Assessing the Catalytic Potential of 12-tungstophosphoric Acid Supported on MCM-41 for the Gas Phase Etherification of Alcohols

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The gas-phase etherification reaction of ethanol with tert-butyl alcohol (TBA) was investigated for the production of an oxygenated fuel additive. The reaction was carried out in a continuous flow reactor, in the presence of 12-tungstophosphoric acid (HPW) dispersed on MCM-41 as catalyst. We have studied the influence of temperature, ethanol:TBA mole ratio, and weight hourly space velocity (WHSV) on the TBA conversion and ETBE selectivity. The optimum operating conditions were found at 110°C temperature, 8:1 ethanol:TBA mole ratio in the feed, and 30% HPW loading on the catalyst. The highest ETBE yield values were obtained at 110 °C and WHSV of 46 h^{-1} and 42 h^{-1}. The HPW/MCM-41 catalyst showed good activity and on-stream stability for the gas-phase synthesis of ETBE at 110°C, thus it is a promising catalyst for etherification reactions and, potentially, for other gas phase acid-catalyzed reactions.

Keywords: ETBE, TBA, gas phase etherification, MCM-41, HPW/MCM-41

The issues of air pollution and health problems caused by automotive vehicle emissions reached a high level of societal concern therefore require significant technical and legislative efforts to reduce automobile emissions [1]. In early 1970s gasoline was formulated by the addition of tetraethyl lead as antiknock agent to increase its octane number. However, the use of this antiknock agent was terminated about twenty years later due to harmful effects to human health of the leaded compounds used in gasoline.

Investigations of oxygenates as alternatives to lead compounds resulted in the usage of alcohols and tertiary ethers for gasoline reformulation [2, 3]. However, tertiary ethers are generally preferred to alcohols as gasoline blending components, due to their lower vapor pressures and better miscibility over alcohols.

Recently, many research reports have been published in the field of gasoline fuel oxygenates used as octane rating boosters. Methyl tert-butyl ether (MTBE) was generally preferred as octane enhancing gasoline additive, due to the availability of methanol produced from natural gas. However, ground water pollution problems created by MTBE leaks from underground storage tanks, and the toxic effects on water and health of the degradation products resulting from MTBE [4-7], diverted the attention of researchers and fuel producers to ethanol based tertiary ethers [8, 9]. Therefore, tertiary alkyl ethers such as ethyl tert-butyl ether (ETBE), tert-amyl ethyl ether (TAEE) and mono-, di-, and tri-tertiary butyl ethers of glycerol (MTBG, DTBG and TTBG) were chosen as alternative oxygenated fuels. These ethers have superior quality as octane enhancers compared to MTBE and can be produced from bioethanol, a renewable source. Also, they exhibit higher octane rating, higher boiling point, lower flash point, lower blending Reid vapor pressure and reasonably high oxygen contents [6, 10–14]. Among these ethers, ETBE was produced by the reaction of isobutene (IB) or tert-butyl alcohol (TBA) with excess ethanol (EtOH).

A significant amount of research has been conducted for the liquid-phase production of ETBE from IB and ethanol [15, 16]. Acidic ion-exchange resins were the subject of a large part of the etherification studies [17, 18]. Production of ETBE using TBA and ethanol was also accomplished by reactive distillation in a study reported by Yang and Goto [19], in which the authors combined the pervaporation process with reactive distillation using Amberlyst-15 as catalyst. The ETBE synthesis was also investigated by various researchers using Amberlyst-15, β-zeolite, and supported polyvinyl alcohol membranes as catalysts [12, 20]. Umar et al. [21, 22] studied the etherification reaction in liquid phase by using ion exchange resins, such as Purolite CT-124, CT-145H, CT-151, CT-175, CT-275, Amberlyst-15, and Amberlyst-35. Yin et al. [17] studied synthesis of ETBE from TBA and ethanol catalyzed by Amberlyst-15 and heteropolyacids (HPAs) in a batch reactor. Although acid ion-exchange resins possess high catalytic activity and selectivity, these materials have some disadvantages, such as low surface areas and lack of thermal stability [17, 21]. Furthermore, ion-exchange sulfonic resins are not stable and release sulfuric acid when exposed to high operating temperatures and pressures, which will decrease their catalytic activity and cause corrosion and environmental problems [24].

We and other authors have showed that etherification of glycerol with isobutene or TBA can be carried out using heterogeneous strong acid catalysts such as ion-exchange resins and heteropolyacids [25-27]. However, in the liquid-phase etherification process there are technological problems arising from the need to use solvents able to dissolve glycerol, and from the complexity induced by the two-liquid phase system causing mass transfer issues [25, 28, 29]. In fact, the use of emulsifiers and TBA, as both reactant and solvent, instead of gaseous isobutene, helped overcoming some of the technological problems, but still presented the drawback of operating at high pressures [7, 25].

