isomers) are much larger than for triptene.

Analogous data in batch reactors with homogeneous catalysts can be obtained from yields of methylation and hydrogenation products from reactions of alkenes, CHD, methanol, and ZnI_2 at temperatures (423 K) below those required for detectable MTT rates. These experiments led to the *exclusive* conversion of triptene to triptane, whereas 2,3-dimethyl-2-butene gave triptyls and 2,3-dimethylbutane, consistent with much higher γ values for 2,3-dimethyl-2-butene than triptene.[18] Similar experiments with other alkenes, using varying amounts of CHD, led to *relative* γ values that are compared with those measured on H-BEA (recast in relative terms to account for differences in reaction conditions) in Table 3. The trends are similar for these two catalyst systems, but the preference for hydrogen transfer over methylation for triptyls seems stronger for the homogeneous system. This difference may reflect intrinsic catalyst properties or the lower temperatures of the ZnI_2 experiments and may account for the low isobutane yields in homogeneous systems, since isobutane is formed via β-scission of chains that grow beyond triptane. The relative rates inferred from the data at 423 K were used in a mathematical model that reproduces most of the essential features of homogeneously catalyzed MTT reactions, particularly the high selectivity for triptyls.[18]

The Nature of the Active Acid Sites and Catalytic Consequences of Acid Strength

Acid sites mediate two critical MTT steps: the formation of active methylating species from methanol/DME and the (reversible) protonation of intermediate alkenes to their carbenium ion equivalents, which undergo hydride transfer, isomerization, or β-scission via cationic transition states. Heterogeneous MTT reactions are clearly catalyzed by Brønsted acid sites, and alkene protonation must involve Brønsted acids in homogeneous systems. Other homogeneous reactions may also be mediated by protons, but their mechanism is less clear. A 5 M aqueous solution of ZnI_2 has a pH of about 1,[26] and the pH of solutions with substoichiometric water/Zn ratios (<4:1) may be even lower but would increase with water content because of the leveling effect. Homogeneous systems may also contain Lewis acid sites that could activate methanol or DME via coordination to Zn^{2+}or In^{3+} ions. Such sites would also coordinate H_2O, making water inhibition consistent with either Brønsted or Lewis acid catalysis.

Acid strength influences both turnover rates and selectivities; a stronger acid preferentially increases hydride transfer and isomerization rates over methylation rates.[27] This is most clearly seen by comparing two mesoporous heterogeneous catalysts of different acid strength: $H_3PW_{12}O_{40}/SiO_2$ polyoxometalate (POM) clusters and amorphous $SiO_2-Al_2O_3$. POM catalysts are stronger acids and give much higher DME homologation turnover rates (7.3×10^{-3} mol C [mol H^+ s]$^{-1}$) vs 0.37×10^{-3} mol C [mol H^+ s]$^{-1}$) but lower selectivities to heavier products (C_{5+}) and to highly branched isomers within each C_n fraction. Turnover rates on H-BEA lie between those for the two mesoporous acids (1.5×10^{-3} mol C [mol H^+ s]$^{-1}$), but H-BEA gives much higher triptyl selectivities, even though it resembles $SiO_2-Al_2O_3$ in acid strength. The higher turnover rates and triptyl selectivities in H-BEA (vs mesoporous aluminosilicates) reflect the effects of solvation by confinement within voids of molecular size, which leads to higher DME homologation rates via van der Waals interactions that stabilize transition states preferentially over reactants. (We expect that the liquid phase in the homogeneous systems similarly solvates transition states preferentially over reactants, thus leading to higher rates and selectivities than expected from the acid strength of the

TABLE 4. Methylative Homologation of Alkanes Catalyzed by InI_3/Adamantane[a]

alkane	adamantane (mol % relative to alkane)	conversion (%)	selectivity (%, carbon basis)[b]
DMB	0	37	39
DMB	1.2	70	55
isopentane[c]	5.9	48	41
isobutane[d]	7.1	47	36

[a] Reactions of equimolar alkane and methanol carried out for 30 min at 453 K, except as noted. [b] Selectivity to maximally branched higher alkanes: triptane from DMB; triptane + DMB from isopentane; triptane + DMB + isopentane from isobutane. [c] Reaction time = 60 min. [d] Reaction time = 300 min; $T = 473$ K.

prevalent acid sites, although there are no rigorous methods to compare acid strengths in solid acids and solutions of ZnI_2 or InI_3.) These confinement effects are more effective for methylation and hydride transfer than for isomerization because two molecules are stabilized within zeolite pores in methylation and hydride transfer transition states but only one is stabilized in isomerization transition states.

