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Kinetic evaluation of the direct synthesis of ethers from alcohols over sulfonated resin catalysts

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Abstract

The acidic Amberlyst-35 sulfonated resin effectively catalyzes the coupling of methanol + isobutanol and ethanol + isobutanol mixtures in the gas-phase to give methyl isobutyl ether and ethyl isobutyl ether, respectively. The reaction occurs via a S_N2 reaction pathway involving two adsorbed alcohol molecules and is successfully described by a simple Langmuir–Hinshelwood kinetics.

Keywords: Sulfonated resin catalysts; Ethers, direct synthesis from alcohols; Kinetics

1. Introduction

The use of high octane ethers, e.g., methyl tertiary butyl ether (MTBE), is a current alternative for the replacement of the hazardous lead additives in automotive fuel blends. The production of MTBE, which is industrially carried out from isobutene and methanol [1], is however limited by the availability of isobutene, for which a shortage is foreseen in the near future. This has led to a general interest in alternative routes for synthesizing high value oxygenates, e.g., fuel-grade C_5–C_6 ethers, from non-petroleum feed stocks. One of these routes is the direct coupling of alcohols over acidic catalysts. Isobutanol is a desirable source for the tert.-butyl group because it can be synthesized, along with methanol, directly from syngas over alkali-modified methanol synthesis catalysts. Also the use of ethanol is of potential interest in view of the recent EPA rule stating that 30% of all the oxygenates in the gasoline must come from 'renewable' sources. Accordingly, the synthesis of ETBE, ethyl tert.-butyl ether, has became of great industrial and academic interest.

In previous studies, the direct coupling of methanol and isobutanol over a series of acidic catalysts has been investigated [2–5]. In particular, it has been shown that the reaction selectivity to mixed ethers is generally difficult to control because a number of reaction products can be formed by parallel and/or consecutive reactions (e.g., dehydration to olefins and self-coupling of the alcohol molecules). The overall process selectivity is governed by the catalyst employed and by the reaction conditions as well.

In this work, a detailed mechanistic and kinetic investigation of the direct coupling of alcohols in the gas-phase over a strongly acidic sulfonated resin catalyst (Amberlyst-35) has been

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addressed. The synthesis of ethers from methanol + isobutanol and ethanol + isobutanol mixtures has been investigated and the chemical and physical factors controlling the vapor-phase dehydration of alcohols have been quantitatively described.

2. Experimental

The gas-phase alcohol coupling reactions were carried out in a stainless steel fixed bed reactor in the temperature range 377–403 K and at 1 MPa total pressure with $He + N_2$ as carrier gas. The reactants were fed as liquids to the top of the reactor and vaporized in a preheater section of the reactor. The exit gas from the reactor was periodically sampled using an on-line heated sampling valve and analyzed by means of a model 5890 Hewlett Packard gas-chromatograph. Condensation of the reaction products in a liquid nitrogen cooled trap was also performed for additional GC-MS analysis. Further details on the experimental setup and procedure can be found elsewhere [2].

Methanol (purity > 99.9%, water < 0.05%), ethanol (purity > 99.9%, water < 0.05%) and isobutanol (purity > 99.5%, water < 0.05%) were purchased from Aldrich and were used as received. The Amberlyst-35 catalyst was supplied by Rohm and Haas in the wet form (water 50% w/w); it was washed three times with distilled water and then dried overnight at 110°C.

The stability of the catalyst was periodically checked during the kinetic runs; under the conditions employed in the present study the catalyst did not showed any significant deactivation.

3. Results

In order to obtain more easily interpretable data, the alcohol conversion was kept low (typically < 10–15%) so that the reactor was operated in the differential mode. This was also tested by plotting the alcohol conversion as a function of the reciprocal space velocity. Linear plots with zero intercepts were always obtained under the reaction conditions employed in the present study, thus confirming the differential regime approximation.

