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Mechanism of TAME and TAEE synthesis from diffuse–reflectance FTIR analysis

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Abstract

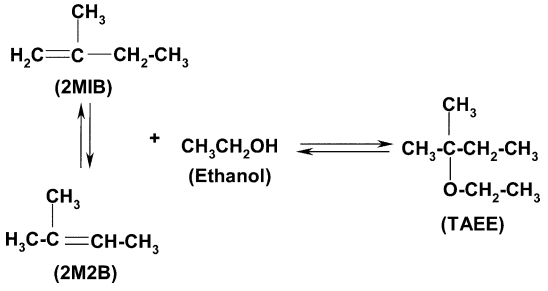
Diffuse–reflectance FTIR results obtained with tert-amyl-methyl-ether (TAME), ethanol, methanol, i-amylenes and mixtures of i-amylenes with alcohols supported a Langmuir–Hinshelwood type reaction mechanism involving adsorbed i-amylene molecules, which form a bridged structure between the adsorbed alcohols and the $–SO_3H$ sites of Amberlyst-15. Number of available sites involved in the adsorption of i-olefins is drastically decreased with an increase in alcohol concentration. The reaction rate model, which was proposed basing on the DRIFTS results, was shown to give good agreement with the published initial rate data for TAEE synthesis. The rate of tert-amyl-ethyl-ether (TAEE) formation was found to give a rather sharp maximum at an ethanol activity smaller than 0.1.

Keywords: TAME; TAEE; Reaction mechanism; Drifts

1. Introduction

Due to their high octane numbers and low volatilities, tert-amyl-ethyl-ether (TAEE) and tert-amyl-methyl-ether (TAME) are considered as attractive alternatives to MTBE as gasoline blending oxygenates [1–4]. Oxygenates are known to improve the burning characteristics of fuels resulting less CO and unburned hydrocarbon exhaust emissions. Bad smell and taste of MTBE, even at very low concentrations in the drinking water, diverted the attention of researchers to other alternate oxygenates for gasoline blending.

TAEE and TAME are produced by the reaction of i-amylenes (2-methyl-2-butene (2M2B) and 2-methyl-1-butene (2M1B)) with ethanol or methanol over acidic macroreticular resin catalysts.



In number of studies, Langmuir–Hinshelwood type rate models involving adsorbed alcohols and i-olefins on the $–SO_3H$ sites of the acidic resin catalysts, were proposed in the production of tert-ethers [4,6–9]. However, in some other studies, Rideal–Eley type mechanisms involving adsorbed alcohol molecules and fluid phase i-olefins were considered [5,10–12]. In the work of Paakkönen et al. [13], a comparison of various kinetic models was presented for TAME synthesis. Our earlier diffuse–reflectance FTIR (DRIFTS) study [14] for MTBE and ETBE synthesis supported a Langmuir–Hinshelwood type reaction mechanism.

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2. Experimental work

In this study, a reaction mechanism was proposed and a rate expression was derived basing on the DRIFTS results of TAME, i-amylenes and alcohols (methanol and ethanol) obtained at different temperatures ranging between 313 and 363 K on Amberlyst-15. Some experiments were also repeated with mixtures of 2M1B with alcohols to follow surface reactions by the DRIFTS technique. These experiments were carried out in the reaction chamber (Graseby Specac) of the DRIFTS cell of the FTIR instrument (MIDAC). Most of these experiments were carried out batch-wise by injecting a pulse of tracer into the reaction chamber, which was filled with nitrogen gas. DRIFTS results obtained for alcohols were obtained with gas mixtures containing 10% alcohol in nitrogen, with a total flow rate of 45 ml/min. About 100 mg of pre-dried catalyst was placed into the sample holder of the DRIFTS reaction cell, which can be heated upto 500 °C. Catalyst sample directly faces the zinc–selenide window of the reaction chamber through which IR beam enters and the diffuse reflected beam leaves. DRIFT spectra thus obtained gave significant information about the surface species involved in adsorption and surface reactions. The distance between the catalyst layer and the zinc–selenide window is rather small (about 7 mm) and our previous results proved that contribution of the gas phase to the IR absorption bands was negligibly small in our DRIFTS results [14]. Also, the differences of spectra obtained with and without the adsorbing/reacting gases were used to eliminate the contributions of the Amberlyst-15 to the DRIFTS bands.

