Systematic kinetic modeling of the propyl *tert*-butyl ether synthesis reaction

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HIGHLIGHTS

- Candidate kinetic models are obtained from a systematic approach.
- All combinations of plausible elementary steps are considered.
- Mathematical and physico-chemical criteria are used to discriminate among models.
- Multimodel inferences based on Akaike Information Criterion are applied.
- The best kinetic model stems from an Eley–Rideal mechanism.

GRAPHICAL ABSTRACT
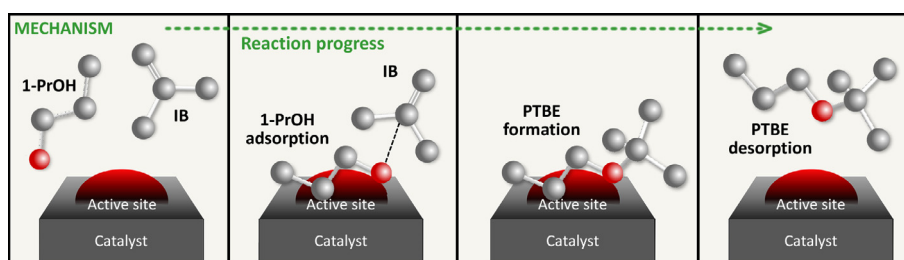
ABSTRACT

The kinetics of the liquid-phase addition of 1-propanol to isobutene to produce propyl *tert*-butyl ether (PTBE) has been studied using the ion-exchange resin Amberlyst™ 35 as the catalyst. Reaction rates free from mass transfer limitations have been experimentally determined in the temperature range 303–352 K, for different initial proportions of alcohol and isobutene, and using two different reactor types (i.e., a batch stirred tank reactor, to obtain most of the experimental data, and a tubular reactor, to validate those results). To find out the best kinetic model, a systematic approach has been adopted. The overall etherification reaction has been decomposed as the result of elementary steps based on Langmuir–Hinshelwood–Hougen–Watson or Eley–Rideal mechanisms. Candidate kinetic equations have been originated from all possible combinations of adsorbed and non-adsorbed compounds, and rate-determining step. The possible effect of the interaction between the reaction medium and the resin on reaction rates has also been examined. Since all experimental data have been used at once in the fit of the kinetic equations, all combinations of significant or non-significant temperature dependence of model parameters have been also considered. As a result, 1404 candidate kinetic equations have been fitted separately to experimental data. Discrimination among models is based on mathematical and physico-chemical criteria. The final choice of the best kinetic model involves multimodel inference. It corresponds to an Eley–Rideal mechanism where one 1-propanol molecule adsorbed on the catalyst reacts with one isobutene molecule from the liquid phase to form one adsorbed PTBE molecule, the surface reaction being the rate-determining step.

1. Introduction

Alkyl *tert*-butyl ethers can be obtained through the addition of an alcohol molecule to 2-methylpropene (isobutene). Common examples of this reaction are the production of methyl *tert*-butyl ether (MTBE) from methanol, and ethyl *tert*-butyl ether (ETBE) from ethanol. Both are used as oxygenate additives for the gasoline pool and they are produced at industrial scale catalyzed by sulfonic macroreticular ion-exchange resins [1–3]. Kinetics of MTBE and ETBE production has been studied extensively for decades now. In the earliest works, kinetic equations were expressed in terms of concentrations [4,5], and later activity-based expressions were found to be more appropriate, given the high
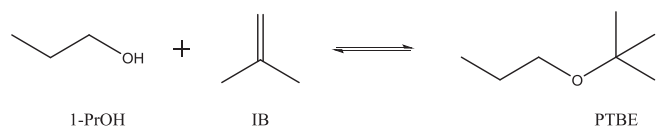
Fig. 1. PTBE synthesis reaction.

non-ideality of olefin-alcohol-ether mixtures [6,7]. Usually, the proposed rate equations for these reactions are derived from Langmuir-–Hinshelwood–Hougen–Watson (LHHW) or Eley–Rideal (ER) mechanisms, where the surface reaction is considered as the rate-determining step. Depending on the assumptions adopted by each author, the reported kinetic models differ mainly on the compounds that adsorb on the catalyst, and on the number of active sites that participate in the rate-determining step of the reaction [6–10].

The next analogous reaction in the alcohol series is the synthesis of propyl *tert*-butyl ether (PTBE), which is obtained by addition of 1-propanol (1-PrOH) to isobutene (IB) (Fig. 1).

PTBE presents suitable properties to be used also as oxygenate additive for the gasoline pool. Moreover, it is good candidate to accomplishing the biofuel target, since 1-propanol can be obtained through fermentative processes of non-edible biomass [11,12]. To date, a kinetic model for the PTBE synthesis in the liquid phase over ion-exchange resins as catalysts cannot be found in the literature. The most relevant references related to this reaction system are the kinetic study of the PTBE gas-phase synthesis by Słomkiewicz [13] and the work on propanol reactivity and equilibrium of the PTBE liquid-phase synthesis by Linnekoski et al. [14], both using Amberlyst™ 15 as the catalyst.