In preliminary experiments, the reactivity of the pure alcohols (methanol, ethanol and isobutanol) has been investigated at 383 K and 1040 kPa. The productivities of the various reaction products as a function of the alcohol partial pressure are displayed in Fig. 1a, Fig. 1b and Fig. 1c. In the case of methanol (Fig. 1a), dimethyl ether (DME) was the only observed reaction product, with a rate of formation that at first increased with increasing the alcohol partial pressure and then reached a constant value. Similar results have been obtained in the case of ethanol (only diethyl ether, DEE, has been formed), whereas a more complex situation was apparent in the case of isobutanol (Fig. 1c). In this case, two major reaction products were detected, namely isobutene (along with minor amounts of 1- and 2-butenes) and tertiary-butyl iso-butyl ether, TBIBE. Minor quantities of di-iso-butyl ether, DIBE and of octenes (not reported in the figure) were also obtained. Upon increasing the isobutanol partial pressure the rates of isobutene and octenes formation showed a maximum, that of TBIBE gradually increased whereas that of DIBE is apparently not affected. Formation of octenes was not detected at high isobutanol partial pressure, thus ruling out any butenes oligomerization at low isobutanol conversion levels.

In the alcohol coupling experiments, methanol + isobutanol and ethanol + isobutanol mixtures were fed over the Amberlyst-35 catalyst at 383 K and 1040 kPa. Experiments have been performed in which the rate of the alcohol dehydration was studied as a function of the partial pressure of each alcohol while keeping constant the partial pressure of the other alcohol.

Fig. 2a and Fig. 2b report the results obtained in the case of the ethanol + isobutanol coupling experiments. In addition to the products obtained in the case of the pure alcohols, the formation of C_6 mixed ethers was also observed. The mixed ethers are ethyl iso-butyl ether, EIBE and ETBE.

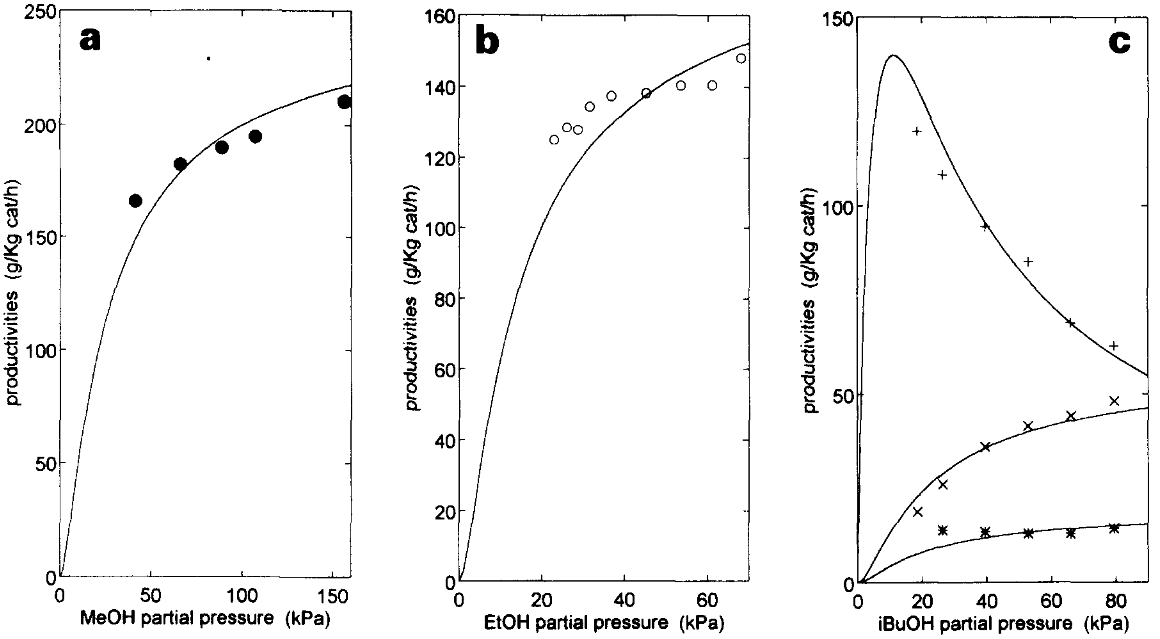

Fig. 1. Rates of formation of DME (●), DEE (o), isobutene (+), TBIBE (x) and DIBE (*) as a function of methanol (a), ethanol (b) and isobutanol (c) partial pressure over Amberlyst-35. $T = 383$ K, $P = 1040$ kPa.

