

## 2.3 Mechanochemistry in Catalysis

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**ABSTRACT:** The use of mechanical energy is an emergent research direction in many sub-disciplines of chemistry. Mechanochemistry in heterogeneous catalysis is only little explored, with the exception of pretreating solid catalysts before they are used in reactions. Over the last years, the department has followed several different approaches for the application of mechanical forces in the context of heterogeneous catalysis. These efforts originated in the work of the group on hydrogen storage materials, where light metal hydrides are milled with catalyst precursors to accelerate hydrogen uptake and release. This experience later initiated highly successful efforts to mechanochemically depolymerize cellulose and lignocellulose. Heterogeneously catalyzed gas-phase reactions were then studied in a specially designed flow-through milling vessel, and strong increase in reactivity was observed in CO-oxidation and PROX. While these reactions served as proof-of-concept systems, the mechanocatalytic chlorination of methane to chloromethane with very high selectivity, and the conversion of carbon-containing solids to hydrocarbons in hydrogen atmosphere extended the work towards more practically relevant systems. Incidentally, during the work on mechano-catalytically assisted gas-phase reactions, pathways for the innovative synthesis of interesting solid catalysts were discovered, i.e. the synthesis of supported metal catalysts from oxide supports and metal powders to yield nanometer-sized metal particles on the supports, and the formation of high surface area  $\alpha$ -alumina with surface areas around 130 m<sup>2</sup>/g from boehmite in short milling times.

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Milling is one of the oldest dry processing methods, used for millennia for diminution of particles to micrometer size. In addition to simple diminution, milling can also be used to effect chemical transformations. The term “mechanochemistry” had already been coined for this more than 100 years ago by W. Ostwald. In ancient times, the synthesis of mercury from cinnabar by grinding was known. In catalysis as well, milling is used frequently. Oxide catalysts are, for instance, activated by milling, producing defects or an amorphous surface layer, which result in higher activity.

As milling constitutes one of the key research expertise of the department since the early work on catalyzed hydrogen storage materials,<sup>1,2</sup> a program was initiated to explore the potential of mechanochemistry in heterogeneous catalysis. The available milling systems include (i) different types of shaker ball mills (Retsch), also suitable for work at low temperature down to -196°C and elevated temperature up to approximately 200°C, (ii) planetary ball mills (Pulverisette P6 and P7 from Fritsch), and (iii)  $E_{max}$  (Retsch) combining milling principles of shaker and planetary mills. Milling in some of the systems is possible also at high pressures up to 300 bar. In order to test the influence of different milling media, milling vessels and balls made from stainless steel, zirconia, tungsten carbide and corundum are available. This broad range of equipment allows in-depth exploration of milling processes over a wide range of conditions.

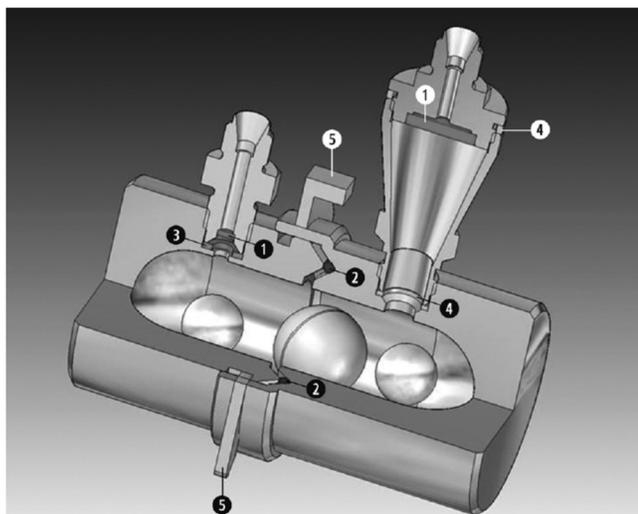
The first success of the extension of mechanochemical approaches beyond hydrogen storage materials was achieved in the mechanocatalytic depolymerization of cellulose and lignocellulose,<sup>3-5</sup> which provided a novel entrypoint into biorefinery schemes. This discovery led to a series of publications on the downstream chemistry of initially obtained celloligomers. As this was covered in previous reports, the following sections will focus on mechanocatalytic

gas-phase reactions and the synthesis of highly interesting catalytic materials by ball milling.

