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2.4.8
Mechanochemical Methods

Bernd Kubias, Martin J. G. Fait, and Robert Schlögl*

2.4.8.1 Introduction

Since the beginning of the last century it has been known that the impact of mechanical energy on a solid leads, besides its comminution and the formation of new free surfaces, to its mechanical activation (MA) and, with increasing activation, to mechanochemical reactions [1, 2].

The term "activation" includes both enhanced activity with respect to reactions of the solid itself and changed physico-chemical properties concerning adsorption and catalytic activity and selectivity. Mechanical activation and mechanochemical reactions are the subject of mechanochemistry, a special branch of chemistry which was first defined by Ostwald at the end of the 19th century [3]. An extensive literature has been devoted to this subject during the past four decades [1, 4–8], whereby it was shown that the occurrence of these reactions cannot be explained only by thermal influence on the system by the exerted mechanical treatments. In contrast, it was proven that this phenomenon is of an independent nature (see Section 2.4.8.2).

During the past years, special domains of mechanochemistry and mechanical activation have been developed

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rapidly [9], such as mechanical alloying and amorphization of metals as well as mechanofusion and the manufacture of new, nanosized materials (see, e.g. Refs. [9–12]). Successful attempts have been made to apply mechanochemistry to pharmacy, synthesis, and to the manufacture of pigments. New approaches to the manufacture of novel or improved catalysts, and for the activation and "selectivation" of known catalysts, have been reported [13–15]. Thus, in addition to "classic" materials processing in engineering, the use of mechanochemistry in catalysis has gained increasing scientific and industrial interest. Many systematic basic and applied investigations have been conducted in this field during the past two decades, especially in the former Soviet Union and Russia, respectively [13–17], based on former fundamental and applied investigations by German and Japanese groups.

The mechanochemically influenced catalytic ("tribocatalytic") reactions known up to 1984 are listed by Heinicke in the monograph *Tribochemistry*, which deals with all aspects of mechanochemistry (in the older German literature the term tribochemistry/Tribochemie was used synonymously for the mechanochemistry of solids). Results from investigations conducted during the past 50 years concerning the mechanochemical preparation of catalysts have been collected in a recently published review by Molchanov and Buyanov [13].

In this chapter, an overview of the methods of MA in the activation and selectivation of catalytic materials, and of the contribution of mechanochemistry to the preparation of catalysts, is presented. Due to its minor importance, the influence of mechanical impact on a running reaction is mentioned only briefly. The first part of the chapter includes some outline information concerning the state of the art of MA. Similarities exist in the use of ultrasonic irradiation, which is also a viable method for the preparation and treatment of solid catalysts (cf. Chapter 8.5).

Mechanical activation and mechanochemical reactions are carried out predominantly in mills, where the milling processes play an important role in chemical industry and are responsible for a large proportion of the process costs [8]. The action of mills and the comminution of solids have formed the basis of many investigations in engineering science for decades, and the findings have led to a deeper understanding of the comminution processes and the development of highly efficient mills [9, 18].

2.4.8.2 The Effect of Mechanical Activation on the Reactivity of Solids

When mechanical energy is applied to a solid by means of pressure and shear, the resulting physicochemical changes are the consequence of relaxation of the field of stresses in the solid during and after the mechanical treatment [13]. The strain field manifests itself by shifts of atoms from the stable equilibrium positions, by changes of bond length and angles and, in some cases, by excitation of the electron subsystem [19]. These changes result in an activated state of the solid. The accumulated energy can lead to destruction of the crystal and finally to amorphization or transition to a metastable polymorphous state. If relaxation of the strain field results in the rupture of chemical bonds, a mechanochemical reaction occurs [2]. Thus, the thermal excitation of chemical reactions, which is also induced by mechanical exertions, is not the only reason for the observed MA results [20].

In all cases the thermodynamic potentials of the treated compounds are changed, and free energy and enthalpy are enhanced. These depend on the size of particles and on the presence of defects in their crystal structure. Often, a direct relationship between the mechanical energy added, the concentration of defects, and the reactivity of the solids has been observed. These relationships have been widely studied for brittle substances, but are also described in some investigations with ductile materials (e.g., Refs. [21–24]). The imperfections are categorized as point defects and extended defects (one- or two-dimensional defects) [25, 26], and are commonly assumed to act as the catalytically active sites.

The non-equilibrium structural and phase states of catalysts arising in the process of their mechanochemical preparation, or by their treatment by MA, tend to anneal during the use of catalysts. As a consequence, the catalytic properties of the treated solids may change to a less-active steady state during their application at higher temperature. Thus, to maintain the enhanced activation for catalytic purposes a permanent addition of mechanical energy may be necessary. However, there are numerous examples of rather high stability of the metastable activated states of solid catalysts at elevated temperatures under real reaction conditions [13, 27]. This is explained by the fact that the thermal annealing of defects is also an activated process. Therefore, some structures with higher reactivity may exist for a rather long time, and the increase in catalytic activity may be used for practical purposes.

On occasion, mechanical treatment is even necessary for the creation of sufficient catalytic activity, as in the case of the activation of Ziegler–Natta catalysts by milling [28]. These catalysts and other mechanically activated catalysts, which are used at lower temperatures, remain stable during their use.

A close correlation between the nature and the concentration of lattice defects and the specific catalytic activity has been found [29–33], and consequently defects such as dislocations [21, 23, 30, 34–37], planes of crystallographic shear [34, 38], and steps in the facets [39] are assumed to be catalytically active sites. However, according to Molchanov and Buyanov [13, 40], only a few studies [23, 41] have provided direct experimental evidence for the role of well-defined defects in the increase in the catalytic activity and allowed a description of the structure of active sites at the atomic level.