Reliable estimates of acid strength for relevant species in ZnI_2 and InI_3 systems at MTT conditions are unavailable, but solutions in protic solvents are expected to be more strongly acidic for trivalent than divalent cations. If so, their relative MTT rates and selectivities would be consistent with the conclusions reached for heterogeneous acids. InI_3 systems give higher MTT rates, function at lower temperatures, and give lighter and less branched products than ZnI_2. The near-total absence of alkenes and the higher arene yields with InI_3 are consistent with higher hydride transfer rates (relative to methylation) for the stronger trivalent acids.[16] The stronger acid sites in InI_3 are also evident from its ability to activate alkanes and to introduce them into C_1 homologation paths. Branched alkanes are activated during MTT on InI_3 (but not on ZnI_2) at 473 K, as evident from singly labeled triptane formed from unlabeled 2,3-dimethylbutane (DMB) reactions with $^{13}CH_3OH$ and from the ability of branched alkanes to initiate MTT in stirred reactions.[16] These effects were not observed with ZnI_2 except at temperatures above 473 K.[18] The incorporation of branched alkanes into DME homologation pathways also occurs on solid acids, as shown on H-BEA at 473 K (see below).[25]

These data suggest that effective MTT catalysts must contain sites of intermediate acid strength. Cationic transition states for methylation require strong acids for practical homologation rates, but such strong acid sites also favor hydride transfer over methylation, which leads chains to terminate too early along the growth path to triptane. Stronger acids also tend to equilibrate skeletal isomers and convert triptyls and their precursors to more stable isomers, as shown by the lower triptyl selectivities for POM than for H-BEA,[27] and isomer distributions much closer to equilibrium for homogeneous phosphoric acid[8] than for ZnI_2 and InI_3.

Methylative Homologation of Alkanes on Acids

Activation of alkanes at the low temperatures of MTT catalysis provides an alternate route to upgrade these low-value molecules: the homologation of light alkanes by addition of methylene. The stoichiometry of this reaction (eq 1) avoids the rejection of carbon as arenes (otherwise required to balance the MTT stoichiometry). Co-homologation of DMB with methanol/DME on InI_3 was mentioned in the previous section; smaller isoalkanes (e.g., isobutane, isopentane) also react with methanol or DME on InI_3[20] and H-BEA.[21] These isoalkanes are prevalent throughout refinery streams and cause high volatility in gasoline fractions. Methylative homologation provides a potential route for their chain growth into less volatile components.

$$C_nH_{2n+2} + CH_3OH \rightarrow C_{n+1}H_{2n+4} + H_2O \tag{1}$$

The rates of methylative homologation of alkanes on InI_3 and H-BEA are significantly increased by addition of adamantane (AdH) in catalytic amounts, as evident from reactions of equimolar DMB–methanol mixtures on InI_3 at 453 K (Table 4), in which DMB methylation occurs without formation of arenes (hence without MTT). DMB conversion rates and triptane selectivities were markedly increased by adding 1% AdH to reactants. Similar effects were observed for isobutane and isopentane, but alkane conversions and triptane selectivities were lower than those for DMB coreactants (Table 4).[20]

On H-BEA, methylative homologation of alkanes and the cocatalytic effects of AdH are most clearly shown by isotopic labeling studies. Reactions of ^{13}C-labeled DME with unlabeled DMB gave products with a 1.1 $^{12}C/^{13}C$ ratio (a measure of the extent of alkane incorporation) without AdH; this ratio increased to 4.1 with 2.5 mol % AdH in the reactant stream. Triptyl selectivities increased from 15% to 27% when DMB was added to DME feeds, and then to 38% with 2.5% AdH. In contrast to the InI_3-catalyzed reaction, even linear alkanes such as *n*-butane reacted with DME on H-BEA but to a lesser extent than branched alkanes and only when AdH was present.[21]

