KINETIC STUDIES OF THE $NaBH_4$ HYDROLYSIS REACTION IN THE PRESENCE OF $NiCo_2O_4$ AND ITS COMPOSITE WITH MULTIWALLED CARBON NANOTUBES

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КІНЕТИЧНІ ДОСЛІДЖЕННЯ РЕАКЦІЇ ГІДРОЛІЗУ $NaBH_4$ В ПРИСУТНОСТІ $NiCo_2O_4$ ТА ЇЇ КОМПОЗИТУ З БАГАТОШАРОВИМИ ВУГЛЕЦЕВИМИ НАНОТРУБКАМИ

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КИНЕТИЧЕСКИЕ ИССЛЕДОВАНИЯ РЕАКЦИИ ГИДРОЛИЗА $NaBH_4$ В ПРИСУТСТВИИ $NiCo_2O_4$ И ЕЕ КОМПОЗИТА С МНОГОСЛОЙНЫМИ УГЛЕРОДНЫМИ НАНОТРУБКАМИ

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Search and study of catalytically active substances are one of the primary tasks in the framework of modern energy issues. In the course of this experiment, the catalytic properties of the spinel of $NiCo_2O_4$ composition, as well as its composite with carbon nanotubes in the heterogeneous-catalytic hydrolysis reaction of $NaBH_4$, were investigated. The reaction order was established and the rate constants for the reaction were calculated using the graphical method.

Keywords: *composite, spinel, carbon nanotubes, kinetics, sodium borohydride*

Пошук і дослідження каталітично активних речовин є однією з першорядних завдань в рамках сучасної енергетичної проблематики. В ході даного експерименту досліджені каталітичні властивості шпінелі складу $NiCo_2O_4$, а також її композиту з вуглецевими нанотрубками в гетерогенно-каталітичної реакції гідролізу $NaBH_4$. Графічним методом встановлений порядок реакції та розраховані константи швидкості реакцій.

Ключові слова: *композит, шпінель, вуглецеві нанотрубки, кінетика, борогідрид натрію*

Поиск и исследование каталитически активных веществ является одной из первостепенных задач в рамках современной энергетической проблематики. В ходе данного эксперимента исследованы каталитические свойства шпинели состава $NiCo_2O_4$, а также её композита с углеродными нанотрубками в гетерогенно-каталитической реакции гидролиза $NaBH_4$. Графическим методом установлен порядок реакции и рассчитаны константы скорости реакций.

Ключевые слова: *композит, шпинель, углеродные нанотрубки, кинетика, борогидрид натрия*

INTRODUCTION

In the context of the current energy crisis, it is crucial to find and explore alternative sources of energy, as well as to improve existing options for introducing clean energetics. In recent years, the increasing attention of researchers has been attracted by the "green" hydrogen energy, which can be an alternative to fossil resources. However, the introduction of hydrogen energy in wide use has certain difficulties. Thus, the hydrogen transportation in gaseous form is extremely difficult and dangerous because of the possibility of an explosion, for the same reason, further work with hydrogen becomes more complicated. The solution to this problem can be the binding of hydrogen to stable compounds, which would greatly simplify transportation. Such compounds must meet a number of requirements, they should decompose rapidly with hydrogen evolution under certain conditions, be relatively inexpensive and non-toxic. An example of such compounds can be borohydrides, the most suitable of which for this purpose is sodium borohydride [1].

However, its decomposition rate is rather low, which prevents its widespread use. The solution to this problem can be the use of an effective catalyst such as Ni-spinel. In addition to using as a hydrolysis catalyst, spinel has a wide range of applications, for example, as catalysts for oxygen reduction and oxygen evolution reactions, in fuel cells, supercapacitors and lithium-air batteries [2], for glucose sensor, for hydrogen generation by $NaBH_4$ hydrolysis [3] and for many other purposes.

Thus, the kinetic parameters calculation of the sodium borohydride hydrolysis reaction is important from the point of view of evaluating the effectiveness of catalyzing the reaction by certain catalysts as well as the choice of the most effective catalyst under these conditions.

EXPERIMENTAL METHOD

In the present research for the preparation of samples, a simple and cost-effective co-precipitation method was used. To obtain the sample of pure spinel's, during the first synthesis stage, the saturated solutions of nickel and cobalt nitrate hexahydrates were mixed in stoichiometric composition. The equal volumes of the obtained solutions were mixed and the pH of 12.4 was adjusted using sodium hydroxide. The resulting mixture was stirred for 40 minutes and left for aging for 7 days, than the obtained precipitate was filtered, dried for 1 hour at 110°C, and then calcinated in at 350°C for 3 hours.

To obtain a composite sample with multi-walled carbon nanotubes, nanotubes were added at the aging stage with the spinel content calculation in the final product of 20 %.

The samples catalytic activity was investigated at atmospheric pressure and temperature 50 and 60ºC in a model liquid-phase oxidation-reducing heterogeneously catalytic reaction of sodium borohydride hydrolysis by volumetric method (as a source of hydrogen, 10,6 % by weight):

$$NaBH_4 + 2H_2O = 4H_2 + NaBO_2.$$

The results of catalytic studies at 50 and 60ºC in the form of kinetic curves are presented in fig. 1.