Systematic studies of the effects of different types of stress during MA showed [42] that the activation effects depend on the types of stress valid for the different comminution machines. Whereas impact stress changes the microstructure in the whole bulk of the particle, pressure and shear stresses cause a significant enhancement of defects at the surface of the treated particles. Among the factors controlling defect development, the energy input of the mills and the efficiency of the energy transfer in the mills are the most important [43]. In the case of complex reactions, MA-effected changes in the catalytic properties can also include altered properties of selectivity (see Section 2.4.8.5.2).

The MA-effected changes of the structure of solids may be characterized by the usual methods of structural and morphological characterization of solids such as X-ray diffraction (XRD) (real structure analysis: crystallite size, amorphous fraction, microstructure), laser diffraction (particle size distribution), BET and porosity measurements (specific surface area, pore structure), density measurements, calorimetry and thermal analysis, and transmission and scanning electron microscopy (TEM, SEM). Vibrational spectroscopy [Raman, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), DR-UV-visible] and electron paramagnetic resonance (EPR) spectroscopy were also used to characterize the defect structures of mechanically activated materials (e.g., Refs. [44–48]). A detailed description of the methods mentioned with respect to MA can be found in Refs. [1, 49], and in the respective chapters of this Handbook.

2.4.8.3 Mills

In general, mills are used for the comminution and mechanochemical treatment of solids. It should be pointed out that although normally used mills are developed for optimal comminution, and not for optimum activation, they have nonetheless proved to be useful tools for mechanical activation.

In the case of a given uniform chemical compound, comminution by milling results in the formation of a middle particle size of the material with increasing milling duration, independent of the particle size of the starting material; in other words, the so-called Hüttig milling equilibrium is reached [50]. Here, typical particle sizes are ca. 10 μm in case of fine grinding with ball mills, and ca. 1 μm (super-fine grinding with attritors). Under special conditions, comminution may be used for the synthesis of a wide range of nanopowders with mean particle sizes as small as 4 nm [51]. As shown by Rehbinder et al., the addition of surfactants to the treated materials leads to a diminished strength of the milled metals [19, 52, 53] (the Rehbinder effect; see Section 2.4.8.3.3) and, thus, enables an efficient comminution.

Due to the importance of comminution for industrial materials processing, the types of crushers and mills available are many and diverse. Despite the progress, which has been made during the past decade in understanding the milling process, the choice of the best suited mill for any given comminution or activation task and, of the "right" conditions, has been until now a question of experiment and experience. This is due mainly to the fact that today the description of a comminution process is possible, but only to a limited extent using appropriate models [54].

The comminution process may be traced by means of standard methods for solids characterization, as listed in Section 2.4.8.2.

As mentioned above, mechanical activation comprises the complex structural changes of the solid in the micro and macro scale. For MA in the laboratory, a number of excellent mills have particularly proved their worth. The different types of stress mechanism exerted in these different mills lead to different grinding results and different structural changes, depending on the material's behavior. A short description of the different stress types is presented below, and an overview is also provided of the main characteristics of selected types of laboratory mill from the point of view of an experimentalist. Some examples will be used to illustrate the mode of action and use of mills in the treatment of solids.

2.4.8.3.1 Stress Types

The micro processes which occur during the comminution can be classified after Rumpf, according to the types of exerted stresses [55, 56].

A Stress Between Two Surfaces (cf. Fig. 1) In this case, the material is stressed individually or collectively between two surfaces. If the influence is vertical, then a compressive stress takes place resulting in pressure and percussion stress. With an additional tangential movement of the milling areas, shearing and friction stress takes place. In practice both stresses occur together. Whereas pressure and percussion dominate at crushing and rolling, shearing dominates at trituration and cutting. At distinct parameters of the mill the transition to percussion stress is adjustable, which is valid especially for planetary mills if their construction allows the independent adjustment of the relevant components.

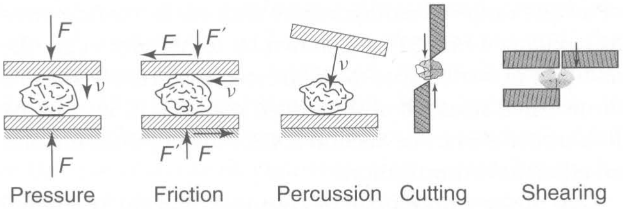

Fig. 1 Comminution principles according to Rumpf [57]: stress between two surfaces (from Ref. [56]). F = force; F' = force directed perpendicular to F; ν = stress velocity.

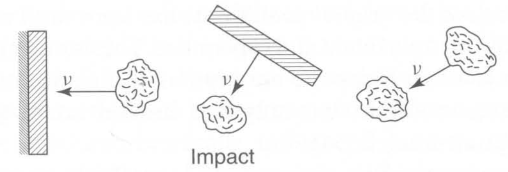

Fig. 2 Comminution principles according to Rumpf [57]: stress at a single surface; ν = stress velocity (From Ref. [56]).

B Stress at a Single Surface (cf. Fig. 2) This type of stress is exerted by a single surface and appears as impact stress. The material is stressed by its striking against the face of the grinding medium, by the striking of the grinding medium against the material, or by mutual impact of the material. The stress intensity is a function of the velocity. This type of stress occurs mainly in a high peripheral-speed pin mill (disintegrator), a jet mill, and an attritor (see Section 2.4.8.3.2).

C Stress Without Milling Faces Energy can also be transmitted to solids by surrounding liquid and gaseous media, for example, by a jet of gases. However, this type of energy input is of minor interest for the comminution and mechanical activation and, therefore, is not mentioned in the following.

2.4.8.3.2 **Types and Mode of Action of Mills** In the following section, the mode of action of some selected laboratory mills are described in order to provide an impression of their application, as well as the problems connected with their practical use. The family of crushers will not be described at this point (see Ref. [56]). A detailed description of a variety of mills from the viewpoint of process engineering can be found in Refs. [56, 58, 59], while the monograph of Höffl [60] concerns the constructive characteristics of different industrial grinding machines.

Well-known members of the family of grinders with two grinding surfaces are the vibratory mill, the mortar grinder, and the planetary ball mills, which are selected here as examples to demonstrate the possible function of mills.