Heteropolyacids have gained increasing attention in recent years, exhibiting good activity in ETBE production [30, 31]. They are known as strong acid catalysts and were immobilized on solid supports and used as acid and oxidation catalysts [32-34]. However, HPAs suffer from two major drawbacks, namely, (i) very low solid phase surface area (below 10 m^2g^{-1}), and (ii) high solubility in polar

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solvents. To avoid dissolution of HPAs in the liquid phase, porous materials have been used to immobilize these soluble acids [35, 36]. Anchoring HPAs onto the surface of porous materials like silica, zeolites, or mesoporous materials, prevented their dissolution or elution and preserved their catalytic properties [37, 38].

Use of M41S and of other mesoporous materials [39] as supports for 12-tugstophosphoric acid (HPW) is expected to greatly expand the catalytic surface area of HPW for some applications. This is because such mesoporous materials, which have uniform mesopores and very high surface areas, have relatively small diffusion hindrance and facilitate the access of bulky organic molecules in and out of their pores [40]. In recent years, many researchers reported on MCM-41 type heterogeneous catalysts used in alkylation and acylation reactions [41-43], acetalyzation [44] and esterification [45, 46]. However, to the best of our knowledge, HPW/MCM-41 catalysts have not been involved in either liquid, or gas phase synthesis of ETBE.

We have recently prepared and characterized MCM-41 supports by ultrasonic irradiation under basic *p*H, used them to obtain HPW/MCM-41 catalysts, and demonstrated that the synthesized materials retained the characteristic MCM-41 mesoporous structure after impregnation of the active phase onto the mesoporous surface. Details on the synthesis route and characterization results of the HPW/MCM-41 catalysts are given elsewhere [47].

In this contribution we report on the performance of our synthesized HPW/MCM-41 catalysts in the gas phase reaction between tert-butyl alcohol and ethanol under different reaction conditions. The effects of the HPW loading, reaction temperature, TBA/EtOH molar ratio, and weight hourly space velocity (WHSV) were systematically investigated aiming to identify the optimal reaction conditions and assess the performance of these catalysts for an industry-relevant process.

Experimental part

Chemicals and catalyst

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 further purification.

MCM-41support were prepared by ultrasonic irradiation under basic environment and the HPW/MCM-41 catalysts were obtained by impregnating the heteropolyacid on the synthesized supports as described in detail elsewhere [47]. BET areas between 1435 and 460 m^2g^{-1}, and pore volumes between 0.914 and 0.208 cm^3g^{-1} were obtained for the samples when the HPW loading increased from 0 to 30 wt%.

Synthesis of ETBE in a continuous-flow reactor

The etherification of TBA with ethanol was investigated in a continuous flow quartz reactor (15mm OD, 12mm ID and 350mm length) heated in a cylindrical electric furnace. In all experiments, approximately 0.5g of HPW/MCM-41 catalysts (40-60 mesh fraction) were packed in the reactor. A schematic diagram of the continuous flow reactor system is shown in figure 1.

The homogeneous solution of reactants, ethanol and TBA, at a 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 by a temperature controller, and a needle valve was used as manual backpressure controller. Ethanol and TBA with

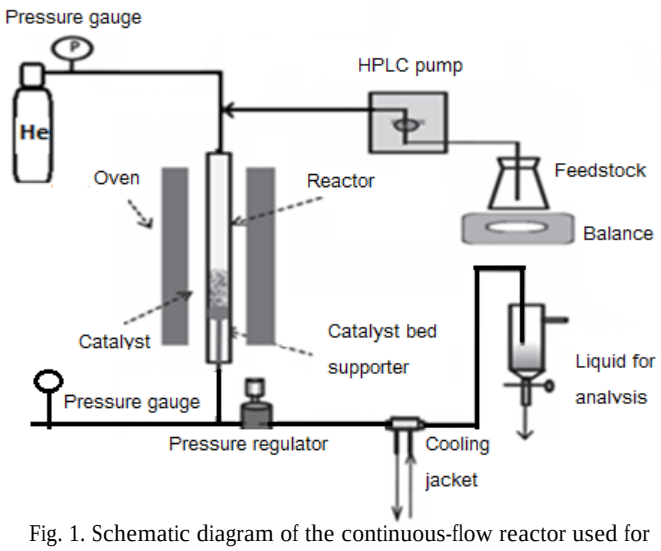

Fig. 1. Schematic diagram of the continuous-flow reactor used for ETBE synthesis

molar ratios from 1 to 10 were mixed and sent to the reactor in a helium flow. The helium flow at 50 mL · min^{-1} must be introduced into the reactor as a carrier gas in order to maintain a steady operation and to equilibrate the adsorption-desorption processes [48]. Reaction was carried out at 1 atm. The flow rate of the reactant mixture was maintained constant for each experiment, and varied between 0.15 and 1 $cm^{-3}\cdot min^{-1}$ for different experiments. Reaction tests were performed in the temperature range from 110 to 150°C. The reaction products collected during the whole duration of an experiment 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. The only product identified in the chromatographic analysis besides unreacted ethanol and TBA, was and the ETBE formed. This is clear evidence that there are no other secondary etherification reactions taking place with formation of diethyl ether or di-tert-butyl ether.

