Catalysis Today 144 (2009) 212–218

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Mechanochemical activation as a tool of increasing catalytic activity

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ARTICLE INFO

Article history:
Available online 14 April 2009

Keywords:
Catalysis
Catalyst
Mechanochemical activation
Catalytic activity
Selectivity

ABSTRACT

The role of structure–energy properties of mechanically induced defects in the crystal structure of heterogeneous catalysts is considered. The main concepts of the mechanochemical activation effect on the activity and selectivity of catalysts are discussed. The wasteless and energy-saving methods of preparation of some catalysts are presented. Rigorous experimental proofs of the influence of defects in the crystal structure of catalysts on their specific catalytic activity are obtained. High performance of mechanochemical catalysis application for hydrogenation, oxidation, amination and hydroalumination processes is shown. For the first time catalytic reactions under the conditions of mechanochemical activation at elevated temperature and increased pressure of gases are carried out.

1. Introduction and definition of the problem

The development of mechanochemical activation (MCA) of solids has shown its considerable promise for the preparation of catalysts with novel properties and improvement of the catalyst activity and selectivity. During MCA a solid (a catalyst in our case) accumulates an excess potential energy as elastic and plastic deformations and great variety of defects accompanied by an increase in its reactivity. This excess energy can considerably affect both the reactivity and activity of catalysts. The system reactivity is universal in the sense that it appears as a universal tendency for the decrease of its thermodynamic parameters. This tendency can involve different relaxation channels, including catalytic reactions yielding the desired products.

MCA allows creating defects of a fixed type, to form a surface by faces and edges not typical of catalysts in the usual state. All this extends a range of bond energies and properties of the intermediate surface species and is the reason of change in activity and selectivity.

In the present work we make an attempt to consider specific features of the synthesis and preparation of catalysts using MCA, the nature of its effect on the catalytic activity and selectivity, and thereupon to define the problem in detail.

2. Possible MCA applications in catalysis

The principle sections of the catalysis science are as follows.

2.1. Development of the scientific basis for catalyst synthesis

The main problem of this division/section is the development of methods to prepare catalysts with desired properties. These are: specific surface area, porous structure, phase composition, crystallization degree, morphological properties of crystals, defectiveness, dispersion, thermal stability, structural and mechanical properties, component distributions on the supports, etc.

To solve the problem one should study physicochemical regularities determining the features of the synthesis and action of materials during all preparation stages of separate families of similar materials (catalysts in our case) [1].

2.2. Development of the scientific basis for prediction of catalytic action

This section includes the most complicated and important problems such as:

- The chemical nature, structure and action mechanism of the active sites during operation on the catalyst surface.
- The nature and relations between catalytically active sites of the main and side reactions, means and methods of affecting the above in order to increase the selectivity towards the desired product.
- The effect of physical characteristics of the catalyst surface, the role of defects and energy-non-equilibrium states in the chemical nature and efficiency of active sites.
- Stability, resistance, lifetime of the active sites and reasons of their deactivation.

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0920-5861/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cattod.2009.02.042

Let us consider specific features and potential of MCA in catalysis.

3. Preparation of catalysts using MCA

3.1. Brief review of the theoretical and practical background of the MCA application for catalyst synthesis

Traditional methods used for synthesis of heterogeneous catalysts include, as a rule, several stages and have a number of significant disadvantages. For instance, the reactivity is usually increased by performing processes in solution or at high temperatures. As a result, the known methods do not meet the present-day ecological and energetic requirements.

The development of highly efficient mechanical activators made it possible to use MCA as an independent and in some cases as the main stage for increasing the reactivity of the solids involved in the catalyst preparation.

A considerable number of articles, reviews and monographs [2–9] are devoted to the theory and practical applications of MCA in the preparation of multi-component solid systems. In this application field, the emphasis is placed on the processes occurring in the bulk. Various phenomena occurring on the solid surface are of secondary importance and become critical only if one considers the nature of the catalytic action.

The preparation of two and multi-component solid systems by MCA involves chemical as well as other types of interaction between solid ingredients. Their rate is limited by such parameters as contact area, mass transfer processes and activation barriers.

Dispersion of solid phases increases the ratio between the particle surfaces areas and their volumes, and thus increases the total contact area between the solid phases.

