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Kinetics of Butene Isomer Methylation with Dimethyl Ether over Zeolite Catalysts

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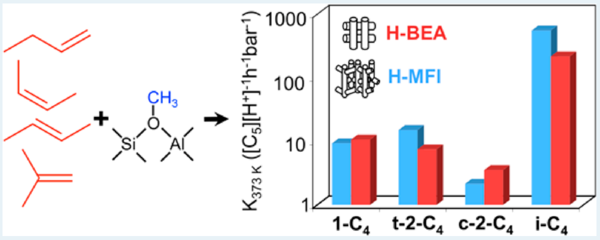
Ⓢ *Supporting Information*



ABSTRACT: The systematic investigation of 1-butene, *trans*-2-butene, *cis*-2-butene, and isobutene methylation with dimethyl ether (DME) over acidic zeolites FER, MFI, MOR, and BEA at low conversions (<0.1%) and high DME:olefin ratios (>15:1) showed linear rate dependencies on butene pressure and no dependence on DME pressure. Such dependencies are consistent with the zeolite surface being predominantly covered by DME-derived species, which either directly reacts with butene species in the rate-determining step or through the formation and subsequent degradation of a coadsorbed complex. A comparison of rate constants for butene methylation across isomers over MFI and BEA shows that, in the absence of hydride shift, a 10-fold increase is observed for reactants capable of forming more substituted carbenium ion-like transition states, as predicted for carbocation mediated mechanisms. High *cis*-2-butene pressure experiments over BEA show linear dependencies of the butene methylation rate on butene pressure for olefin to DME ratios as high as a ∼1.5, indicating that surface-bound DME derived species react with butene in Eley−Rideal type kinetics at low temperatures. Titration with water after steady-state methylation of *cis*-2-butene over BEA results in DME-derived intermediates being removed as methanol in a 1:1 ratio with zeolite Al suggesting that surface methyl groups are involved in olefin methylation reactions.

KEYWORDS: *olefin methylation, zeolites, Brønsted acid catalysis, methanol-to-gasoline conversion, butenes*

1. INTRODUCTION

The mechanism underlying the methanol to hydrocarbons (MTH) process over acidic zeolites has been a topic of debate since its discovery by Mobil in 1977.[1,2] The failure of direct methanol C−C coupling to explain prolonged induction periods with increasing methanol purity,[3] product isotopomer distributions in labeling experiments,[4−6] and high activation barriers for ylide formation via computational methods[7−9] supports an indirect "hydrocarbon pool" mechanism first proposed by Stein and Kolboe.[10−12] This mechanism states that unsaturated hydrocarbons trapped within the zeolite framework undergo methylation, dealkylation, and hydrogen transfer reactions to generate the observed MTH products over zeolite and zeotype materials, in effect, acting as cocatalysts. Olefins and aromatics have been shown to be present within the zeolite framework under MTH reaction conditions through spectroscopic[13,14] and analytical[15−17] techniques. Experiments cofeeding propene or toluene with DME over MFI at 548 and 623 K have shown that olefins increase product selectivity to C$_4$ to C$_7$ aliphatic hydrocarbons and aromatics increase selectivity to methylbenzenes and ethene. The overall product selectivity over MFI can be selected using varying mole fractions of both propene and toluene in 4 kPa cofeed stream.[18]

Aromatic methylation and subsequent dealkylation determine product selectivity toward aromatics and light olefins for MTH reactions, as observed via ^{12}C/^{13}C methanol switching experiments over SAPO-34,[19] BEA,[16,17] and MFI.[20] These experiments allowed the authors to attribute the differences in propene/ethene selectivity to differences in the degree of methylation of the aromatic hydrocarbon pool. Polymethylbenzenes comprise the major aromatic species entrained within the zeolite framework as observed by in situ ^{13}C MAS NMR[17] and via GCMS analysis of the HF digest from the spent zeolite/zeotype catalyst.[16,17,19,20] These studies showed that larger pore BEA[16,17] and SAPO-34[19] have penta- and hexa- methylbenzenes as the most active methylation and dealkylation species, while MFI[20] showed higher alkylation activity for di-, tri-, and tetra- methylbenzenes.

