Modeling of Heterogeneous Catalytic Reduction Process of Aldehydes

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Abstract – The article considers the mathematical model of the reduction reaction of anisyl aldehyde by the Meerwein-Ponndorf-Verley mechanism. The activity of the zeolite catalyst with the assistance of which the reaction took place has been analyzed and calculated the rate constant of reaction.

Key words – aldehydes, heterogeneous catalysis, mathematical model, Meerwein-Ponndorf-Verley mechanism, zeolites.

I. Introduction

The actuality of this study is due to the use of new zeolite catalysts that has been developed at the L.V. Pisarzhevskii Institute of Physical Chemistry of the NAS of Ukraine, which provide a high degree of conversion of the process and also the development of heterogeneous catalytic technologies of organic products synthesis that are more environmentally friendly and cheaper.

There is a need in catalysis and green chemistry for eco friendly technologies of obtaining substances using heterogeneous catalysts.

In the synthesis of ethers with a homogeneous catalyst is often necessary to use an additional solvent and restore the catalyst due to its deactivation. These problems considerably complicate the process of obtaining organic compounds [1].

In contrast to the homogeneous catalyst, the heterogeneous catalyst can be reused and it is much easier to separate this catalyst from the reaction products (with application of mechanical methods of separation).

Therefore, the realization of organic synthesis in the presence of a heterogeneous catalyst is an important scientific task.

In the L.V. Pisarzhevsky Institute of Physical Chemistry it have been investigated zeolites systems of structure group beta (β) in which ions of Al (aluminum) and Sn (tin) were incorporated. The main difference of these zeolites from already known is that they have micro- and meso- pores (dual porosity structure) [1].

The purpose of research is modelling of heterogeneous catalytic reduction process of anisyl aldehyde and calculation of the reaction rate constants [2].

To achieve this goal settled the following tasks:

- A scientific experiment with the reduction reaction of anisyl aldehyde to anisyl alcohol with further esterification in the presence of zeolite catalysts;
- Conducted analysis of the experimental data in an automated mathematical package MathCad 15.0;
- Analyzed the results of calculations.

II. Mathematical model

During carrying out of scientific - research experiment on the reduction of anisyl aldehyde through the Meerwein-Ponndorf-Verley mechanism on SnAl zeolite catalyst and further esterification of obtained anisyl alcohol it has been obtained a dependency of the concentrations of these substances on time and the mathematical processing of the experiment has been done. The obtained dependency of the reaction components concentrations are given in Table 1.

TABLE 1

CONCENTRATIONS OF REACTION COMPONENTS

t, h	Ca, kmol/m^3	Cb, kmol/m^3	Cc, kmol/m^3
0	0,234	0	0
0,33	0,225	0,00424	0,00487
1	0,214	0,00653	0,013
2	0,21	0,00617	0,018
4	0,2	0,00566	0,028

As a result the mathematical model of this process has been obtained [2].

The mechanism of anisyl aldehyde reduction reaction (1):

$$A \xrightarrow[-buthanon]{+2\ buthanol} B \xrightarrow[-H_2O]{+2\ buthanol} C \qquad (1)$$

where A – anisyl aldehyde;

B - anisyl alcohol;

C - p-methoxybenzyl 1-methylpropyl ether.

The reaction Eq. (1) is named as a tandem reaction [3].

The assumptions that have been nominated in modeling the kinetics of the reduction process of anisyl aldehyde [1]:

1. The layer of catalyst is a quasi homogeneous environment.
2. The layer of catalyst is isothermal.
3. The substances are moving in an ideal mixing mode.
4. The transfer of substance in the direction of axis is not included.

A mathematical model of the process on the basis of assumptions is Eqs. (2):

$$\begin{cases} \dfrac{dCa}{dt} = -k_1 \cdot Ca \\ \dfrac{dCb}{dt} = k_1 \cdot Ca - k_2 \cdot Cb \\ \dfrac{dCc}{dt} = k_2 \cdot Cb \end{cases} \qquad (2)$$

with initial conditions: $Ca\ (0) = 0.234\ kmol/m^3$; $Cb\ (0) = 0\ kmol/m^3$; $Cc\ (0) = 0\ kmol/m^3$.

With using of mathematical model Eqs. (2) have been calculated the rate constants k_1 (reaction of anisyl aldehyde reduction to anisyl alcohol) and k_2 (reaction of anisyl alcohol esterification).

III. Results of rate constants calculation

The rate constants have been calculated in an automated mathematical package MathCad 15.0.

The obtained constants are given in Table 2.

TABLE 2

CALCULATED RATE CONSTANTS

Reaction	Symbol	Rate constants, s^{-1}
$A \xrightarrow{k_1} B \xrightarrow{k_2} C$	k_1	0,0323
	k_2	0,4738

As we can see from obtained results, second reaction – the reaction of esterification – is passes more quickly then reaction of anisyl aldehyde reduction.

Also in MathCad 15.0 have been built the dependency of the reaction components concentrations on time (Fig.1).

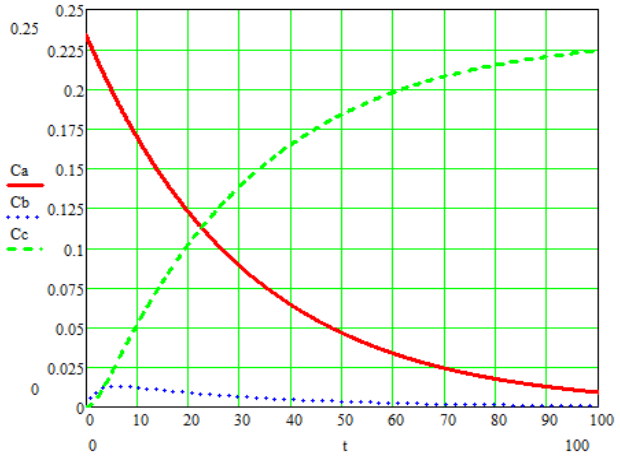

Fig. 1. The dependency of the reaction components concentrations on time

The Fig.1 shows that the most rapidly is changing the concentrations of anisyl aldehyde (Ca) and p-methoxybenzyl 1-methylpropyl ether (Cc).

The concentration of anisyl alcohol slightly increase (Cb) and approximately 5 hours after beginning of the reaction reached the peak, whereupon the concentration is going to down.

Finally, the mathematical model Eqs. (2) with considering the calculated rate constants will be as follows:

$$\begin{cases} \dfrac{dCa}{dt} = -0{,}0323 \cdot Ca \\ \dfrac{dCb}{dt} = 0{,}0323 \cdot Ca - 0{,}4738 \cdot Cb \\ \dfrac{dCc}{dt} = 0{,}4738 \cdot Cb \end{cases} \quad (3)$$

The adequacy of the mathematical model Eqs. (3) have been proved by Fisher's criterion.

Conclusion

With the use of the aforementioned mathematical model in the MathCad software the rate constants of the reaction of reduction of anisyl aldehyde have been calculated.

The calculated values of the rate constants can be used to solve the direct problem of chemical kinetics, as well as for modelling of chemical reactors.

References

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