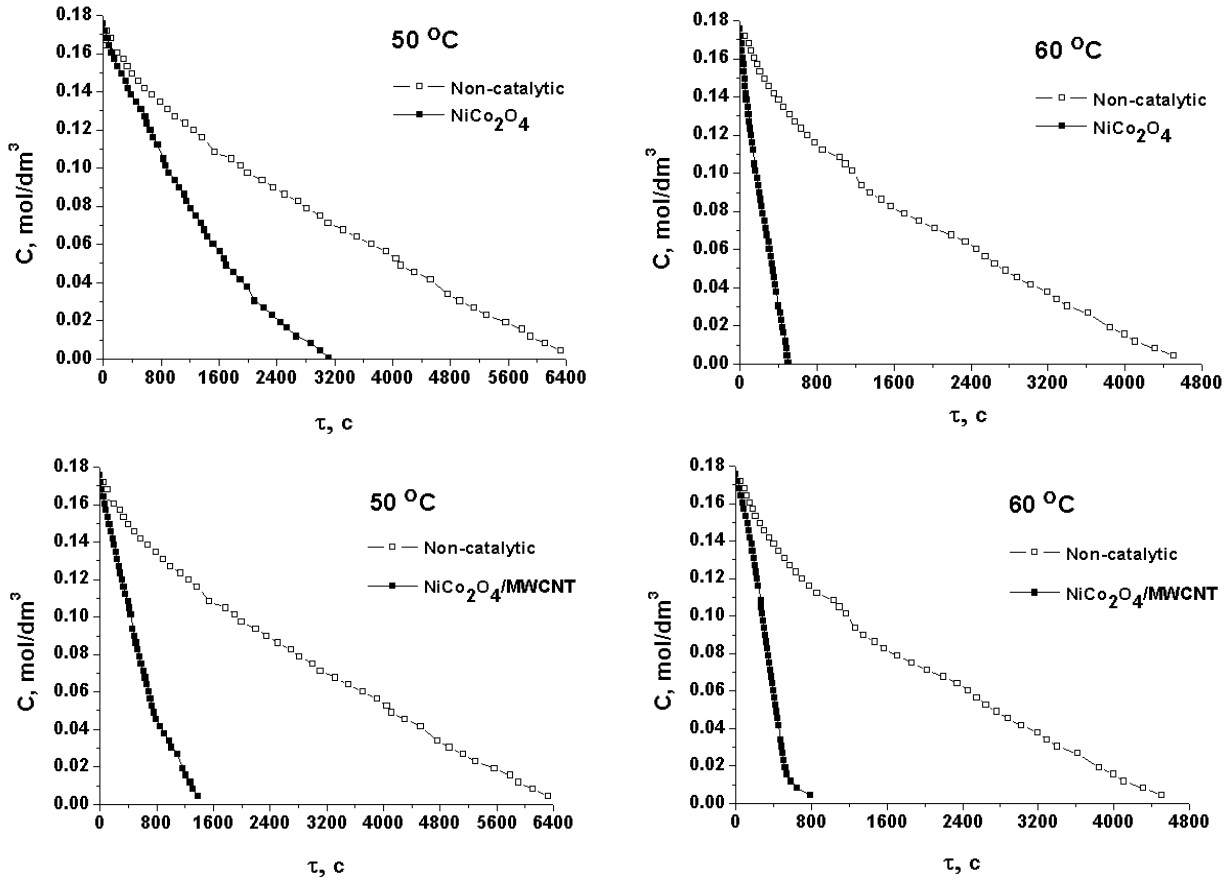

Fig. 1. Kinetic curves

A graphical method was used to calculate the reaction order. As can be seen from the fig. 2, the graph turned out to be straightforward in coordinates $\lg\frac{C}{C_0} = f(\tau)$, which means that this reaction is successfully described by first-order kinetics. The correlation coefficient ranges from 0.97 to 0.99.

The constants calculated by the graphics method are presented in the form of comparative diagrams, from which one can see the undoubted presence of the catalytic effect of both pure spinel's and their composites with carbon nanotubes.

As can be seen from the diagram in the fig. 3, the constant rate of sodium borohydride hydrolysis at 50°C is $0.3 \cdot 10^{-3}$ sec^{-1}, and in the presence of pure spinel, it increases in 3 times. In the presence of a composite with carbon nanotubes, it increases nearly 6 times. At a temperature of 60 °C, the trend is different: the rate constant in the presence of pure spinel's and their composite with carbon nanotubes increases 9 and almost 7 times, respectively.

CONCLUSIONS

Thus, it can be concluded that the kinetics of sodium borohydride hydrolysis reaction is successfully described by dependencies for the first order.