The *pinned disc mill*, as a representative of a comminution machine with one grinding surface, utilizes a high-speed rotor with one or more rows of rods that propel particles into stationary pins that mesh with the rotor. In *jet mills*, the material is accelerated by means of propellant air or gas jets; comminution then occurs by particle impact with a surface (target), or by interparticle collision. The *attritor* is a mill containing balls in liquid media, which is internally agitated by a stirrer; however, the liquid must be removed after grinding and this may affect the properties of the material treated.

A Vibratory Mills Vibratory mills achieve size reduction through the combination of impact and friction. An electromagnetically powered mortar generates vibrations (see Fig. 3), which are transferred to the grinding ball via the grinding material. The impact energy of the grinding ball can be controlled by adjusting the amplitude. The vibrating mill has proved its worth as a good mechanical activation machine, and is often used for the investigations of mechanical activation effects.

B Mortar Grinder The principle of action of a mortar grinder (Fig. 4) is similar to that of a hand mortar, in that the material to be ground is reduced in size between the pestle and the mortar bowl through pressure, friction, shearing, and cutting. Pressure is applied by the pestle on the mortar wall in horizontal as well as vertical directions. Pressure arises by the pestle's own weight and by preloaded adjustable springs, or by an additional

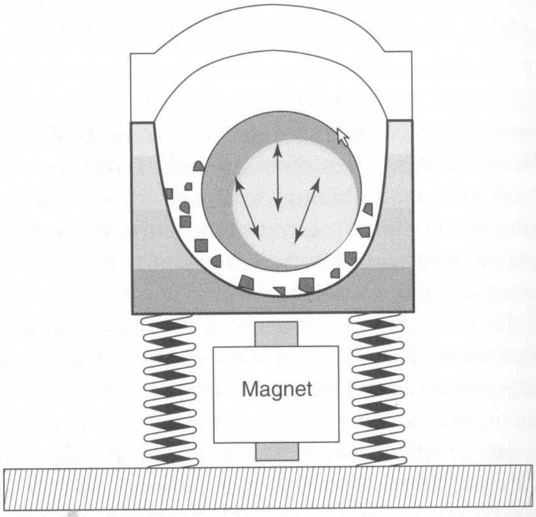

Fig. 3 Schematic view of a vibratory mill with one grinding ball. (Illustration reproduced with permission from Fritsch GmbH.)

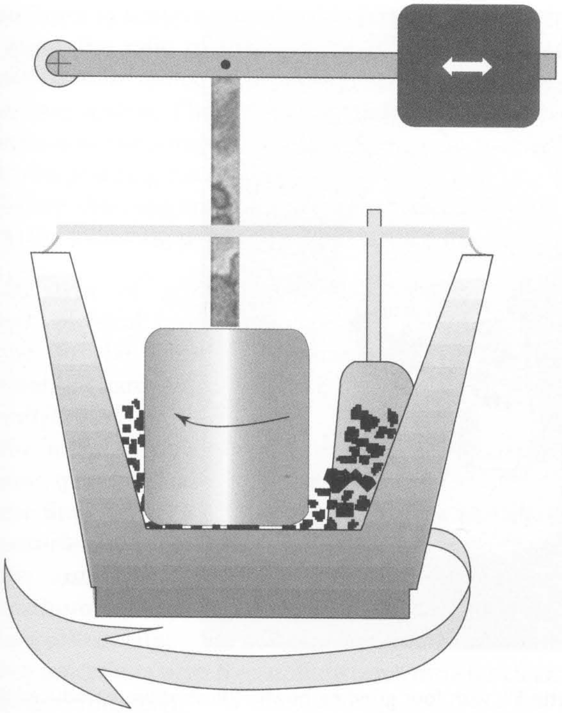

Fig. 4 Schematic view of a mortar grinder. (Illustration reproduced with permission from Fritsch GmbH.)

weight acting on the pestle axis. A fixed scraper turns the material and guides the whole sample amount back to the pestle. The mortar grinder seems to be suited especially for materials with a layered structure, and especially if the layers must be spread in order to expose the catalytically active and selective surfaces.

C Planetary Ball Mill In the planetary ball mill (Fig. 5), the sample material is primarily comminuted by the high-energy impact of grinding balls, together with friction between the balls and the wall of the grinding bowl. The grinding bowls, when filled with the grinding material and balls, rotate around their own axis on a counter-rotating supporting disc (the sun disc). The centrifugal forces caused by the rotation of the grinding bowls and supporting disc work on the grinding material. The force resulting from rotation of the grinding bowl when the mill is started causes the rotating balls to rub against the inside wall of the bowl (sliding regime; Fig. 6a). With increasing centrifugal force, comminution by percussion is reached (throwing regime; Fig. 6b). Depending on the revolution of the grinding bowls and supporting disc, turbulence and circle regimes may occur (Fig. 6c,d). The various milling regimes result in different main stress mechanisms of percussion, shearing, or pressure. In these mills, by using an appropriate geometric arrangement of the trajectories, and by selecting suitable rotation times, accelerations of 600 to 1000 m s^{-2} (ca. 60–100 *g*) can be achieved, ensuring very high mechanical activation effects.

An adjustment of different types of stress is possible in a specially designed planetary mill (type FIA; UVR-FIA GmbH, Freiberg, Germany) by appropriate choice of the characteristic machine parameters; this allows the transfer from friction stress via a transition region to impact stress, as demonstrated in the case of mechanical alloying of binary mixtures of metals [9]. In a similar manner, the creation of new surfaces and structural distortions, respectively, can be influenced specifically in the same mill. This effect was studied, for example with quartz [61], using a vibration mill and by varying the revolutions and the amplitude.

