Surface Species Formed and Their Reactivity during the Alkylation of Toluene by Methanol and Dimethyl Ether on Zeolites As Determined by *in Situ* ^{13}C MAS NMR

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^{13}C MAS NMR has been performed *in situ* to investigate the mechanism of toluene alkylation with methanol (MeOH) or dimethyl ether (DME) at 433 K over H−ZSM-11 catalyst. The reaction protocol used allowed to separate the main reaction stages: MeOH and DME adsorption, activation, and reaction with toluene. In both cases, five strongly bound species were identified upon activation at 433 K, namely, MeOH and DME side-on and end-on adsorption complexes and methoxy species. End-on adsorbed complexes and methoxy species were found to be reactive in toluene alkylation, the reactivity of end-on adsorbed complexes being much higher.

1. Introduction

The elucidation of the reaction mechanism for the alkylation of toluene with methanol on zeolites is not only of fundamental interest but also can help to optimize the reaction conditions and catalyst design for a reaction of potential commercial interest for the production of xylenes.[1] The elucidation of this mechanism requires a detailed knowledge of the surface species formed upon methanol adsorption and their interaction with the surface of the catalyst and the reactivity of these species during the toluene alkylation. While the first point has been well understood after IR[2] and NMR[3] spectroscopic studies and theoretical calculations,[4] the second one remains a source of much controversy. Some authors conclude that the alkylating species are methoxy species,[1a,5,6] while others suppose that methoxonium-like species are responsible for alkylation.[7] In addition, it is known that DME is always formed in the reaction conditions,[1a,7a,8,9] and there are indications that DME may also intervene in ring alkylation under certain reaction conditions.[9−11]

In our previous study,[9] the ^{13}C MAS NMR technique has been used to monitor *in situ* the reaction of toluene and methanol over H−ZSM-11. The main reaction pathways observed in our NMR/batch experiment (alkylation, isomerization, and MTG chemistry) corresponded to those observed in continuous-flow reactor tests,[1d] suggesting that the reaction proceeds in a similar way under both experimental conditions. The advantage of the *in situ* NMR techniques relies on the possibility to tailor specifically the reaction protocol which enables to minimize the coupling of parallel and consecutive reaction steps. As a result, the individual steps of the reaction can be followed by carrying out separated experiments.

In this paper, we consider in more detail the alkylation step, which according to the previous study[9] can be monitored selectively at 433 K over H−ZSM-11, since under these condition MTG chemistry is not superimposed. The reaction protocol used allows to separate two main reaction stages, namely, formation of surface species (precursors for alkylation) and their reaction with toluene. As a result, the surface species formed upon interaction of MeOH or DME with H−ZSM-11 were identified, and the reactivity of these species with subsequently adsorbed toluene was determined. The results

obtained allow to get better understanding of the mechanism of toluene methylation over zeolites.

2. Experimental Section

Materials. The study was performed on a H−ZSM-11 zeolite catalyst with Si/Al ratio equal to 23. The sample was pure ZSM-11 with very high crystallinity as confirmed by XRD (Phillips P.W. 1349/30 diffractometer) and SEM (Phillips XL 20 microscope). The average particle size of the crystallites was 1 μm. According to ^{27}Al MAS NMR data combined with ^{29}Si MAS NMR, all Al were incorporated into the framework of the zeolite as Al^{IV}. No extraframework Al was detected. Owing to the high Si/Al ratio of the zeolite and as is deduced from ^{29}Si MAS NMR, all framework Al are isolated, and consequently, all acid sites should be of equivalent acid strength. Methanol-^{13}C (99.9% enriched) was obtained from ICON Services Inc. Dimethyl ether-^{13}C (99.9% enriched) was synthesized from labeled methanol.

^{13}C MAS NMR Measurements in Controlled Atmosphere. NMR experiments were performed in sealed glass NMR cells containing a catalyst and an adsorbate and fitting precisely into MAS rotors. The NMR cell preparation is described elsewhere.[9] The samples and conditions of their preparation are reported in Table 1. The reaction was carried out by heating the sealed NMR cells outside of the spectrometer at 433 K. The ^{13}C MAS NMR measurements were performed at ambient temperature after quenching of the sample cells. For the kinetic studies, the reaction time was stepped incrementally from 2 to 640 min. ^{13}C MAS NMR measurements were carried out on a Varian VXR-400S WB spectrometer operating at 100.6 MHz. Spinning rates were within 4.5−5 kHz. Quantitative conditions were achieved using high-power gated proton decoupling with the suppressed NOE effect (5 μs 90° pulse, recycling delay 8−14 s). The relaxation time T_1 measurements (inversion recovery method) and cross-polarization experiments (contact time 5−10 ms) were performed to distinguish between the species with different mobilities. In several cases, in order to study the binding strength of surface species, the sample, after being loaded with reactants and heated to reaction temperature, was evacuated before sealing (Table 1).

