# Kinetics of Gas Phase Synthesis of Ethyl-tert-butyl Ether (ETBE) on $H_3PW_{12}O_{40}$/MCM-41 Catalyst

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*The mechanism and kinetics of gas phase synthesis of ethyl-tert-butyl ether (ETBE) in the reaction between tert-butyl alcohol (TBA) and ethanol (EtOH) were investigated performing the reaction in a continuous flow quartz reactor at different temperatures and atmospheric pressure, using a heteropoliacid catalyst with 30wt% loading, dispersed on MCM-41. The Eley-Rideal reaction mechanism was previously proposed based on experimental observations that showed the rate of ETBE increased when partial pressure of tert-butyl alcohol increased, and the partial pressure of ethanol decreased, without significant effects on product selectivity. The kinetic model based on the Eley-Rideal mechanism was proposed and successfully employed to model accurately the experimental data at three different temperatures. The apparent activation energy and the frequency factor of the etherification reaction were 39.42 kJ/mol and 1.69 x $10^8$ mol/kg . h . bar, respectively.*

*Keywords: ETBE, Heteropolyacid, Etherification, HPW/MCM-41, Kinetic modelling*

Lead additives, which were traditionally used as additives to raise the octane number of gasolines, have been replaced by oxygenated compounds in the last two decades. Because of the high demand of such oxygenated compounds, besides the methyl tert-butyl ether (MTBE) originally used as octane booster, other tertiary ethers were synthesized and used to formulate high octane gasolines, such as methyl tert-amyl ether (TAME), ethyl tert-amyl ether (TAEE), and ethyl tert-butyl ether (ETBE) [1-4]. Introduction of such oxygenated compounds to the gasoline pool proved feasible and also opens the route to introducing bio-derived components in the fuel, and to decrease the $CO_2$ fingerprint of gasoline.

Ethers with high molecular mass have low vapor pressure and high boiling point, which is plus for gasoline blending [4-6]. The MTBE, synthesized in the liquid phase reaction of methanol and isobutylene over an acid catalyst, is the most popular fuel additive [7, 8]. However, in recent years, for environmental reasons, objections have been raised against its use. The ETBE is considered to degrade faster than MTBE in soils and water and is less soluble in water, hence the increased interest in wider utilization of ETBE [9, 10].

Most of the kinetic studies on ETBE synthesis were performed using isobutene and ethanol (EtOH) as reactants [11-14]. However, in kinetic studies of ether synthesis on ion-exchange resins, there are contradictory reports concerning the suitable kinetic model for fitting and interpreting the experimental data [15-19]. Kinetic data obtained in liquid and gas phases for the synthesis of MTBE, ETBE, TAME and TAEE have been very well correlated with both the Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) models. Fite at al. [15] studied the kinetics assuming the ER mechanism for the formation of ETBE in liquid phase. According to these authors, ethanol is adsorbed preferentially on the active sites and reacts with isobutene in solution. They assumed two adjacent centers are involved in this step and the surface reaction is the rate limiting step. In fact, MTBE synthesis was frequently described in the terms of the ER mechanism in which isobutene from the solution reacts with methanol adsorbed on ion-exchange resins [20]. This mechanism can be considered to reasonably explain the behavior of olefin-alcohol mixtures when alcohol in excess is present. However, it is difficult to explain the formation of di-isobutene as by-product without recognizing that at least some adsorption of isobutene occurs at the surface, even if it is weak.

On the other hand, other researchers reported the LH kinetic model for gas phase production of ether from ethanol and isobutanol on Amberlyst-35 catalyst. They proposed the LH kinetic model explains quantitatively the formation of the main reaction products (Methyl iso-buthyl ether (MIBE), ethyl iso-buthyl ether (EIBE)) with the kinetic parameters having values of physical significance. The formation of MTBE, ETBE and tert-butyl isobutyl ether (TBIBE) has not been investigated in detail; however, these authors have mentioned that the reaction mechanism involves the reaction between a carbocation or an olefinic intermediate and a gas phase molecule following the ER mechanism [21].

Umar et al. [9] performed the kinetic modeling of liquid phase synthesis of ETBE using ethanol and TBA on purolite CT-124 catalyst. According to their results, heterogeneous kinetic models ER and LH could not predict the behavior of the etherification reaction, while a quasi-homogeneous model (QH) represented the system very well under a wide range of reaction conditions.