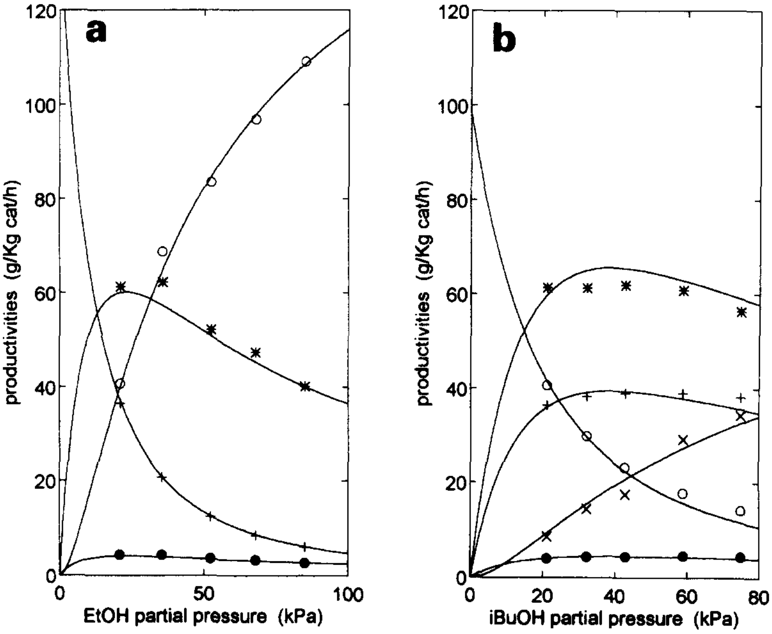

Fig. 2. Rates of formation of EIBE (*), DEE (o), isobutene (+), TBIBE (x) and ETBE (●) as a function of (a) ethanol partial pressure ($P_{BuOH} = 21$ kPa) and (b) isobutanol partial pressure ($P_{EtOH} = 21$ kPa) over Amberlyst-35. $T = 383$ K, $P = 1040$ kPa.

The rate of formation of EIBE was significantly higher than that of ETBE.

A comparison of Fig. 1b and Fig. 1c with Fig. 2a and Fig. 2b clearly shows that the space time yields of the products originating from the pure alcohol dehydration experiments (e.g., butenes, DEE, TBIBE) are significantly depressed by the presence of the other alcohol reactant. This effect was particularly evident in the case of butenes, whose formation was reduced by roughly a factor of 3 by the presence of ethanol. The formation of the mixed C_6 ethers, on the other hand, shows maxima on the dependencies on partial pressure of both ethanol and isobutanol.

Similar results have been obtained in the case of the methanol + isobutanol coupling experiments, where the formation of C_5 ethers (methyl iso-butyl ether, MIBE and MTBE) has been observed. As in the case of the ethanol + isobutanol mixtures, the formation of MIBE was favored with respect to MTBE. Butenes formation was strongly hindered by the presence of methanol and the formation of the mixed C_5 ethers showed maxima on the dependencies on partial pressure of both alcohols.

The effect of the reaction temperature on the ethanol + isobutanol coupling has also been investigated. Accordingly, the partial pressure dependence studies have been performed at different reaction temperatures, e.g., 377, 389 and 403 K. The results, not reported for the sake of brevity, showed that increasing temperature enhanced the rate of formation of all the reaction products.