Commonly, the adopted procedure in kinetic modeling is to propose a reduced number of candidate equations and to discriminate among them by selecting the one that better predicts experimental rate data. If temperature dependence is analyzed, kinetic equations are usually fitted using separately data subsets, each obtained from different reaction temperature experiments. The main weak points are: i) one cannot assure that the true model is included in the set of candidate equations; ii) when fitting separately data subsets, the best fitting equation could differ for some subset, although the actual mechanism does not change; iii) the true model could be discarded if overfitting occurs, because at least one fitted parameter is statistically non significant.

In the present work, some actions have been undertaken to overcome the commented weak points in the search of the true kinetic model of the synthesis of PTBE:

i) Trying to ensure that the true model is contained in the set of candidate models, the overall etherification reaction has been decomposed in the elementary steps, according to LHHW and ER mechanisms: reactants adsorption on the catalyst, surface reaction and product desorption. A kinetic equation has been derived from every combination of these steps, i.e., the choice of adsorbed compounds and rate-determining step. In addition, it has been considered that the reaction medium can affect the catalyst activity, hence reaction rates. A kinetic equation has been derived from every combination of elementary steps and the possible effect of the reaction medium, what results in the base set of candidate kinetic equations.

ii) All terms of every kinetic equation have been expressed as a function of the experimental variables (composition and temperature), so all experimental data are used at once to fit each kinetic equation.

iii) For every kinetic equation in the base set, all plausible combinations of significant and non-significant parameters have been considered, each combination originating a different kinetic equation to be fitted.

A more detailed explanation on obtaining the base set of kinetic equations and the derived equations to be fitted is described in Section 3.2.

Some studies adopting this kinetic analysis approach for a similar reaction system can be found in the literature: the kinetics of the ETBE synthesis, from ethanol and an industrial FCC C_4 cut as the isobutene source [15] and, recently, the kinetics of a more complex reaction system, the simultaneous synthesis of ETBE and TAEE (*tert*-amyl ethyl ether) by etherification of isobutene and isoamylenes with ethanol [16]. In those investigations, several combinations of adsorbed and non-adsorbed species on the catalyst, and the possible temperature-dependence of parameters were considered. Also, the inclusion in the kinetic model of a term that accounts for the possible effect of the interaction between the reaction medium and the catalyst on reaction rates was taken into account.

2. Experimental section

2.1. Materials

Reactants were 1-propanol (> 99.7% GC, Sigma-Aldrich) and isobutene, supplied as pure isobutene (> 99.9% GC; Air Liquide) or as a component of a synthetic C_4 mixture (25%wt isobutene, 40%wt isobutane, 35%wt *trans*-2-butene; Abelló-Linde). Chemical standards were used for chromatographic analysis: 2-methyl-2-propanol (TBA, > 99.7% GC, Panreac), 2,4,4-trimethyl-1-pentene (TMP-1, > 98% GC, Sigma-Aldrich), 2,4,4-trimethyl-2-pentene (TMP-2, > 98% GC, Sigma-Aldrich). 2-Methyl-2-propoxypropane (PTBE, > 99% GC) was synthesized and purified in our laboratory.

As the catalyst, the ion-exchange resin Amberlyst™ 35 (A35, The Dow Chemical Company) was used. A35 is a sulfonic macroreticular polymer of styrene-divinylbenzene. Physical properties are listed in Table 1.

2.2. Apparatus, procedure, and analysis

Experiments have been performed at temperatures ranging from 303 to 352 K in two different reactor setups: most of experiments were run in a batch stirred tank reactor, the rest in a continuously operated fixed-bed catalytic reactor, with the main purpose of validating the results obtained in the batch reactor. The initial reaction mixture in batch experiments, and the reactor feed in continuous experiments did not contain ether. Catalyst beads were crushed and sieved to obtain a specific particle diameter, d_p, of 0.25–0.40 mm that avoids internal mass transfer effects on the measured reaction rate, according to a previous work [19].

2.2.1. Batch stirred tank reactor setup

This setup consisted of a 200 cm^3 stainless-steel jacketed batch

Table 1
Physical properties of A35.

Catalyst		Amberlyst 35
Structure		Macroreticular
Divinylbenzene	[%]	20
Skeletal density, ρ_{sk}	[g cm^{-3}]	1.542
Acid Capacity[a]	[meq H$^+$ g^{-1}]	5.32
Mean particle diameter, $d_{p,m}$[b]	[µm]	623
BET surface area, S_{BET}	[m^2 g^{-1}]	29.0
Swollen-state pore volume, V_g[c]	[cm^3 g^{-1}]	0.720
Volume of the swollen polymer phase, V_{sp}[c]	[cm^3 g^{-1}]	0.613
Porosity in polar medium, ϕ_P[d]		0.513
Max. temperature operation, T_{max}	[K]	423

[a] Titration against standard base.
[b] Laser diffraction technique in air.
[c] Inverse Steric Exclusion Chromatography technique [17,18].
[d] $\phi_P = (V_g + V_{sp} - 1/\rho_{sk})/(V_g + V_{sp})$.