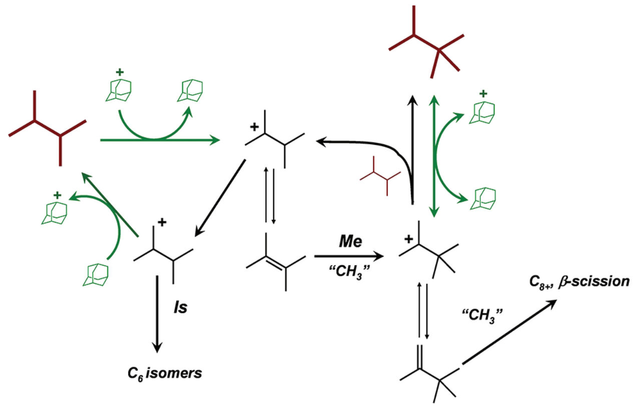
AdH functions as a cocatalyst for the transfer of hydride from alkanes to carbenium ions,[28] allowing alkanes to participate in MTT chemistry. AdH can also "quench" (via H-transfer) reactive intermediates for isomerization and cracking, thus improving selectivity to the most desired products (although alkanes can also re-enter chain growth, overgrow, and crack). These effects are illustrated (for the case of DMB homologation to triptane) in Scheme 2.

MTT Stoichiometric Balance and External Hydrogen Sources

The MTT stoichiometry requires that carbon be rejected (as methyl arenes), limiting carbon yields to 63% even when triptane is the only aliphatic product (eq 2). The rejection of carbon as arenes also causes deactivation in solid acids via retention of nonvolatile residues. These stoichiometric deficiencies and their consequences can be avoided if hydrogen atoms from other sources (preferably H_2) could be brought in active form into MTT reactions.

$$33CH_3OCH_3 \rightarrow 6C_7H_{16} + 2C_6(CH_3)_6 + 33H_2O \quad (2)$$

SCHEME 2. Proposed Mechanism for Homologation of DMB to Triptane with AdH as Co-catalyst[a]



[a]Intermediates are represented as carbenium ions for simplicity.[20,21]

An H_2 activation function was introduced into H-BEA zeolites by exchange with Ga^{3+} cations; this function was so efficient that alkenes (cofed or formed during MTT) were hydrogenated before significant methylation, forming small alkanes as the main products. Adamantane, however, brought these alkanes back into the chain growth path by promoting hydrogen transfer. In these systems, alkenes act as H_2 carriers that shuttle H-atoms from Ga sites, where H_2 is activated, to acid sites, where adamantane facilitates the transfer of these H-atoms to surface alkoxides.[29]

Selectivities depend on H_2 pressure in a complex manner. For example, higher H_2 pressures led to higher triptyl selectivity from DME/*trans*-2-butene/AdH, because C_5-C_7 products of *trans*-2-butene methylation terminate before subsequent growth, via deprotonation and Ga-catalyzed hydrogenation of the resulting alkenes. With branched alkene cofeeds, however, higher H_2 pressures led to lower triptyl selectivities, because branched alkanes formed via hydrogenation become the predominant hydride donors in AdH-catalyzed termination of alkoxides. Thus, triptyl selectivities decreased (and isopentane selectivity increased) with increasing H_2 pressure for DME/isobutene/AdH feeds, because isobutane formed at Ga sites re-entered chain growth but terminated after a single methylation through hydrogen

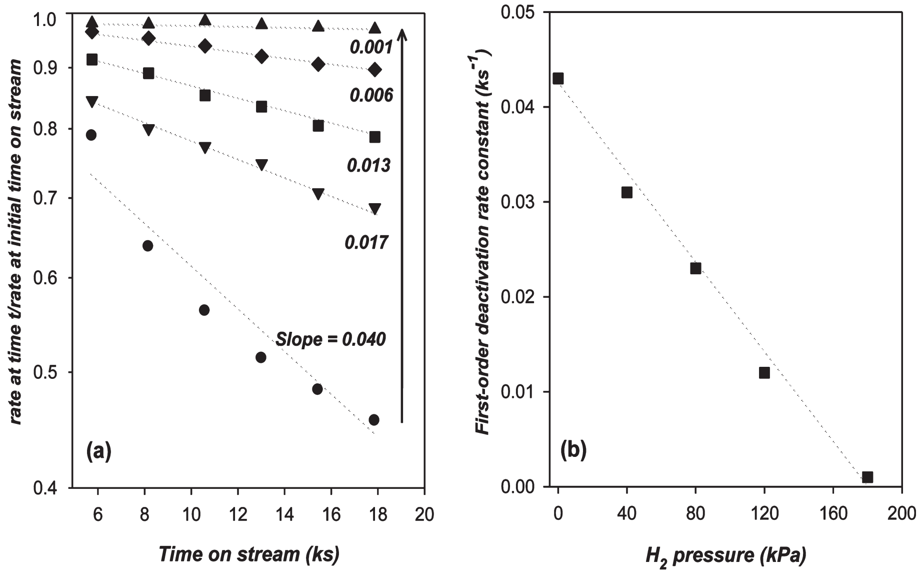
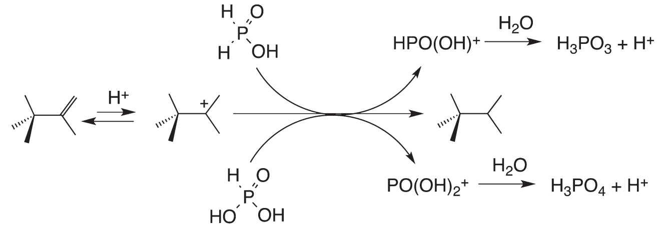