Most ETBE synthesis studies were undertaken using isobutene and ethanol as reactants and ion-exchange resins as catalysts [11-19]. Despite the increasing interest for longer ethers and ethers based on ethanol, to the best of our knowledge, few kinetic studies have been reported on ETBE synthesis from TBA and ethanol. Since the available kinetic data predominantly refers to the reaction of TBA with methanol and ethanol using ion-exchange resins as catalyst, studying the etherification of TBA with ethanol using an alternative catalyst, such as heteropolyacids (HPW) supported on MCM-41, may prove to be a relevant contribution. Moreover, since tert-butyl alcohol is a major

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by-product in the production of propylene oxide, the etherification reaction with ethanol may also be of practical relevance. Therefore, this work is dedicated to the investigation of the gas phase etherification process in order to understand the reaction mechanism and to measure the kinetic parameters of the reaction between TBA and ethanol on the HPW/MCM-41 type catalysts synthesized and characterized previously [22] and were proved to be effective in the gas phase etherification [3].

## Experimental part

*Chemicals*

All reactants - TBA (99%, Aldrich Chemical Co.), EtOH (99.8%, Aldrich Chemical Co.), ETBE (99%, GC, Aldrich Chemical Co.), iso-propanol (99.5%, GC, Aldrich Chemical Co.) – employed in our ETBE synthesis experiments were used without other purification.

*Catalysts and characterization*

The MCM-41 support was prepared by ultrasonic irradiation at high pH and the HPW/MCM-41 catalysts were obtained by impregnating the heteropolyacid on the synthesized supports, as described elsewhere [22]. BET areas between 1435 and 460 $m^2g^{-1}$, and pore volumes between 0.914 and 0.208$cm^3g^{-1}$ were obtained for samples as the HPW loading increased from 0 to 30 wt%.

Fourier transform infrared spectra (FT-IR) of samples pressed in KBr pellets were recorded from 400 to 4000 $cm^{-1}$ on a Bruker VERTEX70 instrument at 4 $cm^{-1}$ resolution, and in each case the sample was referenced against a blank KBr pellet.

Transmission electron microscopy (TEM) images of MCM-4 and HPW/MCM-41 were taken on a TECNAI F30 G2 HRTEM microscope.

*Reaction procedure and product analysis*

Reactivity experiments were carried out in a continuous flow quartz reactor (15mm OD, 12mm ID and 350mm length) heated in a cylindrical electric furnace described in detail in our previous contribution [3]. The homogeneous mixture of reactants, ethanol and TBA, at the desired molar ratio, was fed to the reactor using a HPLC pump at a specific constant flow rate while the reaction system was maintained at the desired constant temperature and pressure. The temperature was controlled within ±1°C by a temperature controller, and a needle valve was used as manual backpressure controller. The pressure was kept constant at 1atm to maintain gas phase operation at all temperatures. In all experiments, approximately 0.5 grams of HPW/MCM-41 catalyst (40-60 mesh fractions) were packed in the reactor. The etherification of TBA with ethanol was carried out in the temperature range from 110 to 130°C, as described in detail elsewhere [3]. The feed and the reactor effluent were analyzed on a Varian 450 gas chromatograph equipped with flame ionization detector (FID) and a Cp-Wax57CB (0.12µm x 0.15mm x 30m) column. In order to ensure a pulse – free flow, the reaction mixture was fed to the reactor in a helium stream at 50 mL . $min^{-1}$. The state of the system (flow, pressure, and temperature) was kept constant for 1h, and repeated analyses of the reactor effluent were performed to ensure the steady state was reached.

## Results and discussions

Characterization of catalyst

The FT-IR spectra (fig. 1) of the mesoporous framework vibrations and of the Keggin structures of pure HPW and supported HPW/MCM-41 were obtained using KBr disks of