3. Results and discussions

DRIFTS results obtained at 333 K with 2M1B, methanol and ethanol are shown in Fig. 1. The strong IR absorption bands observed between 2800 and 3040 cm^{-1} in the DRIFT spectrum of 2M1B correspond to the CH_3 stretching bands. The strong CH_2 wag-band observed at 890 cm^{-1} and the small CH_2 asym. stretching band observed at 3085 cm^{-1} are characteristic bands for isoamyl species. The qualitative behavior of DRIFT spectrum is quite similar to the IR spectrum of gas phase 2M1B. However, in the gas phase spectrum, CH_2 wag-band was expected to be sharper at a higher wave number (at 940 cm^{-1}) [15]. The shift of this band to a lower wave number is an indication that CH_2 group was involved in the adsorption of 2M1B to the $–SO_3H$ sites of the catalyst. For the other bands observed at 1384 cm^{-1} (CH_3 s-deform) and at 1457 cm^{-1} (CH_3 d-deform), no significant shift of the band position was observed as compared to the corresponding values reported in the literature for gas-phase IR spectra. The band observed at 1651 cm^{-1} corresponds to the C=C stretching. In the gas phase, this band was expected at about 1660 cm^{-1}. The relative intensity of this band with respect to the CH_3 stretching bands showed a decreasing trend from 0.14 to 0.11 with an increase in temperature from 313 to 353 K. This decreasing trend indicated the weakening of the C=C bond of adsorbed 2M1B species with an increase in temperature. A similar result was reported for adsorption of isobutylene on Amberlyst-15 in our previous study [14].

DRIFT spectra of methanol and ethanol reported in Fig. 1 are similar to the DRIFT spectra reported in our previous publication at a different temperature [14]. The broad IR absorbtion bands observed between 3080 and 3630 cm^{-1} correspond to the OH stretching of hydrogen bonded adsorbed alcohol molecules. Such broad bands are expected in the spectra of liquid phase alcohols, but not in the vapor phase spectra. These results indicated rather strong adsorption of alcohols on the surface, resulting a hydrogen bonded liquid like behavior. Further discussion of the DRIFT spectra of alcohols were reported in our previous publication [14].

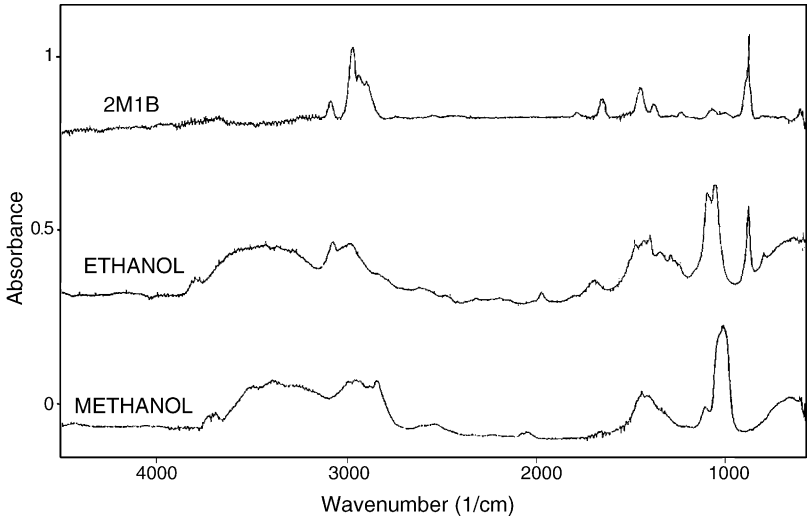

Fig. 1. DRIFTS results for 2M1B, ethanol, and methanol at 333 K on Amberlyst-15.