3. Results and Discussion

3.1. Adsorption. ^{13}C CP MAS NMR spectra obtained immediately after adsorption of methanol and dimethyl ether

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TABLE 1: Sample Preparation

experiment	A1	A2	A3	A4	B1	B2	B3
I. adsorption of the first reactant	MEOH, 1 molec/uc	MEOH, 1 molec/uc	MEOH, 1 molec/uc	MEOH, 1 molec/uc	DME, 1 molec/uc	DME, 1 molec/uc	DME, 1 molec/uc
II. preactivation		433 K, 5 h; evac, 1 h	433 K, 5 h; evac, 1 h			433 K, 5 h; evac, 1 h	433 K, 5 h; evac, 1 h
III. adsorption of the second reactant			toluene, 2 molec/uc	toluene, 2 molec/uc			toluene, 2 molec/uc

TABLE 2: Strongly Bound Surface Species Formed upon MeOH and DME Adsorption or Reaction over H−ZSM-11

| NMR lines characteristics	DME H-bounded neutral complexes		MeOH H-bounded neutral complexes		methoxy species
	side-on	end-on	side-on	end-on	
chemical shift (ppm)	62.5	59.5	53	51	49
T_1 (s)	2−3	0.4 ± 0.1	2−3	0.5 ± 0.1	3.5 ± 0.7
comparative mobility according to CP exp	rigid	mobile	rigid	mobile	very rigid
stability					
vacuum, 433 K	+	+	+	+	+
toluene coads	−	+	−	+	+
H$_2$O coads	−	+	−	+	−
in excess of DME or MeOH	−	+	−	+	+

on H−ZSM-11 are presented in the upper part of Figure 1 (experiments A1 and B1, respectively). Both spectra contain two NMR signals at 50.5 and 53 ppm for MeOH and 59.5 and 62.5 ppm for DME. It should be mentioned that the observation of two NMR signals, which could, in principle, be associated with two different conformations of adsorbed methanol or DME on zeolite surfaces, is a peculiarity of the experimental conditions chosen in this study, namely, extremely low adsorbate loadings (0.3 mol equiv relative to the amount of Bronsted sites in zeolite). At higher loadings, as is usually done in analogous studies reported in the literature, only single resonances corresponding to adsorbed methanol (50−51 ppm) or DME (60 ppm) were found[3,8−10] due to increased probability of intermolecular collisions and therefore faster exchange process, averaging various molecular states produced by adsorption.

Theoretical calculations based on both quantum chemical studies[4a] and density functional theory[4b] also point to two possible conformations of adsorbed methanol on zeolite surface: (1) end-on adsorption, when a methanol molecule is perpendicular to the zeolite surface; (2) side-on adsorption, when methanol molecule is parallel to the zeolite surface:

side-on MeOH (53 ppm)   end-on MeOH (50.5 ppm)
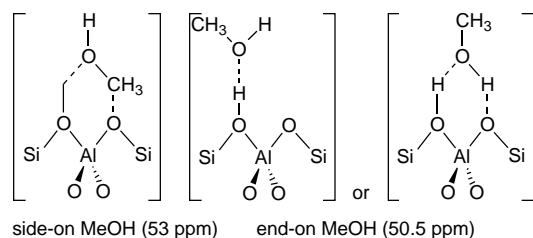
The side-on structure is less stable and less abundant according to theoretical calculations. The methyl group of this structure should be less mobile with respect to that of the end-on structure, and consequently, the NMR line corresponding to the former may be slightly shifted to the lower field due to the weak bonding to zeolite basic oxygen. On the basis of the comparison of theoretical data and the main characteristics of the observed resonances summarized in Table 2, we assigned the NMR line at 53 ppm corresponding to less mobile, less stable, and less abundant species to the side-on adsorption complex and the one at 50.5 ppm to the end-on adsorption complex.