Dessau and La Pierre[21−23] proposed a methylation cycle of olefins over MFI. The slow methylation of ethene and the promotion of longer-chain olefins to aromatics were included in their model from primary product reaction studies performed by monitoring product selectivity at high space velocities. Chen et al.[24] noted that cofeeding olefins led to the increased production of higher olefins in MTH reactions and occurred much faster than ethene formation. Langner et al.[25] noted that the induction period observed for MTH reactions could be decreased by up to 18-fold through the addition of alcohols, which rapidly dehydrate to olefins at 473 K over acid catalysts. Medium channel TON has been shown to selectively methylate

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olefins in the absence of cyclization and dealkylation reactions.[26] Ethene methylation reactions run over this framework showed that propene and subsequent olefins selectively added carbon from ^{13}C labeled methanol at 623 K.[26] Experimental work on MFI by Svelle et al.[27,28] has shown that, at 623 K and 1:1 methanol and olefin pressures, rate constants and activation energies can be obtained by extrapolating reaction rates to infinite space velocities for ethene, propene, and 1-butene. These studies found that the methylation rate constant increases as olefin substitution increases concurrently with a systematic decrease in the apparent activation energy. Pressure dependence studies found that the reaction rate is independent of methanol partial pressures, but monotonically increases with olefin pressures.[27,28] Computational modeling of these reaction systems based on hybrid MP2:DFT on clusters with periodic corrections[29] and simplified clusters using a harmonic oscillator approximation for zeolite framework bonds[30,31] has verified these reaction parameters based on mechanisms involving the coadsorption of methanol and an olefin at a single zeolite acid site. The coadsorption mechanism considers methylation reactions to proceed through the decomposition of a methanol-olefin coadsorbed complex. An alternative mechanism involves the initial dehydration of methanol/DME to form surface methyl groups and subsequent reactions of these methyl groups with olefins. The existence and persistence of surface methoxides on zeolites has been clearly demonstrated by FTIR[32] and ^{13}C MAS NMR[33,34] studies at 453 K and above, consistent with the inability of surface CH_3 groups to desorb from the surface except by reaction. The discrepancy between theoretical results and spectroscopic studies is indicative of the ongoing debate arising from the two mechanisms, and a basis to explain the origins of these conflicting observations is necessary to elucidate the identity of the methylating agent.[35]

This work aims to systematically quantify rate constants and activation energies for butene methylation over zeolites of varying structures, continuing work that explored zeolite topology effects on ethene and propene methylation.[36,37] On the basis of the elementary-step rate parameters reported herein, rate constants increase substantially as intermediate carbocation substitution increases. In addition, high butene pressure experiments were performed to test the kinetic behavior of methylation reactions based on predictions for the coadsorbed mechanism and the surface methoxide-mediated mechanism, and titration of DME-derived intermediates subsequent to butene methylation reactions enabled the identification of surface intermediates present during steady-state olefin methylation.

2. MATERIALS AND METHODS

2.1. Catalyst Preparation. Zeolites FER, MFI, MOR, and BEA were obtained from Zeolyst in their NH_4^+ form and ICP-OES elemental analysis performed by Galbraith Laboratories was used to determine the aluminum content of each material (See the Supporting Information, Table S.1 for results from elemental analysis, DME titration experiments, N_2 adsorption experiments, and XRD). Zeolites were sieved to aggregate sizes between 180 and 425 μm and treated in dry air (1.67 cm^3 s^{-1} NTP, ultrapure, Minneapolis Oxygen) with a 0.0167 K s^{-1} temperature ramp to 773 K and holding for 4 h to obtain the H$^+$ counterion. Protonated zeolite catalysts used in this study are referred to as H-FER, H-MFI, H-MOR, and H-BEA.

2.2. Steady-State Catalytic Conversion of DME and Butene Isomers. Steady-state methylation reactions of 1-butene, *trans*-2-butene, *cis*-2-butene, and isobutene were performed in a 10 mm inner diameter packed-bed quartz reactor at atmospheric pressure and differential conversions (<0.1% pentene + hexene formation). Catalysts were supported on a quartz frit inside the reactor, and the temperature was controlled using a furnace (National Electric Furnace FA120 type) connected to a Watlow Temperature Controller (96 series). Catalyst temperatures were measured using a K-type thermocouple at the bottom of a well penetrating the catalyst bed. Samples (0.005−0.010 g, diluted in quartz sand) were treated in flowing He (1.67 cm^3 s^{-1}, ultrapure, Minneapolis Oxygen) at 773 K (0.0334 K s^{-1} temperature ramp) for 4 h prior to cooling to reaction temperatures (258−333 K). A mixture of dimethyl ether (DME), argon, and methane (50:49:1; Praxair certified standard grade) (0.15−0.98 bar) was combined with C_4H_8 (Sigma-Aldrich, >99%) (0.001−0.03 bar) stream and He to maintain a total flow rate of 1.67 cm^3 s^{-1} (*trans*-2-butene, *cis*-2-butene, and 1-butene) or 0.84 cm^3 s^{-1} (isobutene). Reaction order dependencies were determined by varying either DME or olefin flow rates in the feed stream while keeping the other constant and adjusting He flow to compensate for the change in overall reactant flow rate. Reactor effluent composition was monitored via gas chromatography (Agilent 7890) through a methyl-siloxane capillary column (HP-1, 50.0 m x 320 μm × 0.52 μm) connected to a flame ionization detector and a packed column (Supelco HAYSEP DB packed column, 12 ft) connected to a thermal conductivity detector.