Mechanistic aspects of the alcohol coupling reaction have been addressed by means of isotopic labelling experiments in which $CH_3^{18}OH$ + isobutanol and $CH_3CH_2^{18}OH$ + isobutanol mixtures were fed to the catalyst. In the case of the $CH_3CH_2^{18}OH$ + isobutanol experiment, DEE contained almost exclusively ^{18}O, whereas only ^{16}O was present in the C_8 ethers TBIBE and DIBE, thus indicating that no oxygen scrambling had occurred during the experiment. EIBE retained the ^{16}O of isobutanol, whereas ETBE incorporated the ^{18}O of $CH_3CH_2^{18}OH$.

Similar results were obtained in the case of the $CH_3^{18}OH$ + isobutanol coupling experiments. Indeed, MIBE retained the ^{16}O of isobutanol whereas ETBE incorporated the ^{18}O of the labelled methanol. This clearly indicates that the formation of the ethers containing the iso-butyl or the tert.-butyl group (e.g., MIBE and EIBE vs MTBE and ETBE) occurs via different reaction paths.

4. Discussion

The nature of the reaction products obtained in the methanol + isobutanol and ethanol + isobutanol coupling and the results of the isotopic labelling experiments as well, point out that the formation of the ethers cannot be completely ascribed to an acid catalysis involving carbenium ion intermediates. The S_N1 pathway would lead to the formation of a stable tert.-butyl carbenium ion from isobutanol, which in turn would form MTBE or ETBE upon addition of methanol or ethanol, respectively. However, these species are observed only in minor amounts during the alcohol coupling experiments. Accordingly, a different and parallel reaction pathway that accounts for the formation of MIBE and EIBE must be considered. The isomerization of MTBE or ETBE to MIBE or EIBE, respectively, has been ruled out on the basis of the isotopic labelling experiments previously reported and by specific experiments in which MTBE and ETBE have been fed to the reactor.

A possible route that accounts for the formation of MIBE and EIBE is the direct coupling of two alcohol molecules via a S_N2 mechanism. Accordingly, MIBE (or EIBE) is formed via an isobutanol molecule attacking a methanol (or ethanol) molecule. The attack of methanol (or ethanol) on isobutanol is ruled out on the basis of the steric hindrances of the isobutanol molecule, in line with the chemistry of the S_N2 reaction [6]. The resulting ethers MIBE and EIBE retain the isobutanol oxygen atom, in line with the results of the isotopic labelling experiments. Along similar lines, the formation of DME, DEE or DIBE is expected to involve a S_N2 reaction between two methanol, ethanol or isobutanol molecules, respectively.

In the coupling of the two alcohol molecules, the reactants have to be activated. The nature of the adsorbed reactive intermediates is still unclear, beyond the exclusion of the tertiary carbenium ion. The participation of (i) alcohol molecules hydrogen-bonded to the $-SO_3H$ acid sites, or (ii) oxonium ions formed according to the reaction:

$$\text{-SO}_3\text{H} + \text{ROH} \rightarrow \text{-SO}_3^- \ {}^+\text{H}_2\text{OR}$$

or (iii) sulfonic esters formed according to the stoichiometry:

$$\text{-SO}_3\text{H} + \text{ROH} \rightarrow \text{-SO}_3\text{R} + \text{H}_2\text{O}$$

has been proposed [2]. The coupling may occur through the reaction between an adsorbed alcohol molecule and an alcohol molecule supplied by the gas-phase, according to an Eley–Rideal mechanism, or between two adsorbed molecules. However, the data obtained by varying the alcohol partial pressure showed that (i) the formation of DME, DEE and DIBE follows a 'saturation' kinetics since the rates of formation of these species at first increases upon increasing the alcohol partial pressure and then became constant at high alcohol partial pressures; (ii) the rates of formation of MIBE and EIBE from methanol + isobutanol and ethanol + isobutanol mixtures show maxima when the partial pressure of either alcohol was varied, thus indicating a competitive adsorption of the two alcohols. Therefore, a mechanism involving two surface bound alcohols seems appropriate [7].

