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Kinetics of heterogeneously MgO-catalyzed transesterification

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Abstract

The transesterification of ethyl acetate with methanol over magnesium oxide as solid base catalyst was investigated. Intrinsic kinetic data have been obtained in a perfectly mixed slurry batch reactor. The influence of the temperature (283–323 K) and the initial methanol to ethyl acetate molar ratio (M/E: from 0.1 to 10) was investigated over a broad ethyl acetate conversion range (1–95%). A kinetic model was developed based on a three-step 'Eley–Rideal' type of mechanism applied in liquid phase, describing the experimental data over the investigated range of experimental conditions. Transesterification reaction occurs between methanol adsorbed on a magnesium oxide free basic site and ethyl acetate from the liquid phase. Methanol adsorption is assumed to be rate-determining. Other models derived from other mechanisms were rejected based on statistical analysis, mechanistic considerations and physicochemical interpretation of the parameters. The calculation of activity coefficients accounting for non-ideality had to be incorporated in the parameter estimation procedure.

Keywords: Transesterification; Kinetics; Elementary reactions; Solid base catalyst; Magnesium oxide

1. Introduction

Transesterification of alkyl esters plays an important industrial role with numerous applications, such as the production of biodiesel [1], the production of polyester in the polymer industry and the curing of resins in the paint industry [2]. Transesterification reactions can be performed using acid catalysts, such as sulfuric, sulfonic, phosphoric and hydrochloric acids [2,3] or using base catalysts, such as metal hydroxides [4], metal alkoxides [5], alkaline-earth oxides [6] or hydrotalcites [7]. However, base catalysts are preferred to acid catalysts because of the higher reaction rates and the lower process temperatures as compared to acid-catalyzed transesterification [4]. Nowadays, most industrial applications are performed in batch or continuous stirred tank reactors at temperatures ranging from 60 to 200 °C using homogeneous base catalysts, such as alkaline hydroxides or metal alkoxides [2,8]. However, the use of homogeneous base catalysts requires neutralization and separation from the reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy. Heterogeneous solid base catalysts, able to catalyze the transesterification of alkyl esters could solve these issues; they can be easily separated from the reaction mixture without any solvent, show easy regeneration and have a less corrosive character, leading to safer, cheaper and more environment-friendly operation. Therefore, it is of interest to investigate the possibility to replace the homogeneous base catalysts by solid base catalysts in transesterification reactions, and in particular, to study the kinetics of the heterogeneously base-catalyzed process in order to evaluate its industrial applicability.

Although several authors investigated the kinetics of transesterification catalyzed by homogeneous base catalysts [4,5,9,10], there is very little information concerning the kinetics of heterogeneous base-catalyzed transesterification. Hattori et al. [11] have proposed a mechanism for the transesterification of ethyl acetate with different alcohols catalyzed by a variety of solid base catalysts, particularly

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Abbreviations: EtOAc, ethyl acetate; EtOH, ethanol; LHHW, Langmuir–Hinshelwood–Hougen–Watson; M/E, methanol to ethyl acetate; MeOAc, methyl acetate; MeOH, methanol; MgO, magnesium oxide; RSSQ, residual sum of squares

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Nomenclature

a_i	activity of component i (mol m^{-3})
A	pre-exponential factor (m^3 kg_{cat}^{-1} s^{-1})
A^*	reparameterized pre-exponential factor (m^3 kg_{cat}^{-1} s^{-1})
$A_{peak,i}$	Surface peak area of component i (V s^{-1})
b	parameter vector
CF_i	calibration factor of component i with regards to *n*-octane
$d_{1,2}$	Flory–Huggins combinatorial term
d_I	impeller diameter (m)
d_p	solid particle diameter (m)
$E_{a,i}$	activation energy of adsorption of component i (J mol^{-1})
g	acceleration of the gravity (m^2 s^{-1})
k_i	reaction rate coefficient of adsorption of component i (m^3 kg_{cat}^{-1} s^{-1})
K_{eq}	equilibrium constant of the overall reaction
K_A	equilibrium constant of alcohol adsorption (m^3 mol^{-1})
L_i	surface concentration of component i (mol m^{-2})
N	total number of experimental points or components
n_i	number of moles of component i (experimental) (mol)
$\hat{n}_i$	number of moles of component i (calculated) (mol)
N_I	impeller revolution speed (s^{-1})
p	number of parameters
$P_{A,B}$	probability ratio between Models A and B
q	induction parameter
r	reaction rate (mol kg_{cat}^{-1} s^{-1})
r_p	average catalyst pore radius (m)
S	objective function
S_{BET}	catalyst BET surface area (m^2 g^{-1})
t	time (s)
W	weight of catalyst (kg_{cat})
X_i	conversion of component i

Greek symbols

α	acidity parameter
β	basicity parameter
γ_i	activity coefficient of component i
γ_i^∞	activity coefficient of component i at infinite dilution
ε_p	catalyst porosity
ε_s	solid fraction in the slurry reactor
θ	fractional surface coverage
λ	dispersion parameter
$\Lambda_{i,j}$	Wilson binary parameter of component i in solvent j
ν	liquid molar volume at 293 K (cm^3 mol^{-1})
ξ	asymmetry parameter due to hydrogen bonding
$\rho_{i,j}$	binary correlation coefficient between parameter i and j
ρ_L	liquid density (kg m^{-3})
ρ_p	catalyst density (kg m^{-3})
$\rho_{p,wet}$	density of the catalyst particle filled with liquid (kg m^{-3})
τ	polar parameter
ψ	asymmetry parameter due to polarity difference

Subscripts and superscripts

0	initial condition
*	basic site
A	Model A (Eley–Rideal-type mechanism, MeOH adsorption rate-determining)
B	Model B (Eley–Rideal-type mechanism, surface reaction quasi-equilibrated)
cat	catalyst
eq	equilibrium
i	component/parameter i
I	impeller
j	parameter j
k	kth experimental point
p	catalyst pellet
s	solvent
tot	total

alkaline earth-metal oxides. The proposed reaction mechanism consists of five steps as shown in Fig. 1. The first two steps (steps 1a and 1b) describe the adsorption of alcohol and ethyl acetate on two neighboring free catalytic sites. The two adsorbed species then react to form a surface intermediate (step 2) that further decomposes to methyl acetate and adsorbed ethanol (step 3) that finally desorbs (step 4). Hattori et al. also proposed different rate-determining steps according to the basicity of the catalyst. With catalysts such as MgO, La_2O_3 or KF/alumina, methanol adsorption is assumed to be the rate-determining step of this mechanism while the surface reaction step becomes rate determining with catalysts having a higher basicity, such as BaO, CaO or SrO. However, this mechanistic study did not provide values of activation energies or rate constants. Kinetic studies using homogeneous base catalysts proposed a pseudo-second-order rate law with activation energies ranging from 22 to 83 kJ mol^{-1}, depending on the type of alcohol and ester used [3–5,8,9].

Our goal was to develop a kinetic model based on a fundamental reaction mechanism that describes the transesterification reaction of ethyl acetate with methanol catalyzed by magnesium oxide. Therefore, intrinsic kinetic experiments have been performed in a perfectly mixed slurry batch reactor.