One problem of mechanochemical processing is relevant for all different systems: abrasion from the milling jars and milling media can be substantial and always has to be considered. If the fundamentals of gas-phase reactions under milling are studied, typically different milling media were used in order to assess their influence. If materials are produced, such as supported catalysts or nano-corundum, one should use inert milling media, so that the properties of the produced solid are not substantially affected by the contamination due to abrasion. For the synthesis of nano-corundum, milling jar and media made of corundum are ideal. Alternatively, one can employ milling media, which can be selectively leached out, i.e. tungsten carbide in the synthesis of nano-corundum.

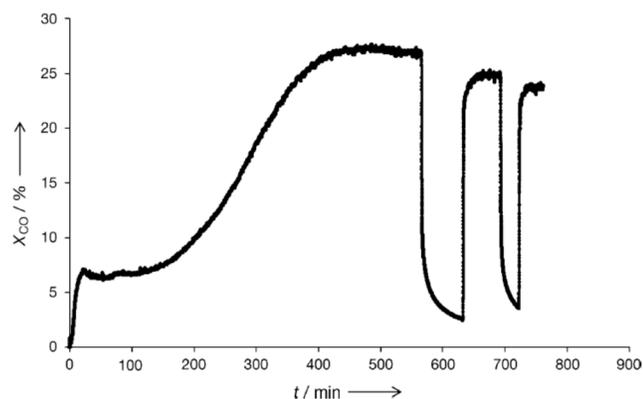
For mechanocatalytic gas-phase processes it was soon realized that batch operation was unsuitable, since it is almost impossible to follow the course of reaction properly in batch operation, and also sampling and analysis is more difficult than in continuous mode. Thus, a flow-through milling vial was constructed, which essentially operates as a continuously stirred tank reactor (Fig. 1). The flow-through vial has the same dimensions as a regular milling vessel, but it is equipped with two fittings for gas in- and outlet. At the outlet, a funnel is added, which acts to some extent like a cyclone filter, allowing the powder to slip back into the milling vial, which would otherwise be carried out with the gas stream. Here, also a thermocouple can be brought into the vial in order to monitor the temperature on-line. The milling vial can also be fitted to the cryo-mill for experiments at low temperatures; elevated temperatures are achieved by a heating jacket. Product gases are analyzed on-line, either by non-dispersive IR-spectroscopy (URAS), GC, or mass-spectrometry.

First CO oxidation was investigated,<sup>6</sup> since this reaction is simple and very well studied, also in the group. It thus appeared to be an ideal model system to explore the effects of mechanical energy during a catalytic reaction.



**Figure 1.** Schematic drawing of flow-through milling vial. 1 frit, 2 rubber sealing, 3 brass sealing, 4 plastic sealing, 5 clamp holding vial together.

Surprisingly, milling has a very pronounced influence on the conversion observed over different solids. Catalysts that are normally not active at room temperature, showed appreciable conversion, when milling was started. Conversion stopped, after the mill had been switched off (Fig. 2). The relatively rapid decay of conversion immediately after stopping the mill might be related to the vanishing of possible hot-spots, which could be present during milling. However, this would not explain the slower decrease of conversion over the course of several ten minutes. The enhanced activity of the catalysts was tentatively attributed to transient defects with higher intrinsic activity, which heal on time-scales of minutes.



**Figure 2.** Typical CO conversion curve for an in-situ milling experiment. Catalyst 1 g Cr<sub>2</sub>O<sub>3</sub>, 50 ml/min 1% CO in air,  $f = 25$  Hz, two balls  $d = 10$  mm, one ball  $d = 15$  mm, balls and vial made of stainless steel.

