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CATALYSIS AND ITS TYPES

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Abstract. This paper presents all types of catalysis, considers the main stages of conversion with a surface catalyst, presents such methods of catalyst synthesis as impregnation by moisture capacity, sol-gel method, hydrothermal synthesis of nanozeolites.

Introduction

The concept of "catalysis" has an ancient history, associated primarily with the fermentation process (fermentations), absolutely all biochemical processes create protein macromolecules called enzymes. For the first time in 1814, K. Kirchhoff enzymatic catalysis was a study of the principle of converting starch into carbohydrates. Then I. Berzelius and E. Mitscherlich determined the nature of enzymatic catalysis and classified it as an organic catalytic phenomenon. In the 19th century, the German chemist E. Fischer A hypothesis has been put forward about the steric correspondence between the substrate and the active centers of enzymes. Currently, the study of enzymatic catalysis and its application in obtaining compounds such as acetone, lower alcohols, direct current energy, synthetic oil and favorable environmental characteristics of processes based on it make biocatalysis applicable to industry and science. Nowadays, the topic is confirmed that over the past decade, the number of scientific publications devoted to biocatalysis is about 5000 scientific articles on the Elsevier platform. The principle of enzymatic catalysis was transferred by scientists - chemists to organic chemistry, where it was successfully consolidated and more than 70% of new compounds are obtained by catalytic processes. Then the so-called chemical catalysis was divided into two main directions - homogeneous and heterogeneous, there is also photo-catalysis, electrocatalysis.

1. Homogeneous catalysis

Homogeneous catalysis occurs in a single phase of liquid or gas, where catalysts and reagents interact to obtain target compounds. In homogeneous catalysis, block reactors are usually used - a Slurry reactor, an autoclave. After the process

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is completed, it is necessary to separate the catalyst from the products. Homogeneous catalysis is mainly divided into acid and metal complex, where protic acids (nitric acid HNO_3, acetic acid CH_3COOH, carbonic acid H_2CO_3, phosphoric acid H_3PO_4, etc.) releasing a proton H^+ and metal complexes $HgSO_4$-H_2SO_4-$Fe_2(SO_4)_3$, $Ni[P(OR)_3]$, $ZnCl_2$, Pd (II), Cu (I)/Cu(II) are used as catalysts. One of the striking examples is the stereoregular polymerization of olefins and dienes, which was first performed by Ziegler and Natta on homogeneous organometallic catalytic complexes $TiCl_4$-$AlEt_3$, $TiCl_3$-AlR_3 (C_5H_5) $TiCl_2Al$ $(C_2H_5)_2$, for which they were awarded the Nobel Prize in 1963. A homogeneous method for synthesizing vinyl acetate was proposed by Soviet scientists on palladium complexes PD(II) in 1960 – the Moiseev reaction.

2. Heterogeneous catalysis

Heterogeneous catalysis has three phases: gas, liquid and solid. The solid phase serves as a catalyst and, depending on the reaction, a carrier (substrate) is selected with a certain specific surface area, promoted by metals. The pore size of the sample taken is also important in the case of zeolites, the molecular – sieve effect, where, depending on the pore diameter, the starting substance is selected whose molecule size “passes” through the pore with maximum conversion and selectivity. The formation of target substances in heterogeneous catalysis occurs in three stages: 1-evaporation, 2-contact-adsorption, 3-condensation-desorption. At the contact stage, the evaporated molecules interact with the surface of the sample (adsorption) and then penetrate through the pores (channels) of the catalyst and are converted into by-products along with the target product. In the absence of a catalyst, the reaction does not occur or occurs at a very slow rate, the catalyst is not consumed, its mass is much less than the raw materials processed on it. However, after a certain time, it must be regenerated to remove coke (compaction products) from its pores and surface. Before assessing the ”suitability” of the reaction and conducting it specifically within the framework of heterogeneous and homogeneous catalysis, a thermodynamic calculation is used, where the free energy ΔG^0 is determined by the formula:

