

THE INFLUENCE OF THE CATALYST ON THE RATE CONSTANT OF THE CHEMICAL REACTION OF ESTERIFICATION OF OLEIC ACID WITH METHANOL

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Abstract: Catalysis and catalysts play an important role in modern technology. Catalysis means a change in the rate of a chemical reaction under the influence of a substance that does not change chemically as a result of the reaction. This substance is called a catalyst. The catalyzed reaction proceeds on a different reaction path than the uncatalyzed reaction, thanks to the participation of the catalyst. The reactants are adsorbed on the surface of the catalyst, and then a mutual reaction of the adsorbed species occurs. The reaction produces a product that is desorbed from the surface, while the catalyst remains unchanged and ready for a new reaction cycle. An important piece of information for evaluating the quality of a catalyst is the rate of the reaction in which it participates. The subject of kinetic research is the study of the influence of process parameters on the reaction rate. It is safe to say that the study of reaction kinetics is a central part of chemical reaction engineering. Therefore, the study of the kinetics of real heterogeneous catalysts is of particular importance, both for the improvement of existing catalysts and for the development of new ones. These tests involve determining the influence of process parameters such as the type of catalyst present, temperature, pressure, and concentration of reactants and products on the reaction rate. In this work, the influence of the mass of the catalyst at a certain temperature on the rate constant of the chemical reaction of esterification of oleic acid with methanol was studied. The catalyst used was mesoporous silica, an amorphous solid that can be obtained by drying hydrogels. It was found that as the mass of the catalyst increases, the rate of the chemical reaction constant also increases, i.e. the rate of the esterification reaction increases.

Keywords: catalyst, reaction rate constant, kinetic model, temperature.

1. INTRODUCTION

In practice, the effect of the catalyst is most easily seen in the reduction of the reaction temperature compared to the same reaction without a catalyst. Nowadays, catalytic processes are widely used. Catalysts are used in the chemical and petrochemical industries, in the production of fuels and in environmental protection. One of the most important features of catalytic reactions is the high efficiency of the catalyst, thanks to which the amount of catalyst is often negligible in relation

to the total amount of reactants and products that come into contact with it per unit time. An important feature of catalytic reactions is their specificity, which is reflected in a potentially large number of alternative products from the same reactant. The most important properties of a catalyst that define its quality are activity, selectivity, yield, stability, lifetime, grain shape, mechanical strength, texture, energy consumption, environmental impact, possibility of regeneration, possibility of reproducing the properties during synthesis, hazardousness during handling, price [1-3].

Activity and selectivity are the properties on which the effectiveness of the catalyst most directly depends, which can ultimately be quantified by the yield of the product. Stability is a property of a catalyst that refers to its ability to operate under defined operating conditions for as long as possible while maintaining designed activity and selectivity. The lifetime can be defined by time units of its total duration, i.e. the duration between two regenerations. The shape and size of the catalyst grains are important data for its specification, as information for the designer to determine the diameter of the reactor and the height of the catalytic charge in it, and also for calculating the pressure drop through the catalytic layer. The nature of the catalyst includes its specific surface area, pore structure, and bulk density. The potential of the catalyst as well as the hydrodynamic conditions in the reactor, and thus the final efficiency of the process, depend on these properties. The consideration of energy consumption starts from the thermal effect of the catalytic reaction and is related to the general requirement of minimum energy consumption in the process. The risk in handling the catalyst is determined by its flammability, toxicity, and the possibility of safely disposing of the spent catalyst. Environmental impact of catalysts - the environmental impact of catalysts can be direct or indirect. Solutions that provide multiple regeneration and eventual recovery of a fully deactivated catalyst are becoming more necessary and less of an alternative to disposal of the spent catalyst. As for the price of the catalyst, it is not a decisive factor in the choice, as it is many times lower than the value of the total products produced [1].

In terms of the number and character of the phases present, catalytic reactions can be divided into homogeneous and heterogeneous. In homogeneous reactions, the catalyst and all other participants in the reaction are in one phase, usually in liquid form. A process in which the catalyst and one of the reactants are in a liquid state is often referred to as homogeneous catalysis, regardless of the fact that the other reactant is in a gaseous state. Homogeneous catalytic processes are characterized by a very high utilization of the catalyst and therefore not particularly harsh operating conditions. As a result, we have high selectivity of homogeneous catalysts, because when we have harsh regime conditions (process conditions), the selectivity is usually lower. The disadvantages of

homogeneous catalysis include: the difficult and expensive separation of the product from the catalyst, the possibility of product contamination, frequently corrosion of the equipment when the catalyst is a liquid acid, and the problem of waste when the catalyst is regenerated or recycled. All these problems have led to the increasing use of heterogeneous catalysis in modern industry [2, 3].

