



Working-state morphologies of ion exchange catalysts and their influence on reaction kinetics

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ABSTRACT

The esterification of fatty acids is an important pretreatment step in the production of biodiesel from low-cost raw materials. It was thus used as a model reaction in a study of the influence of concentration variations of the polar component (methanol) in a reaction mixture on the morphology and functioning of ion exchange catalysts. For a gel-type ion exchange catalyst, a decrease in the methanol concentration proved to have unambiguously negative effects, as it induced de-swelling of the polymer matrix and diminished the accessibility of the active centers. For macroreticular ion exchange catalysts, on the other hand, the drop in methanol concentration had a positive influence on the efficiency of the catalytic action mechanism of the acidic centers. This was due to the existence of some swelling-independent porosity, causing a shift from a general to a specific catalysis-like mechanism.

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1. Introduction

A specific property of ion exchange catalysts is their ability to swell when in contact with the reaction environment. For the gel-type kind of these materials, the accessibility of all the usable active centers strongly depends on the swelling of their polymer skeletons. Macroreticular ion exchangers, on the other hand, exhibit a certain amount of porosity that is independent of swelling, and these materials thus remain open even in the dry state. However, with such pores, only a fraction of the supported active groups are directly accessible. Macroreticular ion exchangers also swell in contact with the reaction environment, and in this case, the swelling causes the opening of both additional “true” pores and pores within the swollen polymer gel. The selection of a proper ion exchange catalyst for a particular reaction therefore strongly depends on the ability of the reaction mixture to induce swelling of the catalyst.

Gel-type polymers offer potentially much higher supporting capacities than their macroreticular counterparts. The surface area of polymer chains in 1 g of styrenic polymers can be as high as 2000–4000 m²/g [1]. However, a full exploitation of this enormous potential support capacity would require an extremely high expansion (swelling) of the polymer network, which, in turn, would result in unacceptable mechanical properties. Hence, in practical applications, the accessibility of the supported centers is always somewhat limited, depending on the expansion (swelling) of the polymer

matrix and the steric demands of a particular reaction (i.e., the molecular size of the reactants and/or the activated complex).

Macroreticular supports contain pores that remain open even in the absence of swelling. In the dry state, commercial ion exchange catalysts exhibit a BET surface area that is usually lower than about 50 m²/g. Such small surface areas can accommodate only very limited fractions of the supported active centers. In spite of this, this type of catalyst has been successfully used in a number of industrial processes involving reagents in poorly swelling polymer matrices (e.g. [2]). Apparently, in the macroreticular catalysts, even poorly swelling solvents are able to cause additional porosity and improve access to more active centers than the size of the dry surface area would suggest. However, the polymer matrix of macroreticular materials is generally much more crosslinked than the polymer mass of the gel types, signifying that in macroreticular materials, even the best swelling solvent can render accessible only a fraction of the amount of active centers that, under similar conditions, are accessible in low-crosslinked polymer gel-type supports (e.g. [3]). For polar reaction environments, the reasonably swelling polymer matrix of gel-type ion exchange catalysts is definitely the preferred choice. Macroreticular ion exchangers become a viable option when all the reaction components swell the ion exchange catalyst only poorly, e.g., phenol alkylation with olefins, or when the swelling component of the reaction mixture is almost completely consumed during the course of the process, e.g., synthesis of MTBE or ETBE.

Differences between gel and macroreticular morphologies influence more than the accessibility of the active centers. The present investigation describes other possible effects that can be obtained. The work was performed with a reaction system within which a

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relevant range of reaction conditions was achievable in order to control the swelling of the catalyst polymer matrix. This was done by changing the composition of the reaction mixture.

One such reaction is esterification of fatty acids with methanol; the important preliminary step in the production of biodiesel from non-edible, low-cost raw materials [4]. These raw materials frequently contain significant amounts of free fatty acids (up to 20 wt.% or more). For the most widely used process of biodiesel production based on base-catalyzed reesterification of triglycerides, the presence of fatty acids represents a serious complication because of soap formation and loss of the basic catalyst [5]. For the economy to be acceptable, it is required that the supplied raw materials contain no more than about 1 wt.% of free fatty acids. In more acidic raw materials, the content of free acids must be reduced, which can be most conveniently performed by acid-catalyzed esterification. Generally, this pre-treatment frequently employs a liquid sulfuric acid catalyst which must subsequently be neutralized and either disposed of or recycled. Such a technology is connected with a number of environmental problems. Ion exchange catalysts are in this respect an attractive alternative as they not only help to diminish the production of waste, but also render it possible to convert batch arrangements, typical of homogeneously catalyzed reactions, into continuous processes using flow-through, fixed-bed reactors.