2.3. In Situ Titration of Surface Species Present during Olefin Methylation. Steady state methylation of *cis*-2-butene with 200 mg BEA at 273 and 282 K and 0.03 bar olefin in the presence of 0.6 bar DME was maintained for 2 h prior to switching to 0.83 cm^3 s^{-1} He. Temperature was increased to 423 K at a rate of 0.25 K s^{-1} and held for 0.5 h, followed by introduction of 0.08 cm^3 s^{-1} water using a syringe pump. Effluent compositions were monitored online using an MKS Cirrus quadrupole mass spectrometer and quantified using Ar as an internal standard.

3. RESULTS AND DISCUSSION

We have systematically examined the kinetics and mechanism of butene isomer methylation to quantitatively assess the dependence of reaction rates, rate constants, and activation energies on olefin substitution and zeolite pore structure. These studies were performed in the absence of olefin isomerization, oligomerization, and hydride transfer reactions. Arguments regarding the identity of the DME-derived methylating agent on the zeolite surface are included based on derived kinetics and direct titration of surface intermediates.

3.1. Effect of Zeolite Topology on 1-Butene Methylation. DME and 1-butene pressure dependence studies were performed over zeolites BEA, MOR, MFI, and FER. The rate of methylation is first order in 1-butene pressure and zero order in DME (Figure 1), showing similar trends to those observed for ethene and propene methylation.[36,37] Work from Svelle et al.[27,28] has also observed these same pressure dependencies for MFI at 623 K and equal pressures of ^{13}C methanol and olefin (50 mbar) by extrapolating rates to zero contact times. These results indicate that 1-butene methylation proceeds via the formation of an active DME-derived species, followed by the rate-limiting addition of the activated C_1 to the olefin.

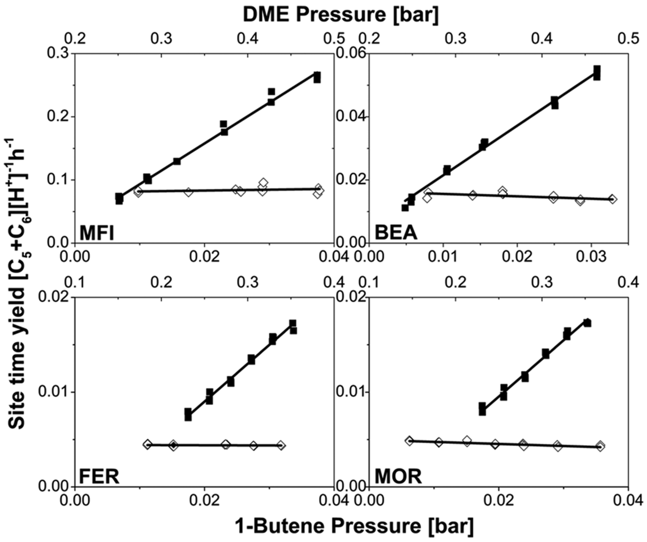


Figure 1. 1-Butene methylation olefin and DME pressure dependence plots. (■) 1-Butene pressure dependence. (◇) DME pressure dependence.

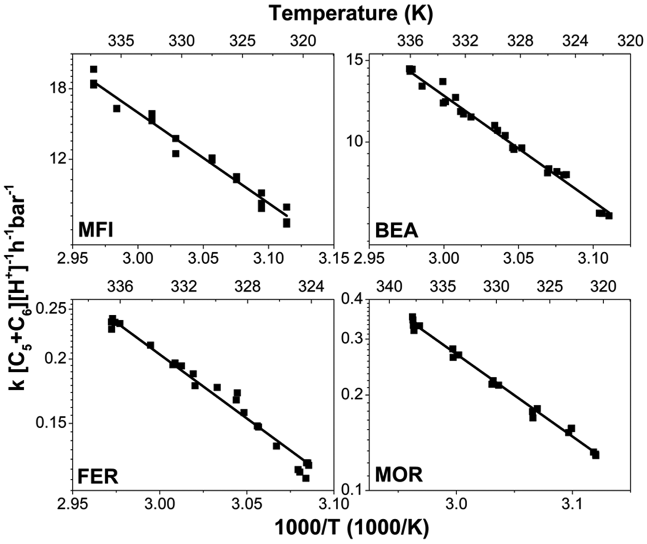


Figure 2. Arrhenius plots for 1-butene methylation from temperature dependence studies.