In heterogeneous catalysis, the catalyst and the reaction system form separate phases and the catalytic reaction takes place at the boundary between these phases. Usually, the catalyst is a solid substance and the reaction system forms a gaseous or liquid phase [3].

There are the following types of catalytic reactions: redox and acid-base reactions. Redox reactions include oxidation, hydrogenation, dehydrogenation, and halogenation and are catalyzed by metals and semiconductors. Acid-catalyzed reactions include: isomerization of double bonds, structural isomerization, hydrogen transfer, polymerization, alkylation, cracking, hydration, dehydration, and etherification. Acid catalysts owe their properties to the formation of carbo-cations in the organic molecule [3, 4].

Reductions catalyzed by bases, some of which belong to the group that can also be catalyzed by acid catalysts, are highly selective. However, reactions catalyzed by bases are less common in industrial practice because the corresponding catalysts are easily deactivated upon contact with the atmosphere [1, 4, 5].

2. ELEMENTS OF THE CATALYTIC SYSTEM

A catalytic reaction system consists of a catalyst and its environment. The catalyst consists of a primary component and a secondary component. The primary component is the one that is catalytically active, i.e., it is the substance with which the catalytic reaction is carried out. It may be accompanied by a secondary component - a promoter, which supports the action of the primary component by various mechanisms, but does not itself catalytically accelerate the given reaction. The primary component and possibly the promoter form the active phase of the catalyst. It is possible that the catalyst in its entirety consists only of the active phase. This is an example of a so-called compact catalyst (bulk catalyst), in which the active phase is in proportion to the total volume of the catalyst grains.

In contrast to this, although less common, concept of a catalyst is that in which the active substance is dispersed on an inert support. Supported catalysts differ from compact catalysts in that the active phase of the former consists of particles separated by the support particles. The proportions of individual components in the catalyst can vary: usually there are 10-100 times more primary than secondary components, and the proportion of the carrier dominates and is usually 70-99% of the total mass of the catalyst [1, 4].

As a primary substance, the active component is a necessary part of any catalyst. It is usually a metal or metal oxide, but various other chemical forms such as sulfides, carbides, chlorides, etc., may also exhibit catalytic activity.

The promoter is a secondary component of the catalyst, usually not catalytically active itself, but its presence improves the quality of the catalyst. The mechanism of action of promoters can be different, but their effect is reflected in the improvement of all important properties of the catalyst, its activity, selectivity and stability. In terms of the mechanism of action, promoters are divided into structural and textural promoters [1, 4].

The most commonly used catalyst support is alumina (a name for aluminum oxide). It is divided into three classes according to the number of hydroxide groups present: $\text{Al}(\text{OH})_3$ (gibbsite, bayerite, northern strandite), $\text{AlO}(\text{OH}) \cdot x\text{H}_2\text{O}$ (boehmite, diasporite), and $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, of which only the last form is stable and suitable as a catalyst support. Proper-

ties that characterize each support and are of interest from the catalysis point of view are: texture, activity/inertness, stability and acidity.

Other traditional catalyst supports are silicon dioxide (SiO_2), magnesium (MgO), titanium (TiO_2), zirconium (ZrO_2), and also some mixed oxides, the best known of which is silica-alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) [1, 5, 6].

Modern catalyst supports include zeolites, natural or synthetic crystalline microporous solids with a well-defined crystal structure. The zeolite structure defined in this way results in pores with well-defined sizes. Depending on the type of zeolite, the pores extend in one or more directions, forming a three-dimensional network of ordered channels that repeat in a precise arrangement. Because these channels are the size of molecules, zeolites are used very successfully as adsorbents, hence their additional name - molecular sieves. Zeolites are characterized by a very large specific surface area. In addition, their very regular spatial tetrahedral structure contributes to their considerable thermal stability [1, 4, 7].