The reaction mixture for the esterification contains basically two types of components: methanol, which is able to swell the ion exchange catalyst, and triglycerides with fatty acids, which have practically no swelling effect what so ever on the strongly acidic ion exchange catalyst. Changes of the proportions of the swelling and non-swelling components (alcohol/oil ratio) can, in addition to influencing the intrinsic kinetics of the esterification reaction, also affect the working-state morphology of the ion exchange catalyst. This paper describes the investigation of these effects on a series of ion exchange catalysts of both gel and macroreticular type.

2. Experimental part

2.1. Materials

The experiments were performed using a model mixture prepared by dissolving 5 wt.% of pure stearic acid (>97%, Fluka, Germany) in a low-acid vegetable oil (0.04%) purchased at the local supermarket. Methanol of p.a. quality (Lachner, Czech Republic) was used as delivered, without any additional purification. The gel-type ion exchanger Amberlyst BD20 (Dow Chemicals, USA) and sulfonated macroreticular polymers M15, M40 and M60 crosslinked with 15, 40 and 60 mol.% divinylbenzene (research samples prepared at the Research Institute for Synthetic Resins and Coatings, Czech Republic) were before use washed with 10% hydrochloric acid and then with deionized water, in order to make sure that they were fully converted into H^+ form. After washing, they were dried at 110 °C overnight and stored over phosphorus pentoxide.

2.2. Apparatus and kinetic experiments

The activity of the ion exchange catalysts was tested in a flow-through arrangement using the apparatus schematically depicted in Fig. 1.

A glass column with PTFE end pieces (3 × 100 mm, Omnifit, USA) was employed as the reactor. Methanol and oil were dosed by separate, computer-controlled pumps (Sanwa Tsusho, Japan). In order to keep the stearic acid dissolved in the oil, the relevant parts of the experimental setup were located in an enclosure in which the temperature was maintained at 60 °C. Catalytic experiments were

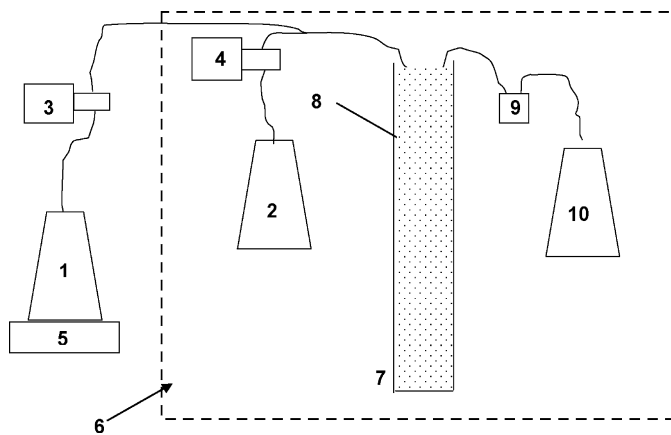


Fig. 1. Scheme of the reactor system. 1,2 – Methanol and oil reservoirs; 3,4 – precise pumps for methanol and oil; 5 – digital balances; 6 – heated enclosure; 7 – water thermostatic bath; 8 – glass reactor; 9 – pressure regulator; 10 – reservoir for products.

performed at a temperature above the methanol boiling point and the pressure in the apparatus was kept at 500 kPa in order to prevent the formation of vapor bubbles. The reactor was charged with dry catalyst and then rapidly filled with methanol. The catalyst was left to swell for a few hours, after which the surplus methanol was aspirated, and the reactor was connected to the apparatus. The pumps were started and the reactor was filled with the reaction mixture, making sure that all air was expelled from the reactor and that a homogeneous catalyst bed was formed. The reactor was subsequently immersed in the thermostatic bath. The pressure regulator (SSI Flow-Through Back-Pressure Regulator, Supelco, USA) connected to the reactor output maintained a pressure of about 500 kPa inside the apparatus, thus keeping the reaction mixture in the liquid state even when the temperature was well above the atmospheric boiling point of methanol.