Similarly, in case of DME adsorption, the following structures were supposed to account for our NMR results:

side-on DME (53 ppm)   end-on DME (50.5 ppm)
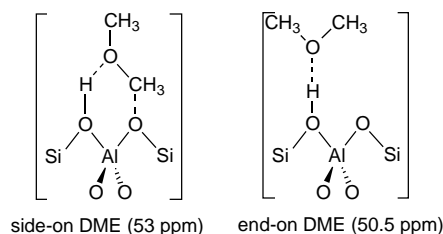
3.2. Activation Step. It is currently accepted that toluene ring alkylation with methanol proceeds via initial methanol activation on zeolite active sites followed by reaction with weakly adsorbed toluene. Therefore, MeOH activation on H−ZSM-11 was initially monitored in the absence of toluene. In order to do that, the catalyst sample with adsorbed methanol was heated to an optimal alkylation temperature (433 K), maintained at this temperature for 5 h, and then evacuated for 1 h at the same temperature to ensure the observation of all strongly adsorbed surface species formed upon MeOH activation (Table 1, experiment A2). A similar experiment was performed with DME (Table 1, experiment B2). Both experiments (A2 and B2) resulted in the observation of nearly identical NMR spectra. The ^{13}C CP MAS NMR spectrum is depicted in the lower part of Figure 1, and the spectrum obtained in quantitative conditions is presented in the upper part of Figure 2. From those results the following features emerge:

Five different species are observed upon MeOH or DME activation on H−ZSM-11. Four of them correspond to MeOH and DME side-on and end-on adsorption complexes already present and identified during the study of the adsorption process (Figure 1).

The new line appearing at 49 ppm is the most sensitive (amenable) to CP conditions and has the longest value of relaxation time T_1 (Table 2), indicating that it corresponds to very rigid strongly bound species. As evidenced by additional experiments, these species are stable in the presence of toluene or excess of MeOH or DME, but they are hydrolyzed in the presence of water already at room temperature (Table 2). From these observations one may conclude that the nature of this
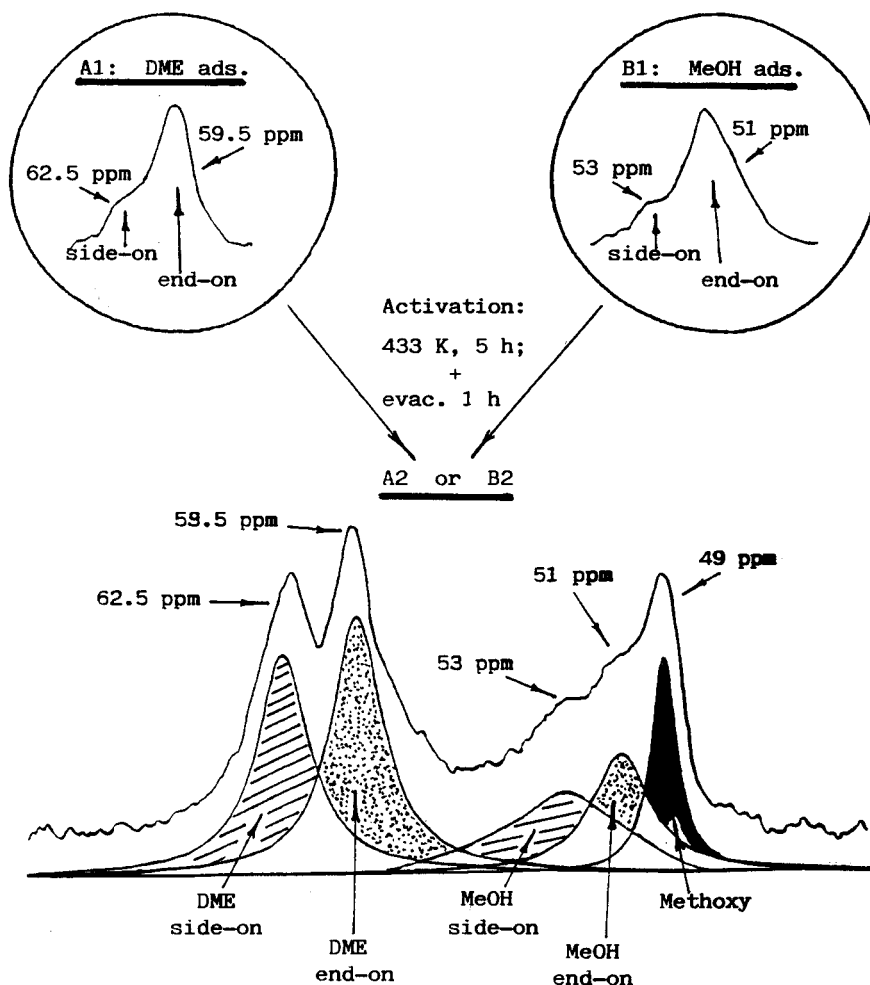
Figure 1. ^{13}C CP MAS NMR spectra observed after adsorption of MeOH (A1) and DME (B1) and and their activation on H−ZSM-11 at 433 K (A2, B2). (See Table 1 for sample preparation.)

