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Methyl *tert*-Amyl Ether Synthesis Catalyzed by a Sulfonic Cation Exchanger: The Effect of the Degree of Hydration of the Cation Exchanger on the Catalytic Activity and Reaction Mechanism

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Abstract—The catalytic properties of the fibrous sulfonic acid cation exchanger FIBAN K-1 in methyl *tert*-amyl ether synthesis are studied as a function of its water content. Reducing the degree of hydration of the cation exchanger to <2 H_2O molecules per SO_3H group diminishes the proportion of the desired product in the catalysate. According to ^{13}C NMR data, protonation of methylbutenes in the air-dry cation exchanger phase (which contains 4 H_2O molecules per SO_3H group) involves $[nH_2O] \cdot H^+$ species and is accompanied by olefin hydration and the formation of protonated *tert*-amyl alcohol.

Methyl *tert*-alkyl ethers are industrially synthesized with the use of granulated macroporous sulfonic acid resins [1–4]. It was demonstrated in an earlier study [5] that the fibrous sulfonic cation exchanger FIBAN K-1 (Institute of Physicoorganic Chemistry, Belarussian Academy of Sciences), which is produced by spatial radiation grafting of a styrene (98 wt %)–divinylbenzene (2 wt %) copolymer on polypropylene staple followed by sulfonation of the resulting matrix with concentrated sulfuric acid [6], is a potent catalyst for the synthesis of methyl *tert*-amyl ether (MTAE).

It was found that water content is a significant factor in the activity of FIBAN K-1 in alcohol dehydration [7, 8]. Although this point is of obvious importance, none of the publications devoted to methyl *tert*-alkyl ether synthesis has paid due attention to the effect of the degree of hydration of sulfonic acid cation exchangers on their catalytic properties.

In the present paper, we report the effect of the water content of FIBAN K-1 on the catalytic properties of this material and on the reactions involved in MTAE synthesis.

EXPERIMENTAL

The cation exchanger FIBAN K-1 (H-form) had an ion-exchange capacity of 3.1 mg-equiv/g. All chemicals were pure-grade.

The water content of cation exchanger specimens dried at various temperatures was determined gravimetrically.

The total water content of the cation exchanger (m_{tot}) was determined as the difference between the weight of an air-dry sample and the weight of the same sample dried at the maximum possible temperature (120°C). The residual water content of the cation exchanger (m_{res}) was determined as the difference between m_{tot} and the weight lost by the sample at a given temperature (Δm): $m_{res} = m_{tot} - \Delta m$. The value of m_{res} is necessary to calculate the number of H_2O molecules per SO_3H group, which appeared to be a measure of the degree of hydration of the cation exchanger.

Methylbutenes were obtained by dehydrating isopropyl alcohol on γ-Al_2O_3 at 310–330°C and drying the product with $CaCl_2$. The resulting methylbutene mixture had the following composition (wt %): 3-methylbutene-1, 45.8; 2-methylbutene-1, 19.4; and 2-methylbutene-2, 34.8.

Methanol was dewatered with NaA zeolite.

MTAE was synthesized in a laboratory-scale flow reactor [5] at a pressure of 0.8 MPa, a feed (methanol + methylbutenes) WHSV of 4 g/(g Cat h), a CH_3OH : *iso*-C_5H_{10} molar ratio of 1 : 1, and a temperature of 60–100°C. Under these conditions, the reaction was liquid-phase. The reactor was charged with 1 g of crushed quartz and 1.4 g of air-dry FIBAN K-1. The catalyst was held in flowing helium (predried in a series of columns filled with NaOH, $CaCl_2$, and NaA zeolite) for 4 h at 60, 80, or 100°C.

