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Ion-exchange resin catalyzed transesterification of ethyl acetate with methanol: Gel versus macroporous resins

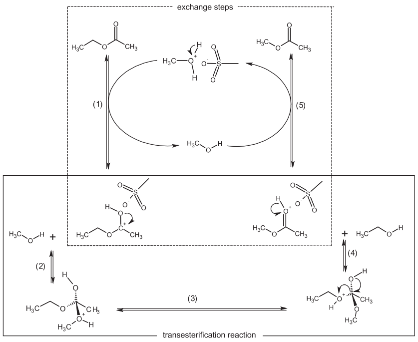
Evelien Van de Steene [a,b], Jeriffa De Clercq [a], Joris W. Thybaut [b,*]

[a] Department of Industrial Technology & Construction, Ghent University, Valentin Vaerwyckweg 1, B-9000 Ghent, Belgium
[b] Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Zwijnaarde, Belgium

HIGHLIGHTS

- Resin swelling determines active site accessibility and, hence, catalytic activity.
- Gel resins outperform macroporous ones in ethyl acetate transesterification with methanol.
- The kinetic model implicitly accounts for swelling by assuming full active site coverage.
- Protonated ethyl acetate reaction with bulk methanol is rate determining.
- The selected Eley–Rideal mechanism is independent of the resin used.

GRAPHICAL ABSTRACT



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ABSTRACT

The liquid-phase transesterification kinetics of ethyl acetate with methanol to ethanol and methyl acetate catalyzed by gel (Lewatit K1221) and macroporous (Lewatit K2640, Lewatit K2629 and Amberlyst 15) ion-exchange resins have been investigated. The effects of the resins' swelling, the initial reactant molar ratio (1:1–10:1) and the temperature (303.15–333.15 K) on the reaction kinetics were assessed. Macroporous Lewatit K2629, Lewatit K2640 and Amberlyst 15 exhibit a clearly inferior catalytic activity compared to the gel type Lewatit K1221, despite the similar number of sulfonic acid active sites. This trend in catalytic activity can be explained by the differences in acid site accessibility, which are related to the resins' swelling behavior and, hence, the extent of divinylbenzene cross-linking in the polymeric structure. A fundamental kinetic model, accounting for the chemical elementary steps as well as for the physical swelling due to solvent sorption, was constructed. According to this model (1) all active sites are initially occupied by protonated methanol, (2) the esters are activated by a proton exchange with protonated methanol and (3) the reaction occurs through an Eley–Rideal mechanism with the surface reaction of protonated ethyl acetate with methanol from the bulk as the rate-determining step. The kinetic model adequately described the experimental data as a function of temperature, initial molar ratio and catalyst resin type. A value of 49 kJ mol^{-1} was obtained for the activation energy, irrespective of the resin used. Differences in catalytic activity caused by the accessibility of the active sites are reflected by the values obtained for the reaction rate coefficient, which is 3–4-fold higher for a gel type resin compared to the macroporous ones.

1. Introduction

Esterification and transesterification reactions are widely used for the synthesis of fine chemicals, pharmaceuticals, plastics

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* Corresponding author. Tel.: +32 9 331 17 52; fax: +32 9 331 17 59.
E-mail address: Joris.Thybaut@Ugent.be (J.W. Thybaut).

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Nomenclature

a_i	activity of component i
A	pre-exponential factor (mol $\text{kg}_{\text{cat}}^{-1}$ s^{-1})
b	parameter estimate
C_i	observed concentration of component i (mol m^{-3})
$\widehat{C}_i$	predicted concentration of component i (mol m^{-3})
E_A	activation energy (kJ mol^{-1})
k_{SR}	surface reaction rate coefficient (mol $\text{g}_{\text{cat}}^{-1}$ s^{-1})
K_{eq}	equilibrium coefficient of the overall reaction
K_i	adsorption/exchange equilibrium coefficient of component i (m^3 mol^{-1}) (–)
m_i	mass of component i (kg)
n_i	number of moles of component i (mol)
N	total number of experimental points or components
p	number of parameters
r	reaction rate (mol $\text{kg}_{\text{cat}}^{-1}$ s^{-1})
R_i	net production rate of component i (mol $\text{kg}_{\text{cat}}^{-1}$ s^{-1})
RSSQ	residual sum of squares
S	swelling ratio
t	time (s)
T	temperature (K)
W	weight of catalyst (kg_{cat})
X_i	conversion of component i

Greek symbols

β	parameter
γ_i	activity coefficient of component i
θ_i	fractional coverage of catalyst surface by component i
v_i	stoichiometric coefficient for component i

Subscripts and superscripts

0	initial conditions
cat	catalyst
eq	at equilibrium
i	component i
T_{ref}	at reference temperature

monomers, and many other products [1,2]. The significant expansion of the biodiesel production capacity in the last decade has reinforced the interest in both reactions and the optimization of their industrial implementation.