$$\Delta G^0 = -RT \ln K_0$$

and the temperature range is determined where the reaction is feasible, based on the given formula if the obtained values are negative, then the reaction is feasible, and in the case of positive numbers, respectively, it is not. That is, the catalyst cannot cause a reaction if it is thermodynamically unacceptable. Since the catalyst is not consumed during the reaction and does not affect the free ΔG^0 and, accordingly, the equilibrium constant, the catalyst does not shift the reaction equilibrium towards the formation of products, but only increases the rate at which this equilibrium is achieved.

Previously, to determine the mechanism of reactions and intermediates, analytics after the reactor block was used, with the help of which the main reaction products and trace impurities were identified using gas, gas-liquid chromatography. This, of course, did not show the complete picture, and a kind of ”black box” was obtained. At the beginning of the 21st century, physical and chemical methods of catalyst analysis have advanced so much that intermediate compounds formed on the surface of catalysts are determined taking into account SEM, X-ray diffraction, X-ray photoelectron spectroscopy, NMR, IR spectroscopy in situ, which brings clarity to the concept of a "black box". However, the above-mentioned methods of analyzing structural and surface characteristics have their limitations associated with the conditions of studying the catalyst sample. The fact is that the environment formed under reaction conditions (catalytic system) differs from that created in analytical devices. Today, advanced technologies allow us to observe the operation of the catalyst during the reaction and on a nano scale too.

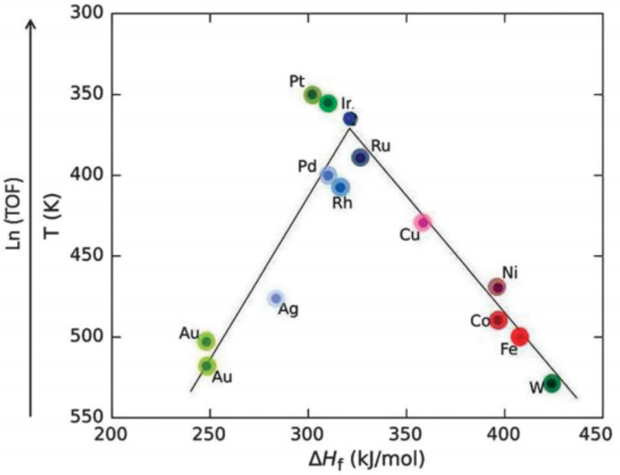

FIGURE 1. Volcanic graph: decomposition temperature at a certain rate - a function of the heat of formation of formate salt.

Nanocatalysts have new quality characteristics, first of all, this is the largest surface area, secondly, the location of the metal (promoter) is more accessible than in single crystals. For each process, it is necessary to select nanoscale dimensions and promoters.

Contact of the raw material with the catalyst has the following stages a) adsorption, b) reaction, c) desorption, and depending on the reaction conditions, the "adsorption-desorption" process occurs to varying degrees. The German scientist and chemist Sabatier clearly depicted on the graph a "volcano" of the dependence of temperature (and LnTOF Ln on the speed of rotation) on the heat of formation of formate. As can be seen from the graph in Figure 1, there is no direct dependence of temperature on ΔH_f heat of formation, and with an increase in it, a maximum is observed at average values, which indicates an average - optimal adsorption energy at which acceptable catalyst activity is maintained [5–7].

3. Nanoheterogeneous catalysis

Nanoheterogeneous catalysis as a separate direction of catalysis was defined in the work of S.N. Khadzhiev, where the main premise was the influence of the size effect on the activity and stability of the catalyst, the influence of this effect itself consisted in changing: 1- the rate of formation of products, 2- the binding energy, 3- the specific catalytic activity.