3. CHEMISTRY OF THE ESTERIFICATION PROCESS

The esterification reaction practically does not occur at the temperature of most industrial processes today. If you increase the temperature, significant conversions occur only at temperatures above 200°C and after several hours. This is because a chemical

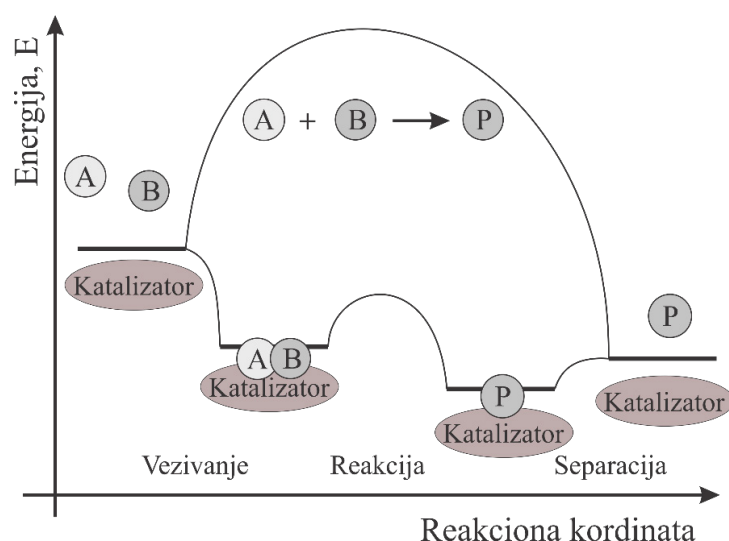


Figure 1. Graphic representation of the reaction path with and without catalyst [3]

reaction is a result of the collision of molecules, and their kinetic energy must be large enough for the collisions to result in a new molecule. The minimum energy that the molecules must have for effective collisions to occur, i.e. for a reaction to take place, is called the activation energy. At the same temperature, a larger number of molecules with an energy equal to or greater than the activation energy is achieved with the help of catalysts that allow a different reaction path with a lower activation energy [3].

The main characteristics of the catalyst are:

- it is not consumed during the reaction and remains unchanged after the end of the reaction,
- by accelerating the reaction, it allows it to be carried out at significantly lower temperatures compared to reactions without a catalyst,
- it does not change the equilibrium constant of the reaction,
- a relatively small amount is sufficient to catalyze the reaction of a large amount of reactants.

Catalytic esterification processes are mainly characterized by the ratio of the aggregate states of reactants, products and catalysts. If the reactants, products and catalysts are in the same phase, the process is homogeneous catalysis, i.e., homogeneous catalysts. The advantage of homogeneous catalysts is good contact with the reactants, i.e. higher effective concentration than heterogeneous catalysts, which usually leads to milder reaction conditions, faster reaction and better selectivity. The disadvantage of this process is the need for separation of unreacted reactants, products and by-products of the reaction. In current industrial practice, homogeneous alkaline catalysts are mostly used. The advantage over acid catalysts is as follows

- high conversion rates under relatively mild reaction conditions,
- short reaction times,
- lower corrosiveness of the reaction conditions allows the use of cheaper materials for the equipment,
- a more favorable ratio of reactants and, as a result, a smaller required volume of the reactor (lower investment costs).

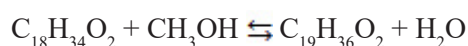
Common catalysts used in acid catalysis of esterification are sulfonic acid and sulfuric acid. The temperature and duration of this reaction are significantly higher than in alkali-catalyzed esterification.

Heterogeneous esterification reaction systems are characterized by a solid catalyst and liquid reactants and products. Therefore, separation of the catalyst from the product is straightforward. The shelf life of solid catalysts can be long. The disadvantage of solid catalysts is usually a much lower effective concentration compared to homogeneous catalysts, so high temperatures are often required to achieve satisfactory conversion in a reasonable time. In addition, the reactants must reach the catalytic sites, which are usually deposited on a solid substrate and, because of the large contact area required, usually in its pores. This requires overcoming the resistance to mass transfer and contributes to the slowing down of the overall reaction. The most commonly studied solid alkaline catalysts are various forms of compounds of alkali or alkaline earth elements, their oxides and carbonates [1, 8].

4. KINETICS OF HETEROGENEOUS CATALYTIC REACTIONS

An important piece of information for evaluating the quality of a catalyst is the rate of the reaction in which it is involved. Information on the rate is primarily of practical importance, since it provides information on the amount of product that can be obtained in a unit of time. In the presence of a catalyst, however, it is not the concentration of the components in the gas phase that is important for the reaction rate, but the concentration of the adsorbed components on the surface of the catalyst. During adsorption of the reactants on the catalyst, saturation of its surface or even inhibition of the reaction by some of the reactants or products may occur. Kinetic models are usually used to obtain a mathematical expression describing the rate of a heterogeneous catalytic reaction.