In a typical run, 94.14 g of ethanol and 74.12 g of TBA (corresponding to 2:1 molar ratio of ethanol:TBA) were mixed, and the composition of the solution was confirmed by GC analysis. The feed flowrate in each run was determined by the amount of catalyst in the reactor and the desired weight hourly space velocity (WHSV, reciprocal of reaction time) defined as follows:

$$\mathrm{WHSV}(h^{-1}) = \frac{Mass\ flow\ of\ feed\ material(g/h)}{Mass\ of\ catalyst\ used(g)} \quad (1)$$

Depending on the feed flowrate, the compositions of the feed and the amount of the catalyst loaded in the reactor for each run, WHSV varied from 13 to 61h^{-1}. In all experiments the catalysts were activated for 1h at 200 °C in helium flow before the mixture of ethanol and TBA was admitted into the reactor.

Product analysis

All the components in the reaction mixture were analyzed by GC on a Varian 450 with Cp-Wax57CB column (0.12 µm x 0.15mm x 30m), using hydrogen as the carrier gas at a flow rate of 0.5mL·s^{-1}. The oven temperature was maintained at 70°C for one min and then increased to 150 at 10°C·min^{-1}. Injector and detector temperature were 200 and 220°C, respectively. Iso-propanol was used as internal standard and separation was achieved for all components. Herewith, ETBE product yield, TBA conversion and product selectivity are defined as follows:

$$\text{Yield}(\%) = \frac{\text{Moles of ETBE formed}}{\text{Initial moles of TBA}} \times 100 \quad (2)$$

$$\text{Conversion}(\%) = \frac{\text{Initial moles of TBA} - \text{Final moles of TBA}}{\text{Initial moles of TBA}} \times 100 \quad (3)$$

$$\text{Selectivity}(\%) = \frac{\text{Moles of ETBE formed}}{\text{Initial moles of TBA} - \text{Final moles of TBA}} \times 100 \quad (4)$$

Material balance for each run

As observed in figure 1, the reaction systems allows collection only for the liquid reaction products, gas products being released to the venting system, therefore the material balance was performed based on two assumptions: (i) the only product leaving the system as gas is the isobutene formed as a byproduct from the dehydration of TBA; and (ii) there is no accumulation of reactants or products into the reaction system, that is all materials entering the reaction system must be either captured in reaction products collection vessel, or released to the vent.

Based on these assumptions, we were able to perform the overall material balance starting from the weight of the reaction products and the stoichiometry of the two competing reactions identified, that are the etherification between ethanol and TBA – as main reaction, and the dehydration reaction of TBA – as the secondary, competing reaction. Therefore, the collected reaction product contains unreacted TBA and ethanol, ETBE resulting from the main reaction, and water resulting from both main and secondary reactions. The difference between the weight of the reactants introduced in the reactor and the weight of the collected reaction products gives the amount of the isobutene formed in the secondary reaction.

The chromatographic analysis of the liquid reaction products only provides information on the ratio of different organic components in the total reaction product, since water cannot be identified by the FID. For instance, if we consider the ratio between the peak areas of ETBE and TBA resulting from the analysis of the final reaction product, we can write:

$$\frac{A_{ETBE}}{A_{TBA}} = \frac{N^f_{ETBE}}{N^f_{TBA}} \quad (5)$$

where N^f_{ETBE} and N^f_{TBA} are the numbers of moles of ETBE and TBA, respectively, in the final product.

Using the stoichiometry for the two reactions occurring simultaneously, one can write:

$$N^f_{ETBE} = N^0_{TBA} - N^f_{TBA} - N^{R2}_{TBA} \quad (6)$$

where N^o_{TBA} is the number of TBA moles introduced in the reactor, and N^{OR2}_{TBA} is the number of TBA moles reacted in the competing reaction and forming isobutene, thus $N^f_{ETBE} = N^f_{TBA}$.