The flow rate of methanol was determined from the changes in weight of the methanol reservoir, and the flow rate of the whole reaction mixture was determined by weighing the amount of reaction mixture collected at the output. The conversion of the fatty acid in samples collected at regular time intervals was obtained by simple titration with sodium hydroxide solution in isopropanol. When the difference in stearic acid conversion between two consecutive samples was lower than 0.1%, this was considered as evidence of steady state operation being reached. This typically required 3–5 h.

2.3. Morphological characterizations

The dry-state morphology of the macroreticular catalysts M15, M40 and M60 was characterized by a nitrogen adsorption/desorption method using a computerized ASAP 2020 M apparatus and associated software (Micromeritics, USA). The swollen-state morphology of the samples was assessed by inverse steric exclusion chromatography (ISEC) using a methodology described elsewhere [6].

3. Results and discussion

The oil and methanol components of the reaction mixture had only a limited miscibility. It was possible to achieve a homogeneous solution when the methanol concentration in the mixture was lower than about 20 wt.%. Above this limit, two separate phases existed in the reaction mixture: a predominant methanol-saturated oil phase and a small volume of an alcohol-rich phase. This solubility behavior was the key factor determining the dependence of the catalyst performance on the methanol concentration. Fig. 2 dis-

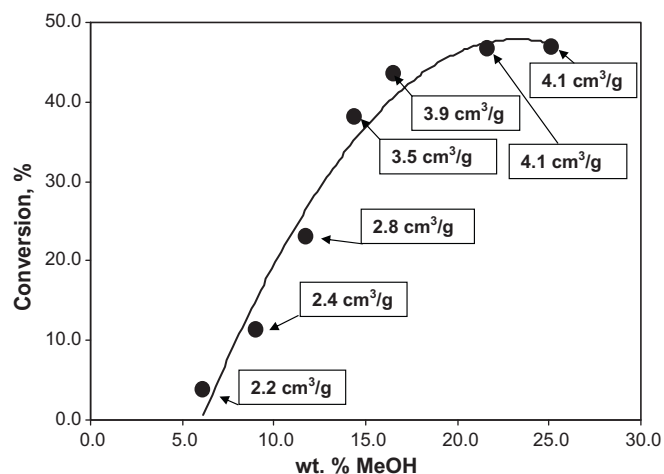


Fig. 2. Dependence of the stearic acid conversion on the methanol concentration in the reaction mixture comprising the gel-type ion exchange catalyst Amberlyst BD20, together with the specific volume of the catalyst bed in the working state. Temperature: 75 °C, 5 wt.% of stearic acid in edible oil, W/F=55 g catal (dry), h/mol stearic acid.

plays the dependence of the stearic acid conversion at a constant reciprocal weight hour space velocity (W/F) for the gel-type ion exchanger Amberlyst BD20.

At a concentration of MeOH above 20 wt.%, the reaction conversion was independent of the methanol concentration due to saturation of the catalyst with the alcohol. However, when its concentration was below this limit, the reaction mixture became unsaturated with methanol and the conversion started to fall. This should not be interpreted as a simple lowering of the reaction rate with the decrease in concentration of a reaction component. The methanol concentration influenced not only the intrinsic reaction kinetics, but also the morphology (swelling degree) of the ion exchange catalysts. In the employed glass reactor, it was easy to follow the changes of the catalyst volume with the methanol concentration.

Each experimental point in Fig. 2 was annotated with the specific volume of the catalyst bed determined at steady-state operation of the reactor at various methanol concentration levels. It was evident that the reduction of the acid conversion closely followed the shrinking of the polymer matrix of the gel-type ion exchange catalyst Amberlyst BD20. Such a shrinking of the polymer matrix signified a decrease of the distances between the polymer chains, and these changes enhanced steric effects of the polymer matrix on the accessibility of the acidic groups for the reactants, which controlled the activity of the ion exchange catalyst.

In an aqueous environment, it was possible to achieve a quantitative correlation between the activity of a large series of ion exchange catalysts and their swollen-state morphology as determined by ISEC [3]. However, in the mixed methanol/oil environment, such a direct comparison of the catalytic activity and morphology data was impossible due to ISEC not being able to provide morphological information on partially swollen polymers [7,8]. However, using a similar approach for a qualitative assessment, it was plausible to conclude that the observed decrease from 4.1 to 2.2 cm³/g of the swollen volume of the catalyst (see Fig. 2) was quite capable of partially blocking the access to the acidic groups inside the swollen polymer gel, especially for molecules as big as those of stearic acid.