Arrhenius plots of temperature dependence studies (Figure 2) show that rate constants for 1-butene methylation vary by an order of magnitude for different zeolite frameworks, namely, MFI and BEA have higher rate constants than MOR and FER, consistent with rate constants for ethene and propene methylation previously reported[36,37] (Table 1). Apparent activation energies remain relatively constant between frameworks, indicating that pore wall stabilization of adsorbed species is either (i) offset by transition state destabilization or (ii) small compared to other contributions to the activation barrier. DFT +D models using the PBE exchange-correlation functional of ethene methylation over many zeolite frameworks have shown that activation energies and heats of physisorption vary among zeolites to different extents.[38] It is the balance of these two values that encompass variations in methylation rates among different zeolites structures The activation energy of 1-butene methylation over MFI, 44 kJ mol^{-1}, is in good agreement with the previously reported experimental value of 45 kJ mol^{-1},[27] MP2:DFT calculated value of 48 kJ mol^{-1},[29] and a value of 45 kJ mol^{-1} calculated using ONIOM methods.[30] Furthermore, an extrapolation of the experimental rate constant in this account is within a factor of 0.7 with the previously determined value of 3.6 × 10^4 h^{-1} bar^{-1} at 623 K.[27]

3.2. Effect of Butene Isomer on Methylation Reactions over Zeolites BEA and MFI. Temperature, olefin pressure, and DME pressure dependence experiments were performed for the three other butene isomers: *cis*-2-butene, *trans*-2-butene, and isobutene over MFI and BEA, shown in Figures 3 and 4,

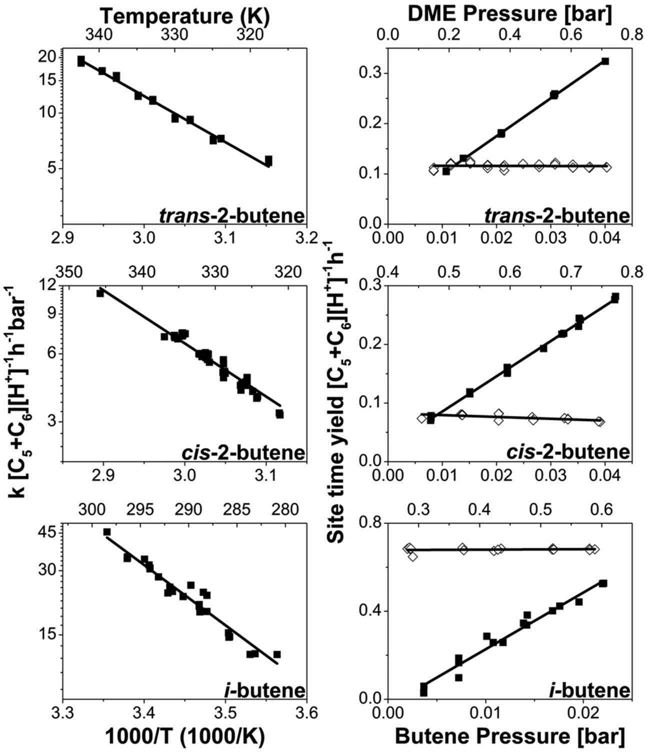


Figure 3. Kinetics of butene methylation over MFI for different isomers. Temperature dependence (left) and (■) olefin pressure dependence, (◇) DME pressure dependence (right).

Table 1. Rate Parameters for C$_2$−C$_4$ Olefin Methylation over Zeolites[a]

	C$_2$H$_4$[b]		C$_3$H$_6$[b]		1-C$_4$H$_8$		*trans*-2-C$_4$H$_8$		*cis*-2-C$_4$H$_8$		*i*-C$_4$H$_8$	
sample	*k*	E_a	*k*	E_a	*k*	E_a	*k*	E_a	*k*	E_a	*k*	E_a
BEA	0.12	64 ± 2	2.8	54 ± 2	72.5	45 ± 3	63.7	29 ± 1	17.5	42 ± 1	2995	34 ± 1
MOR	0.01	61 ± 3	0.20	58 ± 4	1.8	49 ± 1						
MFI	0.06	98 ± 3	3.7	62 ± 3	89.1	44 ± 2	74.2	46 ± 1	40.6	49 ± 1	3509	56 ± 3
FER	0.03	84 ± 2	0.12	57 ± 2	1.2	50 ± 3						