The dehydration of the alcohols to the corresponding olefins also presents striking mechanistic features. Indeed, the partial pressure dependence study clearly shows that the rate of isobutene formation exhibited a maximum with the isobutanol pressure and was strongly depressed by the presence of methanol or ethanol. This clearly indicates a self-poisoning effect of isobutanol and a retarding effect of the other alcohol molecules. Accordingly, a dual-site mechanism could be invoked to explain the dehydration of isobutanol to isobutene. One site is possibly activating the alcohol molecule and a second empty acid acts in a cooperative fashion in the dehydration step. The reaction might occur via a concerted E_2 mechanism or with the participation of a carbenium ion or olefinic intermediate. This latter pathway is also corroborated by the formation of the ethers containing the tertiary butyl group (e.g., MTBE, ETBE, TBIBE), which are likely formed by attack of methanol, ethanol and isobutanol, respectively, on the olefinic or carbenium ion intermediate. In agreement with this reaction mechanism, the isotopic labelling experiments show that the oxygen atom of methanol or ethanol was retained in the resulting ether.

Based on the mechanistic information provided by the isotopic labelling experiments and by the alcohol partial pressure dependence study, the general reaction pathway for the alcohol dehydration reactions over the Amberlyst-35 catalyst can be summarized as follows:

$$\text{R}_1\text{-OH}_{(a)} + \text{R}_2\text{-OH}_{(a)} \rightarrow \text{R}_1\text{-O-R}_{2(g)} + \text{H}_2\text{O}_{(a)} \quad (1)$$

$$\text{iB-OH}_{(a)} + \text{-SO}_3\text{H} \rightarrow [\text{-SO}_3\text{-tB}^+] + \text{H}_2\text{O}_{(a)} \quad (2)$$

$$[\text{-SO}_3\text{-tB}^+] \rightarrow \text{isobutene}_{(g)} + \text{-SO}_3\text{H} \quad (2a)$$

$$[\text{-SO}_3\text{-tB}^+] + \text{R}_2\text{-OH}_{(g)} \rightarrow \text{tB-O-R}_{2(g)} + \text{-SO}_3\text{H} \quad (2b)$$

where (a) and (g) stand for adsorbed and gas-phase, respectively; R_1, R_2 = methyl, ethyl or isobutyl groups; iB = isobutyl group; $-SO_3H$ = acid site; tB^+ = tertiary butyl carbocation.

Reaction (1) represents the reaction of two adsorbed alcohol molecules according to the S_N2 mechanism previously depicted. It is responsible for the formation of the symmetrical ethers DME, DEE and DIBE (when $R_1- = R_2-$ = methyl, ethyl and isobutyl, respectively) as well as for the formation of MIBE and EIBE (with R_1- = isobutyl and R_2- = methyl or ethyl, respectively).

Reactions (2) and (2a) are representative of the dehydration of isobutanol to isobutene. As previously discussed, the alcohol dehydration likely involves the reaction of an adsorbed alcohol molecule with an empty acid site $-SO_3H$. It is noted that only isobutanol has been considered as a participant in this reaction, since no ethylene formation has been observed from ethanol. The intermediacy of an adsorbed tert.-butyl carbocation, originating from the rearrangement of the isobutyl primary carbocation, has been invoked.

Table 1
Kinetic expressions for the dehydration of alcohols over Amberlyst-35

$$r_{\mathrm{DEE}} = k_{\mathrm{DEE}} \theta_{\mathrm{E}}^2 = \frac{k_{\mathrm{DEE}} K_{\mathrm{E}}^2 P_{\mathrm{E}}^2}{(1 + K_{\mathrm{E}} P_{\mathrm{E}} + K_{\mathrm{B}} P_{\mathrm{B}})^2}$$