Nowadays, both a gas pressure and temperature measuring system (GTM system, Fritsch GmbH) and a means of providing an inert atmosphere are available for ball mills. Such systems enable a planetary mill to be converted, for example, into an *in-situ* measuring system. Without any modification of the mill itself, the grinding bowl is substituted by a bowl with a transmitter integrated into the lid. The data are transferred by wireless mode to a computer, where they can be visualized and analyzed.

Direct observation of the self-combustion of elemental powders during the course of ball-milling treatment by using quartz, transparent reaction vessels and a high-speed image-acquisition system has been described [62].

2.4.8.3.3 The Practical Use of Mills: Some Comments

The different comminution machines vary by three orders of magnitude in their maximum power input related to the milling body mass [63]. The respective maximum values are in the range of 40 W kg^{-1} (vibration mill), ca. 100 W kg^{-1} (planetary ball mill; type "Pulverisette 5", Fritsch GmbH, Germany), and up to 4 kW kg^{-1} (planetary ball mill; type FIA, UVR-FIA GmbH, Germany). An especially powerful high-energy mill is the Spex mill 8000 (SPEX CertiPrep, USA), which enables a power input of up to 30 kW kg^{-1}. The energy input is correlated directly to the milling time; mills transferring a very high energy permit short milling times in the range of minutes, whereas mills with lower power input require longer milling durations that range from several hours up to days.

The key points of carrying out effective grinding, such as optimum filling, cleaning procedures of grinding sets, and safety requirements, are summarized with respect to analytical aspects in Ref. [64]. In this section, only the

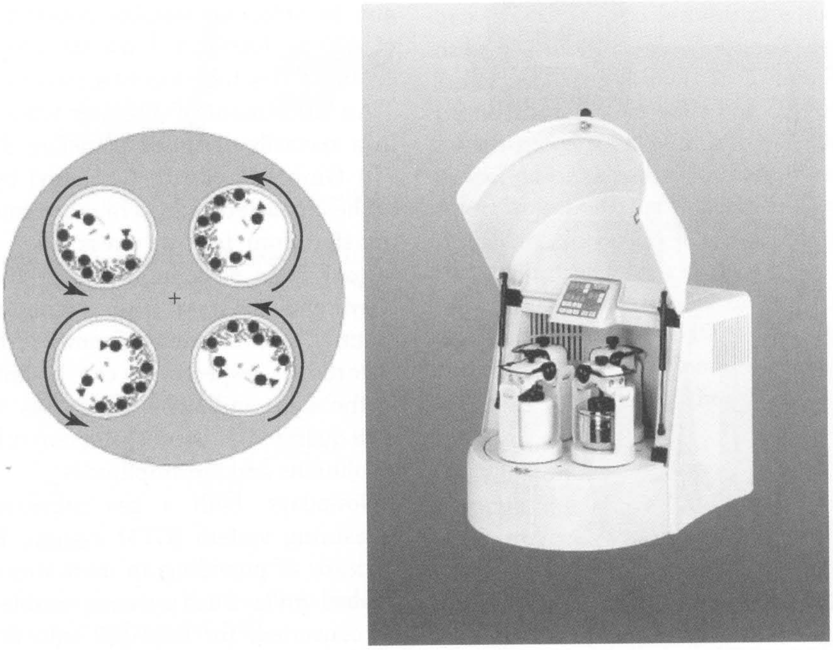

Fig. 5 Left: a schematic view of a planetary ball mill. Right: A "Pulverisette 5", with four grinding bowls. (Illustration reproduced with permission from Fritsch GmbH.)

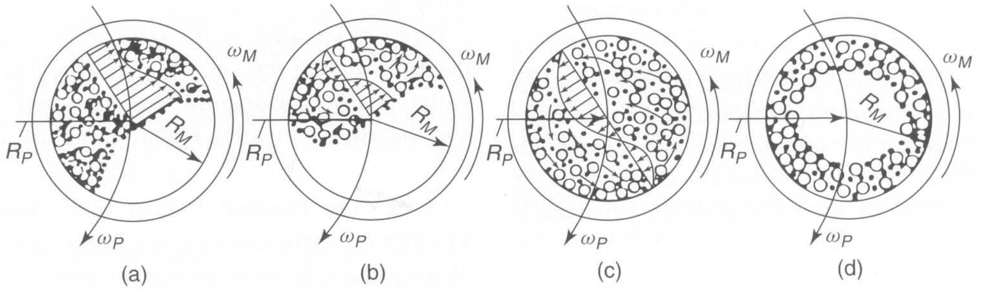

Fig. 6 Different milling regimes depending on the operating parameters in a planetary ball mill (from Ref. [60]). R_P = radius of the supporting disc; R_M = radius of the grinding bowl; ω_P = angular velocity of the supporting disc; ω_M = angular velocity of the grinding bowl. (a) Sliding regime; (b) throwing regime; (c) turbulence regime; (d) circle regime

problems of contamination and agglomeration will be detailed.

In general terms, contamination of the milled materials must be considered, mainly as a result of abrasion of the mill's grinding parts. For example, it could be expected that a milled material would contain iron if the grinding part were to be made from stainless steel [65]. In order to overcome this problem, the vessels should be lined with appropriate materials (e.g., semiprecious stone). Moreover, for catalytically relevant studies, grinding media with high abrasion resistance should be used, such as agate, sintered corundum, and zirconia.

One undesired effect during grinding is that of agglomeration or "caking"; this may be caused by electrostatic charge accumulation and/or the fusion of particles under pressure or humidity, and in turn leads to an inhibition of further particle size reduction. The multichoice of grinding aids available (slurry grinding) makes this technique an "art". The theoretical background of efficient grinding in suspension is termed the "Rehbinder effect", which consists of a decrease in the surface tension of a solid under the action of an ambient medium such as water, alcohol, or other liquids. These media are added to the sample before grinding begins, and are removed afterwards. The effect results in an abated strength of the solid, and thus favors the evolution of defects and comminution at a lower level of mechanical stress.