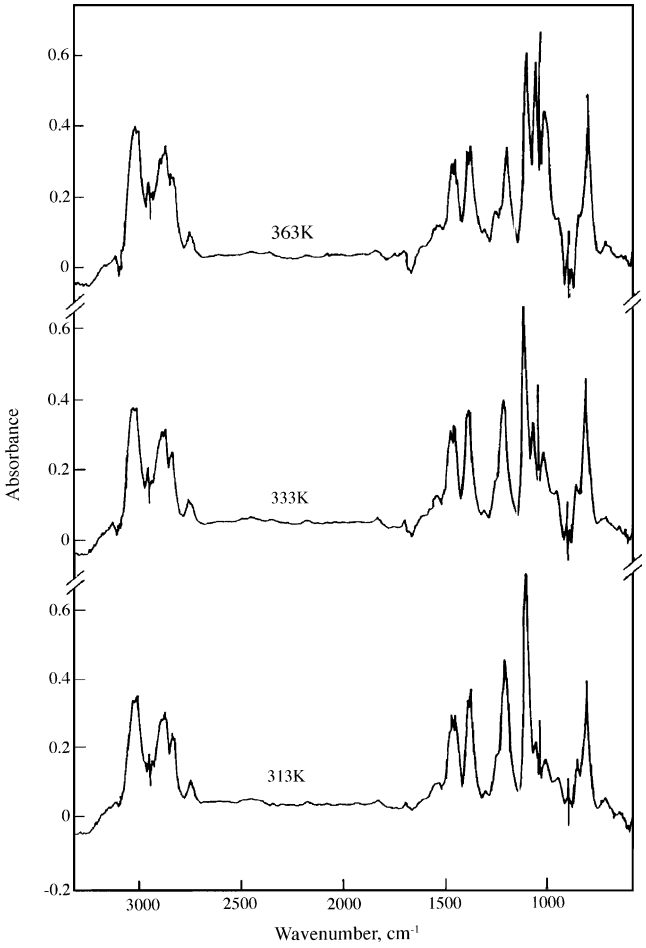

Fig. 2. DRIFTS results for TAME on Amberlyst-15 [17].

DRIFTS results obtained with TAME at different temperatures, ranging between 313 and 363 K, are given in Fig. 2 [17]. Similar to the spectra obtained with 2M1B, characteristic CH_3 stretching bands (between 2780 and 3040 cm^{-1}) and CH_3 deformation bands (at 1457 and 1380 cm^{-1}) were also detected in the DRIFT spectrum of TAME. One of the major differences of the spectrum of TAME from the spectrum of 2M1B is the strong band observed at 1085 cm^{-1}. This band is the characteristic band of aliphatic ethers (C–O–C). As it is shown in Fig. 2, the relative intensity of this band (observed at 1085 cm^{-1}), with respect to the CH_3 stretching and deformation bands, decreased significantly with an increase in temperature from 313 to 363 K. This decrease of the 1085 cm^{-1} band intensity was accompanied with an increase of the characteristic band at 1030 cm^{-1}. This 1030 cm^{-1} band corresponds to the characteristic CO stretching band of methanol [14,15]. The intensity of this band observed at 1030 cm^{-1} was very small at 313 K. However, its intensity significantly increased with an increase in temperature. The ratio of IR absorption band heights of 1085–1030 cm^{-1} decreased from 3.0 to 0.9 with an increase of temperature from 313 to 363 K. The decrease of the intensity of the band at 1085 cm^{-1} with a corresponding increase of the intensity of the band observed at 1030 cm^{-1} is an indication of the decomposition of the adsorbed TAME molecules on the surface forming adsorbed methanol by the association of the hydrogen from the $–SO_3H$ sites of the catalyst. Also, the increasing intensity of the band observed at 890 cm^{-1} with an increase in temperature is an indication of the formation of 2M1B on the surface.

Basing on these results, adsorbed species involved during the formation of TAME in the reaction of methanol with 2M1B is schematically illustrated in Fig. 3. Similar conclusions had been reached in the formation of other tert-ethers (MTBE, ETBE, etc.) in our previous work [14,18] and also for the formation of TAEE. Basing on the DRIFTS results, following reaction mechanism was proposed for the formation of TAME or TAEE over Amberlyst-15.

