

Kinetic Model Heterogeneous Reaction Self-assembly on Nanocomposit Sorbent and Their Peculiarity

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Abstract: Kinetic modeling of self-assembly reactions occurring on a nanocomposite with the formation of dimers in a solvent cell and molecular complexes in micelles is presented. In this self-organization occurs due to the synergistic effect, due to a combination of nonvalent interactions. This approach opens up new possibilities in the field of chromatographic and separation technologies related to the analysis of complex mixtures. The coefficient α of the self-assembling processes at the nanocomposite. It is shown that α can have different values, for example, for pyridine dimer in cage solvent this coefficient is 2.5~3.4. Quantum chemical calculations show that the surface of the nanocomposite is doped with alkaline metal, which restores hydrogen atoms, turning them into H. This is used in a chromate-mass spectrometer in identify environmental toxicants, the technique of determining metaphase in food products.

Key words: Self-assembly reaction, nanocomposit, equation N.I. Brensted, intercaljacia, chromate-mass-spectrometrija, metaphos, helium.

1. Introduction

The problem of control over the selectivity of catalytic systems is one of the main problems in petrochemical and organic systems. The attention of researches is attracted by supramolecular catalysis, which involves the use as components of catalytic systems of compounds capable of forming complexes of inclusion of the guest-host type with various organic compounds. This approach opens up opportunities to create new highly active metal complex catalysts with substrate, region and chemoselectivity [1]. A distinctive feature of nanostructured composites is the high sorption activity of their surface and chemical activity, which is manifested both in the geometry of the active center (geometric factor) and in its energy state (electronic factor). Catalytic centers of nanomaterials can serve not only the active component of the catalyst, located on its surface, but also pores, defects, dislocations that

occurs in surface volumes in the film coating technology. The dominant role of the sorption processes on the interphase surfaces of nanocomposites belongs to the self-organization processes occurring in thin films with controlled architecture and structure. In this self-organization occurs due to the synergistic effect, due to a combination of nonvalent interactions. This contributes to the development of chromatographic and separation technologies, related to the analysis of complex mixtures. Catalytic organic reactions usually involve polyatomic molecules [2], which may occupy several places on the catalyst surface during adsorption. Therefore, reliable kinetic models describing the rate of reactions are necessary for the simulation of chemical reactors, for technological design and for solving problems of intensification of industrial processes [3, 4]. Despite the rapid development of modern experimental methods in situ, the acute lack of detailed microscopic information of such reactions serves almost as the main obstacle to the calculation of kinetic parameters of real electrochemical systems in the framework of modern

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quantum-chemical theory. In this sense, quantum chemistry serves as a “bridge” through which the general provisions of the theory can be brought to a direct comparison with the experiment [5]. In the present work chromatographic studies of gas sorption on nanocomposition sorbent, on the surface of which a polymer film is applied, capable of selectively binding the substrate, thereby increasing efficiency and selectivity, were carried out.

2. Experiments

Researches carry out by a method gas chromatograph with application of a column 1 m, with an internal diameter of 3 mm and a sorbent of 10% 3-nitripropanamin on colorchrome (fr. 0.14/0.25 mm). The nanocomposite sorbent represents electrochemical active heteroborder [6] “the proton conductor-hydrogenated metal”. For formation of an ionic heterojunction a necessary condition is present of edential element in an electrode and in electrolyte. Borders of heterostructures settle down close, therefore decisive role belong dimensional affects. Through heteroborder “the firm proton conductor-hydrogenated metal” can realize an reversible and direct, i.e. with catalyst participation, exchange of protons. As gas carrier used hydrogen and air, temperature column varied from 90 to 190 °C. Experiment made on the “Crystal-2000M” chromatograph with ardently-ionizatsionnym detector. The chromatograph provide with programme securing “Chromatec analyst”. In quality adsorbate we investigated toluene, pyridine, benzene. By calculation the method of intersecting parabolas [7] and the method DFT were used [8].