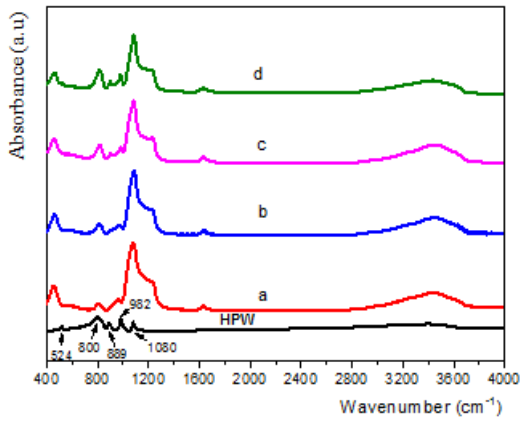



Fig. 1. FT-IR spectra of HPW and 30% HPW/MCM-41: (a) Si-MCM-41. (b) 10% HPW/MCM-41, (c) 20% HPW/MCM-41, (d) 30% HPW/MCM-41

samples at ambient temperature. The IR spectrum (KBr pellets) of the Keggin structure of pure HPW shows four strong bands at 1080 $cm^{-1}$ (P-O), 982 $cm^{-1}$ (W=O), 889 $cm^{-1}$ and 800 $cm^{-1}$ (W-O-W) and one weak band at 524 $cm^{-1}$ (W-O-P) [23, 24]. Because the infrared framework vibration of Si-MCM-41 are at 1230, 1080, 961, 808 and 458 $cm^{-1}$, they easily overlap with the spectral features of the Keggin structure of HPW centered at 1080, 982, 800, and 524 $cm^{-1}$. For the HPW/MCM-41 sample with 10% loading none of the HPW spectral features were observable, except for a slight increase in the intensity at 800 $cm^{-1}$. With the increase of the HPW loading to 30 wt%, features at 889 and 982 $cm^{-1}$ became visible, and their intensity was enhanced. Additionally, it was observed that the increase in intensity of the 800 $cm^{-1}$ band was correlated with the increase of the HPW loading on MCM-41 due to the increased number of oscillators.

On the other hand, FT-IR spectra in the 3800-3000 $cm^{-1}$ region of the Si-MCM-41 and the HPW/MCM-41 samples show that the relative coverage of surface hydroxyl groups decreases with increasing HPW loading. Owing to the rather weak hydroxyl bands of pure HPW, the decreasing absorbance in the aforementioned spectral regions is most likely due to the coverage of dispersed HPW on the surface of Si-MCM-41, and/or to the interaction of HPW with surface hydroxyl groups of Si-MCM-41. FT-IR results are consistent with previous XRD, BET surface area, and pore size analysis [22]. Furthermore, the pore volume of the HPW/MCM-41 catalysts is much less than that of pure MCM-41, indicating that large amounts of crystalline nanoparticles of HPW are present inside the pore system of MCM-41.

Besides our previous XRD and $N_2$ sorption investigations [22], the structure of the catalyst after incorporation of HPW on MCM-41 was also investigated by TEM. The array of regularly sized holes of about 2.17 nm diameter separated by approximately 1.5-2 nm thick silica walls are shown in figure 2, confirming the values obtained from XRD and $N_2$

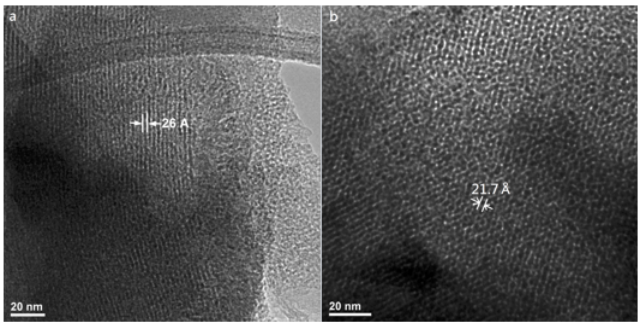



Fig. 2. TEM images of MCM-41 (a) and 30% HPW/MCM-41 (b)

adsorption measurements [22]. These results indicate the HPW/MCM-41 catalysts prepared by impregnation maintained regular mesoporous structure observed for the support.