$$\mathrm{A(methanol\ or\ ethanol)} + \underline{\mathrm{S}} \overset{K_\mathrm{A}}{\rightleftarrows} \underline{\mathrm{AS}} \tag{1}$$

$$\mathrm{B(i\text{-}amylene)} + \underline{\mathrm{AS}} + \underline{\mathrm{S}} \overset{K_\mathrm{B}}{\rightleftarrows} \underline{\mathrm{ABSS}} \tag{2}$$

$$\underline{\mathrm{ABSS}} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \underline{\mathrm{ESS}} \quad \mathrm{(rate\ determining\ step)} \tag{3}$$

$$\underline{\mathrm{ESS}} \overset{K_\mathrm{E}}{\rightleftarrows} \mathrm{E(TAME\ or\ TAEE)} + 2\underline{\mathrm{S}} \tag{4}$$

The rate expression derived basing on this reaction mechanism is given by Eq. (5).

$$r = k\left(a_\mathrm{A}a_\mathrm{B} - \frac{a_\mathrm{E}}{K}\right) \times \left[\frac{[(1+K_\mathrm{A}a_\mathrm{A})^2 + k''(a_\mathrm{A}a_\mathrm{B} + (K_\mathrm{E}/K_\mathrm{A}K_\mathrm{B})a_\mathrm{E})]^{1/2} - (1+K_\mathrm{A}a_\mathrm{A})}{(K_\mathrm{A}K_\mathrm{B}a_\mathrm{A}a_\mathrm{B} + K_\mathrm{E}a_\mathrm{E})}\right]^2 \tag{5}$$

Here k and k'' correspond to $k = (k_3K_\mathrm{A}K_\mathrm{B})/16$ and $k'' = 8(K_\mathrm{B}S_\mathrm{o})K_\mathrm{A}$, respectively. S_o is the total number of sites per unit mass of catalyst (mol/g). Considering the non-idealities of the alcohol–isoamylene–tert-ether mixtures, activities are used in Eq. (5). The equilibrium constant K of etherification reaction for the synthesis of TAEE is given by Kitchaiya and Datta [16].

$$\ln K = 26.779 + \frac{2078.6}{T} - 6.5925\ln T + 0.0231T - 1.126\times10^{-5}T^2 - 1.414\times10^{-8}T^3 \tag{6}$$

As it was reported in the literature [19], the adsorption equilibrium constants of alcohols are more than two orders of magnitude greater than the adsorption equilibrium constants of i-olefins (i-butylene, 2M1B, 2M2B) and tert-ethers. Consequently, the orders of magnitude of the terms containing the adsorption equilibrium constant of tert-ether (K_E) in Eq. (5) are expected to be rather small.

In our previous publications [3,20], initial rate data obtained in a fixed bed differential flow reactor were reported for the synthesis of TAEE. Those data, together with the rate data reported by other researchers [8,21] were used for the evaluation of the rate parameters. In the analysis

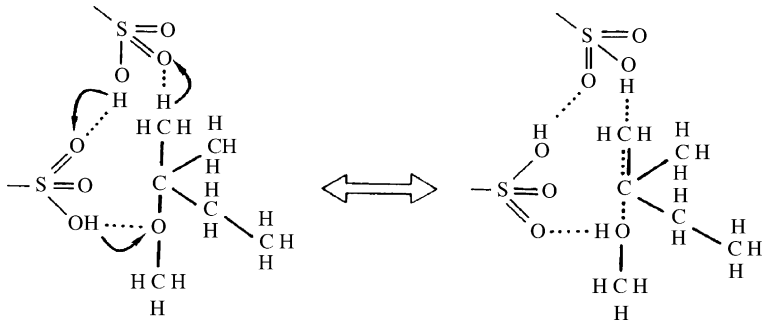

Fig. 3. Schematic representation of TAME decomposition on Amberlyst-15.

of the initial rate data, the terms containing activity of ether (a_E) becomes negligible in Eq. (5) and the rate expression reduces to:

$$r = k'\left(\frac{a_A}{a_B}\right) \times \left\{\left[\left(\frac{1}{a_A}+K_A\right)^2 + k''\left(\frac{a_B}{a_A}\right)\right]^{1/2} - \left(\frac{1}{a_A}+K_A\right)\right\}^2 \quad \text{(initial rate)} \tag{7}$$