Since for each mole of TBA reacting in the secondary reaction a mole of isobutene is formed, based on our assumption, we can determine the number of moles of isobutene formed by dividing the weight difference between the materials fed to the reactor and the liquid products collected to the molecular mass of isobutene. Thus, equation (5) becomes:

$$\frac{A_{ETBE}}{A_{TBA}} = \frac{N^0_{TBA} - N^f_{iB} - N^f_{TBA}}{N^f_{TBA}} \quad (7)$$

Rearranging terms in equation (7) and writing material balance equations for each component, the number of moles of each component in the final product can be calculated with equations (8):

$$N^f_{TBA} = \frac{N^0_{TBA} - N^f_{iB}}{1 + \frac{A_{ETBE}}{A_{TBA}}};$$

$$N^f_{ETBE} = N^0_{TBA} - N^f_{TBA} - N^f_{iB};$$

$$N^f_{EtOH} = N^0_{EtOH} - N^f_{ETBE}; \quad (8)$$

$$N^f_{H2O} = N^f_{ETBE} + N^f_{iB};$$

with N^x_{ABC} indicating the number of moles – where x is 0 for initial, and f for final – of component ABC – where EtOH stands for ethanol, H_2O for water, and iB for isobutene.

The resulting computed values were compared to the experimental ones and errors were assessed. In all our experiments, following the procedure described above, the resulting material balance errors varied between 2 and 7%, within acceptable margins.

Results and discussions

Stability of the catalytic activity and selectivity

The stability of the catalytic performance for long time-on-stream – up to 14 h– was investigated under the following experimental conditions: 110°C, 1 atm, ethanol:TBA molar ratio of 2:1, and WHSV of 29 and 43 h^{-1}. Results of the stability test are shown in figure 2. The HPW/MCM-41 catalyst exhibited good stability of both TBA conversion and ETBE selectivity over long time-on-stream, with TBA conversions of 70 and 60%, respectively, and ETBA selectivity of 32 and 40%, respectively, during the whole course of the experimental run up to 14 h on-stream.

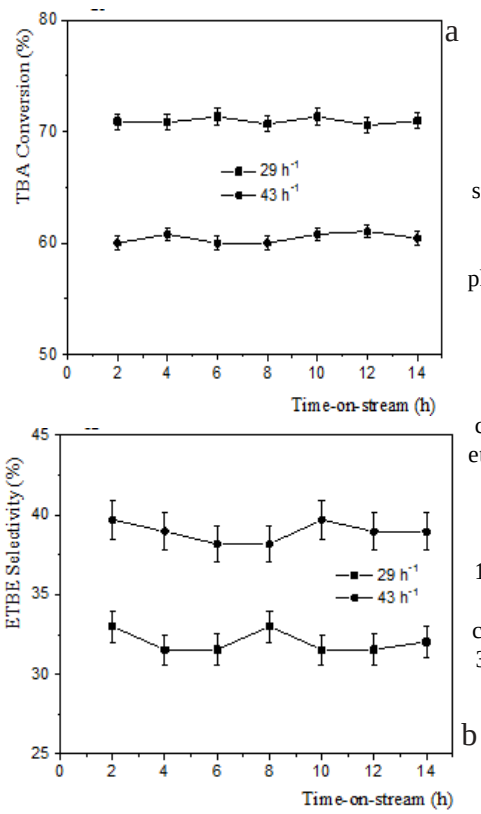

Fig. 2. The on-stream stability of HPW/MCM-41 catalyst for gas-phase synthesis of ETBE: a; conversion, b; selectivity. Experimental conditions: 1atm, ethanol/TBA molar ratio of 2.0, reaction temperature, 110° C. Error bars are at 1% for conversion and at 3% for selectivity

These results indicate that our experimental procedure is sound, and cumulative samples collected after reaction over several tens of minutes are representative for the process, with no major changes in conversion and selectivity. As seen in figure 2, errors for conversion measurements are within ± 1% for conversion and ± 3% for selectivity, values that are considered very good taking into account the procedure for establishing the material balance. Therefore, the results discussed further were obtained after reacting for up to 3 h and collecting the reaction products for the entire duration of the experiment. We should also mention that no clogging or pressure excursions were observed under the reaction conditions used in our experiments.

Effect of the HPW loading on MCM-41

To investigate the effect of the HPW loading, etherification reaction tests were carried out with increasing the HPW loading from 10 to 30 wt%. The results are presented in figure 3. As expected, both TBA conversion and ETBE yield increase with the increase of the HPW loading on the catalyst. At 30 wt% HPW loading the ETBE yield and TBA conversion achieved their highest values of 38.76 and 53.86%, respectively.