*Catalytic activity*

Effect of space time

In the present works, the only ether detected was ETBE. Besides the etherification reaction, the dehydration reaction of TBA to IB and water also occurred. The effect of space time on the conversion of tert-butyl alcohol and on the selectivity of ETBE were studied at temperatures between 110 and 130°C (fig. 3). As it can be seen in figure 3, the TBA conversion increases almost linearly as the space time increases to about 70000 g·s·mol$^{-1}$ at 110°C indicating the absence of any mass transfer limitations under these conditions. The ETBE selectivity decreased linearly with increasing space time, as seen in figure 4, confirming the hypothesis discussed above. At 130°C, the linear portion of the conversion variation with space time is limited to space time values below 60000 g·s·mol$^{-1}$, indicating that at higher temperatures there may be a regime controlled by transport, which would alter kinetic measurements. For this reason, the kinetic experiments to check the rate equation and measure the kinetic parameters should be performed at space time values below 60000 g·s·mol$^{-1}$. At short space times, the reaction does not reach the thermodynamic equilibrium and is controlled by the degree of surface coverage with carbocation intermediates, therefore isobutene formation reaction can be considerably limited. At the same time, these interpretations are also consistent with the hypothesis of a reaction mechanism involving the assistance of several surface acidic centers to form ETBE, while isobutene formation can take place on a single acidic site. These assumptions will be tested by carrying out kinetic experiments to be analyzed using analytical rate equations developed on the basis of the proposed reaction mechanism.

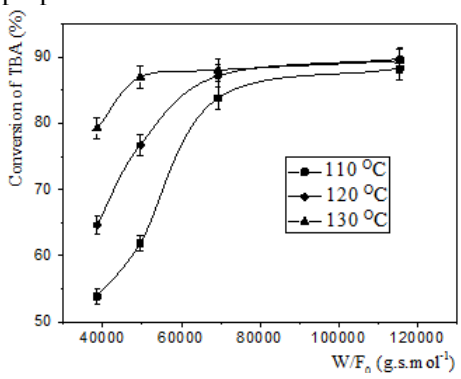



Fig. 3. The effect of space time on TBA conversion at different temperatures

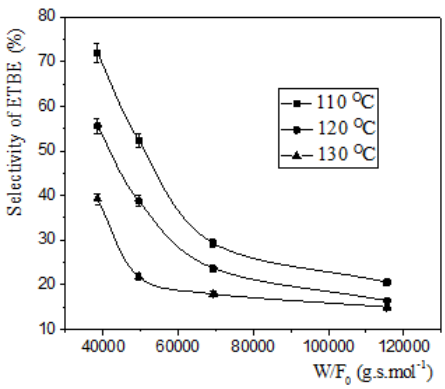



Fig. 4. The effect of space time on ETBE selectivity at different temperatures

Effect of partial pressure of TBA and ethanol on the reaction rate

The 30% HPW/MCM-41 catalyst was used for kinetic experiments.

The rate of ETBE formation was expressed as:

$$r = F\frac{x}{m} \quad (1)$$

where F is the flowrate of tert-butyl alcohol in the feed (mol·h$^{-1}$), x the TBA conversion, and m is the mass of catalyst (g).

If we consider an empirical expression of the reaction rate for etherification of the form $r = kp_{EtOH}^{\alpha}p_{TBA}^{\beta}$, the rate of ETBE formation on the HPW/MCM-41 catalyst can be represented in the logarithmic graphs according to the partial pressures of TBA, $p_{TBA}$, and ethanol, $p_{EtOH}$, as depicted in figure 5. As it can be seen in figure 5, the rate of ETBE formation reaction varies linearly with the partial pressures of ethanol and tert-butyl alcohol, with the difference that the increase in partial pressure of the ethanol results in a decrease in the reaction rate, while the increase in partial pressure of TBA induces an increase in rate of the ETBE formation reaction. These results suggest a positive apparent reaction order of with respect to TBA, and a negative one with respect to ethanol. The values of the apparent reaction orders calculated from the experimental dates plotted in figure 5 are -3.8 with respect to ethanol and 0.95 with respect to TBA. As we already noted in our previous contribution [3], this kinetic behavior confirms that excess ethanol prevents the adsorption of TBA on the surface of the catalyst, and is consistent with the Eley-Rideal reaction mechanism in which tert-butyl carbocation intermediates react with ethanol molecules in the gas phase.