In order to prevent extra dehydration of the cation exchanger, MTAE was synthesized at a temperature not exceeding the catalyst drying temperature (table). However, extra dehydration was not totally ruled out because the catalyst was in contact with absolute methanol. For estimation of the extent of dehydration, we developed a procedure based on measuring the refractive index (n_D^{20}) of the catalysate as a function of its water content. In this procedure, n_D^{20} was measured before and after the product mixture was dried over

Catalysate composition (wt %) as a function of process temperature for MTAE synthesis on FIBAN K-1 with various degrees of hydration

Components	Process temperature, °C				
	60	70	80	90	100
*Air-dry cation exchanger					
MTAE	11.9	29.4	42.9	39.3	33.0
Methanol	27.4	20.9	16.5	17.2	19.5
Methylbutenes	60.7	49.7	40.6	43.5	47.5
**Cation exchanger dried at 60°C					
MTAE	11.0	–	–	–	–
Methanol	28.1	–	–	–	–
Methylbutenes	60.9	–	–	–	–
**Cation exchanger dried at 80°C					
MTAE	9.0	23.0	34.9	–	–
Methanol	28.3	23.8	19.9	–	–
Methylbutenes	62.7	53.2	45.2	–	–
**Cation exchanger dried at 100°C					
MTAE	8.6	15.7	22.6	26.0	29.8
Methanol	27.7	27.0	24.0	21.7	20.9
Methylbutenes	63.7	57.3	53.4	52.3	49.3

Note: Pressure, 0.8 MPa; feed WHSV, 4 g/(g Cat h); methanol-to-methybutenes molar ratio, 1 : 1.

* The reactants were not dried.

** Predried reactants.

freshly calcined NaA zeolite. Certain amounts of water were added to the dry catalysate to obtain a calibration curve on the water content–refractive index coordinates. Using this curve, it was possible to derive the water content of the real catalysate from its n_D^{20}. The water content of the cation exchanger after the run was calculated from the weight and water content of the cation exchanger charged into the reactor and the weight of water contained in the catalysate.

^{13}C NMR spectra were recorded on a BS-587A spectrometer operating at 20.2 MHz in the quantitative mode. The interpulse delay time was longer than $>5T_1$, where T_1 is the spin–lattice relaxation time. The pulse sequence ruled out the Overhauser effect.

The air-dry cation exchanger (0.4–0.5 g) was tamped in a glass insertion ampule ($d = 7$ mm), and ~1 ml of the reaction mixture (methylbutenes + methanol or *tert*-amyl alcohol (TAA) + methanol) was added up to the cation exchanger bed level. The molar ratio of methylbutenes or TAA to methanol was 3 : 1, because the swelling capacity of FIBAN K-1 is 2–3 times higher for methanol than for methylbutenes or TAA. The insertion ampule was cooled with liquid nitrogen, sealed up, and placed in an NMR ampule ($d = 10$ mm). The field-to-frequency ratio was stabilized by locking on the signal from D_6 benzene placed between the walls of the insertion and NMR ampules. The reaction was conducted at 40°C, and the composition of the reaction mixture was determined at regular time intervals.

RESULTS AND DISCUSSION

The ultimate weight loss for the H-form of FIBAN K-1 at 60, 80, 100, and 120°C is, respectively, 12.2, 13.8, 15.6, and 18.4 wt % (Fig. 1, curves *1*–*4*). As the cation exchanger is held at 130°C, it loses weight