The conversion was strongly dependent on the conditions of the milling, such as milling frequency, size of balls, or ball-to-powder ratio. A higher mechanical energy input typically led to an increased

conversion – as would be expected, if the mechanical energy is affecting the catalyst's activity.

In order to compare the activity during milling with that observed in a conventional plug-flow reactor, the activity of the pre-milled catalyst (surface area increased by a factor of six during milling; thus, in order to exclude surface area effects, the pre-milled catalyst was studied) was studied at different temperatures in a regular plug-flow reactor. At room temperature, no activity for CO-oxidation was observed at the same space velocity as in the milling reactor. Reaction only started at observable rates slightly above 100°C in the plug-flow system. From these experiments, it could be concluded that milling increased reaction rates by up to three orders of magnitude.

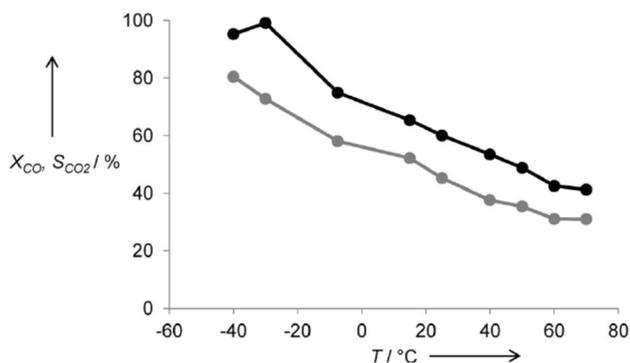
Such increased activity was not only observed for chromium oxide as catalyst, but also for a number of other solids, both bulk catalysts and supported systems. Especially interesting were supported gold catalysts. Bulk gold is normally inactive at room temperature in CO oxidation, but if gold powder was milled under a flow of CO in air, full conversion of CO was reached at room temperature. These experiments were also extended to a mixture of support oxides and gold powder, and incidentally, the formation of supported gold nanoparticles was observed under these conditions (see below).

CO oxidation was chosen as the initial example, since it is simple considering that no selectivity issues arise as CO<sub>2</sub> is the only possible product. Next, to study the effect of milling on selectivity in a catalytic gas-phase reaction, the preferential oxidation of CO in hydrogen (PROX) was investigated. Herein, CO can be oxidized to CO<sub>2</sub>, hydrogen to water, and even CO might react with hydrogen in syn-gas type reactions (this is improbable in the presence of oxygen, and no corresponding products were observed in our studies). This reaction is also of technological importance, since it is used to remove traces of CO from hydrogen for use in PEM fuel cells.

In initial screening experiments, various different solids were explored under milling conditions as catalyst for this reaction.<sup>7</sup> Metal oxides alone were only slightly active at room temperature, even under milling. Copper, milled together with metal oxides, was found to be surprisingly active under these conditions, and Cu-Cr<sub>2</sub>O<sub>3</sub> was found to give the highest activity system, with a conversion of 45% and a selectivity of 55% in a gas mixture of 1% CO, 1% H<sub>2</sub>, 50% O<sub>2</sub>, and 48% N<sub>2</sub> at room temperature. In-depth studies of the PROX reaction were thus carried out with Cu-Cr<sub>2</sub>O<sub>3</sub> in a ratio of 1:3. Also in this case, the performance of the system was highly dependent on the milling parameters.

Interestingly, the conversion and the selectivity for CO oxidation increases with decreasing temperature. At -40°C the conversion is close to 100% at a selectivity of around 80% for CO oxidation (Fig. 3). In control experiments with pre-milled catalyst in the plug-flow reactor, a temperature of 100°C was required to achieve such high conversion, and the high selectivities observed in the ball mill were never reached in the plug flow reactor. This supports the notion that it is not just high local temperatures which are responsible for the catalytic performance during milling, because then the behaviour observed in the milling reactor should be observed in the plug-flow reactor at sufficiently high temperatures. Also in the case of PROX, the high activity and selectivity for CO oxidation is attributed to short-lived defects. The slightly negative apparent activation energy

would then be due to almost similar activation energies for the surface reaction itself and the healing of defects, which cancel each other.