It was established [2] that MCA reactions in solid mixtures follow two regimes. For low intensity MCA, solids undergo crushing. In this case, the reaction rate depends on the number and area of contacts between the reacting particles. At high intensity MCA, we observed the plastic deformation regime, at least for one reacting component. This results in a contact throughout the whole surface of a hard-to-grind material. Note that at the initial period, the chemical interaction of the components is a rate-limiting process stage. As the formed product layer begins to isolate the reacting products from each other, the diffusion mass transfer begins to define the reaction rate.

Under plastic deformation conditions, the solid phase acquires the properties of a “quasi-liquid”. This state is associated with the formation of dislocations, linear and point defects, anion and cation vacancies and the appearance of external and internal interfaces, that is, total disorder of crystals. Available data [3] suggest that for the vacancy mechanism of material transfer, the diffusion coefficient is proportional to the vacancy concentration. As the MCA intensity is sufficiently high, the saturation with defects reaches a point where a solid transforms into a “cold melting” state.

The tension gradient noticeably affects the mass transfer in such dissipative systems. The system non-equilibrium is responsible for the formation of a large variety of structural, energetic, chemical and physical properties depending on the MCA intensity. This extends the area of objects and potentialities which may be of interest for catalysis.

Similar substances (ionic salts, metals) subjected to MCA may be mixed at the atomic level via a dislocation-diffusion mechanism. Thus, the substance mass transfer occurs due to plastic flow and diffusion resulting from movement of linear and point defects.

It was shown [3] that under elastic crystal deformation conditions, the excess energy of MCA is distributed throughout the volume of dislocations and defects. Such energy distribution is thermodynamically more efficient than uniform distribution through all bonds. This feature of the substance crystalline state defines the nature of MCA conversions.

Synthesis of multi-component systems under MCA conditions should be considered with regards to the process thermodynamics. During MCA, the reacting solid phases increase Gibbs energy $\Delta G = \Delta U - T\Delta S$, which is related with the equilibrium constant K by equation $\Delta G = -RT \ln K$. Such relation leads to a seemingly paradox conclusion that it is possible to create metastable systems. However, this paradox can be explained from the thermodynamic viewpoint. Under MCA conditions the energies of reacting phases significantly differ from the reference data corresponding to the standard conditions. For this reason, non-equilibrium systems can appear under such conditions. As the energy stops to dissipate, such energy-intensive systems undergo an extinction relaxation process towards standard characteristics. This is an activated process. Owing to internal friction and retardation of atoms, relaxation decays and complete equilibrium is not attained. This results in a metastable non-equilibrium system [7,9].

It is pertinent to note that some individual crystal materials, which were treated by MCA but did not experience chemical conversion, change their structure and properties to such an extent that they could be considered as new substances having the same composition as the initial substance.

This brief description of the present-day concepts on the mechanism, regularities and peculiar features of MCA is aimed at promoting the interest to this promising method and its application in the development of the scientific basis for preparation of catalysts [1].

Let us mention some areas where significant results have been already obtained:

1. Substitution of the process stages employing solutions by mechanically activated homogenization of systems or mechanical alloying, which permits one to obtain new structures and prevent ecologically harmful wastes; direct synthesis of catalysts under MCA conditions (mechanochemical synthesis).
2. Synthesis of new solid materials (catalysts) due to an increase in the reactivity of reacting solid phases under MCA conditions.
3. Preparation of non-equilibrium solid systems that cannot be prepared by traditional methods, including solid solutions with concentrations significantly higher than the equilibrium ones.
4. Temperature decrease and easy interaction of phases during further treatments such as calcination, hydration, sorption, reduction, etc.
5. Decrease in the synthesis temperature of binary and more complex systems owing to MCA, resulting in improved structural and other characteristics.
6. Modification of the operation properties (formability, strength, texture, etc.).
7. Preparation of finely dispersed and nano-sized systems.
8. Simplification of technologies by reducing the number of stages and aggregate costs.

3.2. Some MCA applications for catalyst synthesis

We would like to present several examples to illustrate the MCA potential in the preparation of catalysts.

The treatment of powdered mixtures of magnesium and iron group metals by MCA produced a number of mechanical alloys that after subsequent hydrogenation in hydrogen at 10–17 atm