species should be substantially different from that of the other four species observed before, and it may have its origin in the attachment of methyl group to a bridging zeolitic oxygen as shown below:

methoxy (49 ppm)
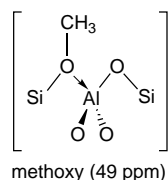
It is worth mentioning that there is no general agreement in the literature on the assignment of the signals corresponding to methoxy groups. Various signals in the comparatively large spectral region from 45 to 62 ppm were assigned to this group by different authors.[3,8,12] Then, it is difficult to directly extrapolate these assignments to the present work, since the position of the signals corresponding to methoxy groups in the NMR spectra seems to depend on many factors, namely, zeolite structure, its composition, the activation procedure, the state of adsorbate, and the presence of coadsorbate which can interact with surface methoxide. However, the signal and its characteristics correspond to what could be expected for a surface methoxy.

In conclusion, the activation of MeOH or DME on a H−ZSM-11 zeolite catalyst results in the formation of five strongly bound surface species, namely, MeOH and DME side-on and end-on adsorption complexes and surface methoxides,
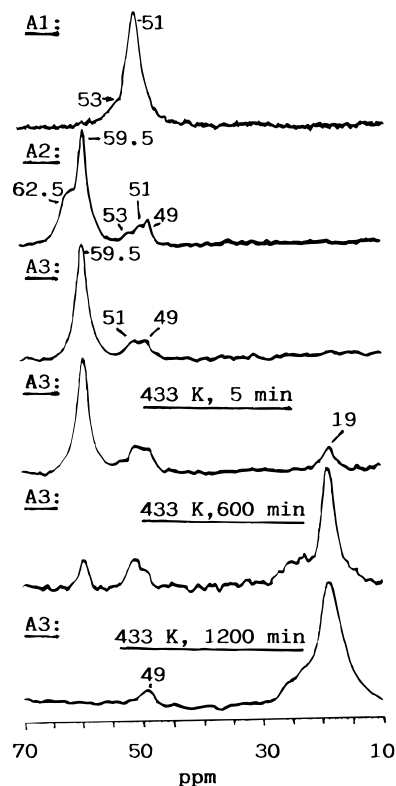