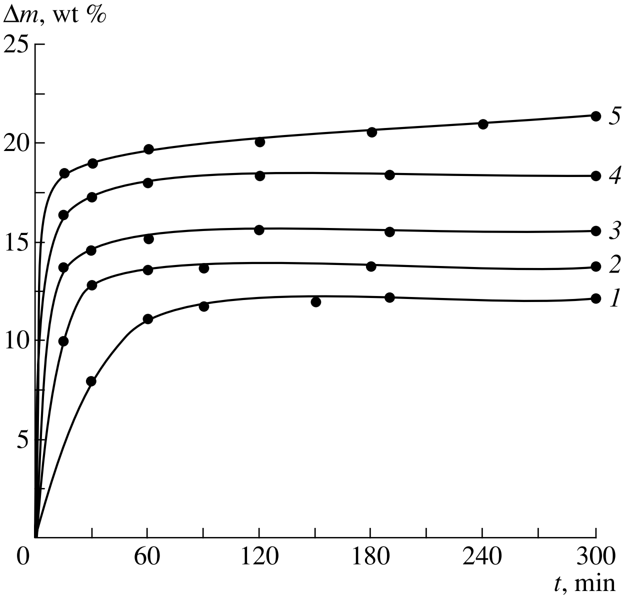


Fig. 1. Time dependence of the weight lost by air-dry FIBAN K-1 (Δ*m*) at (*1*) 60, (*2*) 80, (*3*) 100, (*4*) 120, and (*5*) 130°C.

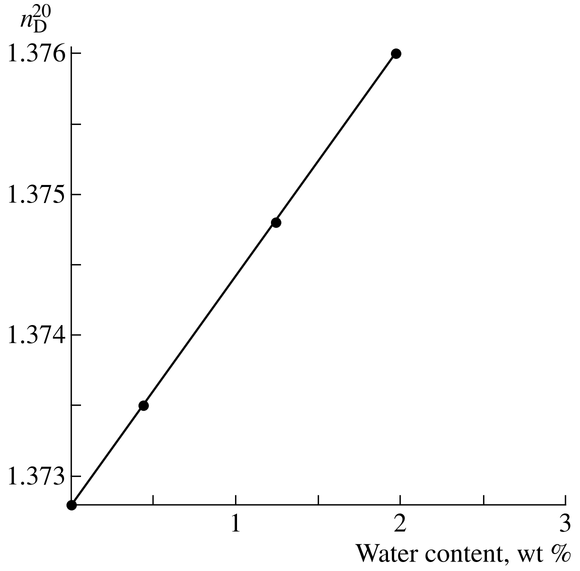


Fig. 2. Refractive index versus water content for the catalysate obtained at 80°C.

steadily (curve 5), apparently because of progressive decomposition.

A computer-based quantum chemical method was suggested for modeling hydrate structures and was applied to *p*-ethylbenzenesulfonic acid and its salts (analogues of the monomer unit of sulfonated styrene resins) [9]. The mutual arrangement of ions and water molecules was determined for various hydration stages. For example, it was demonstrated that, depending on the degree of hydration, H_2O molecules can be in qualitatively different states. In the H^+-form of *p*-ethylbenzenesulfonic acid containing one H_2O molecule per SO_3H group, this molecule is bonded only to a proton. If there are two water molecules per SO_3H group, one is bonded to the proton and an oxygen atom of the SO_3H group and the other is bonded only to an oxygen atom of the SO_3H group. If there are three water molecules, two of them are bonded to both the proton and an oxygen atom of the SO_3H group and the third is bonded only to an oxygen atom of the SO_3H group. In the case of four hydration molecules, one is bonded only to the proton, one is bonded to both the proton and an oxygen atom of the SO_3H group, one is bonded only to an oxygen atom of the SO_3H group, and the fourth is free, bonded neither to the proton nor to an oxygen atom of the SO_3H group.

Therefore, free water can be present only in the air-dry cation exchanger. In specimens dried to constant weight at 60, 80, or 100°C (which contain 1.4, 1.0, and 0.6 water molecules per SO_3H group, respectively), H_2O molecules are bonded to the proton and an oxygen atom of the SO_3H group or only to the proton. The fractional numbers of water molecules per SO_3H group indicate that SO_3H groups are energetically different. For example, the specimen dried to constant weight at 60°C must contain SO_3H groups binding either one or two water molecules.

