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Nature and Regularities of the Effect of Mechanochemical Activation on Catalytic Activity

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Abstract

Changes in thermodynamic and kinetic characteristics of catalytic processes under mechanochemical activation of catalysts (mechanochemical catalysis) are considered. It is shown that the activity of catalysts should increase under the mechanochemical activation, while selectivity can vary depending on the relations between the changes in the target reaction and side processes. The considered phenomena are formulated as a new research area which is at the very beginning of its development.

INTRODUCTION

Creation of high-energy mechanical activators of solids has promoted several new research areas. One of them has recently become investigation of the effect of mechanochemical activation (MCA) on the activity of catalysts. It should be noted that only unpretentious, purely empirical investigations have yet been performed in this area; they just illustrated the fact of such an influence [1]. However, we already can distinguish two research areas which are not equivalent to each other in the complexity:

1) The effect of MCA on the properties of catalysts after treatment;

2) The effect of MCA on the catalytic activity during the activation of a catalyst.

In the present paper, we mainly consider the general notions of and approaches to the problems of the second area, which is the most complicated one.

ANALYSIS OF THE PROBLEM

Influence of MCA on the properties of catalysts after the its cessation

Questions related to the traditional heterogeneous catalysis arise: what is the role of defects, unsaturated bonds, distorted coordination and the structure of catalyst in the formation of its catalytic activity and selectivity in light of the modern understanding of the nature of catalysis stage? In general, the set of questions connected with the effect of MCA on catalytic properties comprise a serious direction of fundamental science.

On the basis of scarce experimental data available at present [1] and general considerations, we can assume that the effect of MCA should be positive in the major part of cases. This conclusion is promoted by the fact that a catalyst subjected to mechanochemical activation is characterized by decreased particle size and by heterogeneity. Being in such a state, it possesses excess energy accumulated during MCA, and higher specific reactivity (*i. e.*, per unit surface). It is natural to ask what is the reason of such an increase in the reactivity: an increase in the activity of separate active centres or an increase in their concentration, *i. e.*, their number per unit surface. This principal question makes an independent problem for researchers in the area of catalysis. It should be taken into account that the mechanism of catalytic reactions known today, such as acid-basic, redox, *etc.*, are determined by the corresponding nature of catalyst and reaction conditions. One more question arises, which is not less urgent, too: whether MCA can destroy some active centres and induce other ones, of different nature, which can in principle lead to changes in both the activity and selectivity. The problem is to reveal the nature and mechanism of the effect of MCA on the catalysts of the above-mentioned types, *i. e.*, to understand how the consequences of MCA affect the specific properties and active centres of initial catalysts which determine their activity and selectivity.

It should be noted that the methodology of investigation and the required instrumentation remain traditional for heterogeneous catalysts.

Effect of MCA on catalytic activity during the activation of catalyst

In this case, we observe unusual dissipative structure of the system [2]. Pulsed character of the action on solids under MCA causes two oppositely directed processes to pass at each given moment in such a system. They are: deformation and relaxation; some equilibrium is established between them. Such an open system is maintained in the steady state due to constant energy and substance fluxes from the environment. As a result of self-organization, its structure gains spatial order and specific properties [2].

In this new activated state with constant MCA energy input and increased reactivity, along with other known relaxation channels [3], part of energy is transformed into chemical energy through the excitation of active centres, which is expressed as an increase in catalytic activity. Question arises: how does this specific channel of energy relaxation (*i. e.*, catalytic reaction) function? This new research area is incommensurably more complicated than that dealing with problems connected with the MCA aftereffect on catalyst.

Finally, there is a question to which extent is energy dissipation in this case similar to temperature judging from results of action, or, in other words, is MCA able to change the equilibrium constant of a catalytic reaction? If this is possible, we will thus change the ratio of the rates of target and side reactions, *i. e.*, selectivity of the process.

We will consider only these questions though they do not embrace the whole problem.

NATURE OF CHANGES IN CATALYTIC ACTIVITY DURING ACTIVATION (BASIC NOTIONS)

One may expect that the application of the theory of absolute reaction rates [4] to catalytic reactions under MCA conditions will allow substantial advance in understanding their mechanisms. The possibility exists to consider the transformation of mechanical energy into other kinds [3] which determine acceleration of catalytic step, taking into account catalyst type and catalytic reaction itself, that is, one can consider the whole course of system's relaxation along the channel of catalytic reaction. To some extent, the problem concerning efficiency of energy consumption in mechanochemical catalysis is also connected with this question, because the efficiency factor is determined by the part of energy relaxing through this channel.

In a dissipative system, catalyst is in the special state [2, 5, 6] due to substantial excess of free energy resulting from stationary inflow of MCA energy. This new state of the substance causes acceleration of reactions, which is called mechanochemical catalysis [1]. If we accept that steady distribution of energy between all the participants of catalytic step is established in such a system, it will be possible to estimate the rate of catalytic reaction under the MCA conditions.