Transesterification reactions can be performed using base catalysts, such as metal hydroxides, metal alkoxides, alkaline-earth oxides or hydrotalcites or using acid catalysts, such as sulphuric, sulfonic, phosphoric, hydrochloric acids and acid ion-exchange resins [3]. Amongst this wide variety of catalysts, acid ion-exchange resins are gaining popularity as transesterification catalyst [4], as they are ecofriendly, noncorrosive, heterogeneous and have a good stability and reusability. Transesterification has been investigated both in a qualitative as a quantitative manner [4–15]. Pseudo-homogeneous (PH) as well as adsorption-based mechanisms, such as Eley–Rideal (ER) and Langmuir–Hinshelwood (LH) mechanisms have been used for this purpose [6,13,14,16]. The most commonly used one is the simpler pseudo-homogeneous model that gave similar simulation results as the Langmuir–Hinshelwood model [14]. However, pseudo-homogeneous models lack any adsorption or swelling phenomena and, hence, more advanced models are required when assessing the kinetics on a series of heterogeneous catalysts with varying properties, such as the resins considered in the present work.

Swelling due to solvent sorption is of particular importance in the use of ion-exchange resins [17,18]. When a dry resin, which inherently has a very low surface area, is brought into contact with a solvent, it can swell. The solvent is sorbed by the resin until equilibrium is reached with the liquid bulk phase. Because of the flexible structure of the polymeric resin, its volume increases during solvent sorption. When, e.g., water diffuses into the resin, it interacts with its sulfonic acid sites, forms protonated water molecules and primary solvation shells. As a consequence of this solvation additional water molecules are attracted into the gel phase and further extend the solvation shell. This phenomenon is observed at the macro scale as the swelling of the resin, thanks to the elastic properties of the polymeric network [17,19,20].

When contacted with multicomponent mixtures, different components tend to sorb on a resin to a different extent [19,21–24]. Sorption results in significant partitioning of the components between the bulk phase on the one hand and the resin on the other. The partitioning as well as the resins' swelling depend on the physicochemical characteristics of the components and the resin involved. These include not only the liquid phase composition and temperature but also the functional groups and the structure of the polymeric resin, i.e. type of polymer, polystyrene or polyacrylic and degree of cross-linking [24].

A comprehensive theory for describing sorption and swelling behavior of various components on a wide range of resins, related to resin catalyzed kinetics is not available yet [25]. Nevertheless, for the esterification of free fatty acids with methanol, Tesser et al. [17] accounted already for swelling phenomena in their kinetic model, by the use of a physical phase equilibrium relationship between the resin-absorbed and the external liquid phase.

Two types of morphology in cross-linked polymer resins are commercially available and have been investigated: a gel type such as Lewatit K1221 and macroporous type resins such as Lewatit K2640, Lewatit K2629, and Amberlyst 15. Gel type resins are available as a hard glassy transparent resin bead which consists of a homogeneous matrix on a microscopic scale without discontinuities [4]. When dry, it has a very low surface area: typically less than 10 $\text{m}^2\ \text{g}^{-1}$ as measured by BET. Even small molecules diffuse very slowly through this polymeric resin, which does not have permanent pores. As described above, these resins swell when brought into contact with a solvent, with the swelling degree typically being inversely related to the divinylbenzene (DVB) content. Swelling creates space or 'solvent porosity' inside the resin and allows ready access to the polymer network for small molecules [26]. A macroporous type resin, on the other hand, is available as a hard opaque bead which has permanent pores and is relatively rigid. Hence, it typically exhibits a less pronounced swelling behavior compared to a gel type resin. The polymer matrix can be regarded as a conglomerate of permanent macropores and small gel particles. As a result, these materials have much higher surface areas in the dry state, typically ranging from $\sim$50–1000 $\text{m}^2\ \text{g}^{-1}$, and allow already more easy access to their interior without swelling [26]. The macropore structure does not appreciably vary with the solvent [27]. Nevertheless, when a macroporous resin is contacted with a solvent gel particle swelling occurs to some extent [26]. Studies on the kinetics of the acetic acid and amyl alcohol esterification catalyzed by gel and macroporous resins [9,28] typically observed a higher activity of the gel type resin versus the macroporous one, e.g. Amberlyst 15.

Several authors have reported that esterification reactions, catalyzed by macroporous ion-exchange resins, occur on the functional groups in the small gel particles of the resin [21,24,26,29]. For the esterification of phenol and acetic acid, Ihm et al. [30] found that the conversion increased with the resins' swelling capability. It was, hence, concluded that the reactant molecules can