According to our experimental data (table), the highest activity is attained with the air-dry cation exchanger (which contains four H_2O molecules per SO_3H group) at a reaction temperature of 60°C without preliminarily drying the reactants. Preliminarily heat-treating the cation exchanger at 60°C (resulting in 1.4 H_2O per SO_3H) and feeding dry reactants into the reaction zone changes the catalytic activity, but only slightly. The cation exchanger specimens predried at a higher temperature are much less active. For example, for the specimen dried at 80°C (1.0 H_2O per SO_3H) and the air-dry specimen, the MTAE content of the catalysate is 34.9 and 42.9 wt %, respectively. The specimen dried at 100°C, with 0.6 H_2O per SO_3H, is the least active. No methylbutene dimers were detected in the product.

Drying a catalysate changes its refractive index insignificantly. For the catalysate obtained at 80°C, n_D^{20} before and after drying is 1.3730 and 1.3728, respectively. According to the calibration plot (Fig. 2), the water content of this catalysate is 0.11 wt %. Hence, the water content of the cation exchanger is reduced by 0.4 wt % (<10 rel % of the initial value) as a result of the reaction.

Therefore, the cation exchanger predried at the reaction temperature undergoes further dehydration when in contact with dry reactants, primarily methanol. However, the extent of this reactant-induced dehydration is not so great as to influence the basic inferences following from this study.

The MTAE synthesis data indicate that the cation exchanger loses activity as it is dehydrated. This result is consistent with the fact that protonated water species of composition $H_5O_2^+$ or $H_9O_4^+$, which are effective proton transfer agents, exist in hydrated poly(styrenesulfonic acid) [10]. Dehydration of the cation exchanger decomposes these species, yielding hydronium ions (H_3O^+), which also show a high protonating activity. Further dehydration of the cation exchanger to a water content below 1 H_2O molecule per SO_3H group brings part of the SO_3H groups into the nondissociated state and causes the formation of association species. This probably results in a reduction in the protonating activity of the cation exchanger.

Methyl *tert*-alkyl ether synthesis catalyzed by sulfonic acid cation exchangers may proceed by two fundamentally different mechanisms, namely, an ionic mechanism involving solvated protons and a concerted mechanism involving nondissociated and associated SO_3H groups [11].

The carbonium ion mechanism of methyl *tert*-alkyl ether synthesis on acid catalysts includes three steps: the formation of a carbocation by olefin protonation; the formation of a carbanion through interaction between methanol and an acid anion; and interaction