[a] All *k* values reported are in h^{-1} bar^{-1} and normalized to 373 K. Activation energies are reported in kJ mol^{-1}. [b] Reported previously.[36,37]

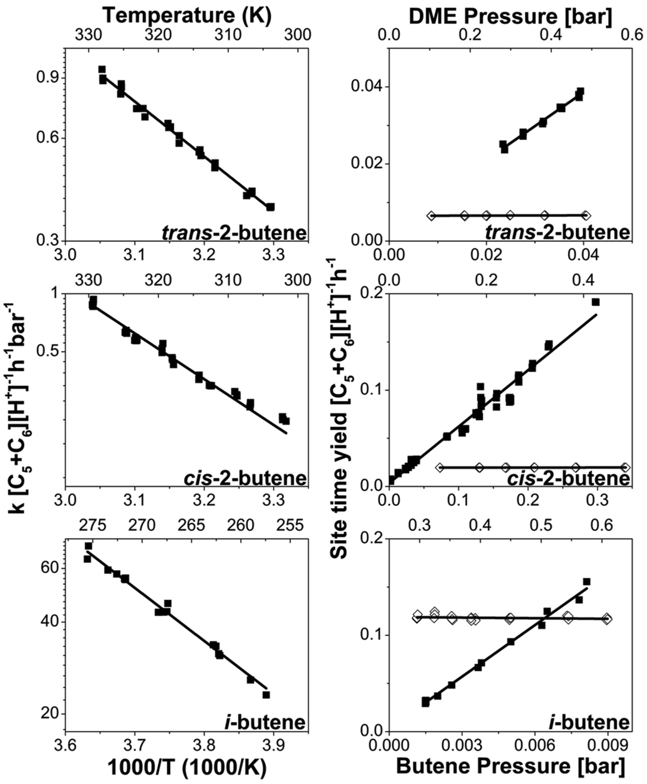
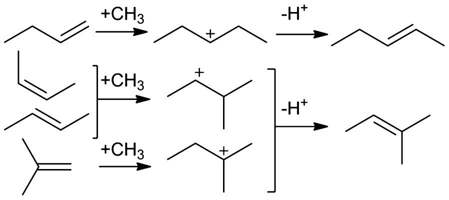


Figure 4. Kinetics of butene methylation over BEA for different isomers. Temperature dependence (left) and (■) olefin pressure dependence, (◇) DME pressure dependence (right).

respectively. These zeolites were chosen as consistently higher reaction rates are noted on MFI and BEA compared to MOR and FER. A compilation of our data in Table 1 shows that the 2-butene isomers have similar activation barriers toward methylation. The rate of methylation of 1-butene is on the order of propene at 373 K.[36,37] The rate constant for isobutene methylation exceeds those for all other isomers by an order of magnitude at 373 K. These data suggest that the rate of methylation is directly related to the degree of substitution about the double bond, which stabilizes intermediate carbocations through inductive electron donation. The ranking of carbocation or cyclopropyl-type intermediates is as follows: primary (C_2H_4) < secondary (C_3H_6) < secondary (1-C_4H_8, *trans*-2-C_4H_8, *cis*-2-C_4H_8) < tertiary (*iso*-C_4H_8). The role of olefin methylation[39] and zeolite structure[40] in the overall reaction network leading to selective 2,2,3 trimethylbutane formation has shown that the formation of branched alkanes arises because of increased carbocation stability of reactive intermediates and proceeds over BEA with the highest rate. Propene and butene isomer methylation reactions with ^{13}C DME over BEA at 473 K were performed by Simonetti et al.[39] using isotope tracing. These experiments yielded rates, when taken as first-order rate constants at 473 K, within the range of 24 h^{-1} bar^{-1} for isobutene methylation to 49 h^{-1} bar^{-1} for 1-butene methylation for C_3 and C_4 cofeeds. We attribute the conflicting observations regarding the methylation rate of isobutene to the difference in reaction conditions and, specifically, the presence of hydride transfer. Isobutene is the only isomer capable of forming a tertiary carbocation upon methylation at the most kinetically favored position in the absence of hydride transfer (Scheme 1). Comparing rate constants in Table 1 and the carbenium ion-like transition states formed, compounds with similar bond order about the carbocation have similar rate constants toward methylation with an order of magnitude gap between subsequent groups.

Scheme 1. Methylation Pathway for Butene Isomers



3.3. Reaction Rate Expression Derivation for Butene Methylation.

The identity of the surface species responsible for methylation reactions on zeolites remains a topic of debate in the field of MTH.[35] Two possible species are considered to be active for the methylation of olefins: a complex involving a physisorbed methanol/DME molecule on a Brønsted acid site with a subsequently physisorbed olefin, or a chemisorbed methoxide bound directly to the zeolite lattice.