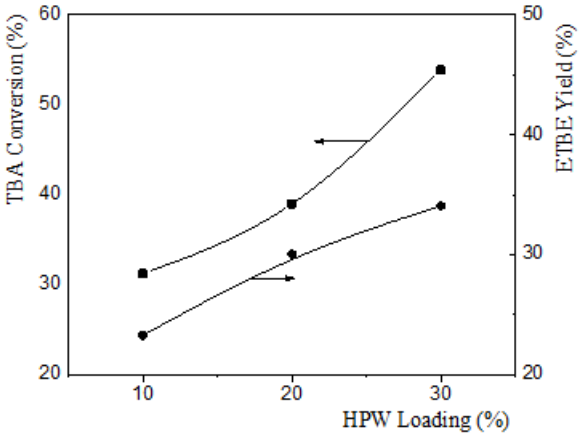

Fig. 3. Effect of HPW loading in MCM-41 on the performance of the catalyst. Reaction conditions: amount of catalyst, 0.5g; mole ratio of ethanol/TBA, 8:1; reaction temperature, 110°C; pressure, 1atm; WHSV, 42 h^{-1}

This behavior is most likely due to the increased number of Brönsted acid sites per unit surface area at higher HPW loading, these sites playing a critical role in the activity of catalysts. Since the reaction mechanism involves the formation of tert-butyl carbenium ion intermediates, followed by the nucleophilic attack of ethanol molecules [21], it is expected that an increase of the surface acidity will favor TBA conversion. Due to its relative high activity over a wide range of operating conditions, the catalyst with 30% HPW loading was selected for further detailed investigations.

Effect of the EtOH:TBA mole ratio in the feed

The etherification reaction is an equilibrium-controlled reaction [49]. In order to overcome the equilibrium limitation, it is necessary to carry out the reaction using one of the reactants in excess. Yields can be increased by increasing the concentration of either ethanol or TBA. In practical applications, for obvious economic reasons, the less expensive reactant is usually taken in excess to obtain maximum yield. For this reason, in our investigation we chose ethanol as the excess reactant. The influence of the ethanol:TBA molar ratio on TBA conversion and ETBE selectivity was investigated at 110°C, 1 atm and WHSV of 38 h^{-1}. Different ethanol:TBA molar ratios varying from 1:1 to 10:1 were tested and the corresponding results are

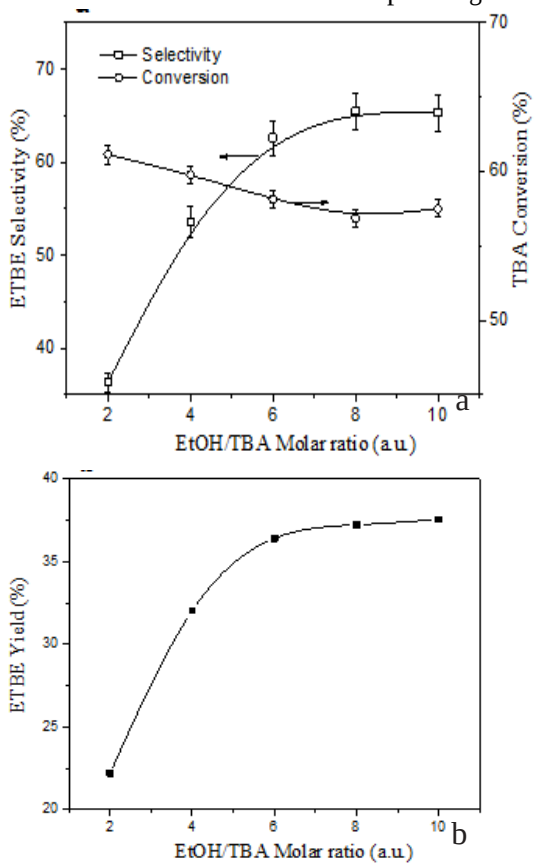

Fig. 4. Effect of the EtOH:TBA mole ratio on the performance of the HPW/MCM-41 catalyst: a – conversion and ETBE selectivity; b – ETBE yield. Reaction conditions: amount of catalyst, 0.5g; reaction temperature, 110°C; pressure, 1atm; WHSV, 38 h^{-1}.

presented in figure 4.

As shown in figure 4, increasing the ethanol:TBA molar ratio from 1:1 to 10:1 resulted in a clear decrease of the TBA conversion, and a significant increase in the ETBE selectivity. However, as the molar ratio increases beyond 8:1, the decrease in TBA conversion was less intense, as well as the increase in ETBE selectivity.

On a catalytic surface with strong Brönsted acid sites – which is the case for the HPW/MCM-41 catalyst – both alcohols are expected to compete for available acid sites and react to form the corresponding protonated oxonium species. Nevertheless, TBA is favored in this competition since it is a stronger base than ethanol and will give a more stable oxonium ion than the protonated ethanol species. Moreover, under our reaction conditions, i.e. at 110°C, the oxonium ion resulting from TBA can, and will eliminate a water molecule to form a tert-butyl carbenium ion bound to the surface, while the protonated ethanol species needs considerably higher temperature to follow the same reaction pathway with the formation of a surface stabilized ethyl carbenium ion [50]. Once formed at the surface, the tert-butyl carbocation can either react with an ethanol molecule to form a protonated ETBE molecule that will further desorb to the gas phase and regenerate the acid site at the surface, or it can be stabilized by desorption as isobutene with the regeneration of the active site. Therefore, both competing reactions proceed through the same intermediary species. Thus, as the concentration of ethanol increases, the partial pressure of TBA decreases, such that the reduction of TBA conversion is actually expected, as the ethanol excess likely impedes adsorption of TBA on the catalyst surface, slowing down the rate of TBA reaction.