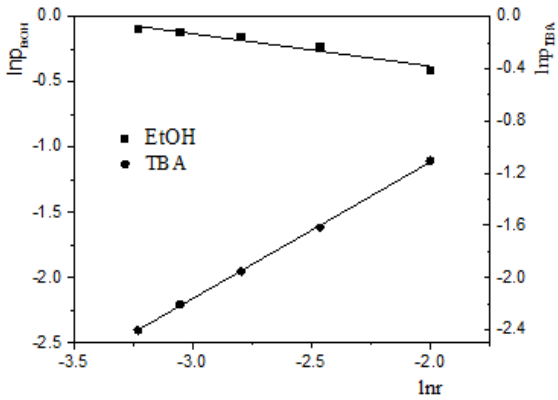


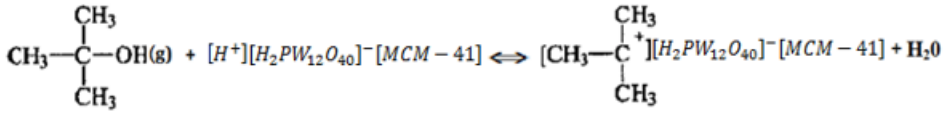

Fig. 5. Logarithmic plot of the reaction rate vs. TBA and ethanol partial pressures (T=110°C, WHSV=43341 g.s.mol$^{-1}$)

Kinetic experiments for the synthesis of ETBE and MTBE by reaction of isobutene with ethanol or methanol were performed in gas phase on Wells-Dawson catalyst [25, 26]. The results for both ethers were qualitatively similar to those obtained in our experiments on kinetics of ETBE formation from TBA and ethanol: the increase in the partial pressure of alcohol was accompanied by a decrease in the reaction rate, and the increase in the partial pressure of isobutene resulted in an increase in the reaction rate. The above results allowed us to propose an Eley-Rideal kinetic model in which the gas phase ethanol molecules react with surface tert-butyl carbocations resulting from the adsorption of TBA molecules on catalyst acid sites, followed by removal of a water molecule.

*Mechanism of reaction*

The etherification reaction of TBA with ethanol on the HPW/MCM-41 catalyst is a nucleophilic substitution reaction in which the Brönsted acid sites on the catalyst surface are responsible for generating tert-butyl carbocation from tert-butyl alcohol by removing a water molecule. Therefore, the catalytic activity is expected to depend on the number and strength of the Brönsted acid sites. Synthesis of ETBE

from TBA and ethanol on HPW/MCM-41 catalyst is produced according to a mechanism that can be described through the following steps:



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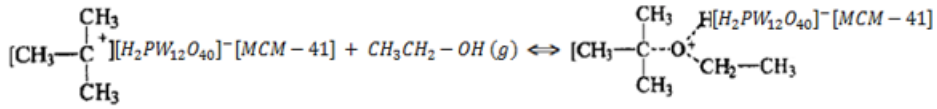

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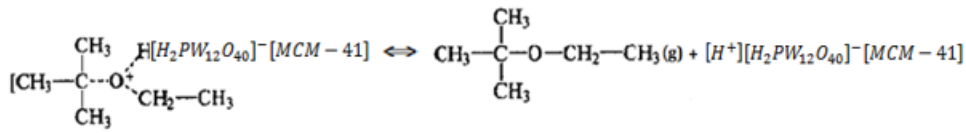

(4)

The first step is the protonation of tert-butyl alcohol over HPW/MCM-41 catalyst, to give a tert-butyl oxonium ion. It should be noted that, at the temperatures of our experiments, dehydration of the oxonium ion formed by TBA protonation is possible and leads to the formation of a surface stabilized tert-butyl carbocation, while dehydration of the oxonium ion derived from ethanol requires higher temperatures and would generate a less stable, secondary carbocation on the surface of the catalyst [27]. Thus, it is assumed that the dominant surface species is the tert-butyl carbocation, which can either react with ethanol molecules from the gas phase, or with surface protonated ethanol molecules to form adsorbed ETBE molecules - or it can be desorbed in the form of isobutene, restoring the acid center. It is noted that no traces of dimers of isobutene were detected in the reaction products.

In the last step, the adsorbed reaction product is desorbed as ETBE in the gas phase restoring the acidic site. The surface reaction is considered to be the rate-limiting step for this reaction mechanism. The Eley-Rideal mechanism is most likely the candidate suggested by the absence of dimethyl ether in the reaction product, confirming the ethanol does not generate carbocations on the surface.