In order to achieve reproducible results, it is necessary to know the ratio of the mass of balls to the mass of material to be milled, as well as the filling degree of the grinding vessels. These data, together with the velocity, determines the amount of energy which is transferred into the grinding material [9].

Before choosing and using a distinct laboratory mill for MA, the following points must be clarified [66]:

- the type of grinding material (i.e., its chemical and physical properties, especially hardness according to the classification hard/tough, hard/brittle, medium hard/tough, medium hard/brittle, soft/tough, soft/brittle)
- the initial sample characteristics (i.e., initial particle size, quantity, and number of samples)
- the final sample characteristics (i.e., fine particle size, particle size range, contamination, abrasion)
- the universal applicability (i.e., milling in a slurry medium or in an inert atmosphere and under vacuum, sample cooling)
- the processing time (i.e., milling time, time for cleaning of grinding sets).

2.4.8.4 **The Use of Mechanochemistry for the Synthesis of Catalysts**

In this section, selected examples of the application of mechanochemistry in the synthesis of catalysts, and for the control of their performance, are presented. Today, catalyst synthesis represents a specialized area of mechanochemistry in the production of new or improved materials.

According to Molchanov and Buyanov [13], mechanochemical syntheses can be successfully carried out if: (i) the crystalline structures of the solids to be converted are similar; (ii) in the case of an interaction of acid–base type, one of the reactants is a strong acid or base; or (iii) in the formation of pseudomelts, an intensive mechanical treatment increases the mobilities of molecules of at least one reagent to the level of their mobilities in a melt.

One of the most impressive examples of improving catalytic properties by mechanical treatment is the preparation of polymerization catalysts of the Ziegler–Natta type. The ball milling of $TiCl_3$ was found to cause a large increase in catalyst activity in the stereoselective production of isotactic propylene [28]. The reason for this is that, under the conditions of milling, formation of the δ-$TiCl_3$ phase is favored, which shows a higher activity than the α- and γ-phases and proved to be necessary for high stereospecificity [67]. The processes occurring during the manufacture of Al–Ti-chloride catalysts by the mechanical treatment of $Al/TiCl_4$ or $Ti/AlCl_3$ or chloride/alkylaluminum mixtures were investigated by Tornquist et al. [68–70], who showed that activation was due to the formation of a solid solution of the δ-$TiCl_3$ structure [68].

An additional example of the successful use of MA has been the synthesis of hydrides of intermetallic Mg compounds as selective hydrogenation catalysts [71, 72]. These catalysts are used for the purification of olefin monomers from undesired alkine and diene contaminations. As yet, the known noble metal hydrogenation catalysts have too-low selectivities in these reactions but, as was shown during the 1980s, the discovered hydrides of intermetallic compounds proved to be active and selective in these hydrogenation reactions due to their highly mobile hydrogen [73–75]. In fact, the mechanically prepared alloys were found to be readily hydrogenated without any long-lasting hydrogenation/dehydrogenation treatments. As shown by Molchanov et al., under the conditions of high hydrogen pressure, new Mg intermetallic compounds such as Mg_2FeH_6, Mg_3CoH_5, and Mg_2CoH_5 can easily be prepared via the stage of mechanical alloying [40]. These mechanochemically obtained catalysts show 100% selectivities in the hydrogenation of butadiene to butenes and acetylene to ethylene, and also proved to be active in the hydrogenation of nitrogen to ammonia.

Novel waste-free methods for the manufacture of heteropoly acids (HPA) by the mechanical treatment of the constituents, allow for the preparation of these compounds [76], which are efficient catalysts for acid–base and oxidation reactions [77]. A direct synthesis from the oxides of tungsten, molybdenum, and vanadium was possible due to an increase in their reactivity by suitable milling procedures. More recently, new methods developed by Molchanov et al. for the synthesis of P–Mo–V– and P–Mo–HPA's comprise more the MA of the respective oxides and their mixtures in interaction with phosphoric acid [76].

According to Maksimov et al. [78], mechanochemically prepared HPA catalysts proved successful (instead of oleum) for the synthesis of diacetone L-sorbose, an intermediate product in the synthesis of vitamin C. This new technology is also said to include a method for the recovery of spent catalysts, thereby allowing the easy recycling of catalytic materials and avoiding the loss of expensive constituents.

Mechanical activation may also be successfully applied in the preparation of hydrocarbon decomposition catalysts for the manufacture of filamentous carbons. These catalysts are normally obtained by the catalytic decomposition of hydrocarbons on iron subgroup metals or their alloys with other metals such as Cu. The traditional method of catalyst preparation is to coprecipitate the hydroxides of metals and supports to obtain metal or alloy particles with a size of less than 50 nm [79]. The MA of Ni oxide

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or its mixture with other oxides, together with suitable lamellar-structured supports in planetary mills, yielded catalysts with better activities compared to the conventionally prepared materials [80, 81]. Moreover, their good long-term stability makes them attractive for use in the production of hydrogen and carbonaceous materials from suitable hydrocarbons.

Mechanical activation proved also to be helpful in the manufacture of skeletal catalysts for the hydrogenation of organic compounds, as shown by Boldyrev et al. [82] and Fasman et al. [83]. Thus, the mechanical alloying of mixtures of powders of Ni and Al metals by means of planetary-centrifugal and vibratory mills leads to Raney catalysts with improved activity, which can be easily leached [82, 83]. In addition, energy-consuming pyrometallurgical steps for the preparation of alloys are avoided. Mechanical activation may also be successfully applied in the regeneration of spent skeletal catalysts, leading to catalysts with higher activity compared to the original catalysts. This result is attributed to the formation of a metastable compound with a Ni–Al structure, whereas conventional Raney catalysts contain Ni as a face-centered cubic lattice [84].