The coadsorbed mechanism has been used to explain experimental observations[41] and used as a theoretical basis for computational studies.[8,29,41] This mechanism postulates an active coadsorbed complex between the methylating agent and a cofed olefin on a zeolite acid site. The energy associated with the formation of coadsorbed complexes has been shown to mostly derive from the interaction of the methylating agent, that is, methanol or DME, with the zeolite acid center. Svelle et al.[29] have reported the heat of adsorption of ethylene onto a physisorbed methanol molecule differs by only 2 kJ mol^{-1} between a purely silaceous framework and with one containing Al using hybrid MP2:DFT calculations with periodic boundary conditions. This suggests that the addition of ethylene onto the physisorbed methylating agent is not driven by ionic interactions with methanol, but rather van der Waals interactions with the zeolite pore walls. The differential heat of adsorption with the addition of an olefin onto a physisorbed methanol is −37 and −53 kJ mol^{-1} for C_2H_4 and C_3H_6 coadsorption, respectively.[29] In contrast, Blaszkowski and van Santen[42] have shown that the adsorption of a single methanol molecule on a Brønsted acid site has an enthalpy of adsorption, $\Delta H_{ads} = -75$ kJ mol^{-1} and the formation of methanol dimers has a $\Delta H_{ads} = -121$–130 (1T vs 3T cluster) kJ mol^{-1} using self-consistent nonlocal corrected DFT. The similar contributions to the adsorption energy from a coadsorbed olefin and a second methanol molecule indicate that methanol dimers are potentially in competition with coadsorbed species, as methanol does not exhibit a significant change in the heat of adsorption, $\Delta H_{ads} = -115 \pm 5$ kJ/mol, on MFI until loadings above 2 molecules per Al are achieved, as observed by microcalorimetry at 400 K.[43] Molecular dynamics simulations have shown that methanol dimers are considered inactive for the methylation of olefins because of their enhanced stabilization through mutual H-bonding.[44] Methylation via coadsorbed complexes is traditionally viewed as being less energetically taxing compared to the activated formation of a methoxide, yielding barriers around 100 kJ mol^{-1} for ethylene methylation[29] compared to barriers between 215–223 kJ mol^{-1} for the formation of surface methoxides.[8,45,46] A recent study by Boronat et al.[47] has shown that dispersion effects play an important role in the stabilization of methoxide species by using 121–130 atom clusters with DFT-D dispersion corrections, yielding intrinsic barriers of 39−150 kJ mol^{-1} for 12-membered ring channels in MOR.

A formal derivation of rate equations is provided to further understand the kinetic behavior of the two proposed active surface species. It is assumed in each derived rate expression that only one surface species is responsible and the others act to inhibit the rate by occupying acid sites. Equation 1 below outlines the site balance used for both rate models, based on the discussion provided above:

$$\begin{aligned}[H^+]_0 &= H^* + H{\cdot}CH_3OCH_3^* + H{\cdot}CH_3OH^* \\ &\quad + H{\cdot}Dimer^* + H{\cdot}CH_3OCH_3{\cdot}O_n^* \\ &\quad + H{\cdot}CH_3OH{\cdot}O_n^* + CH_3^* + CH_3{\cdot}O_n^* \end{aligned} \qquad (1)$$

The terms in eq 1 refer to unoccupied acid sites; physisorbed DME, methanol, methanol dimers, DME/olefin, and MeOH/olefin coadsorption complexes; and chemisorbed methoxy groups and an olefin adsorbed on a methoxide, respectively.

The accompanying rate equation for coadsorbed complex mediated olefin methylation is given in eq 2.

$$\begin{array}{lll} (i) & CH_3OCH_3 + H^* \leftrightarrow H{\cdot}CH_3OCH_3^* & K_a \\ (ii) & H{\cdot}CH_3OCH_3^* + O_n \leftrightarrow H{\cdot}CH_3OCH_3{\cdot}O_n^* & K_C \\ (iii) & H{\cdot}CH_3OCH_3{\cdot}O_n^* \rightarrow O_{n+1} + H^* + CH_3OH & k_C \\ (iv) & CH_3OH + H^* \leftrightarrow H{\cdot}CH_3OH^* & K_a' \\ (v) & H{\cdot}CH_3OH^* + O_n \leftrightarrow H{\cdot}CH_3OH{\cdot}O_n^* & K_C' \\ (vi) & H{\cdot}CH_3OH^* + CH_3OH \leftrightarrow H{\cdot}Dimer^* & K_D \\ (vii) & H{\cdot}CH_3OH{\cdot}O_n^* \rightarrow O_{n+1} + H^* + H_2O & k_C' \\ (viii) & H{\cdot}CH_3OCH_3^* \leftrightarrow CH_3OH + CH_3^* & K_M \\ (ix) & H{\cdot}CH_3OH^* \leftrightarrow H_2O + CH_3^* & K_M' \\ (x) & CH_3^* + O_n \leftrightarrow CH_3{\cdot}O_n^* & K_O \end{array} \qquad (2)$$