In this work, the esterification of oleic acid with methanol was carried out using mesoporous silica MCM-41 as a catalyst. The reaction can be represented by a stoichiometric equation:



The Langmuir-Hinshelwood-Hougen-Watson model was used to obtain a mathematical expression describing the rate of a heterogeneous catalytic reaction:

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(M - X_A) \quad (1)$$

where:

X_A - conversion (%)

$$M = \frac{C_{B0}}{C_{A0}} = 520,1$$

k – reaction rate constant ($\text{dm}^3\text{mol}^{-1}\text{h}^{-1}$)

Equation (2) was obtained from equation (1) by separating the variables

$$\frac{dX_A}{(1-X_A)(M-X_A)} = kC_{A0}dt \quad (2)$$

Solving the given differential equation yields equation (3)

$$\ln \frac{M-X_A}{M(1-X_A)} = kC_{A0}t \quad (3)$$

The esterification reaction was carried out with different catalyst masses (0.05, 0.075, 0.1, 0.125 and 0.15 g) at temperature 64.5°C.

The obtained values for the reaction rate constants are given in Table 1.

Table 1. Dependence of the constant k on the mass of the catalyst for a temperature 64.5°C

| Catalyst mass, g | 0.05 | 0.075 | 0.1 | 0.125 | 0.15 |
|---|-------|-------|-------|-------|-------|
| $k \cdot 10^3, \text{dm}^3\text{mol}^{-1}\text{h}^{-1}$ | 2.083 | 3.701 | 4.211 | 5.452 | 6.368 |

As expected, the reaction rate constants are higher at higher temperatures. The comparison of the experimental data with the data calculated according to the Langmuir-Hinshelwood-Hougen-Watson model is shown in Figure 2.

From Figure 2, we can see that the proposed Langmuir-Hinshelwood-Hougen-Watson model fits our experimental data very well. We can also see that the conversion increases with increasing mass of the catalyst.

5. CONCLUSION

Catalyst quality is a very broad term that depends on numerous factors. Accordingly, the testing of catalyst activity is a complex process that first of all requires a properly chosen strategy. In this work, testing was performed in laboratory conditions by determining the degree of conversion of the transesterification reaction by measuring the concentration of oleic acid and methyl oleate using the GC-FID method. It was concluded that with the increase in

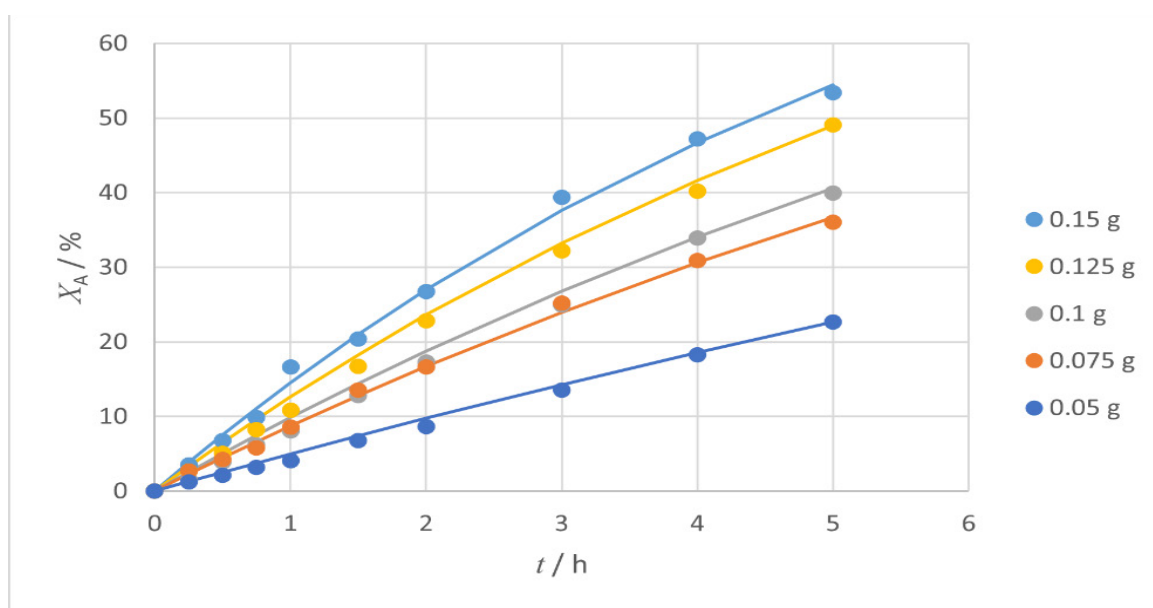


Figure 2. Conversion of oleic acid regarding time of the reaction at different masses of the catalyst and 64.5°C (symbol – experimental data, line – LHHW model).