An impressive example of the advantage of mechanical treatment in the synthesis of supported metal catalysts is the milling of a mixture of metallic Ni with quartz in a vibratory mill. As shown by Schrader et al. [85], this procedure led to a coating of quartz with Ni and, consequently, to an improvement of the hydrogenation activity with respect to benzene. The increased activity is assumed to be due to distortions of the crystal lattice of Ni. If Cr, V, and Mo on silica gel were treated in a vibratory mill in different media, the catalysts obtained showed increased activities for ethylene polymerization [86], propylene metathesis [87], and the selective oxidation of methane to formaldehyde [88].

A further example of the successful application of mechanochemical methods for the manufacture of catalysts, namely the preparation of supported oxide monolayer catalysts from mechanical mixtures of the respective oxides, is discussed in Chapter 2.4.7. The preparation of catalysts for total oxidation on the basis of Co/Cu oxides, the synthesis of phosphate catalysts with improved strength, the preparation of alumina-based catalysts and of supports including hydroxyaluminates, alumosilicates, and zeolites have been described by Molchanov and Buyanov [13, and references cited therein].

It follows from the above-mentioned examples that mechanochemistry might help to identify new solutions with reduced expenditures for the purification of liquid and gaseous emissions, and that this will in turn make a major contribution to reducing the costs associated with catalyst production. As some of these mechanochemical syntheses show great potential with regards to not only energy saving but also improved safety, this technology should prove to be highly attractive when substituting conventional catalyst preparations.

2.4.8.5 The Influence of Mechanical Activation on Catalytic Properties

Evidence suggests that MA of catalytic materials prior to their use as catalysts may have a major influence on both the activity and selectivity. Whereas the influence of mechanical treatment on catalytic activity was realized during the initial investigations on catalytic effects caused by MA, the improvements in selectivity in complex reactions has become increasingly important only during the past 20 years.

2.4.8.5.1 The Influence of Mechanical Activation on Catalytic Activity

The effect of MA on the catalytic activity of metals and metal oxides has been demonstrated in numerous experiments, and is well documented in the literature. As a rule, mechanical treatments result in a considerable increase in the catalytic activity of solids – in some cases by several orders of magnitude [89].

Such an effect on the catalytic activity of metals was first realized during the 1930s [90], when Eckell observed that the rolling of a Ni foil led to an increase in its activity for ethylene hydrogenation. However, this enhanced activity was seen to disappear following annealing of the foil at temperatures in excess of 200 °C.

From later studies with different noble and other metal catalysts, it was concluded that dislocations and point defects were responsible for the observed increase in catalytic activity [91, 92]. Further, it was recognized that thermal annealing resulted in a decrease in activity to a level identical with the activity of the untreated metal.

Systematic studies of the influence of MA on the catalytic properties of metals were conducted by Uhara et al. and Kishimoto and Nishioka during the 1960s. These groups demonstrated increases in the catalytic activities of Cu [21, 30], Ni [35, 36], Ag [37], Au [93], and Pt [94] in a series of reactions such as the decomposition of diazonium chloride, the dehydrogenation and oxidation of ethanol, the hydrogenation of cinnamic acid, and the decomposition of formic acid. Dislocations were concluded to act as active sites, although in some cases the increase in activity was also attributed to the occurrance of vacancies [35, 36, 94].

At the same time, Schrader et al. [41, 95–99] showed that the activity of Co and Ni powder in the hydrogenation of benzene and ocenol, as a model reactant for fats, depended heavily on the duration of treatment in the applied ball and vibratory mills, and correlated well with the presence of defects and their density, as well as distortions of the crystal lattice. In the case of cobalt, Schottky defects were identified as active sites [99]. Again, the deactivation of catalysts by heating was attributed to the annihilation of vacancies [99].

The effects of MA on the catalytic activity of oxides were first observed by Clark and Rowan in 1941, while studying the catalytic activity of lead oxide in the decomposition of hydrogen peroxide [100]. Later studies by Paudert [101, 102] and by Schrader et al. [95, 96, 103, 104] concerning the activation behavior of different oxides (e.g., α-Fe_2O_3 in the oxidation of SO_2 and CO) revealed that the increase in activity caused by grinding the oxide in a vibratory mill was due rather to distortions of the crystal lattice than to the observed enlargement of the surface area. Analogously, the activation of α-Fe_2O_3 in a ball mill led to an enhanced activity in the selective catalytic reduction of NO with CO, which was shown to be caused by defects in the oxygen lattice [27]. Other types of mechanical impacts, such as compacting pressure and shock waves, were also found to cause higher activities of the treated mixed oxides or solid acids (e.g., tungstic acid and potassium hydrogensulfate) in different types of reactions such as polymerization, hydration/dehydration, hydrogenolysis, and oxidation [105–108].

The responsibility of defects for this increased activity was also clearly evidenced by Avvakumov et al. in a study of the MA of TiO_2 in the oxidation of CO. These authors' results revealed a quantitative dependence of the specific rate of CO oxidation on the concentration of the defects such as the concentration of the planes of crystallographic shear, which emerged on the surface of TiO_2 [38].

The above-mentioned examples show clearly that several effects may be responsible for the mechanochemically effected changes in the activity of a catalytic material. In most cases, the high concentration of defects in the solids as the result of treatments led to a decrease in activation energy and, therefore, to an increased activity. If, at the same time, an inhibitory effect caused by adsorbed molecules on the catalyst surface was to be lifted by the formation of fresh surfaces, a particularly strong increase in catalytic activity would be expected to appear [109].

There are also examples, however, when mechanical treatment leads to a *reduction* in activity; an example is the case of aluminum oxide which, after milling, no longer possess any activity for coke formation [110]. According to Buyanov et al. [15], the MA of rutile in air resulted in a decrease in specific activity for the oxidation of CO by one order of magnitude, whereas in the presence of Ar, MA led to almost complete deactivation. Another example of the somewhat surprising effects of MA was that such treatment of α-Fe_2O_3 in a ball mill, with up to 90% amorphization, caused a negative effect on the solid-state reactivity for reduction by hydrogen; this inhibitory effect was thought to be caused by diffusion of the Fe ions [27].