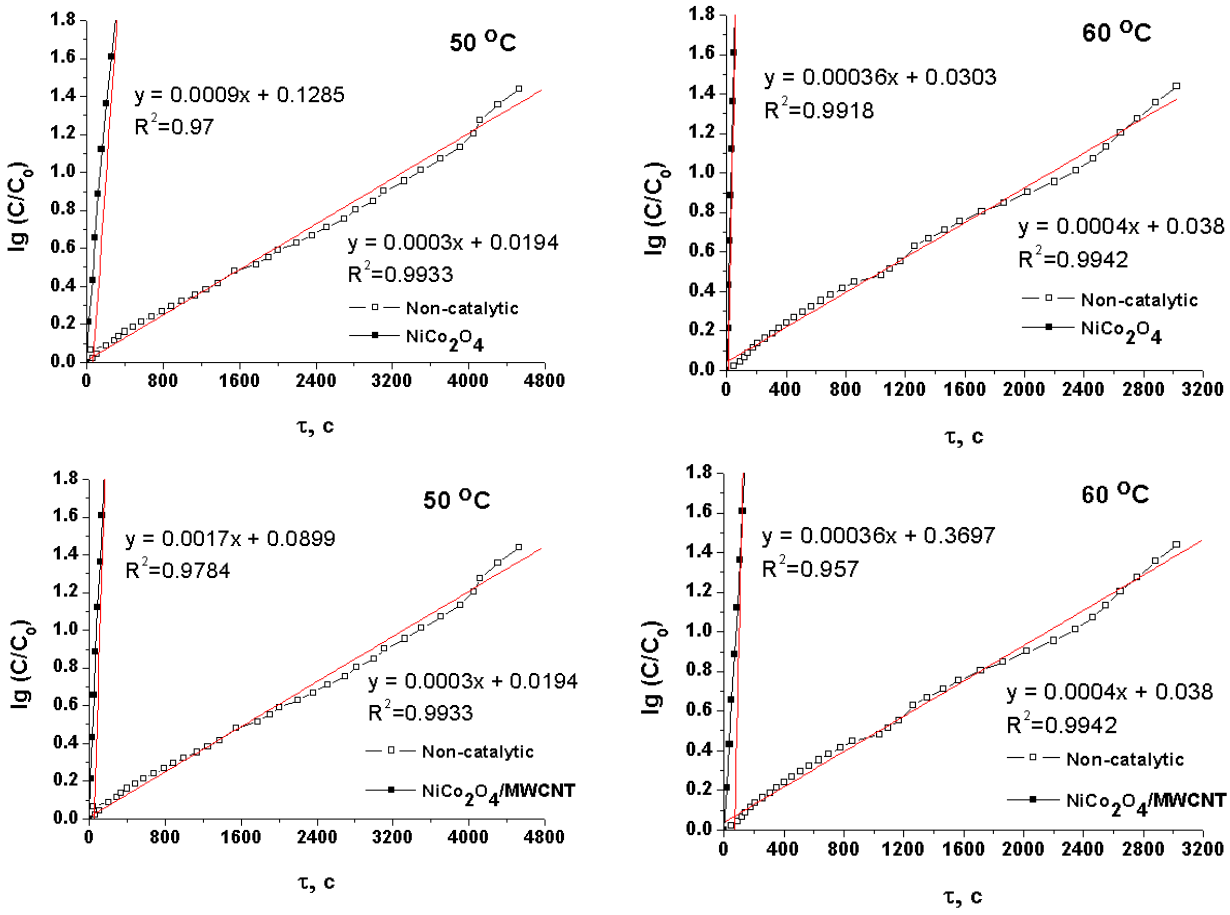

Fig. 2. Graphic determination of the reaction order

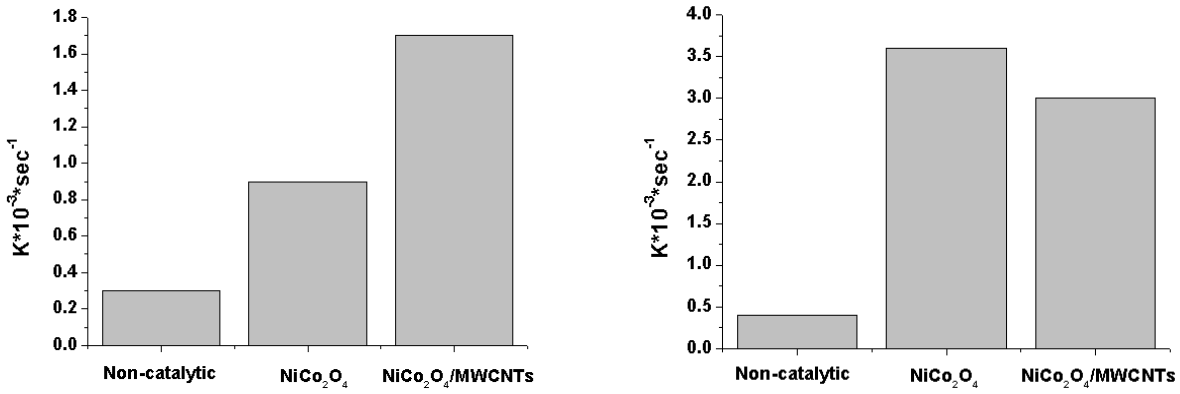

Fig. 3. The rate constants of sodium borohydride hydrolysis at **a** 50°C **b** 60°C

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