Over the past decades, the most widely used catalysts with a positive size effect are zeolites (molecular sieves), where pores and crystals brought to nanoscale provide high activity and selectivity of processes. The authors[9, 10] were the first to obtain samples of nanosized zeolite catalysts of the Y and ZSM-5 type with superacid centers, the structural characteristics of which are similar to liquid Ola superacids, and were substantiated by quantum-chemical calculations. High activity of acidic centers of nanozeolites easily breaks C-C bond of hydrocarbons in comparison with classical amorphous aluminosilicates, in connection with which zeolites have displaced them from industrial processes of oil refining and petrochemistry. Nanosized structure of zeolite catalysts provides activity not only by surface characteristics, but also by diffusion of reagents into pores with further transformation - configuration selectivity (shape selectivity). Pores can contain Brønsted acidic centers, ions of transition metals or metal clusters. To form four bonds, the Al atom needs an additional electron. Thus, the framework carries a negative charge, which is balanced by cations that are not part of the link and, therefore, are easily exchanged. H^+ exchange leads to Bronsted acidic centers, which are very active in alkylation and isomerization reactions. Interestingly, the reaction products do not occur in their thermodynamic equilibrium distribution, even if the reactions are carried out at high temperatures. This is explained by the configurational selectivity that is imposed on the reactants, transition states and products, the principle of which is schematically shown in Figure 2.

Figure 2 shows that the reaction mechanism involving a carbon "pool" also leads to the formation of compaction products - coke. Several such coke particles can completely block and deactivate a one-dimensional pore, while three-dimensional zeolites can remain selective due to additional planes. Zeolites with a three-dimensional pore structure are less susceptible to deactivation, since one coke particle can block only one pore, and there remains the possibility of substrate penetration via other routes through adjacent planes.

4. Synthesis of heterogeneous catalysts

Heterogeneous catalysts are solid samples of metal and non-metal oxides and their mixtures, with a given specific surface area, porosity, structure. Catalyst synthesis is carried out in factories for industrial processes and in laboratories to study its main parameters for new reactions or to improve the conversion and selectivity of a known process. The catalyst basically has two active phases - a carrier and a modifier. The carrier has such characteristics as porosity, structural framework, specific surface area and they are participants in the reaction, by selecting or changing the values of the characteristics, you can change the course of the reaction - increase the speed of the target routes to obtain the desired compound.

The modifier is active metals that are applied to the carrier by various methods, where salts (carbonates) of metals are taken as a basis and the formation of the sediment structure is affected by the concentration of solutions, the speed of the

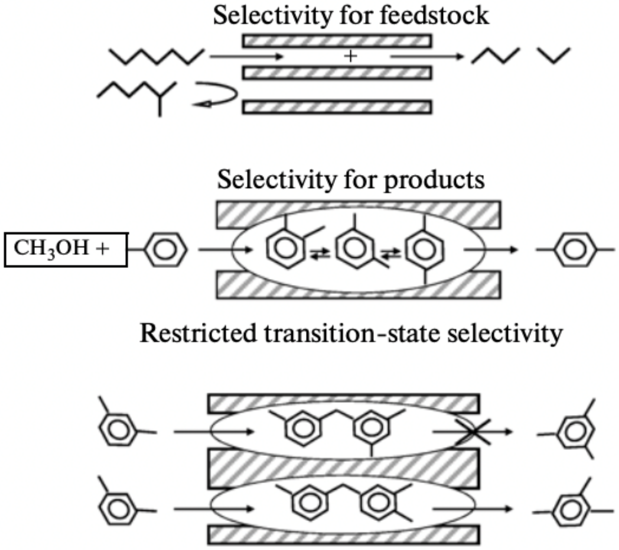

FIGURE 2. Different types of shape selectivity.

process, the drying temperature. The precipitation method is often used to obtain binary systems by the action of ammonia on metal nitrates. As a result, amorphous gels are obtained, which must be dried to obtain a stable structure should be avoided in order to avoid crystallization, which can negatively affect the activity of the catalyst.