Where O_n refers to a general olefin consisting of n-carbons and O_{n+1} refers to the methylated olefin, or butene and pentene in this report, respectively

The mechanism described in eq 2 provides two potential reactions to generate a methylated olefin, corresponding to coadsorbed complexes generated from DME and methanol. Assuming decomposition of these complexes occur on kinetically similar time scales, as reported by Svelle et al.[41] where the rate of DME methylation of propene is ~2.5 times that of methanol when comparing saturated rates at (625 K, 20 mbar C_3H_6 25−75 mbar DME or CH_3OH, 100 mL min^{-1} flow) and 5 times that of methanol based on B3LYP/6-31G(d) + ZPE energy calculations and quasi-IRC techniques, the rate-limiting step is represented by eq 3:

$$\frac{Rate_c}{[H^+]_0} = k_c[H{\cdot}CH_3OCH_3{\cdot}O_n^*] + k'_c[H{\cdot}CH_3OH{\cdot}O_n^*] \qquad (3)$$

Under high DME pressure conditions, the methanol coadsorbed complex contributes a negligible amount to the overall reaction rate, yielding the fully derived form provided in the Supporting Information. Considering a zeolite surface covered in coadsorbed complexes with DME, the rate equation reduces to the following form:

$$\frac{Rate_c}{[H^+]_0} = k_c \qquad (4)$$

The surface methoxide-mediated mechanism is represented by the following sequence of reaction steps:

$$\begin{array}{lll} (i) & CH_3OCH_3 + H^* \leftrightarrow H{\cdot}CH_3OCH_3^* & K_a \\ (ii) & H{\cdot}CH_3OCH_3^* \leftrightarrow CH_3OH + CH_3^* & K_M \\ (iii) & CH_3^* + O_n \leftrightarrow CH_3{\cdot}O_n^* & K_O \\ (iv) & CH_3{\cdot}O_n^* \rightarrow O_{n+1} + H^* & k_M \\ (v) & CH_3OH + H^* \leftrightarrow H{\cdot}CH_3OH^* & K_a' \\ (vi) & H{\cdot}CH_3OH^* \leftrightarrow H_2O + CH_3^* & K_M' \\ (vii) & H{\cdot}CH_3OCH_3^* + O_n \leftrightarrow H{\cdot}CH_3OCH_3{\cdot}O_n^* & K_C \\ (viii) & H{\cdot}CH_3OH^* + O_n \leftrightarrow H{\cdot}CH_3OH{\cdot}O_n^* & K_C' \\ (ix) & H{\cdot}CH_3OH^* + CH_3OH \leftrightarrow H{\cdot}Dimer^* & K_D \end{array} \qquad (5)$$

The rate-determining step has the following form, with the fully derived equation reported in the Supporting Information:

$$\frac{Rate_M}{[H^+]_0} = k_M[CH_3{\cdot}O_n^*] \qquad (6)$$

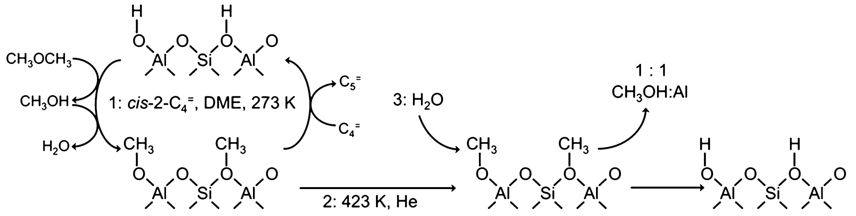
Assuming a zeolite surface covered in methoxide species, the rate equation reduces to the following form:

$$\frac{Rate_M}{[H^+]_0} = K_O k_M P_O \qquad (7)$$

A distinguishing feature between these rate expressions is the rate behavior at high olefin pressures. Saturation of surface sites with both DME and olefin concurrently is only possible for the coadsorbed mechanism, while the surface methoxide mechanism predicts first order rate dependence in either DME or olefin but never saturated in both. Running steady-state *cis*-2-butene methylation at 308 K over BEA with olefin pressures ranging from 0.2−30 kPa in the presence of 20 kPa DME maintains linear behavior, indicating that saturation of the BEA surface with a coadsorbed complex does not occur under these conditions, if these species are formed at all (Figure 4).