*Kinetic model*

It is considered that the ETBE formation reaction from TBA and ethanol is reversible, while dehydration of TBA to IB is irreversible, and these two reactions are competitive:

$$\mathrm{TBA} + \mathrm{EtOH} \rightleftarrows \mathrm{ETBE} + H_2O \quad (5)$$

$$\mathrm{TBA} \rightarrow \mathrm{IB} + H_2O \quad (6)$$

For the Eley-Rideal kinetic model, we made the following assumptions: all adsorption (S) sites on the catalyst are energetically equivalent, and the adsorption of molecules is rapid compared to the surface reaction. Also, ether, water and isobutene molecules, once desorbed from the surface, are not readsorbed on the catalyst.

Analysis of the effect of various parameters and the product profiles suggests that chemisorption of TBA should be the first step followed by other reactions.

$$\mathrm{TBA} + \mathrm{S} \rightleftharpoons \mathrm{TBA} - \mathrm{S} \quad (7)$$

where S is the vacant site

The chemosorbed species reacts according to the following paths:

$$\mathrm{TBA} - \mathrm{S} + \mathrm{EtOH(g)} \xrightarrow{k_1} \mathrm{ETBE} - \mathrm{S} + \mathrm{H_2O(g)} \quad (8)$$

$$\mathrm{TBA} - \mathrm{S} \xrightarrow{k_2} \mathrm{IB} - \mathrm{S} + \mathrm{H_2O(g)} \quad (9)$$

The major side reaction is the dehydration reaction of TBA.

In the absence of external mass transfer limitations, the reaction rate is proportional to the partial pressure of TBA and the yield and selectivity of ETBE remain constant for a given TBA feed rate and temperature. The ETBE yield at constant temperature increases when the ethanol partial pressure in the feed increases, indicating a strong influence of the ethanol partial pressure on the rate of isobutene formation reaction. The isobutene yield is proportional to the partial pressure of TBA. It is also worth noting that TBA conversion increases, and the ETBE yield decreases with increasing temperature at fixed molar ratio of reactants, while the yield of isobutene increases with increasing temperature for all molar ratios studied.

Based on the above observations, only reactions (8) and (9) were found to be relevant. The chemisorption of tert-butyl alcohol (A) and ethanol (B) on a vacant site (S) gives surface species AS and BS. The chemisorbed species AS undergoes two parallel reactions to produce ETBE (E), and IB, while BS can only be desorbed to regenerate the active site and a gas phase ethanol molecule. The reaction was carried out between 110-130°C in vapor phase, and it was found that through preliminary analysis of the data the adsorption terms were insignificant. Thus, the overall rate of reaction of tert-butyl alcohol (A) (mol/s·g-cat), assuming parallel reactions (8) and (9) as rate controlling, is given by the Eley-Rideal model

$$-r_1 = k_1\theta_A p_B \quad (10)$$

$$-r_2 = k_2\theta_A \quad (11)$$

If the adsorption of reactant A (TBA) follows the Langmuir adsorption isotherm;

$$\theta_A = \frac{K_A p_A}{1+K_A p_A} \quad (12)$$

where $K_A$ is associated equilibrium constant for A, $\theta_A$ is the fractional occupancy of adsorbed A.

From relations (10) and (11), it is obtained

$$-r_A = -r_1 - r_2 = k_1\theta_A p_B + k_2\theta_A = (k_1 p_B + k_2)\theta_A \quad (13)$$

$$-r_A = \frac{(k_1 p_B + k_2)K_A p_A}{(1+K_A p_A)} \quad (14)$$

where $p_A$ is partial pressure of A.

However, $p_{Bo} >> p_{Ao}$, the initial concentration of the ethanol is 8 times higher than that of TBA, and if $K_A p_A << 1$, then above equation (14) becomes:

$$-r_A = (k_1 p_B + k_2) K_A p_A \quad (15)$$

$$-r_A = k' p_A \quad (16)$$

where the overall pseudoconstant for the reaction of A (k') is given by

$$k' = (k_1 p_{B_0} + k_2) K_A \quad (17)$$

Now, equation (15) is integrated for a fixed bed vapor phase catalytic reactor to get the following:

$$-\ln(1 - X_A) = k' p_{A_0} \frac{W}{F_{A_0}} \quad (18)$$

Thus, a plot of $-\ln(1-X_A)$ versus $\frac{W}{F_{A_0}}$ was built at different temperatures (fig. 6) to obtain a good fit up to 130°C. However, the fit is not so good over 130°C, because the rate of reaction is very high and, most likely, the reaction no longer remains pseudo-first-order. Since there are substantial changes in the concentration of ethanol over 130°C due to much higher rate of reaction, the first term in equation (15) ($k_1 K_A p_A p_B$) becomes predominant.