To obtain highly dispersed catalysts - metal oxides, the hydroxides and carbonates of heavy metals are heated at high temperatures with the release of water and carbon dioxide; to obtain a loose structure at moderate temperatures, metal oxides can also be obtained by thermal decomposition of organic salts, nitrates of heavy metals.

4.1. Impregnation in an acidic medium. To synthesize a multicomponent catalyst phase, the method of impregnation with solutions of salts of active components in an acidic medium of the carrier is used. The distribution of phases in the grain space can be observed by physicochemical methods (spectrophotometry, in situ XRF, thermogravimetry, IR spectroscopy, ESM). Depending on the degree of sorption of active phases, the impregnation method can be sorption and impregnated. Sorption impregnation implies the strongest fixation of active components (not disturbed during heat treatment) on a carrier with a certain profile of macroscopic distribution. With the impregnated method, the active component diffuses into the internal pores - the carrier capillaries, and further heat treatment leads to the movement of the active component to the radius of the grain, forming a multiphase system. There are four types of macroscopic distribution of the active phase inside the granule in Figure 3.

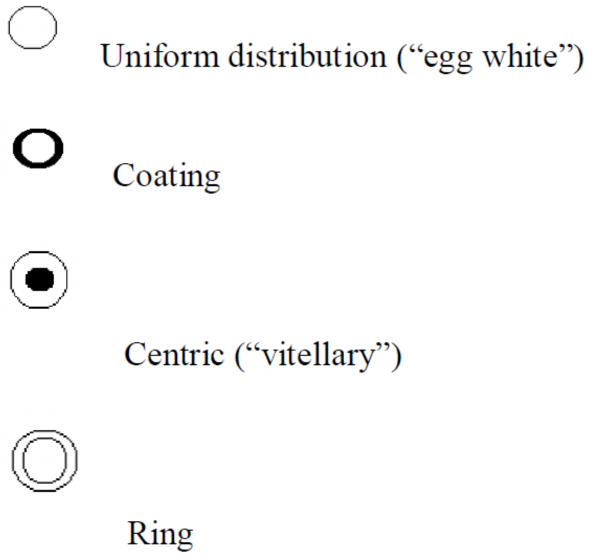

Figure 3. Types of macroscopic distribution of active components in a spherical granule of the catalyst: Uniform distribution (“egg white”), Coating, Centric (“vitellary”), Ring.

To ”bring out” active metals (ions) to the surface of the catalyst sample, competitive Maatman adsorption is used, which consists in weakening the bonds of the precursor with the surface. It can be carried out using electrolytes. The structure of γ-Al_2O_3 looks like this: O-Al-OH and under the influence of Cl^-, OCl^-, OH^-, H^+ ions, the OH groups are replaced, blocked and modified, which makes it possible to regulate the acidity of the carrier according to Lewis and Bronsted. Synthesis of catalysts based on the sol-gel method.

4.2. Synthesis of nanocatalysts using the sol-gel method. Synthesis of nanocatalysts using the sol-gel method based on tetraethoxysilane (TEOS) with subsequent production of a three-dimensional silicon network is obtained in two stages: hydrolysis of TEOS ($Si(OC_2H_5)_4$: C_2H_5OH: H_2O: HNO_3 in a ratio of 1: 1.6: 2.5: 0.001); after obtaining the sol, a dopant of $Mg(NO_3)_2{\cdot}6H_2O$ is used; and to obtain a single gel with Mg built into its network, the resulting sol is kept at room temperature for one week, after which the following cluster ≡Si–O–Mg–O–Si≡ is obtained.