Here, the combined rate constants k' is

$$k' = \frac{k_3}{16K_AK_B} \tag{8}$$

The rate data obtained in our studies in a differential flow reactor and also the initial rate data published in the literature [3,8,20,21] at different temperatures were analyzed using Eq. (7) and the rate parameters were determined using a Quasi–Newton nonlinear regression procedure. Eq. (7) contains three parameters, namely k', k'' and K_A. Regression results became highly dependent on the initial estimates, if all three of these parameters were left as adjustable. The adsorption equilibrium constants of ethanol (K_A) obtained from independent adsorption experiments were reported in our earlier publication [14]. As it was discussed in the earlier publications [14,19,22], adsorption equilibrium constant of liquid ethanol shows an unexpected increasing trend with an increase in temperature at temperatures greater than about 330 K. This behavior was explained by the chemisorption of some of the ethanol molecules on Amberlyst-15. Dehydration reactions of alcohols are expected to take place on the catalyst surface at higher temperatures. Also, due to swelling of the gel-like polymer structure of Amberlyst-15, some changes are expected in the pore structure and penetration of molecules into the gel-like micrograins becomes easier in the presence of alcohols at higher temperatures. This causes an increase in the number of active sites available for the etherification reaction. The adsorption equilibrium constants reported by Dogu et al. [14] were based on fluid phase concentrations. However, the adsorption equilibrium constants which appear in Eqs. (5) and (7) are in terms of activities (K_A = (AS)/(S) a_A). Knowing the temperature, pressure and compositions of the mixtures, activity coefficients of ethanol were evaluated using the UNIFAC program [23] and adsorption equilibrium constants based on activities were estimated from the experimental adsorption equilibrium constants reported in the literature. The temperature dependence of K_A, thus evaluated is illustrated in Table 1. The adsorption equilibrium constants of ethanol evaluated from this analysis are substituted into Eq. (7) and the rate parameters k' and k'' were evaluated by regression analysis of the initial rate data. In this analysis, UNIFAC program was again used for the estimation of activity coefficients. In this analysis, data reported for the reaction of ethanol with 2M1B and also with an i-amylene mixture, which constituted majorly 2M2B (95 wt.% 2M2B, rest being majorly 2M1B), were used. Analysis of the data available in the literature at 333, 343, 353 and 360 K were analyzed to obtain the rate parameters. The rate parameters k' and k'' which were evaluated from the Marquard's nonlinear least squares regression tehnique are also reported in Table 1. The agreement of the proposed rate expression with the data published in the literature [3,8,20,21] was found to be quite good. Typical experimental results and model predictions of the initial rate of TAEE formation from 2M1B and 2M2B are illustrated in Fig. 4a–d. As it is seen in these figures the rate values pass through a sharp maximum as the ratio of activity of ethanol to i-amylene (a_A/a_B) increases. This maximum is also clearly seen in Fig. 5, where the predicted rate values are plotted as a function of activity of ethanol (a_A) (activity of i-amylene (a_B) being the parameter). In the presence of alcohols, most of the surface is expected to be covered by alcohol molecules. As a result of this, number of available

Table 1
Temperature dependence of rate and adsorption equilibrium parameters of the model (Eq. (7))

2M1B	2M2B
ln k' = −6199.3 (1/T) + 16.7 (mol/g s)	ln k' = −4961.1 (1/T) + 13.1 (mol/g s)
ln k'' = −7463.3 (1/T) + 20.8	ln k'' = −5490.2 (1/T) + 15.0
ln (k_3S_o) = −13663 (1/T) + 38.3	ln (k_3S_o) = −10451 (1/T) + 28.8
ln (k_BS_o) = 1901.4 (1/T) − 11.2	ln (k_BS_o) = 3874.5 (1/T) − 17.01
ln K_A = −9364.7(1/T) + 29.9 (ethanol)	