FIGURE 3. (a) Ratio of rate at time *t* to rate at initial time on stream (3.2 ks) at different H_2 partial pressures: 0 kPa (●); 40 kPa (▼); 80 kPa (■); 120 kPa (◆); 180 kPa (▲). (b) Influence of H_2 pressure on the deactivation constant (k_d). The reactant mixture contains DME (65 kPa), isobutene (2 kPa), and adamantane (1 kPa) (473 K, <2.0% total carbon conversion, 0.05 mol [mol Al s]$^{-1}$ space velocity, 0.30 g Ga/H-BEA with 2.0 wt % Ga).[29]

SCHEME 3. Proposed Mechanism for the Role of Phosphorus Reagents As Alternate Hydride Transfer Sources



transfer from another isobutane. We conclude that selectivities for isoalkanes are more sensitive to H_2 pressure than those for *n*-alkanes because isoalkanes undergo more facile Ga-catalyzed hydrogenation and AdH-catalyzed dehydrogenation steps. The combined effects of H_2 activation and AdH also markedly decreased deactivation rates (Figure 3), as expected from the concomitant decrease in arene formation rates.[29]

Analogous attempts to incorporate a hydrogenation function into the ZnI_2 system did not succeed. The solid cocatalysts added were ineffective and homogeneous hydrogenation catalysts did not survive MTT conditions. The addition of phosphorous acid or hypophosphorous acid, however, led to a substantial improvement in triptyl selectivities. Triptyl yields at 473 K were 18% without such additives, 23% with 7% H_3PO_3, and 32% with 7% H_3PO_2; in the latter case, yields were as high as 36% at 448 K. ^{31}P NMR of the reaction mixture showed that the acids were oxidized, ultimately to phosphoric acid, indicating that the added reagent served as a stoichiometric source of hydrogen (Scheme 3). In accord with this conclusion, arene yields decreased by ~50% and products were somewhat lighter, as expected from more effective hydride sources and transfer pathways.[17] In contrast, addition of these phosphorus reagents to InI_3-catalyzed MTT resulted in *decreased* triptyl yields (even though both oxidation of the reagent and suppression of arene formation were observed just as with ZnI_2), a consequence of the higher acidity of InI_3, which would disproportionately accelerate the rate of hydride transfer, favoring termination over growth (large increases in the yields of lighter products, isobutane and isopentane, were also observed).[16]

Conclusions

The different historical and disciplinary contexts and reaction conditions of homogeneous and heterogeneous catalysis are brought together in this Account within a common mechanistic framework based on carbenium ion chemistry mediated by Brønsted acids to account for the unique homologation selectivities common to liquid and solid acids. These selectivities, which appear to be unprecedented in acid catalysis (note that triptane would be obtained in less than 1% yield under thermodynamic control) depend critically on the strength, but *not* the chemical nature, of the acid. This catalytic chemistry provides exemplary evidence for the preferential routes by which carbenium ion transition states mediate acid catalysis and for the ability of reactive alkenes (and less reactive alkanes) to undergo methylative growth, specifically in a manner that adds the C_1 species derived from DME or methanol at backbone positions dictated by the stability of the relevant carbocationic transition states.

Our interpretation of these selectivity trends in terms of elementary steps led to strategies that exploit molecular H-transfer cocatalysts, such as adamantane, to incorporate typically unreactive alkanes into C_1 homologation paths and, in doing so, to provide the stoichiometric hydrogen requirement to form alkanes from DME/methanol without concomitant yield losses otherwise imposed by the need to reject carbon as arenes. H-atoms can also be supplied by sacrificial H-sources, such as H_3PO_2 and H_3PO_3 on homogeneous catalysts and H_2 molecules on solid acids modified by cations that activate H_2. Even though MTT does not appear to be practical at the current stage of development, the ability to devise such enhancements via mechanistic understanding offers considerable encouragement for the eventual application of this or related chemistry.

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