The increase in the ETBE selectivity when the TBA partial pressure decreases suggests that, at lower tert-butyl carbenium ion surface coverage, the reaction rate of the intermediate tert-butyl carbenium ions with ethanol molecules is less influenced than the rate of isobutene desorption. Indeed, the variation of the ETBE yield with the increase in the ethanol:TBA molar ratio depicted in figure 4 shows that, despite the decrease in the TBA conversion, the ETBE yield – that is the number of ETBE moles formed per mole of TBA reacted – keeps increasing, although the TBA partial pressure decreases. This behavior suggests that the rate of ETBE formation is less influenced by the TBA partial pressure and the increase in the ethanol partial pressure is dominant with respect to the rate of ETBE formation.

Based on these results we speculate the isobutene desorption follows a mechanism involving multiple surface carbenium species and/or site cooperation, hence it is favored by a high tert-butyl carbenium ion surface coverage. As the TBA partial pressure decreases, the tert-butyl carbenium ion surface coverage likely decreases with a strong effect on the rate of isobutene formation, and leaving more tert-butyl carbenium ion surface species available for the etherification reaction. This hypothesis is consistent with the etherification reaction following an Eley – Rideal reaction mechanism, with gas phase ethanol molecules reacting with tert-butyl carbenium ion surface species, which is favored by the increase of the ethanol partial pressure as long as there is a sufficient surface coverage with tert-butyl carbenium ion species.

Effect of the reaction temperature

The effect of the reaction temperature on TBA conversion and ETBE selectivity was investigated in two sets of experiments conducted on 0.5g of 30% HPW/MCM-41 catalyst at four different temperatures (110, 120, 130 and 150°C) and several weight hourly spatial velocities, while keeping the reaction pressure at 1 atm and reacting for 3 h. In the first set of experiments the ethanol:TBA molar ratio was 8, and for the second the molar ratio was 2. The results are presented in figures 5 and 6, respectively.

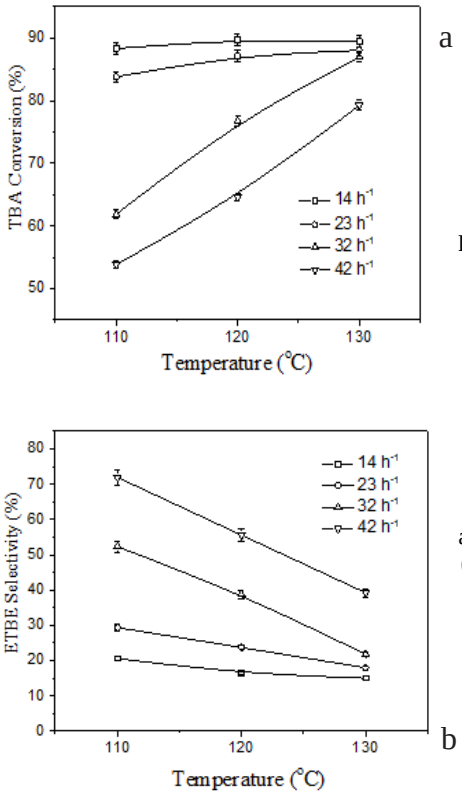

Fig. 5. Effect of the reaction temperature on TBA conversion (a) and ETBE selectivity (b) at different spatial velocities. Reaction conditions: amount of catalyst, 0.5g; mole ratio of ethanol/TBA, 8:1; pressure, 1atm

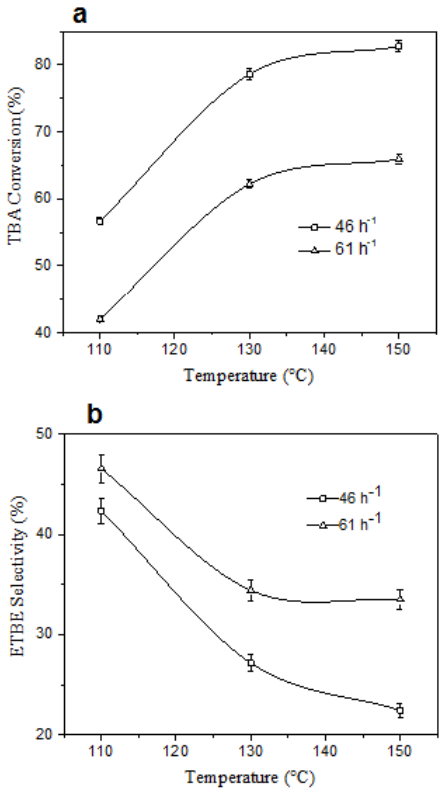

Fig. 6. Effect of the reaction temperature on TBA conversion (a) and ETBE selectivity (b) at different spatial velocities. Reaction conditions: amount of catalyst, 0.5g; mole ratio of ethanol/TBA, 2:1; pressure, 1atm