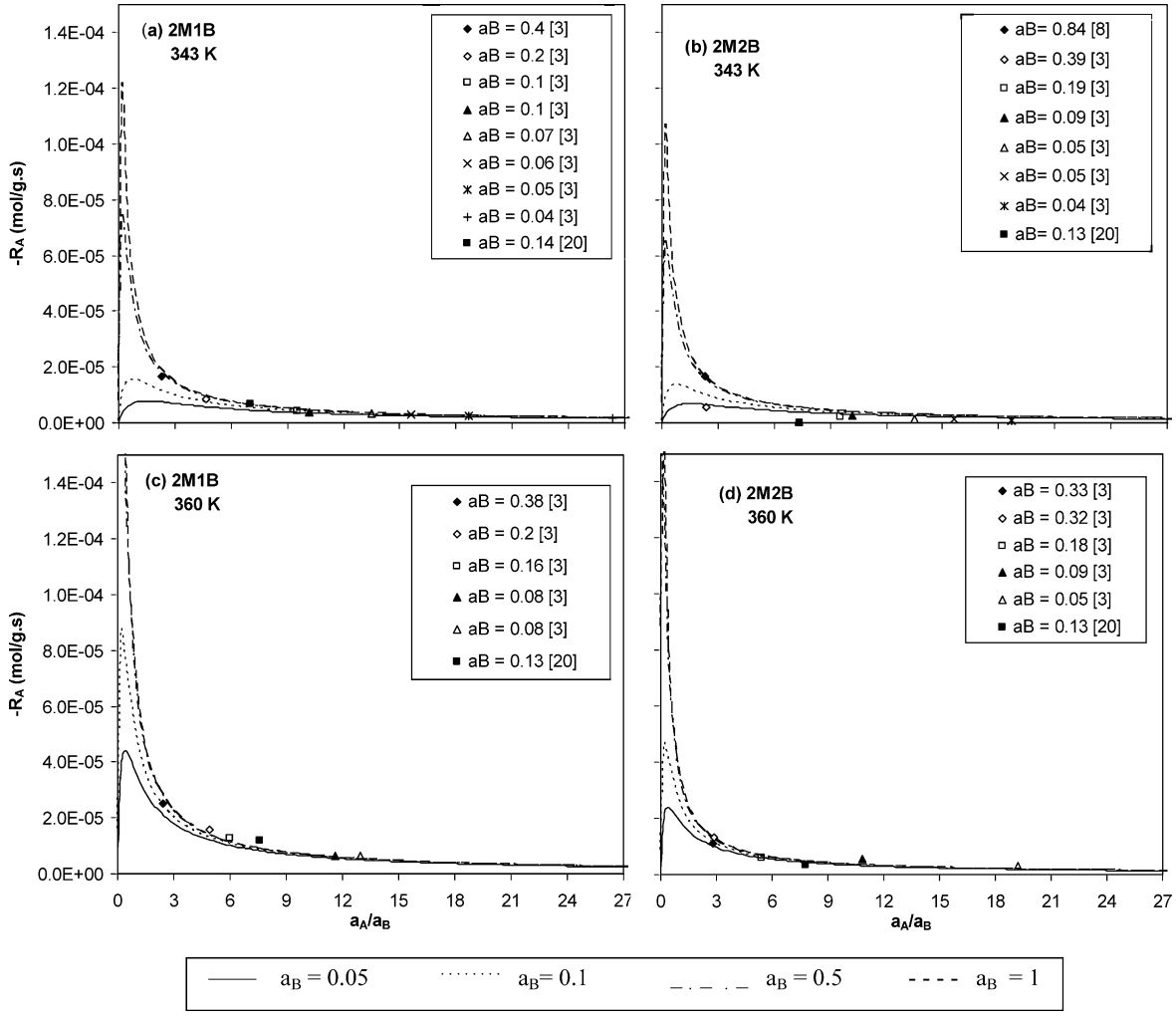

Fig. 4. Rate of TAEE formation using 2M1B (a, c) and 2M2B (b, d).