3. Results and Discussion

3.1 Chromatographic Study of Solvation Processes on Nanocomposition Sorbent

Solvation plays a key role in the regular of many chemical processes of sorption. The energy disparity of active sites on the surface of the nanosorbent leads

to solvation effects of heterogeneous catalytic reactions of self-assembly. The solvent can be used not only as a medium, but also as an effective means to study the nature of chemical interaction and reactivity of substances. Therefore, the understanding and priori estimate of the effects of the environment remain one of the important practical problems of modern chemistry.

The kinetic model of solvation and formation of dimers in the solvent cell is presented by the equation:

$$k_{\text{эксн.}} = k_{\text{асс.}} \cdot k_e' = \frac{k_e + k_{H^+}}{k_s} \quad (1)$$

where k_s —constant bind final product micelle or in cage solvent accordingly; k_e ; k_{H^+} —constant synchron transfer electron and proton accordingly; $k_{\text{асс}}$ —constant association.

The kinetic model of the formation of the final product in the micelle is presented by the equation:

$$k_{\text{эксн.}} = k_{\text{асс.}} \cdot k_{H^+} = \frac{k_e + k_{H^+}}{k_s} \quad (2)$$

In the continuation of studies [9-11] they calculated the coefficient α in the equation I. N. Brensted, $\alpha = \frac{\Delta G}{8G_o^\ddagger}$, where α is a constant characterizing the reaction series and reflecting the sensitivity of the reaction rate to the change of the catalyst, where ΔG —change of free energy in reaction; ΔG_o^\ddagger —internal barrier [12] (the value having sense of energy of thermoneutral reaction, i.e. reaction with zero thermal effect). Data for the dimer pyridine are presented in Table 1.

T °C—temperature column. According to studies, the coefficient α is greater than one. Such anomalies can provide important information about the mechanisms of reactions and structure of the resulting anions [12]. As a rule, they occur when the formation of anion is a sharp change in the distribution of electron density and as a consequence of significant changes in the structure of the solvation sphere. The transition state

Table 1 The data in the formation of the dimer of pyridine in a cage of solvent on the mechanism Langmure-Hinshelwood, analyzed according to equation Brensted I. N.

T (°C)	E _{oe} (J/mol)	ΔG (J/mol)	α	k _o (mol/L·c)	k _a (mol/L)
120	-4,571.3	-1.206 × 10 ⁵	3.3	0.12 × 10 ¹⁷	7.2 × 10 ⁻⁶
130	-4,773.88	-1.263 × 10 ⁵	3.3	3 × 10 ¹⁶	1.55 × 10 ⁻⁵
140	-4,806.63	-1.108 × 10 ⁵	2.9	0.11 × 10 ¹⁵	0.17 × 10 ⁻⁴
150	-4,900.59	-1.326 × 10 ⁵	3.4	2.66 × 10 ¹⁶	0.18 × 10 ⁻⁴
160	-4,977.54	-1.359 × 10 ⁵	3.4	2.88 × 10 ¹⁶	0.19 × 10 ⁻⁴
170	-6,862.77	-1.35 × 10 ⁵	2.5	9.2 × 10 ¹⁵	0.29 × 10 ⁻⁴
180	-6,951.3	-1.413 × 10 ⁵	2.5	2.2 × 10 ¹⁶	0.24 × 10 ⁻⁴

becomes later, as a result, the degree of localization of the unpaired electron on the reaction center increases, which leads to an increase in selectivity. Experiments define work exit electron by 140 °C column, that compose 2.3 eV. Therefore, surface nanocomposit doped alkali metal, which restores hydrogen atoms, reduce to helium.

3.2 Chromato-Mass Spectrometry Determination of Metaphos

The chromatography-mass spectrometry method [13] is based on a combination of gas chromatography and mass spectrometry. The separating ability of chromatography and the ability to identify mass spectrometry with a direct combination of these two methods allows for reliable identification of components of complex mixtures of pollutants of any origin. Equipped with modern computers, chromatography-mass spectra allows detecting in the environment a lot of toxic chemicals and identifying the origin associated with the activities of modern industrial society. Gas chromatography-mass spectrometry allows the detection of ultramicrocomponent on the background of high concentrations of other compounds. In this case, it is necessary that the substance passes through the gas chromatograph column at atmospheric pressure and temperature of 250-300 °C.