Figure 2. ^{13}C CP MAS NMR spectra observed after MeOH adsorption (A1), activation (A2), and reaction with toluene at 433 K (A3). (See Table 1 for sample preparation.)
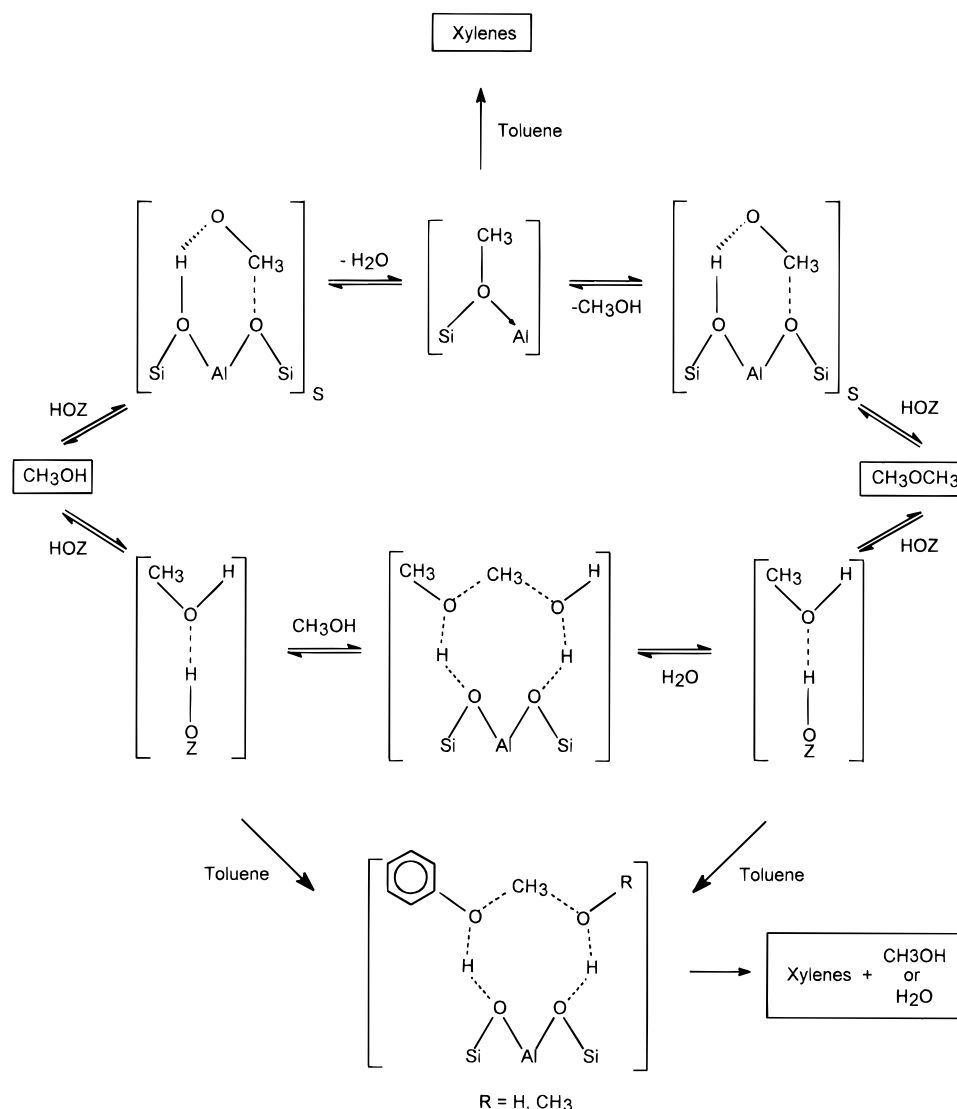
Figure 3. Surface reaction sheme.

the major species being DME side-on adsorption complexes. Methoxonium ions were not identified, supporting the recent theoretical results showing that these species are rather unstable and correspond to a maximum on the potential energy curve.[4]

3.3. Toluene Alkylation. The next step of our study was to find out which of the above species can play the role of precursor in alkylation. For that, toluene was adsorbed on the sample on which methanol and DME were preactivated as described above (Table 1, experiment A3). The ^{13}C MAS NMR spectra obtained in quantitative conditions before and after reaction are presented in Figure 2. As can be seen from the spectra, toluene adsorption at room temperature leads to the disappearance of the NMR lines attributed to side-on adsorption complexes of MeOH and DME. This can be due to the destruction of weak bonding between methyl of the adsorbate and zeolite basic oxygen in the presence of toluene. On the contrary, end-on adsorption complexes and methoxy species are not affected significantly by toluene adsorption at ambient temperature. This result leads to the first obvious conclusion that side-on adsorbed MeOH and DME species cannot be responsible for alkylation step since they disappear before the onset of the reaction.
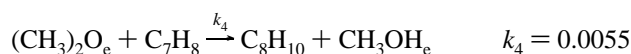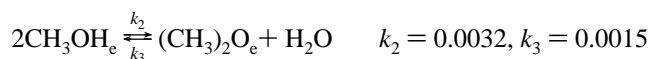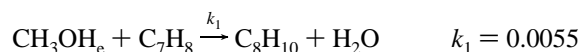
Heating of sample A3 to 433 K results in xylene formation, evidenced by the broad NMR line at ca. 19 ppm, increasing with reaction time (Figure 2). Simultaneously, the intensity of the resonances corresponding to end-on adsorption complexes

decreases. The concentration of methoxy species remains nearly constant during the reaction, and they are not produced or consumed until the very end of the reaction and therefore cannot be considered as intermediates in the interaction of end-on adsorbed species with toluene. Finally, at the very end of the reaction methoxy species are also converted to xylenes, the rate of this reaction being much slower. Consequently, formation of xylenes from surface methoxides, while possible, is not the preferred route for xylene formation, and their reaction rate is much lower than that occuring through end-on adsorption complexes.