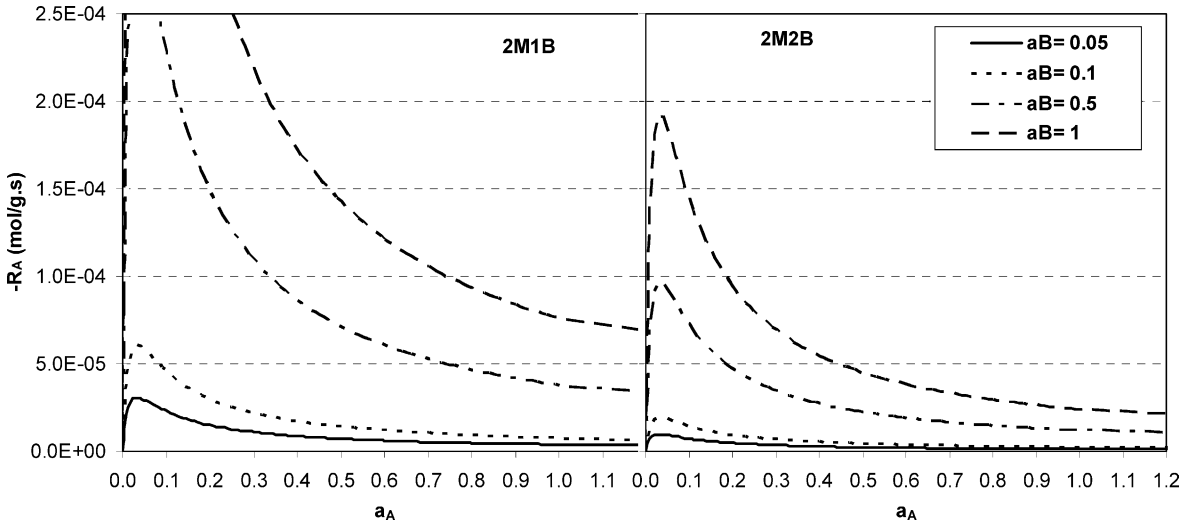

Fig. 5. Dependence of initial rate of TAEE formation on activities of ethanol (a_A) and isoamylenes (a_B) at 353 K.

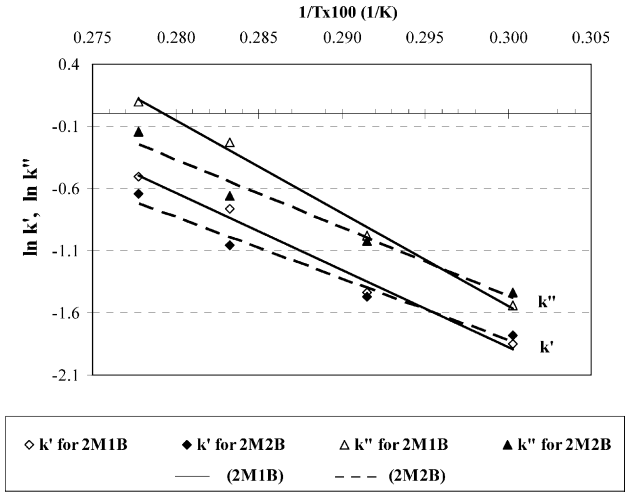

Fig. 6. Temperature dependence of rate constants.

sites involved in the adsorption of i-olefins is drastically decreased with an increase in alcohol concentration. The reaction order with respect to i-olefins is found to be close to one. This behavior of the rate expression is also consistent with the conclusions of Tejero et al. [24] reported for liquid phase synthesis of MTBE.

The temperature dependence of the rate constants k' and k'' obtained for 2M1B + ethanol and 2M2B + ethanol reactions are illustrated in Fig. 6. As it seen in Figs. 4 and 5, the reactivity of 2M1B is higher than the reactivity of i-amylene mixture, which constituted majorly 2M2B. This activity difference becomes more significant at higher temperatures. Activation energies of the rate constants (k' and k'') of 2M1B + ethanol reaction are also higher than the corresponding values of 2M2B + ethanol reaction.

Knowing the k', k'', and K_A values, adsorption equilibrium constant of i-amylenes (2M1B and 2M2B) and the rate constant of the rate determining step of the mechanism are determined using the definitions of k' and k''. Temperature dependence of these parameters is also given in Table 1.

4. Concluding remarks

Basing on the DRIFTS results obtained with TAME at different temperatures and also with i-amylenes, ethanol, methanol, i-amylene–alcohol mixtures, a Langmuir–Hinshelwood type reaction mechanism was shown to take place in the synthesis of TAME and TAEE over Amberlyst-15. Since the adsorption equilibrium constants of alcohols are about two orders of magnitude greater than the adsorption equilibrium constants of i-amylenes and tert-ethers, number of available sites are drastically decreased with an increase in alcohol activities. Consequently, a sharp maximum was observed in the rate of tert-ether formation when plotted as a function of activity ratio of alcohol to i-amylene.

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