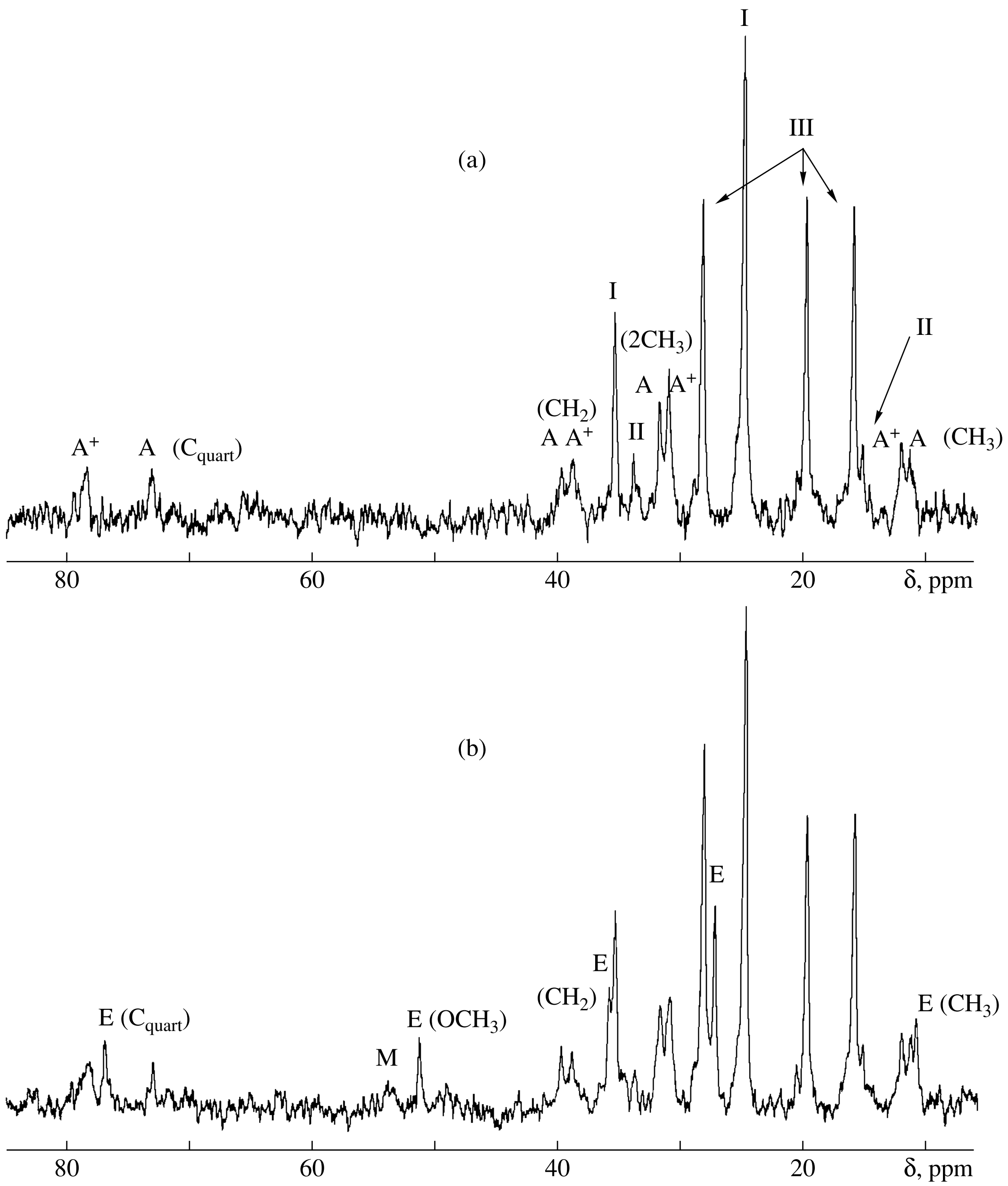
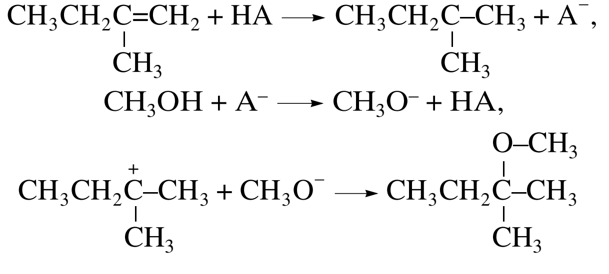


Fig. 3. ^{13}C NMR spectra recorded (a) 1 and (b) 20 h after adding a methylbutenes + methanol (3 : 1) mixture to FIBAN K-1 at 40°C: I = 3-methybutene-1, II = 2-methybutene-1, III = 2-methybutene-2, E = MTAE, A = *tert*-amyl alcohol, A$^+$ = protonated *tert*-amyl alcohol, and M = methanol.

between the carbocation and the carbanion, yielding ether [12]. Accordingly, the synthesis of MTAE can be represented as



$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}{=}CH_2 + HA \longrightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_3 + A^-,$$

$$CH_3OH + A^- \longrightarrow CH_3O^- + HA,$$

$$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_3 + CH_3O^- \longrightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{O-CH_3}{|}}{C}}{-}CH_3$$

After the reaction is conducted for $t = 1$ h, the ^{13}C NMR spectrum of air-dry FIBAN K-1 swollen with a mixture of methanol and methylbutene isomers at 40°C indicates the presence of the starting reactants, TAA, and its protonated form (Fig. 3a). At $t = 3$ h, the spectrum of the reaction system shows signals from MTAE. At $t = 20$ h, the MTAE content is markedly increased, the proportion of 2-methylbutene-1 is decreased, and the amounts of TAA and its protonated form are unchanged (Fig. 3b). After the reaction, the liquid remaining in the insertion ampule was decanted and combined with the eluate resulting from washing of the