Generally, as shown in figures 5 and 6, higher reaction temperatures led to higher TBA conversions. In contrast, lower reaction temperatures led to higher ETBE selectivity. For ethanol:TBA molar ratio of 8, among all tested temperatures, the highest TBA conversion was observed at 130°C, and the best ETBE selectivity resulted for reaction at 110°C, as shown in figure 5. Similarly, for ethanol:TBA molar ratio of 2, the highest values for conversion and selectivity were observed at 150 and 110°C, respectively, as seen in figure 6. These results are consistent with the previous mechanistic discussion concluding that higher temperatures and tert-butyl carbenium surface coverage values favor isobutene formation, while low temperatures favor better ETBE selectivity.

The equilibrium conversions calculated for our experimental conditions at ethanol:TBA molar ratios of 2 and 8 using the equilibrium constant relation given by Ozbay and Oktar [51] are given in table 1. For ethanol:TBA molar ratio of 2, our experimental conversions of 78.58 and 82.76% observed at 1.04 min·g·cm^{-3} space time and 130 and 150°C are below the corresponding predicted equilibrium conversion values, that are approximately 84%. Neither for ethanol:TBA molar ratio of 8 the experimental conversions did not reach the predicted equilibrium conversion of 96%. In addition, we have found that, for ethanol:TBA mole ratio of 8, the conversion of TBA to IB is much higher than that to ETBE for weight hourly spatial velocity below 42 h^{-1}. This suggests that the equilibrium conversion for ETBE formation decreases with increasing reaction temperature, while and the equilibrium conversion for isobutene formation increases, consistent with previously published results [51]. This is expected ETBE formation is an exothermic reaction, while isobutene formation is endothermic.

From these experimental results, we conclude that the ETBE synthesis from ethanol and TBA on HPW/MCM-41 catalyst is rather thermodynamically controlled at high temperatures, and kinetically controlled at low temperatures. On the other hand, Ozbay and Oktar [51] estimated the equilibrium conversion of TBA to ETBE by using Amberlyst-15 as catalyst in the temperature range

Table 1
COMPARISON OF EXPERIMENTAL EQUILIBRIUM CONVERSION AT DIFFERENT ETHANOL:TBA MOLAR RATIO WITH EQUILIBRIUM CONVERSION [51]

Ethanol:TBA / T/K	2.0 (Space time=1.04 g·min·cm^{-3})		8.0 (Space time=3.3 g·min·cm^{-3})	
	TBA Conversion (experimental, %)	Predicted Equilibrium TBA Conversion (from correlation, %)	TBA Conversion (experimental, %)	Predicted Equilibrium TBA Conversion (from correlation, %)
383	56.67	84.7	88.34	96.7
393	-	84.8	89.75	96.9
403	78.58	84.6	89.48	96.7
423	82.76	84.4	-	96.6

from 300 to 800 K. The maximum experimental reaction temperature was selected at 383 K due to the deactivation of Amberlyst-15 at around 393K. According to the results of their study, the equilibrium conversion of TBA has reached the highest value for the ethanol:TBA molar ratio of 10, and the observed experimental conversion was quite in agreement with the predicted equilibrium conversion. In our test, the TBA conversion was close to 90% at 110°C for a molar ratio of 8. The catalytic activity of the 30%HPW/MCM-41 catalyst is not much less than that of Amberlyst-15, which suggests the heteropoliacid would be a good catalyst candidate for the synthesis of ETBE from ethanol and TBA, since the experimental results were obtained in similar test conditions, except for the type of catalyst used.

Effect of the spatial velocity

A separate set of experiments were conducted to investigate the effect of WHSV on the ETBE yield and TBA conversion at WHSV of 14 and 42 h^{-1}, and three temperatures. For these tests the ethanol:TBA molar ratio and pressure were kept constant at 8.0 and 1 atm, respectively.

The results are presented in figure 7, which clearly shows that increasing the WHSV from 14 to 42 h^{-1}, leads to the decrease of the TBA conversion from 88.34 to 53.86% at 110°C, temperature at which we see the most significant effect. The same behavior is also observed for the other two investigated temperatures, 120 and 130°C, respectively, but the influence of the WHSV becomes weaker as the temperature increases. This behavior is consistent with a shorter gas-catalyst contact time at higher velocity of the gas mixture through the catalyst bed. On the other hand, the 30%HPW/MCM-41 catalyst reached almost 72% ETBE selectivity at the highest spatial velocity of 42 h^{-1}. In contrast to the TBA conversion, the ETBE selectivity and the ETBE yield increase when the WHSV increases, as observed in figure 8. These results suggest that, the shorter the reactants' residence time in the reactor, the slower the rate of TBA dehydration, and better process performance, consistent with our previous discussion concerning the reaction not being at equilibrium, but rather under a kinetically controlled regime. They are also consistent with the proposed reaction mechanism where the rate of isobutene formation decreases as the temperature and the surface coverage with tert-butyl carbenium ions decrease. Our findings are also consistent with previously published results showing larger WHSV lead to lower conversion values [52].

