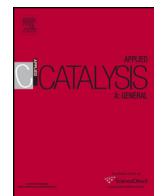




Contents lists available at ScienceDirect

## Applied Catalysis A: General

journal homepage: [www.elsevier.com/locate/apcata](http://www.elsevier.com/locate/apcata)



# Behavior of cation-exchange resins employed as heterogeneous catalysts for esterification of oleic acid with trimethylolpropane

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### ARTICLE INFO

#### Article history:

Received 15 October 2014

Received in revised form

19 December 2014

Accepted 22 December 2014

Available online xxx

#### Keywords:

Ion-exchange resins

Esterification

Biolubricant

Dowex

Amberlyst

Purolite

### ABSTRACT

Four cation-exchange resins (Dowex 50wx2, Amberlyst 36, Purolite CT482 and Purolite CT275DR) were investigated as catalysts in the esterification of oleic acid (OA) with trimethylolpropane (TMP). All four resins accelerated the reaction kinetics. The results showed that in a solvent-free system, the gel-type resin Dowex 50wx2 must be pre-swollen prior to the reaction to achieve high catalytic performance. Contrary, the macro-reticular Amberlyst 36, Purolite CT482 and Purolite CT275DR do not need any pre-treatment to be active. The latter is due to the high crosslinking degree of these resins. Recyclability tests showed that the resins slightly lose their activity after the first use but retain stable activity during the further uses. The activity decay of the recycled resins is referred to the partial blocking of the active sites by the co-produced water. Additional studies confirmed the high stability of the chosen resins toward leaching in polar medium. Overall, both high stability and possibility of reusing through still high catalytic activity make the resins attractive candidates as heterogeneous catalysts for such complex industrial process.

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## 1. Introduction

Esterification of oleic acid (OA) with trimethylolpropane (TMP) is used in the industry for the synthesis of biolubricant – particularly trimethylolpropane trioleate (TMPTO) [1]. Esterification of OA with TMP has not been extensively studied so far. This reaction possesses difficulties among which is the intrinsic molecular hindrance of the reaction components. Besides, high viscosity of the reaction medium negatively impacting the mass transfer and diffusion limitations undoubtedly also minimizes the reaction kinetics. However, this reaction allows performing comparatively clean synthesis of biodegradable TMPTO which makes this process attractive for industrial applications [2–7]. To the best of our knowledge, at the industrial scale, this reaction is catalyzed by homogeneous acidic catalysts (e.g., p-toluenesulfonic acid, tin oxide). This configuration of homogeneous catalysis requests additional separation and purification steps of the final product. The latter challenge could be solved by finding efficient heterogeneous catalysts.

Cation-exchange resins show a high potential for different acid catalyzed liquid phase reactions including esterification of fatty acids [8,9]. The resins are ecofriendly, highly acidic, mechanically stable, chemically versatile and are of low cost [10].

Two different types of resins are known: gel-type and macro-reticular type. The main difference between gel- and macro-reticular types of resins is their textural properties due to their different divinylbenzene content (crosslinking degree). As a consequence of different crosslinking degree, gel and macro-reticular resins possess differences in terms of catalytic behavior, thermal and mechanical stability, and ion-exchange capability. Gel type of resins is characterized by homogeneous matrix with low crosslinking (normally, <12%) and without discontinuities [10]. In the dry state, gel resins have very low surface area and low accessibility of active sites. But when the resin is brought into contact with polar solvents, the polymeric matrix absorbs the solvent thereby increasing its volume and surface area. As a consequence the resin swells. Swelling provides better access to the polymer network for reactant molecules and thus often higher catalytic performance. When the dry gel-type resin is used as a catalyst, a polar solvent is required in order to provide the resin swelling. Otherwise wet form of resin should be used. Contrary to gel resins, macro-reticular resins have high degree of crosslinking and thus possess a more rigid matrix with a lower ability to swelling. Macro-reticular resins

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can be described as agglomerates of very small microspheres that provide higher surface area. The microsphere interstices can be regarded as permanent macropores. The macro-reticular type of resins does not need to be swollen as they have fixed size of pores and rigid texture that provides the access to their interior. Even though they can swell to some little extent [11] (depending on the crosslinking degree), often their swelling is negligible compared to the gel-type of resins.

In this work we investigate the catalytic performance of ion-exchange resins in the esterification of OA with TMP. One gel-type resin (Dowex 50wx2) and three macroreticular resins (Amberlyst 36, Purolite CT482 and Purolite CT275DR) were used as heterogeneous catalysts. Because no additional solvent was used in the reaction, we explored the advantage of an alternative pre-swelling procedure prior the catalytic test for the resins to improve their activity. Moreover, we discussed the catalytic properties of the chosen resins on the basis of their respective texture. This study demonstrates the big potential of ion-exchange resins for complicated industrial process.