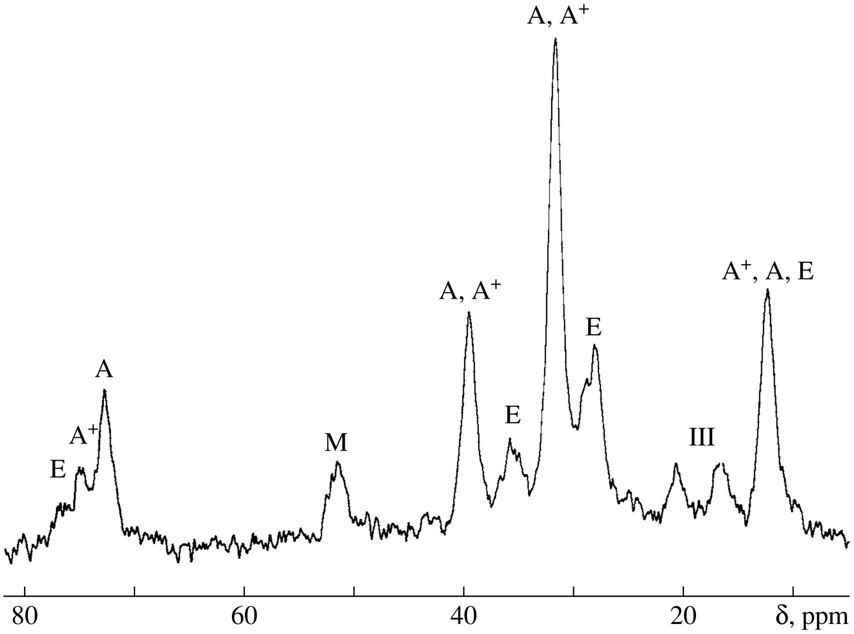


Fig. 4. ^{13}C NMR spectrum recorded 24 h after adding a *tert*-amyl alcohol + methanol (3 : 1) mixture to FIBAN K-1 at 40°C: III = 2-methybutene-2, E = MTAE, A = *tert*-amyl alcohol, A$^+$ = protonated *tert*-amyl alcohol, and M = methanol.

swollen cation exchange with deuterated chloroform. As would be expected, the ^{13}C NMR spectrum of this mixture showed no peak assignable to protonated TAA.

Note that the product mixture contains not only the desired product and starting chemicals but also TAA, indicating the hydration of methylbutenes with a double bond at the tertiary carbon atom. As demonstrated in an earlier study [5], 3-methylbutene-1 does not participate in MTAE synthesis.

The higher conversion of 2-methylbutene-1 as compared to 2-methylbutene-2 is obviously due to the fact that the former is more reactive because of the more favorable position of the double bond. Under the experimental conditions examined, 2-methylbutene-1 is readily protonated, involving $[nH_2O] \cdot H^+$ species, and then undergoes further transformations.

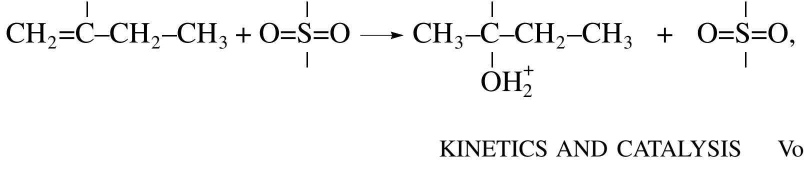
As judged from the composition of the product, a protonated TAA species can transform into a neutral TAA molecule, undergo dehydration to yield 2-methybutene-2 (in accordance with Zaitsev's rule), or participate in MTAE synthesis.