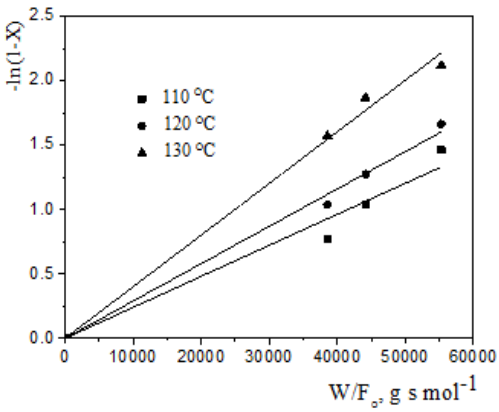


Fig. 6. Pseudo-first-order plot: -ln (1-$X_A$) *vs* W/$F_{Ao}$ for ETBE synthesis

The values of the rate constant (k') were calculated at different temperatures up to 130°C and an Arrhenius plot given in figure 7 allowed us to estimate the frequency factor and the activation energy. The values of the frequency factor and of the apparent activation energy were calculated to be 1.69 x$10^8$ mol . $kg^{-1}$ . $h^{-1}$ . $bar^{-1}$ respectively.

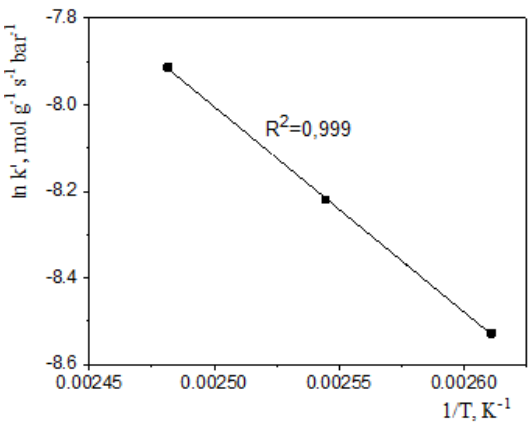


Fig. 7. Arrhenius plot

For a fixed bed reactor with plug flow of vapors, where the mole ratio of ethanol (B) is taken in far excess over tert-butyl alcohol (A), the total overall fractional yield φ of ETBE with reference to the amount of A reacted is obtained from the instantaneous yield as follows:

$$\varphi = \frac{k_1 p_B}{k_1 p_B + k_2} = \frac{1}{1 + \frac{k_2}{k_1 p_B}} \quad (19)$$

When $k_1 p_B << k_2$, then equation (19) is reduced to:

$$\varphi = \frac{k_1 p_B}{k_2} < 1 \quad (20)$$

Equation (20) shows that the ETBE yield increases with increasing partial pressure of ethanol, but it is independent on the TBA partial pressure over a certain value, as observed experimentally in figure 8, thus it is confirmed experimentally. The maximum ETBE yield of 38.76% was reached at an ethanol/TBA molar ratio of 8.0 and 110°C temperature of [3].

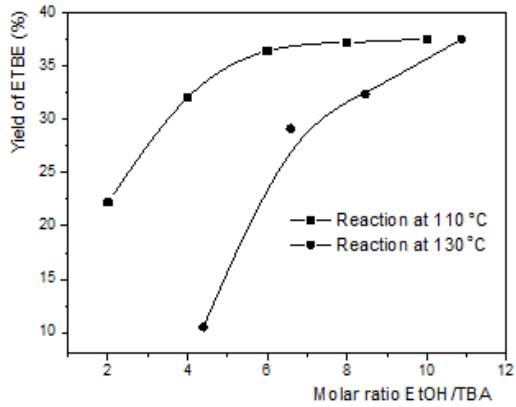


Fig. 8. The ETBE yield *vs.* ethanol/ TBA molar ratio

## Conclusions

Kinetics of the etherification reaction of tert-butyl alcohol with ethanol on HPW/MCM-41 catalyst to produce fuel additives were investigated experimentally. The Eley-Rideal mechanism was considered to developing the kinetic model for the ETBE synthesis. Experimental data were collected under a kinetically controlled reaction regime. The model explains the experimental observations very well. The reaction follows pseudo first order kinetics on HPW/MCM-41 catalyst.

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