The tested macroreticular ion exchange catalyst contained some non-collapsible, swelling-independent pores, which were open even in the dry material. This is evident from values of their BET surface area, listed in Table 1.

Table 1
BET surface area values as determined in dried ion exchange catalysts.

Catalyst	BET surface area (m ² /g)
15% DVB	31
40% DVB	100
60% DVB	233

As can be seen from the table, the dry-state BET surface area increased with an increasing crosslinking degree and consequently also with an increasingly rigid polymer matrix. However, in contact with liquids, the macroreticular ion exchangers swelled and their working-state morphology was believed to differ substantially from that in the dry state. Swelling opens additional “true” pores and also facilitates access to some active centers in the interior of the polymer matrix. One can obtain valuable information on such changes by using ISEC [6,9,10], however, due to specific requirements of this method, it can only be applied to water-swollen ion exchangers and not those swollen by alcohols [7,8]. Information obtained by ISEC analysis of the macroreticular catalysts swollen by water is given in Table 2.

In methanol, the expansion of the polymer network is not as extensive as in water and the discussed application of the quantitative part of the ISEC analysis is thus not fully relevant. Nevertheless, the ISEC results give very valuable qualitative insight into the differences between the three macroreticular catalysts. Polymer A, with the lowest degree of crosslinking, exhibited the most significant difference between surface area of the “true” pores in the dry as opposed to in the fully swollen state. This material also contained the highest amount of swellable polymer mass. On the other hand, in comparison with the dry state in polymer C – the most crosslinked catalyst – contact with the swelling liquid did not lead to the opening of any additional pores and this polymer also exhibited the smallest amount of swellable mass. Due to the high degree of crosslinking in the examined macroreticular polymers, the swellable domains constituted only a small fraction of the polymers’ mass. The range of swollen polymer mass densities detectable by ISEC was about 0.1–1.5 nm³/nm³, covering densities from an extremely low-crosslinked swollen polymer gel to a dense material into which even small molecules could not penetrate without difficulty [6]. Among the tested macroreticular catalysts, only

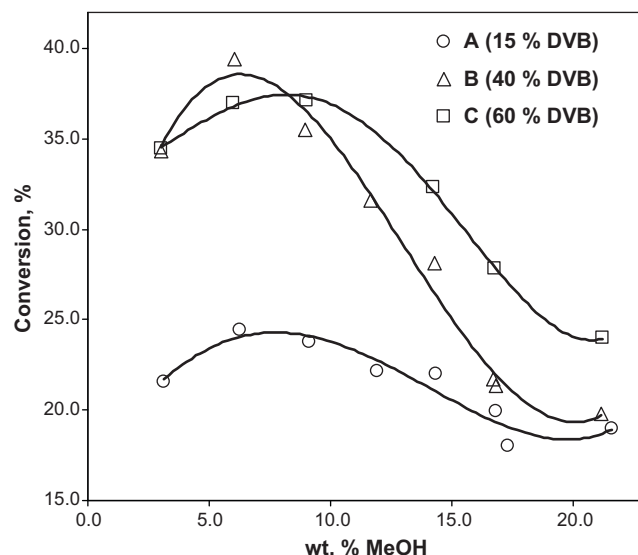


Fig. 3. Dependence of the stearic acid conversion on the methanol concentration in the reaction mixtures of the three macroreticular ion exchange catalysts with varying degrees of crosslinking. Temperature: 85 °C, 5 wt.% of stearic acid in edible oil, W/F=83 g catal (dry), h/mol stearic acid.

Table 2
Results of ISEC characterization of the macroreticular ion exchange catalysts in their water-swollen state.

Catalyst	DVB content (mol.%)	"True" pores			Swollen polymer gel	
		Pore diameter (nm)	Pore volume (cm ³ /g)	Surface area (m ² /g)	Chain density (nm/nm ²)	Gel volume (cm ³ /g)
A	15	22	0.89	156	1.5	0.91
B	40	22	1.39	240	1.5	0.33
C	60	22	1.34	253	1.5	0.18