$$r_{\mathrm{EIBE}} = k_{\mathrm{EIBE}} \theta_{\mathrm{E}} \theta_{\mathrm{B}} = \frac{k_{\mathrm{EIBE}} K_{\mathrm{E}} P_{\mathrm{E}} K_{\mathrm{B}} P_{\mathrm{B}}}{(1 + K_{\mathrm{E}} P_{\mathrm{E}} + K_{\mathrm{B}} P_{\mathrm{B}})^2}$$

$$r_{\mathrm{iB}} = k_{\mathrm{iB}} \theta_{\mathrm{B}} \theta_{\mathrm{V}} = \frac{k_{\mathrm{iB}} K_{\mathrm{B}} P_{\mathrm{B}}}{(1 + K_{\mathrm{E}} P_{\mathrm{E}} + K_{\mathrm{B}} P_{\mathrm{B}})^2}$$

$$r_{\mathrm{ETBE}} = k_{\mathrm{ETBE}} \theta_{\mathrm{B}} \theta_{\mathrm{V}} P_{\mathrm{E}} = \frac{k_{\mathrm{ETBE}} K_{\mathrm{B}} P_{\mathrm{B}} P_{\mathrm{E}}}{(1 + K_{\mathrm{E}} P_{\mathrm{E}} + K_{\mathrm{B}} P_{\mathrm{B}})^2}$$

r = rate of reaction; k = kinetic constant; K = adsorption equilibrium constant; P = partial pressure; θ = surface coverage; E = ethanol; B = isobutanol; iB = isobutene; V = vacant site.

However, the occurrence of a concerted E_2 mechanism cannot be ruled out.

The carbocation or olefinic intermediate might also be attacked by a gas-phase alcohol molecule (reaction 2b) thus forming the ethers with the tert.-butyl group, e.g., TBIBE, MTBE and ETBE. Indeed, addition of isobutene to the alcohol feed led to a significant increase in the formation of TBIBE, MTBE and ETBE.

In the proposed reaction network, reactions (2a) and (2b) have been considered as parallel reactions rather than consecutive. This has been demonstrated by contact time experiments in which the selectivity to the various reaction products is not dependent on space velocity under the operating conditions employed in the present study.

Table 2
Estimates at $T = 383$ K of the kinetic parameters for the alcohol coupling reactions over the Amberlyst-35 catalyst

kinetic constants	estimated value (mol/ ($\mathrm{kg_{cat}}$ h))	adsorption equilibrium constants	estimated value ($\mathrm{kPa^{-1}}$)
k_{DME}	4.52	K_{M}	0.07
k_{DEE}	2.36	K_{B}	0.10
k_{MIBE}	3.34	K_{E}	0.14
k_{EIBE}	3.42		
k_{DIBE}	0.20		
k_{ibut}	11.38		
k_{MTBE}	0.04[a]		
k_{ETBE}	0.03[a]		
k_{TIBE}	0.05[a]		

[a] mol/($\mathrm{kg_{cat}}$hkPa).

On the basis of the reaction scheme depicted above, a kinetic model has been developed by using simple Langmuir–Hinshelwood kinetic rate expressions. In particular, the following assumptions have been utilized:

(i) ethers and isobutene are not adsorbed on the catalyst surface;

(ii) adsorption equilibrium is established for all adsorbed species;

(iii) the rates of formation of DME, DEE, DIBE, MIBE and EIBE according to reaction (1) are proportional to the surface concentrations of the reacting species;

(iv) the rate of isobutene formation according to reactions (2) and (2a) is proportional to the surface concentration of isobutanol and of empty acid sites;

(v) the rates of formation of MTBE, ETBE and IBTBE according to reactions (2) and (2b) are proportional to the surface concentration of isobutanol and of empty sites and to the gas-phase concentration of methanol, ethanol and isobutanol, respectively.

The resulting kinetic expressions following from assumptions (i)–(v) are shown in Table 1 for DEE, EIBE, isobutene and ETBE taken as examples. The rate of formation of the other reaction products can be easily obtained from those reported in Table 1.