In conclusion, two parallel reaction routes for toluene alkylation can be envisaged in our reaction conditions: (1) direct alkylation including end-on adsorbed precursors (fast) and (2) alkylation including methoxy-like intermediates (slow). The preferable realization of the first reaction route can not only be due to the kinetic factor but also because of the restricted formation of side-on adsorption complexes, which were claimed to be precursors for the surface methoxides.[4a,b]

3.4. Kinetics. The above results suggest that MeOH and DME end-on adsorbed species can play a role as precursors in alkylation. On the other hand, it was shown (section 3.2.) that these two species can be easily interconverted one into another under our experimental conditions, and therefore it should be found whether either both MeOH and DME end-on adsorbed complexes can be considered as precursors for alkylation or

only one of them is the real one, and if so which one. In order to determine this, a kinetic study was carried out using sample A4 (Table 1). In this case the only starting species were MeOH end-on adsorbed complexes (CH$_3$OHe) and physisorbed toluene. The reaction was carried out at 433 K, and the kinetic data gave the variations of the NMR line intensities corresponding to CH$_3$OHe, DMEe, toluene, and xylenes as a function of reaction time. From those results the kinetic rate constant for the different surface reaction occurring were calculated, and the results are given below (all rate constants in units of min^{-1} (molecule/uc)$^{-1}$):

$$CH_3OH_e + C_7H_8 \xrightarrow{k_1} C_8H_{10} + H_2O \qquad k_1 = 0.0055$$

$$2CH_3OH_e \underset{k_3}{\overset{k_2}{\rightleftharpoons}} (CH_3)_2O_e + H_2O \qquad k_2 = 0.0032, \ k_3 = 0.0015$$

$$(CH_3)_2O_e + C_7H_8 \xrightarrow{k_4} C_8H_{10} + CH_3OH_e \qquad k_4 = 0.0055$$

These results show that both CH$_3$OHe and (CH$_3$)$_2$Oe species do participate in alkylation. Taking into account that the error associated with the calculated kinetic rate constant can be as high as 30%, it can be concluded that the values for the alkylation with CH$_3$OHe and (CH$_3$)$_2$Oe are rather close, suggesting the existence of transition states of similar nature. It can also be observed that the formation of DME is not much faster than the two alkylation reactions, as one could expect from a macrokinetic point of view. The reason for the observed results relies on the fact that we are working at very low coverages of MeOH and larger concentrations of toluene. Then, under these circumstances the rate of formation of DME which is bimolecular in MeOH should be strongly diminished, being less so than the rate of toluene alkylation.

3.5. Mechanism Proposal. The model presented in Figure 3 further rationalizes all the above observations. MeOH or DME is first adsorbed on H−ZSM-11 to give side-on and end-on adsorbed species. The side-on adsorbed species are the precursors for the formation of surface methoxides which may further react with toluene to give xylenes. It should be mentioned, however, that side-on adsorption is prevented in the presence of toluene, water, or excess MeOH or DME. Methoxy species were found to be quite stable under our reaction conditions (low temperatures), the rate of their reaction with toluene being rather low, and therefore this reaction pathway occurs only to a very small extent.

Starting from the end-on adsorbed species (both MeOH and DME) two different reactions occur: (1) MeOH−DME interconversion, the equilibrium being shifted to DME, and (2) toluene alkylation. The first route occurs in the presence of high local concentrations of MeOH or water, while at low coverages the second route is preferred. It may be possible that both reaction routes proceed via a concerted type mechanism

including eight member type transition states, as shown in Figure 3. However, additional proof is required to support this mechanism.

4. Conclusions

The reaction mechanism for the alkylation of toluene by methanol includes adsorption of MeOH or DME on H−ZSM-11, leading to side-on and end-on adsorption complexes. The end-on adsorbed species are the precursors for MeOH−DME interconversion and toluene alkylation. The occurrence of one or another reaction depends on the local concentrations of MeOH, DME, water, and toluene in the system. The side-on adsorbed species are the precursors for the formation of surface methoxides which may also react with toluene to give xylenes. The latter reaction pathway only occurs to a very small extent, because of prevented side-on adsorption in the presence of toluene and high stability of surface methoxy species under our reaction conditions.

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