**Esterification of myristic acid with methanol using functionalized mesoporous SBA-15**

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**Highlights**

* Propyl-sulfonic acid functionalized SBA-15 catalyst was synthesized.
* The catalyst characterization was performed.
* The esterification reaction of myristic acid with methanol was conducted.
* Kinetic parameters of the reaction were determined.

**1. Introduction**

Acid catalysis is one of the most important catalytic processes in the chemical industry. Industrially important organic transformations include esterifications and transesterifications [1,2]. Solid acid catalysts present an alternative to dangerous and corrosive mineral acid catalysts used in the industry. They contain more environmentally benign components, while providing higher activity and selectivity in comparison with existing homogeneous catalysts.

Mesoporous silicas, a type of solid acid catalyst, are solid inorganic carriers with large surface areas and relatively large ordered pores. Catalysts based on silica are inexpensive, simple to synthesize, and insoluble in most organic solvents, which allow them to be recycled. One type is modified mesoporous silica SBA-15, which is applicable for a wide variety of organic reactions [3].

In this study, mesoporous silica SBA-15 was functionalized with sulfonic acid, a very suitable catalyst for acid-catalyzed reactions. We used a slightly modified single-step synthesis based on simultaneous hydrolysis and condensation. After extensive characterization, the catalyst was tested performing the esterification reaction of myristic acid with methanol.

**2. Methods**

Propyl-sulfonic acid functionalized SBA-15 was synthesized by the one-step co-condensation procedure. The catalyst characterization was performed applying XL-30 scanning electron microscope from Philips and ZetaSizer Nanoseries from Nano, a Tristar II 3020 porosimeter from Micromeritics, FTIR IRAffinity-1 from Shimadzu and TA4000 from Mettler Toledo.

All experiments were performed in a batch reactor at different temperatures, *ϑ* = (55, 60 and 64.5) ºC and stirrer speed, *f*s = 600 min-1, loading of the catalyst, *m*= (0.2, 0.4 and 0.6) g and 10 mL of myristic acid solution in methanol with an initial concentration, *γ* = 15 g/L. The analyses of myristic acid were performed on a Shimadzu GC-2010 equipped with an autosampler AOC-20s and a flame ionization detector (FID).

**3. Results and discussion**

The myristic acid conversion was calculated from determined concentration of myristic acid in the reaction medium. The results at 55 °C are presented in Fig. 1. At 55 °C the conversion of myristic acid after 1 h was 49.9, 68.2, 81.7 % and 93.7, 98.7, 99.0 % after 5 h, applying 0.2, 0.4 and 0.6 g of the catalyst, respectively. We can observe that at the beginning of the reaction the conversion is highly dependent on the amount of catalyst used, while at the end those differences are not so pronounced.



**Figure 1.** Conversion of myristic acid versus time at different catalyst loadings, *ϑ* = 55 °C and *f*s = 600 min-1.

In order to calculate reaction rate constants, the Langmuir-Hinshelwood-Hougen-Watson model was applied. The plots ln((*M* – *X*A)/*M* (1 – *X*A)) versus *t* were constructed for all sets of experimental data. The reaction rate constants were then obtained from the slopes of the lines divided by *c*A0 (*M* – 1) term. The Arrhenius equation was used to calculate activation energies and pre-exponential factors form the determined values of reaction rate constants at different temperatures. The average activation energy for myristic acid esterification was found to be *E*a = 32.2 kJ/mol.

Three subsequent reactions were performed with each batch of the catalyst to test the deactivation between individual repeated reaction. The results revealed that used catalyst is highly resistant to deactivation, because there were practically no differences in the conversion for the 1st, 2nd or 3rd reaction.

**4. Conclusions**

Functionalized mesoporous silica SBA-15 containing sulfonic groups was synthesized with a modified one-step procedure. The results of catalyst characterization reveal that SO3H functional groups are incorporated in the structure of homogenous particles with a random distribution. The catalyst has high catalytic activity in esterification reaction and is easily separated from the reaction medium. We confirmed the high potential of the catalyst’s reuse with no significant loss of activity between consecutive reactions. Additionally, the kinetic parameters of the reaction were determined and they are in accordance with the literature data.

**References**

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