## 2. Materials and methods

### 2.1. Chemicals

Oleic acid 90% (Alfa Aesar), trimethylolpropane 98% (Alfa Aesar), pentadecane 99% (Sigma), N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) (Alfa Aesar), acetonitrile, hexane and dimethylformamide (DMF) were of HPLC grade. Ion-exchange resins: Dowex 50wx2 (mesh 50–100  $\mu\text{m}$ ) (Sigma), Amberlyst 36 (600–850  $\mu\text{m}$ ) (Sigma), Purolite CT482 and Purolite CT275DR were kindly provided by Purolite®.

### 2.2. Drying

Before each characterization and catalytic test all the resins were dried at 105 °C under vacuum for 24 h.

### 2.3. Ion-exchange capacity

1 g of resin was placed into 50 ml of 0.1 N KOH. The mixture was agitated overnight at room temperature. Then 10 ml of filtered solution was titrated with 0.1 N HNO<sub>3</sub>. The ion-exchange capacity was calculated by using equation:

$$\text{ion exchange capacity (meq/g)} = \frac{C_{\text{NaOH}} \times (50 - 5 \times V_{\text{HNO}_3})}{m_{\text{resin}}} \quad (1)$$

### 2.4. Leaching test in DMF (elemental analysis)

0.20 g of dry resin was placed into 10 ml of DMF and refluxed at 120 °C with agitation for 19 h. The amount of leached S was measured in the filtered solution by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP AES) on an Iris Advantage apparatus from Jarrell Ash Corporation.

### 2.5. Scanning electron microscopy (SEM)

SEM imaging of metallized sample was performed with a Hitachi TM-1000 scanning electron microscope operating at 15 kV with a current at 10  $\mu\text{A}$ . The metallization of the samples was done by using Au/Pd electrode.

### 2.6. Catalytic test without pre-swelling step

Known quantities of OA and TMP with molar ratio OA:TMP = 3:1 were placed into the batch reactor. The mixture was heated for

about 1 min to melt TMP, after which the resin (1.6 wt%) was added. No additional solvent was used. The start of the reaction was considered after all components were mixed and the reactor was placed in an oil bath at 120 °C. Before the reaction started, the known amount of internal standard (pentadecane) was added to the mixture to facilitate quantification. The reaction was performed under magnetic agitation at 400 rpm and in an open reactor.

### 2.7. Catalytic test with pre-swelling step

In order to induce resin swelling before the catalytic test, the resin was first placed into TMP and heated at 120 °C for 90 min. Then OA was added to this mixture and the catalytic test started (at 120 °C, 400 rpm, open reactor). Before the reaction started, the known amount of internal standard (pentadecane) was added to the mixture to facilitate quantification. The quantities of OA, TMP and resin were the same as in the test without pre-swelling.

### 2.8. Recyclability tests (re-using of resins without any additional treatment)

To check if the resins are still active after the first catalytic test, the recyclability tests were performed. For the latter, after 24 h of the first catalytic test, the hot reaction medium was first removed immediately (unless specified otherwise) from the reactor with syringe. The resin was left in the same reactor and was not washed or dried after the first catalytic test. Then fresh OA, TMP and internal standard (pentadecane) were placed into the reactor. The reaction was started with the same conditions as in the catalytic test with pre-swelling step (the used resin was first treated with pre-swelling step, then OA was added to this mixture and the reaction was run at 120 °C, 400 rpm in open reactor). This procedure was repeated several cycles (24 h each).

### 2.9. Reaction monitoring

For sampling, 10  $\mu\text{l}$  of the reaction mixture was taken at certain time intervals, derivatized as described, and analyzed by gas chromatography (GC). The separation on the GC system was performed with the method as described elsewhere [12]. For the quantification, internal standard (pentadecane) was used which was added to the reaction mixture in the beginning of the catalytic test. In the chromatogram the evolution of mono-, di- and triesters was followed.

### 2.10. Derivatization of esterification products

To improve the gas chromatography (GC) detection and separation of low volatile compounds, the sample was derivatized with BSTFA following the protocol as in [12] with some modifications. Thus, 10  $\mu\text{l}$  of the reaction mixture was solubilized with 2 ml of acetonitrile. Then 500  $\mu\text{l}$  of BSTFA was added and the final mixture was heated at 60 °C for 30 min with vigorous agitation. After the derivatization was finished, the final products were extracted with 2 ml of hexane. The hexane extract was analyzed by GC. Standard deviations of the GC measurements were in the range of 0.04–0.20 (mol/l) for the detection of monoester, 0.03–0.15 for diester and 0.01–0.11 for the detection of triester.

### 2.11. Response factor estimation for mono-, di-, and triesters

Since no standards for the products of esterification of OA with TMP are available commercially, the response factors were estimated by the following procedure.

For the estimation of response factors of the products, standard solutions of 2-ethylhexyl butyrate (EHB), ethyl stearate (ES),

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