The optimal estimates of the kinetic parameters have been obtained by multiresponse nonlinear regression analysis. The task was to minimize the squared deviations between the calculated and the experimental values. The obtained values of the kinetic constants of the major reaction products and of the adsorption equilibrium constants for the alcohol molecules are reported in Table 2. The solid lines reported in Fig. 1 and 2 illustrate a typical model fit of the experimental data. It appears that the productivities of the various products can be quantitatively represented by the kinetic model. Similar fittings have also been obtained in the case of the methanol + isobutanol experiments, with only the rate of isobutene formation being slightly overestimated.

Inspection of Table 2 shows that the values of the kinetic constants for formation of the ethers are in the range of 2–5 mol/($kg_{cat}h$) and are lower than that of olefin formation. In particular, the rate constant for DME formation is slightly higher than that of DEE formation, in line with the higher reactivity of methanol as compared to ethanol. The high value of the kinetic constant for isobutene formation clearly indicates that the formation of this species is kinetically favored over the Amberlyst-35 catalyst. The values of the adsorption equilibrium constants indicate that ethanol is the strongest adsorbed alcohol molecule and methanol is the weakest adsorbed species. This order of strength of adsorption may result from both the basicity of the alcohol molecules (which is expected to increase in the order isobutanol > ethanol > methanol) and from steric factors as well.

The temperature dependence study for the ethanol + isobutanol mixtures has lead to estimates of the activation energies for the etherification reactions, which are in the range of 22–26 kcal/mol. A slightly higher value (30 kcal/mol) has been calculated from the Arrhenius plot for the dehydration of isobutanol to isobutene. This indicates that a temperature increase will favor the formation of the olefins more than the formation of the ethers.

The values of the enthalpies of adsorption for ethanol and isobutanol estimated from the temperature dependence study are -14 and -12 kcal/mol for ethanol and isobutanol, respectively. These data confirm that ethanol is more strongly bonded to the catalyst surface than isobutanol. The values of the alcohol enthalpies of adsorption are slightly higher than the values of the ΔH of vaporization for ethanol and isobutanol (-9.4 and -10.2 kcal/mol, respectively).

5. Conclusions

The results of the present mechanistic and kinetic investigation of the coupling of methanol and ethanol with isobutanol over Amberlyst-35 yield the following conclusions:

(i) the dehydration of mixtures of methanol + isobutanol and ethanol + isobutanol over the Amberlyst-35 catalyst leads to the formation of the symmetrical ethers (DME, DEE and DIBE) and of the mixed ethers (MIBE, EIBE, MTBE, ETBE). The selectivity towards MIBE and EIBE is significantly higher than that towards MTBE and ETBE. Significant amounts of isobutene were also formed, but no ethanol dehydration to ethylene has been observed.

(ii) The formation of the symmetrical ethers (DME, DEE, DIBE) and of the mixed ethers containing the isobutyl group (MIBE, EIBE) is likely occurring via a S_N2 mechanism involving two adsorbed alcohol molecules. Accordingly, the rate of formation of the symmetrical ethers reaches a constant value upon increasing the alcohol partial pressure, whereas the rate of MIBE and EIBE formation shows maxima on the dependencies on partial pressures of the alcohol molecules.

(iii) Isobutene formation requires an adsorbed isobutanol molecule and a near-by vacant acid site. As a consequence, the rate of isobutene formation shows a self-poisoning effect by isobutanol and is retarded by the presence of other alcohol molecules that block the vacant acid sites. The mechanism of the reaction may involve a carbocation or olefinic intermediate, but the occurrence of an E_2-type reaction cannot be ruled out.

(iv) The formation of the ethers containing the tert.-butyl group (e.g., MTBE, ETBE and TBIBE) has not been investigated in detail; however, it is likely that it involves a reaction between the carbocation or olefinic intermediate previously suggested and a gas-phase alcohol molecule.

(v) Based on the reaction network previously suggested, a simple Langmuir–Hinshelwood kinetic model has been developed that quantitatively accounts for the formation of the major reaction products with values of the kinetic parameters that have physical meaning.

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