These results suggest that HPW/MCM-41 is a promising catalyst for ETBE synthesis from ethanol and TBA, and that the temperature and the WHSV have a major influence on TBA conversion and ETBE selectivity. On the basis of product yield and experimental conditions, the overall results of this study further elucidate the potential advantages of HPW/MCM-41 as acidic catalyst for the gas-phase synthesis of ETBE.

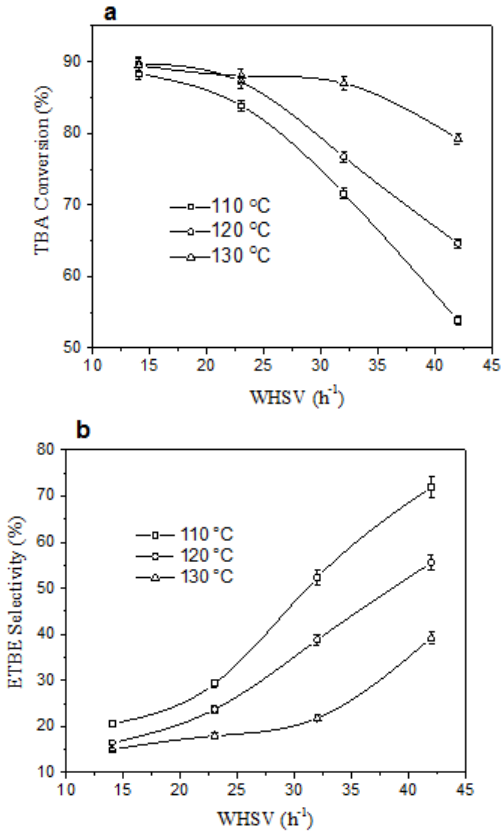

Fig. 7. Effect of the WHSV on TBA conversion (a) and ETBE selectivity (b) at different temperatures. Reaction conditions: amount of catalyst, 0.5g; mole ratio of ethanol/TBA, 8:1; pressure, 1atm

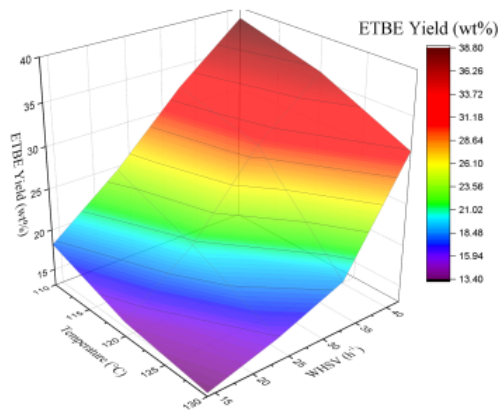

Fig. 8. Effect of the temperature and the WHSV on the ETBE yield. Reaction conditions: amount of catalyst, 0.5g; mole ratio of ethanol/TBA, 8:1; pressure, 1atm

Conclusions

The HPW/MCM-41 catalyst is a promising catalytic material for ETBE synthesis. It shows good conversion and high selectivity values when reaction parameters are carefully selected. Results of experiments performed under different reaction conditions suggest that, although both reacting alcohols may be protonated on the acid sites of the catalyst, only the oxonium ion resulting from TBA is capable, under our experimental conditions, to eliminate water and form a surface stabilized tert-butyl carbenium ion, that is the reaction intermediate for two competing reactions: etherification with the excess ethanol molecules and stabilization by isobutene desorption and regeneration of the acid site. Our experimental results aslo suggest that, while the reaction between tert-butyl carbenium ion species on the surface and the ethanol molecules follow an Eley – Rideal reaction mechanism, TBA dehydration is favored by high temperature and surface coverage with tert-butyl carbenium ions. Based on these findings, we propose that the intramolecular TBA dehydration requires multiple surface carbenium species and/or site cooperation, which allows operating the process under a kinetically controlled regime.

From practical perspective, the HPW/MCM-41 catalyst can be used for gas phase synthesis of ETBE from TBA and ethanol at temperatures near 110°C, fairly large ethanol:TBA ratios and high WHSV values, in order to obtain optimal results. It is speculated that these catalysts are likely to have good performance in gas phase etherification of isobutene that would allow even lower reaction temperatures.

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