The relative stability of physisorbed intermediates compared to surface methoxides provides a basis for probing the identity of the surface species. Surface methoxides have been shown to be thermally stable species as they are able to persist in vacuum at 673 K, monitored via in situ IR spectroscopy, before surface-bound C−H stretches diminish during coke formation.[32] This enhanced stability arises from the absence of mechanisms for surface C_1 species to desorb unlike their higher homologues, which can generate an olefin via β-elimination.[34,48] These species have also been directly observed using solid-state ^{13}C MAS NMR under vacuum[33] and continuous flow[34] conditions on MFI at 473 K. In this report, the temperature of a 200 mg BEA sample was increased to 423 K in 1.67 cm^3 s^{-1} He after steady state cis-2-butene methylation. The steady state rate constant, when extrapolated to 373 K using the activation energy calculated from temperature dependence studies, was 20.4 h^{-1}bar^{-1}, which coincides with the 17.5 h^{-1}bar^{-1} found at higher temperatures and 5 mg BEA (Table 1). Increasing the temperature in He was done to remove residual physisorbed species removed from the zeolite surface and isolate the

Scheme 2. Post-Olefin Methylation Titration of Surface Species with H_2O on Zeolite BEA



reaction intermediate. Water was added in excess using a syringe pump to probe the existence and number of residual methoxides via the formation of methanol, based on reactivity studies performed by Wang et al.[34] who reacted methanol (forming DME), water (forming methanol), and ammonia (forming methylamines) with methoxides from zeolites H−Y and H-ZSM-5 and zeotype H-SAPO-34. Methanol liberated with H_2O amounted to 1.02 ± 0.03 and 1.01 ± 0.04 molecules per Al in BEA for 273 and 282 K experiments, respectively, indicating that the BEA surface is entirely covered in reactive DME-derived surface species at 423 K in He consistent with surface methoxide stability (Scheme 2).

Our studies show that 1-butene methylation reaction rates are first order in olefin pressure and zero order in DME pressure over zeolites BEA, MFI, FER, and MOR. These pressure dependencies are also observed for butene isomers over MFI and BEA, consistent with observations made for ethene and propene methylation that olefin methylation reactions proceed through the same mechanism regardless of the olefin or framework.[36,37] Zeolite pore structures and olefins are distinguished by the varying extents to which they propagate the olefin hydrocarbon pool by different zeolites. The extent olefins propagate the hydrocarbon pool can be classified by the degree of substitution about the most stable carbenium ion-like transition state available based on measured rate constants. High olefin pressure studies and direct titration of methylation intermediates provide further evidence that surface methoxides are the species responsible for methylating olefins to their higher homologues.

4. CONCLUSIONS

The rate of dimethyl ether methylation of 1-butene at temperatures below 350 K in excess DME at differential conversions is independent of DME partial pressure and first order in olefin pressure. This is consistent with results reported for higher conversions with methanol[27] and lighter olefins,[27,28,36] and agrees with a mechanism involving the rapid formation of DME-derived methylating agents reacting with 1-butene in the rate limiting step. These pressure dependencies hold for all butene isomers over BEA and MFI, and rate constants scale with the stability of the intermediate carbenium ion formed. Temperature dependence experiments show good agreement with previous studies[27−30] and little variation between zeolite frameworks.

Methylation reactions with a high *cis*-2-butene to DME ratio (up to 1.5) provide evidence that even in conditions with excess olefin, the reaction rate maintains a first order dependence in olefin pressure. This indicates saturation of the rate in olefin and DME, as predicted for the coadsorbed complex mediated mechanism, would require higher olefin to DME ratios than those probed in this study. Surface species were titrated with H_2O at 423 K in He in a 1:1 ratio with Al. These titrations were performed by first replacing reactant flows with He during steady-state *cis*-2-butene methylation over BEA, followed by increasing the temperature to 423 K. The surface species were shown to persist in a 1:1 ratio with Al at 423 K under He flow consistent with NMR[34] and reaction studies[48] of surface methoxide stability and observed zero order rate dependencies on DME pressure. These experiments give evidence toward an olefin methylation cycle that proceeds through carbenium ion-like transition states, formed by reaction with surface methoxide species on zeolite acid sites.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Dimethyl ether titration of zeolite acid sites, N_2 adsorption experiments with BET fit parameters, XRD patterns of zeolite structures, and rate equations for the coadsorbed complex and surface methoxide mediated mechanisms of olefin methylation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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