So, in the aspect of general considerations, we may start from the expectation that during

MCA the activation energy of catalyst itself should decrease, *i. e.* its reactivity will increase. Of course, this consideration is complicated by superposition of notions concerning the existing types of catalytic reactions (acid-base, redox, radical, *etc.*).

Thus, under the established mode of MCA of catalyst and flow rate of reacting substances, averaged steady distribution of energy in the system among all the participants of the catalytic process is established. With invariable nature of active centres, degree of saturation of chemical affinity of the interacting molecules will determine the potential barrier, that is, activation energy (E) of the reaction. In this case, the rate of chemical interaction will be determined by the probability of the state of reacting substances with energy $>E$ and will increase proportionally to the exponential factor $e^{-E/(RT)}$. This factor should be considered as a measure of the probability for active complex to exist. In the case of catalytic reaction under MCA conditions, active complex is an intermediate compound formed by the reacting molecule and some active centre or fragment of catalyst in the highest point of energy barrier of the most profitable reaction pathway on the potential energy surface.

For elementary reactions, the theory of absolute reaction rates [4] gives an expression for the rate constant $\underline{K}$:

$$\underline{K} = \frac{kT}{h} \frac{Q^{\#}}{Q_{A} Q_{B\ldots}} e^{-E/(RT)}$$

where Q_A and Q_B are the partition functions of reacting participants; $Q^{\#}$ is the same for the active complex; k is Boltzmann constant; h is Planck's constant; T is the absolute temperature. Here kT/h has the dimensionality of frequency and represents the probability for the active complex to pass the highest point of the energy barrier in one direction along the coordinate of complex decomposition.

It was shown [4] that the configuration corresponding to the active complex possesses all the properties of a usual molecule except for the fact that the frequency of normal vibration along the decomposition coordinate is an imaginary value. Because of this, instead of the full partition function of the complex, the function is used which does not include the factor corresponding to degree of freedom of translation movement along the decomposition coordinate. So, if all the necessary structural and spectral characteristics of the active complex of reacting molecule with the active centre of the catalyst were known, the $\underline{K}$ value could be calculated. However, in most cases, we do not know true structure of the active complex, even for reactions without participation of catalysts. As far as the active complex under MCA is concerned, this is even a more ephemeral subject. Because of this, we cannot perform a theoretical quantitative estimation of $\underline{K}$ value. At the same time, it is possible to observe trends and make qualitative estimation.

The equilibrium constant $K^{\#}$ between reacting molecules and active complex can be calculated through the partition functions [7]:

$$K^{\#} = (Q^{\#}/\Pi Q_{R})\, e^{-E/(RT)}$$

However, on the other hand,

$$RT\ln K^{\#} = -G^{\#} \text{ и } \Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

where $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ are the changes in isobaric potential, enthalpy and entropy during the formation of active complex.

In this case,

$$\underline{K} = (kT/h)\, K^{\#} = (kT/h)\, e^{-\Delta G^{\#}/(RT)}$$
$$= (kT/h) e^{-\Delta H^{\#}/(RT)} e^{\Delta S^{\#}/R}$$

This appearance of the expression for rate constant of the catalytic reaction seems more acceptable for qualitative consideration of the effect of MCA on a catalytic process [4].

MCA can affect both the energy and entropy factors of the above equation. The effect of the energy factor is more easily predicted: since the excess energy is «pumped» both in the catalyst and in solid reagents, enthalpy of formation of the activated complex becomes more positive, which leads to an increase in reaction rate.

It is more difficult to predict the effect of MCA on the entropy factor. In our opinion, two versions are possible. As a rule, the formation of active complex gives rise to a more ordered system, which is accompanied by a decrease in entropy. In such a process, $\Delta S^{\#}$ is always smaller than zero. The more ordered is the structure of the transient active complex, the smaller is entropy factor, and the lower is reaction rate. A question arises: how will the entropy of formation of active complex change if we pass from the traditional conditions of heterogeneous catalysis $\Delta S^{\#}$ (1) to those of MCA $\Delta S^{\#}$ (2). The entropy contribution into the rate of catalytic process due to the transition to the conditions of mechanochemical activation of the catalyst will be determined by the difference: $\Delta S^{\#}(2) - \Delta S^{\#}(1) = \Delta S$.

It seems impossible yet to expect some unambiguous ΔS value; this problem requires special consideration. However, for invariable structure of the active complex, the ΔS value is likely to be insignificant. The prevailing contribution will be determined by the energy factor.

So, even such a purely qualitative consideration leads to the conclusion that in the cases when MCA does not destroy the nature of initial active centres of a catalyst, a substantial increase in its activity should be expected.

CONCLUSION

We have generally considered the effect of superposition of MCA on a catalytic process. Even such a consideration allows thinking that mechanochemical catalysis can become a promising method of realization of some catalytic technologies, especially small-scale ones.

In addition, we would like to formulate this problem as an important research area which is at the very beginning of its development and embraces a number of questions for further investigations. We considered some of these questions in the present paper.

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