The NMR spectrum recorded after the addition of a methanol–TAA mixture to the cation exchanger (Fig. 4) indicates that MTAE and 2-methybutene-2 are present in the reaction mixture along with neutral and protonated TAA. Therefore, it is quite possible that protonated TAA takes part in MTAE synthesis and methylbutene isomerization.

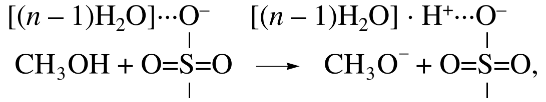
Carbonium ions forming from olefins or alcohols on proton sites of zeolites can be identified by NMR spectroscopy by detecting the corresponding carboxylic acids [13, 14]. These acids result from the reaction of carbonium ions with CO and H_2O at 20–100°C (the Koch reaction).

In order to detect the *tert*-amyl carbonium ion in the FIBAN K-1–methylbutenes system, we conducted a special experiment. An insertion ampule containing air-dry cation exchanger (with 4 H_2O per SO_3H) was charged with methylbutene mixture, and CO was bubbled through the reaction system at 40°C for 2 h. Next, the insertion ampule was cooled with liquid nitrogen and sealed up, and an NMR ^{13}C spectrum was recorded. This spectrum consists only of lines due to the original methybutenes, TAA, and its protonated form. No signals assignable to *tert*-amyl carboxylic acid were detected.

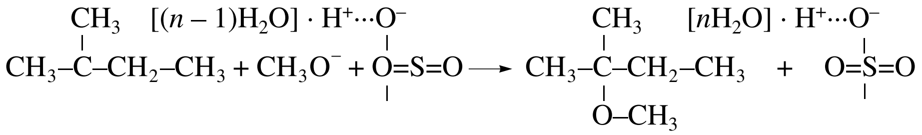
In view of the above data, the carbonium ion mechanism of MTAE formation involving hydrated FIBAN K-1 should be refined by taking into account the participation of $[nH_2O] \cdot H^+$ species in all synthesis steps:



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_2{-}CH_3 + O{=}\underset{|}{\overset{\overset{\displaystyle [nH_2O]H^+\cdots O^-}{|}}{S}}{=}O \longrightarrow CH_3{-}\underset{\underset{\displaystyle OH_2^+}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_2{-}CH_3 + O{=}\underset{|}{\overset{\overset{\displaystyle [(n-1)H_2O]\cdots O^-}{|}}{S}}{=}O,$$



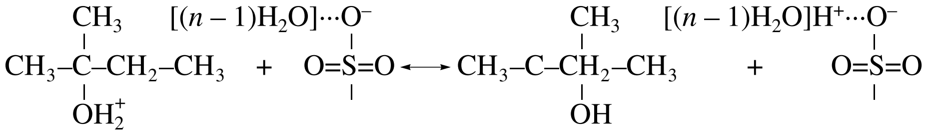
$$CH_3OH + \overset{[(n-1)H_2O]\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}} \longrightarrow CH_3O^- + \overset{[(n-1)H_2O]\cdot H^+\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}},$$



$$CH_3-\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3 + CH_3O^- + \overset{[(n-1)H_2O]\cdot H^+\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{O-CH_3}{|}}{C}}}-CH_2-CH_3 + \overset{[nH_2O]\cdot H^+\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}}$$

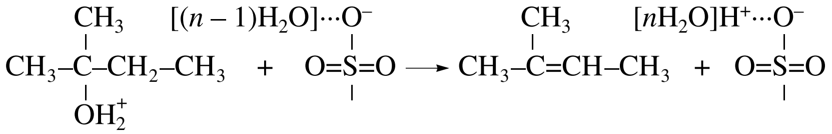
Therefore, if the cation exchanger has a sufficient water content, the first step of MTAE synthesis will include a simultaneous protonation and dehydration of the olefin, without forming any carbocation.