2.4.8.5.2 **The Influence of Mechanical Activation on Catalytic Selectivity** During the past 20 years, an increasing number of studies have been devoted to the effect of MA on the selectivity of catalysts. One such investigation involved the influence of MA on the selectivity of vanadyl pyrophosphate [$(VO)_2P_2O_7$] catalysts in the oxidation of butane to maleic anhydride; this effect is of special interest due to the industrial importance of this oxidation process. A study of the behavior of defects in the treated catalyst precursor, vanadyl hydrogen phosphate hemihydrate, $VOHPO_4 \cdot 0.5H_2O$, showed that structural changes in the precursor induced by MA were preserved due to the topotactic nature of the conversion of the hemihydrate into the pyrophosphate (the "heredity effect") [43]. According to Horowitz et al., the treatment of a suspension of $VOHPO_4 \cdot 0.5H_2O$ in isopropanol in a (not-specified) mill for 24 h improved the maleic anhydride selectivity by about 6% at a butane conversion of 80% [111]. This improvement was attributed to an increased exposure of the catalytically selective face of the $(VO)_2P_2O_7$ catalyst relative to other crystallographic surfaces, this being due to shear forces provided by the wet milling. A rise in the catalytic selectivity and activity of the vanadyl pyrophosphate catalyst was also described by Zazhigalov et al. [112], independent of the fact, whether the samples were obtained after pretreatments of the raw material V_2O_5, the precursor, or of the catalyst itself. These authors suggested that such an effect might be due to an enhanced exposure of the (100) planes of the vanadyl pyrophosphate crystals formed by topotactic transformation of the vanadyl planes (001) of the precursor. In contrast, other groups [113–115] attributed the increase in selectivity of maleic anhydride formation to an increased surface area and the generation of fresh and reactive surfaces. Fait et al. [116] studied the influence of grinding the precursor and catalyst in different mills, thus allowing different mechanisms of mechanical exertions on the real structure parameters. Subsequently, a 5% increase was observed in the selectivities of maleic anhydride, though the area-specific rates did not change significantly. According to these authors, the improved selectivity cannot be explained by catalytic anisotropy but rather by induced lattice imperfections connected with a particle size effect. After conditioning, the changes in selectivity and activity were found to remain constant for more than 70 h while on stream.

A further example of a selectivity-enhancing effect of MA was found in the grinding of MoS_2 in a vibratory mill, with selectivity in thiophene hydrodesulfurization being markedly changed. As shown by Stevens and Edmonds [117], the composition of the medium in the mill had a major influence on the direction of this change. For example, if the grinding was performed

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in heptane, a ratio of the surfaces of basal and edge planes of molybdenum disulfide of ca. 3 : 1 was found, but when ground in air the ratio amounted to 1 : 19. The edge plane was found to be a strong site for thiophene adsorption and for activated hydrogen adsorption, and also appeared to be a strong hydrogenating center. The basal plane of MoS_2 proved to be active for thiophene conversion and was also more selective, producing low levels of thiophene and hydrogen adsorption and low levels of product hydrogenation. The sulfided commercial $CoMo-Al_2O_3$ catalyst resembled heptane-ground MoS_2, which suggested that the main active site of the CoMo catalyst is the MoS_2 basal plane.

As shown by Trovarelli et al. [118], nanophase carbides obtained by the ball milling of elemental Fe and graphite powders at room temperature were found to be more active and selective in the hydrogenation of CO_2 than Fe/C mixtures and coarse-grained, conventionally synthesized carbides. Depending on the milling duration and the formation of iron carbide, the selectivity towards C_{2+} hydrocarbons varied markedly. The alkene/alkane ratio in C_2-C_4 products decreased, indicating that secondary hydrogenation of alkenes was promoted on these samples, with the product distributions following Anderson–Schulz statistics.

As observed by Molchanov [17], grinding may also lead to a decrease in selectivity compared to the behavior of the untreated material. Thus, Molchanov reported a decrease in the selectivity of butadiene formation by dehydrogenation of *n*-butenes on a mechanically activated Fe/K catalyst.

In most cases, the observed changes in selectivity were related to changes in the exposure of special crystallographic planes caused by grinding. However, as mentioned above, studies performed under the conditions of varying exertions of pressure and shear showed clearly that induced imperfections of the catalyst crystals may also have a selectivity-directing effect.

2.4.8.6 Pseudocatalytic and Catalytic Reactions During Mechanical Activation

According to Molchanov and Buyanov [13, 15], heterogeneous reactions, which occur exclusively under the permanent influence of mechanical impacts to a solid, can be discriminated either as "pseudocatalytic" or "catalytic".

Pseudocatalytic reactions are characterized by the repeated transformation of chemical reactants with the continuously activated solid. In this case, the catalyst acts as the initiator of the chemical reaction and is consumed in the process. The driving force of these reactions is the permanent generation of active centers by mechanical impact.

In contrast, in *catalytic reactions* the active sites are regenerated as a result of cyclic chemical transformations. With regards to activation of the reactants, it was postulated [13] that the necessary activation energy is supplied only partially by the transformation of mechanical energy into thermal energy, thus enabling the activation of the molecules in the usual manner. Subsequently, a direct transfer of excess energy concentrated in short-living centers formed by mechanical impact to the reactants was proposed as a more probable means of activation, termed "mechanochemical catalysis".

According to the above definition, examples of pseudocatalytic reactions include the oxidation of C, H_2, and CO during the mechanical activation of quartz [119–122]. Polymerization reactions of vinyl monomers occurring under the influence of vibromilling of Al, Fe, and SiO_2 powders in the medium of the respective monomers are also assumed to belong to this type [123]. Radicals or charged centers of freshly formed surfaces are thought to start these polymerization reactions [124].