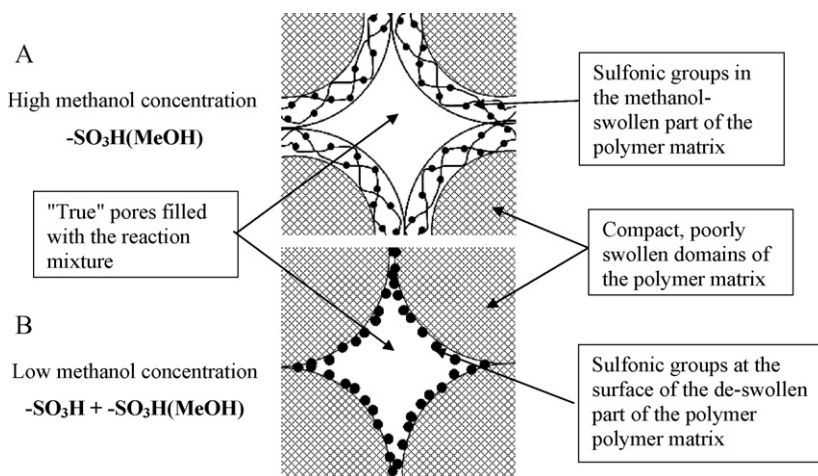


Fig. 4. A schematic offering a simplified description of the situation for macroreticular ion exchange catalysts in contact with (A) the reaction mixture saturated with methanol and (B) the mixture with a low methanol concentration.

the most dense, least swollen polymer gel fraction was detected, but this does not mean that the catalytic reaction could proceed exclusively on the walls of the "true" pores. Most probably, some of the acidic groups located inside the swollen polymer were accessible also for the reactants. However, because this amount was very small, even in the presence of surplus methanol as the swelling agent, the macroreticular ion exchange catalysts were substantially less active than the gel-type Amberlyst BD20. In order to obtain comparable conversions and therefore to carry out all the catalytic tests at similar concentrations of the reaction products, the tests on the macroreticular catalysts were performed at a temperature that was 10 °C higher than that used in the experiments with Amberlyst BD20. The dependency of the stearic acid conversions on the methanol content in the reaction mixture is presented in Fig. 3.

There is evidence that the reaction of the acid conversion, which lowers the methanol concentration in the reaction mixture, is completely different with the macroreticular catalysts as compared to with their gel-type counterparts. For each of the three catalysts, the lowest conversion was observed at conditions when the reaction mixture was saturated with methanol. Subsequently, when the methanol concentration decreased, the conversion increased toward a maximum corresponding to a concentration of 5–10 wt.% of methanol in the reaction mixture. This effect was connected with the response of the macroreticular ion exchange catalyst morphology to changes in the concentration of methanol in the reaction mixture. For the gel-type Amberlyst BD20, de-swelling of the polymer simply closed the access of reaction mixture to the acid centers (Fig. 2), while for the macroreticular catalysts, the situation was more complicated. Nevertheless, Fig. 4 presents a schematic giving a simplified description of the latter case.

Under methanol-saturated conditions, only sulfonic groups occupied with methanol were available for the interaction of the fatty acid molecules with the catalyst. These were located mostly inside the methanol-swollen layer of polymer matrix, on

the walls of the "true" pores. Analogously to general and specific acid catalysis on hydrated and anhydrous sulfonic groups [11,12], methanol-occupied sulfonic groups were much less efficient acid catalysts than their "naked" counterparts. As the methanol concentration in the reaction mixture decreased, this layer collapsed. For stearic acid, on the other hand, there was an increased opportunity to compete with methanol for the sulfonic acid groups, which meant a shift from a slower mechanism of specific acid catalysis to a more efficient mechanism of general acid catalysis. The lower the crosslinking degree of the catalyst, the higher was the sensitivity of its morphology to the degree of swelling. During shrinking from the fully swollen state to the collapsed dry state in the least crosslinked macroreticular ion exchange catalyst A, the surface area of the "true" pore system dropped from 156 to 31 m²/g (cf. Tables 1 and 2). Thus, for catalyst A, the positive effect of the reaction mechanism was almost eliminated by the shrinking of its polymer matrix. For this reason, the dependence of the reaction conversion on the methanol concentration was almost flat in this case. Conversely, in the highly crosslinked catalysts B and C, the difference between the swollen and collapsed morphologies was much smaller and the positive effect of the decrease in methanol concentration on the reaction kinetics were more distinct. With further decrease of methanol concentration prevails the simple effect of lowering of the concentration of one of the key reactants and that is why the conversion goes through a maximum between 5 and 10 wt.% of methanol in the reaction mixture.

4. Conclusions

Changes of the morphology of ion exchange catalysts in response to compositional variations of the reaction environment may influence both the accessibility of the catalytically active centers and the mechanism of their action. A good understanding of these effects may help to optimize catalysts for specific process conditions.

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