The absence of TAA in the MTAE synthesis product may be due to the following two factors arising from the elevated synthesis temperature: displacement of the equilibrium



$$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{OH_2^+}{|}}{C}}}-CH_2-CH_3 + \overset{[(n-1)H_2O]\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}} \longleftrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-CH_2-CH_3 + \overset{[(n-1)H_2O]H^+\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}}$$

to the left and a higher probability of TAA dehydration to 2-methybutene-2,



$$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{OH_2^+}{|}}{C}}}-CH_2-CH_3 + \overset{[(n-1)H_2O]\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH-CH_3 + \overset{[nH_2O]H^+\cdots O^-}{\overset{|}{\underset{|}{O{=}S{=}O}}}$$

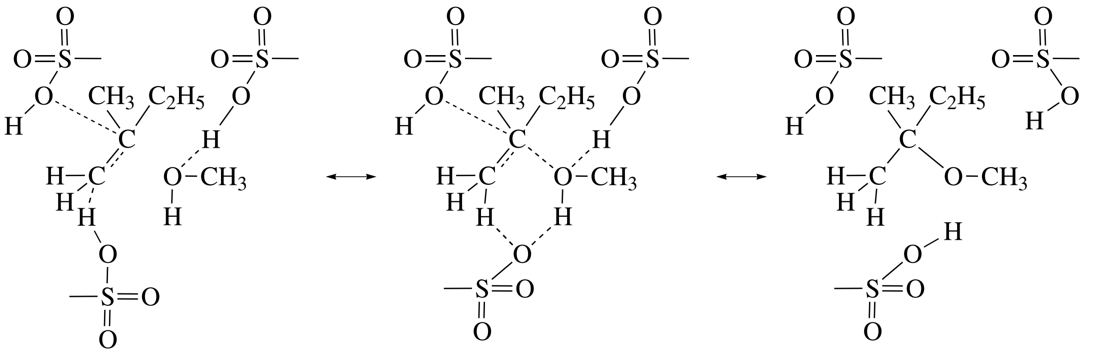
Since 2-methybutene-1 is the most reactive methylbutene isomer, its conversion into 2-methybutene-2 will cause a reduction in the yield of the desired product. Indeed, it is clear from the data presented in the table that a decrease in the MTAE content of the catalysate is observed even for the cation exchanger specimen dried to constant weight at 60°C, in which most of the SO_3H groups are dissociated.

Note that neither TAA nor its protonated form is present in the cation exchanger specimen that was profoundly dehydrated by drying to constant weight at 120°C and then swelled in a methanol–methylbutenes mixture. Oligomers along with the starting chemicals and MTAE were detected in the reaction mixture by NMR spectroscopy.

Reducing the degree of hydration of the cation exchanger is known to bring dissociated SO_3H groups to the nondissociated state [10, 15]. Oxygen atoms of nondissociated SO_3H groups are stronger acceptors in hydrogen bonding than oxygen atoms of dissociated SO_3H groups. Therefore, neighboring OH groups can bind to the former by means of strong hydrogen bonds, yielding association species involving two or more SO_3H groups.

Olefin oligomerization apparently includes protonation by protons of associated SO_3H groups followed by the formation of dimers and trimers. However, the protonated forms of 2-methybutene-1 and 2-methybutene-2 were not detected by NMR spectroscopy. Presumably, these olefin species are spectroscopically undetectable because of their high reactivity and, accordingly, their short lifetime.

The synthesis of MTAE on dehydrated cation exchanger proceeds by a concerted mechanism involving charge transfer [11, 15] rather than by a carbonium ion mechanism:



According to this mechanism, methanol is adsorbed by the cation exchanger, resulting in a hydrogen bond between the oxygen atom of methanol and the proton of an SO_3H group. A molecule of isomeric methylbutene is adsorbed on two SO_3H groups: the proton of one of them binds to the methylene group of the olefin, and the tertiary carbon atom at the double bond, which is deficient in electron density, interacts with the hydroxyl oxygen of the second SO_3H group.

Thus, the degree of hydration is a significant factor not only in the catalytic activity of FIBAN K-1 in MTAE synthesis but also in the mechanism of this synthesis.

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