the amount of catalyst, the reaction rate increased, which was measurable by calculating the reaction rate constant. The given results are in agreement with the fact that the presence of a catalyst reduces the activation energy of the reaction and therefore accelerates it. The Langmuir-Hinshelwood-Hougen Watson model was used to obtain the mathematical expression.

6. LITERATURE

- [1] G. Bošković, *Heterogena kataliza u teoriji i praksi*, Tehnološki fakultet Univerziteta u Novom Sadu, Novi Sad 2007, 34–197
- [2] D. Sinčić, *Biodizel svojstva i tehnologija proizvodnje*, Prehrambeno-biotehnoški fakultet Sveučilišta u Zagrebu, Zagreb 2008, 10–131
- [3] M. Jotanović, V. Mičić, *Hemijsko reakcijsko inženjerstvo*, Tehnološki fakultet Zvornik 2016, 25–78
- [4] Stanka Zrnčević, *Kataliza i katalizatori*, HINUS Zagreb 2005, 10–175
- [5] C. H. Bartholomew, R. J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, John Wiley & Sons 2010, 35–215
- [6] K.A.Petersen, et al., *Natural gas to synthesis gas-Catalysts and catalytic processes*, Journal of Natural Gas Science and Engineering Vol. 3–2 (2011) 423–459
- [7] R.J. Schmidt, *Industrial catalytic processes -production*, Applied Catalysis A:General, Vol. 280–1 (2005) 89–103
- [8] V.V. Ranade, S.S.Joshi, *Industrial Catalytic Processes for fine and specialty chemicals*, Elsevier 2016, 1–14

UTICAJ KATALIZATORA NA KONSTANTU BRZINE HEMIJSKE REAKCIJE ESTERIFIKACIJE OLEINSKE KISELINE METANOLOM

Sažetak: Kataliza i katalizatori igraju primarnu ulogu u savremenoj tehnologiji. Pod katalizom se podrazumeva promena brzine hemijske reakcije pod uticajem supstance koja se hemijski ne menja kao rezultat odigravanja reakcije. Ova supstanca se naziva katalizator. Katalizovana reakcija se odigrava drugim reakcionim putem u odnosu na nekatalizovanu reakciju zahvaljujući učešću upravo katalizatora. Na njegovoj površini dolazi do adsorpcije reaktanata, a zatim i do međusobne reakcije adsorbovanih vrsta. Reakcijom nastaje proizvod koji se desorbuje sa površine, a katalizator je ostao nepromenjen i spreman za novi reakcioni ciklus. Bitna informacija za ocenu kvaliteta nekog katalizatora je brzina reakcije u kojoj ovaj učestvuje. Predmet kinetičkih istraživanja je ispitivanje uticaja parametara procesa na brzinu reakcije. Može se slobodno reći da je ispitivanje kinetike reakcije centralni deo reakcionog hemijskog inženjerstva. Zato je proučavanje kinetike realnih heterogenih katalizatora od posebnog značaja, kako u poboljšavanju postojećih tako i u projektovanju novih katalizatora. Ova ispitivanja podrazumevaju određivanje uticaja procesnih parametara, kao što su: vrsta prisutnog katalizatora, temperatura, pritisak, koncentracija reaktanata i produkata na brzinu reakcije. U ovom radu vršeno je ispitivanje uticaja mase katalizatora na određenoj temperaturi na konstantu brzine hemijske reakcije esterifikacije oleinske kiseline sa metanolom. Kao katalizator korišćena je mezoporozna silika, amorfnja čvrsta materija koja se može dobiti sušenjem hidrogela. Zaključeno je da se sa povećanjem mase katalizatora povećava konstanta brzine hemijske reakcije, odnosno da raste brzina reakcije esterifikacije.

Ključne reči: catalyst, reaction rate constant, kinetic model, temperature.

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