The precursor drying process takes place in a muffle oven with stepwise heating from 100°C to 350°C for 15 hours. The resulting white MgO/SiO_2 powder was molded into tablets using a rotary tablet press. The distribution of metals in the silicon matrix is shown in Figure 4. In the form of a diagram, metal nanoparticles

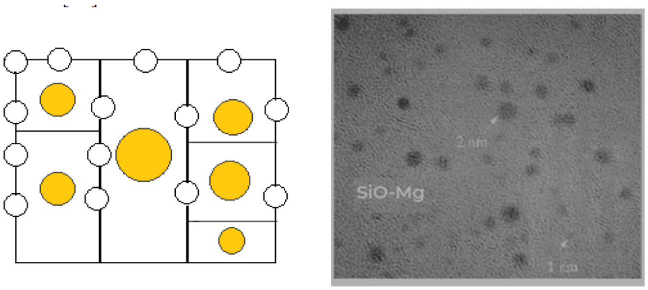

Figure 4. Schematic diagram of the gel structural network with metal dopant nanoparticles distributed in its loops (a); photograph taken using a scanning electron microscope with the dimension in nanometers indicated (b).

are shown in yellow circles a) photograph taken using a scanning electron microscope, where black dots show the uniform distribution of metal throughout the entire volume of the sample taken b).

5. Nanozeolites - hydrothermal synthesis

Zeolite catalysts play a key role in petrochemical and oil refining processes. Nanosized zeolites based on micro-mesoporous materials turned out to be more effective (better stability, high selectivity), which is due to the availability of active acid centers and a decrease in diffusion limitations. The most well-known in terms of use in the petrochemical and gas chemical industries are zeolites with the following structures FAU, BEA, MFI, MOR. The basis for the synthesis of these zeolites is hydrothermal crystallization using various templates to obtain the desired nanocrystallites with certain pores for the targeted synthesis of the desired hydrocarbons. Depending on the specifics of the synthesis of nanozeolites, the crystal size is in the range from 20 to 300 nm, while the formation of agglomerates with sizes from 100 to 600 nm takes place. Improvement of the main properties of methanol conversion and glycerol dehydration on Fe-MFI zeolite with a crystal size of 100 nm is demonstrated in Figure 5.

Hydrothermal synthesis of nanozeolites was carried out in Mori-type autoclaves, where the gel obtained from solutions of $Al(O\text{-}i\text{-}Pr)_3$ - TEAOH and NaOH - SiO_2 – TEAOH (taken in the required ratios) was placed. The resulting nanocrystals were dried at 100°C for 12 hours. The availability of active centers and the increase in selectivity for target substances in processes such as catalytic cracking, hydrocracking, oligomerization, and oxygenate conversion on the obtained nanozeolites is one of the new and promising areas in catalysis, which open up new opportunities not only in the synthesis of nanocatalysts based on zeolites, but also in other catalytic systems known to heterogeneous catalysis[14–16].

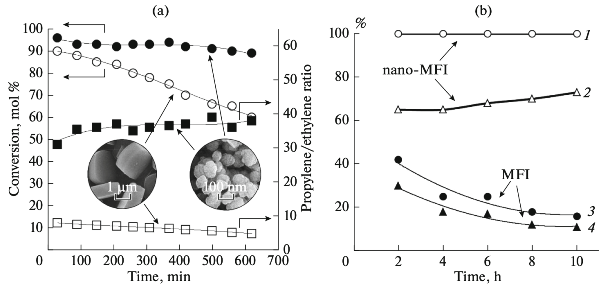

Figure 5. Effect of crystal size on its catalytic properties in petrochemical processes: a Fe-MFI zeolite, methanol conversion, b-MFI zeolite, glycerol dehydration. Curves 1,3 – glycerol conversion, 2,4 – glycerol formation selectivity (placeholder).

6. Conclusion

Over two centuries, catalysis has formed as a separate scientific and industrial direction, on the basis of which many industrial processes of oil refining, petrochemistry, and organic chemistry exist. Within the framework of fundamental science, much attention is paid to quantum-chemical modeling of frameworks - structures of heterogeneous catalysts. The use of spectrometers to study the surface in order to establish intermediate products that are included in the database provides more complete information taking into account the structural characteristics and the use of physical devices (XRF, XPS, NMR, ESM).

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