To determine and identify trace concentrations of pesticides (FOS) in food products, a method has been developed, including extraction by organic solvents and subsequent use of gas chromatographic mass

spectrometry (GC-MS) on the gas chromatograph “Crystal-2000M”, using the software “Chromatek-analyst”. For the basis we have taken the method of gas-liquid chromatography, based on the extraction of pesticides (FOP) from acidified water with hexane [14, 15], and then with chloroform, and chromatography on the chromatograph “Color-106” with thermionic detector (T_{col}—190~230 °C; T_{isp.}—200~230 °C; flow rate of nitrogen 60~75 mL/min, hydrogen 18; air 180, relative retention time of metaphos 1.0).

A sample of cucumber juice was dissolved by us in water, then extracted with butanol and acetone in a ratio of 1:1. Experience shows that in the organic phase from the aqueous solution of the substance passes into the electro-neutral particles: coordination compounds, ionic associates, etc. GC-MS analysis was carried out by the detector PID 2 mode: T_{det.}—150 °C; T_{isp.}—150 °C; T_{col} key. —150 °C. Carrier gas-helium. The GC-MS method [16] consists in the fact that the gas sample is sorbed by the sorbent of the gas chromatographic column, ionized, while fragmentation of the molecule occurs—its disintegration into separate charged particles (“fragments”) with different mass. The process of ionization is carried out as a result of ion-molecular reactions with helium. These charged particles are accelerated by an electric field, under the action of which they deviate in different ways, depending on their mass, and are divided into bundles each of which includes only particles of the same mass. The detector registers these beams in the form of chromato-mass spectrum.

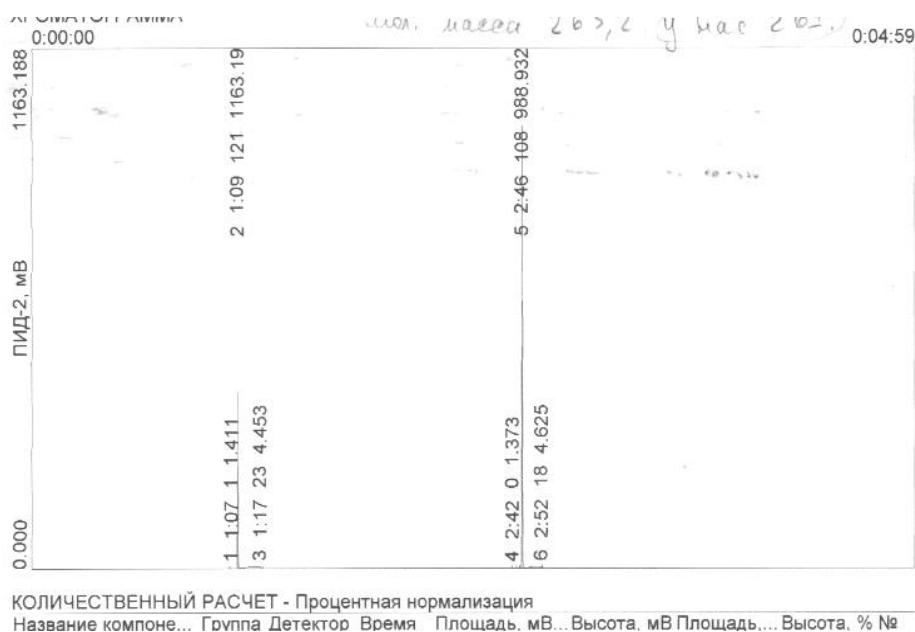


Fig. 1 Chromato-mass-spectrometric determine metaphos in food products.

Detected carry out on ion with m/z 121, 23, 116 for metaphos, which use in agriculture. Maintenance metaphos in vegetables not possible sanepidem supervision ($LD_{50} = 20$ mg/kg).

4. Conclusion

Thus, the coefficient α of self-assembly reactions occurring on the surface of the nanosorbent in the solvent cell indicates the reactions occurring at quantum dots. Surface nanocomposit intercalacion alkaline metal. These metal restore hydrogen atoms, reduce to helium. The gas chromatograph can be used as chromato-mass-spectrometer. The method of determination of metaphos in food products is developed.

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