Catalytic reactions were first observed by Heinicke et al. [119, 125], who studied the formation of NH_3 during the treatment of an industrial catalyst with carborundum particles in either a jet mill [119, 125] or in a ball mill [126] at room temperature. The catalytic reaction [126] was found to take place only during the treatment process. As shown by Lischke and Heinicke, the hydrogenation of benzene on Ni metal under mechanical exertion took place even in the presence of the strong catalyst poison thiophene if corundum particles were added to Ni [127, 128]. Studies at elevated temperature comprised the oxidation of SO_2 on V_2O_5 in a vibratory mill at 350–500 °C [101]. In addition to these reactions, Molchanov et al. [129] highlighted the fact that the pyrolysis of butane on MgO, the hydrogenolysis of butadiene on intermetallides of Mg, and the synthesis of boric esters on zeolites also take place under MA conditions.

2.4.8.7 Conclusions

As shown in this chapter, the mechanochemistry of catalysts and catalysis has developed rapidly during the past few decades. Comprehensive reviews characterizing the state of the art and providing detailed information and access to the original papers are available. Today, mechanochemistry provides a valuable tool, with multiple choice, for the syntheses of catalytic materials and for the activation and selectivation of catalysts. A variety of novel, environmentally friendly approaches to the manufacture of catalysts has been developed, with the MA of known catalysts proving to be most successful in the preparation of more active catalysts with sufficient long-term stability and enhanced selectivity. Notably, the investigation of the latter possibility should open new routes to the development of improved catalysts.

In addition, MA has contributed to a better understanding of catalytic processes by providing deeper insights into the nature of active sites. With further development of the methods of characterization, it is expected that open questions concerning mechanisms at the atomic level will be answered within the next few years. In particular, knowledge of the types, concentration, and distribution of induced imperfections in solids should be expanded in order to gain a more detailed understanding of the relationships between structure and activity/selectivity for mechanically activated solids. This includes the development and application of methods for the investigation of single defects and the separation of amorphous, partly crystalline, and crystalline parts of the treated solids [2].

For the reader's information, current manufacturers of mills for laboratory applications include:

- Fritsch GmbH, Industriestraße 8, D-55743 Idar-Oberstein, Germany, www.fritsch.de
- Retsch GmbH, Rheinische Straße 36, D-42781 Haan, Germany, www.retsch.de
- SPEX CertiPrep, 203 Norcross Avenue, Metuchen, NJ 08840, USA, www.spexcsp.com
- UVR-FIA GmbH, Chemnitzer Straße 40, D-09599 Freiberg, Germany
- Pascall Engineering, Capco Test Equipment Ltd., Wickham Market, Suffolk, IP13 OTA UK, United Kingdom, www.capco.co.uk
- Tema B.V. Chemical & Mineral Process Equipment, Steenplaetsstraat 22–26, 2288 AA Rijswijk, The Netherlands, www.tema.nl
- Herzog Maschinenfabrik GmbH & Co., Auf dem Gehren 1, D-49086 Osnabrück, Germany, www.herzog-maschinenfabrik.de
- Bühler AG, CH-9240 Uzwil, Switzerland, www.buhlergroup.com
- Siebtechnik GmbH, Platanenallee 46, D-45478 Mülheim an der Ruhr, Germany, www.siebtechnik-gmbh.de
- Bico Braum International, 3116 Valhalla Dr, Burbank, CA 91505, USA, www.bicoinc.com

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2.4.9
Immobilization of Molecular Catalysts

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2.4.9.1 Introduction and Scope

The beneficial effects of molecular catalyst immobilization (IMC; immobilized molecular catalyst) have been substantiated by numerous scientific reports in the fields of homogeneous, heterogeneous, and bio(enzyme)-catalysis [1, 2]. Such IMCs are also referred to as heterogenized homogeneous catalysts, anchored catalysts, supported catalysts, or hybrid catalysts [3–9]. Conceptually, molecular catalysts are immobilized in order to evoke synergistic effects between homogeneous catalysis, heterogeneous catalysis, and enzyme catalysis (Fig. 1).

IMCs provide access to environmentally benign chemical syntheses due to the ease of product separation and concomitant waste decrease; these prominent "classical" issues also comprise catalyst recovery and reusability, as well as the application of such IMCs in both batch and fluidized-bed processes [10–12]. Moreover, catalyst immobilization facilitates combinatorial library generation via simplification and automation of synthesis and characterization procedures ("high-throughput screening") [12]. Finally, modern catalyst immobilization techniques not only aim at the superior performance and facile reactivity control of molecularly well-defined catalytic sites [13]. The quest for tailor-made catalysts featuring *improved* catalytic performance (enhanced reaction rate, conversion, and selectivity) and/or new reactivity pathways are the ultimate challenge. This can be achieved by emulating and adapting the exceptional catalytic performance of metalloproteins which is imparted by site isolation, coordination confinement [keywords: entatic state (Greek "entasis" = under tension), local environment] and the intriguing protein environment of the active center (keywords: lock-and-key principle, micro- and mesoenvironment) [13, 14]. Importantly, site isolation and limited mobility of the catalytically active moieties counteract bimolecular decomposition pathways/collisional deactivation [13].

Accordingly, the "active" promoter role of the support material is no longer determined exclusively by its chemical composition. The implications of the topology ("architecture") and prefunctionalization of the (hybrid) organic/inorganic host for the catalytic performance are additional delicate issues (keywords: "molecular factories", "nanoreactors", "zeozymes", "mesozymes") [15]. The formation of precise reaction chambers can be accomplished via multicomponent self-assembly or via the use of nanoscopic host materials (e.g., periodically nanoporous silica or dendrimers) [16–18]. Such advanced concepts of catalyst immobilization involve nanostructured catalysts which are supposed to narrow the gap between nature and innovation [19, 20]. Catalyst encapsulation can counteract catalyst deactivation, and simultaneously enhance product selectivity. Furthermore, the molecular precursor route to tailor-made nanostructured host materials according to a soft chemistry approach ("chimie douce") facilitates bioinspired catalysis [21] and advanced methods

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