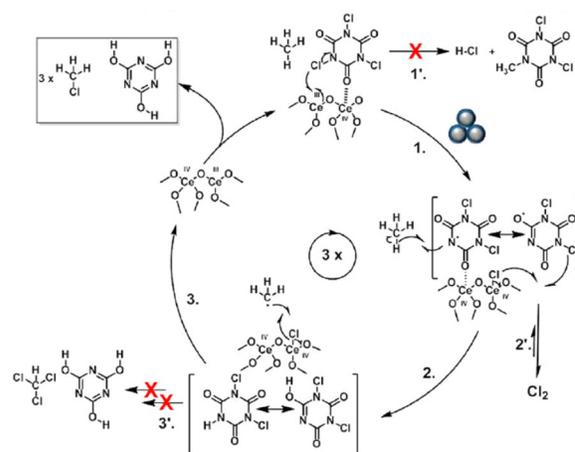
**Figure 3.** Comparison of conversion (black) and selectivity (grey) for CO-PROX under milling at different temperature. 500 mg Cu, 1500 mg Cr<sub>2</sub>O<sub>3</sub>, CO/H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> (1:1:50:48) 50 ml/min, six balls 10 mm made from WC,  $f = 25$  Hz.

With respect to applications, the most interesting mechanocatalytic reaction studied is the chlorination of methane with trichloroisocyanuric acid (TCCA) over Lewis acidic catalysts, like alumina or ceria.<sup>8</sup> Various solid Lewis acids were tested, and ceria was found to be the most active catalyst. Under optimized, relatively mild conditions (seven 5 mm  $\varnothing$  WC balls,  $f = 10$  Hz), a gravimetric productivity of 150 g CH<sub>3</sub>Cl kg<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup> could be achieved, which is in the range of large scale technical processes. Experiments to elucidate the mechanism suggest a radical process (Fig. 4), in which TCCA is activated by homolytic N-C bond cleavage, the N<sup>•</sup> radical abstracts hydrogen from methane to yield methyl radicals, and the Cl<sup>•</sup> radical combines with the methyl species to chloromethane. During the laboratory experiments, only about one third of the chlorine in the TCCA is used for the chlorination of methane, the rest of the TCCA is decomposed to cyanuric acid and gas phase chlorine. For a technical process, it will probably be possible to suppress this decomposition by adjusting the rate of radical generation and the residence time of methane in the reactor. Alternatively, one could regenerate TCCA from the product cyanuric acid and the chlorine, since these are the starting materials for industrial TCCA synthesis in any case.

During work on these mechanocatalytic gas-phase reactions, several serendipitous observations led to additional lines of work. On the one hand, it was discovered that carbon-containing solids can be hydrogenated under hydrogen pressure during milling to hydrocarbons in the presence of suitable catalysts. This work is still in progress, and will probably be submitted or published at the time of the SAB meeting. Other projects were targeted at the synthesis of catalytically interesting materials, i.e. supported metal catalysts and  $\alpha$ -alumina with exceedingly high surface area.

Normally, supported catalysts are synthesized using wet chemical methods, requiring a number of different steps. There are also scattered reports in the literature that for specific cases milling of metal compounds, accompanied or followed by reduction reactions, can be used to produce supported catalysts. In one publication, as one of

three alternative synthetic processes, elemental silver was used as precursor of a high activity Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized by ball milling. Also milling oxides with preformed nanoparticles resulted in a supported catalyst. However, mechanochemical synthesis as a general approach to synthesize supported metal catalysts from macroscopic metal powder had not been explored before. In the studies of catalytic reactions during milling, in some cases, when starting from metal powder and oxides, the solid after the reaction did not consist of separated metal and oxide particles, but in nanometer sized metal particles supported on the oxide, exactly as in conventional supported catalysts. In order to explore the potential of this process in detail, this effect was studied systematically.<sup>9</sup>



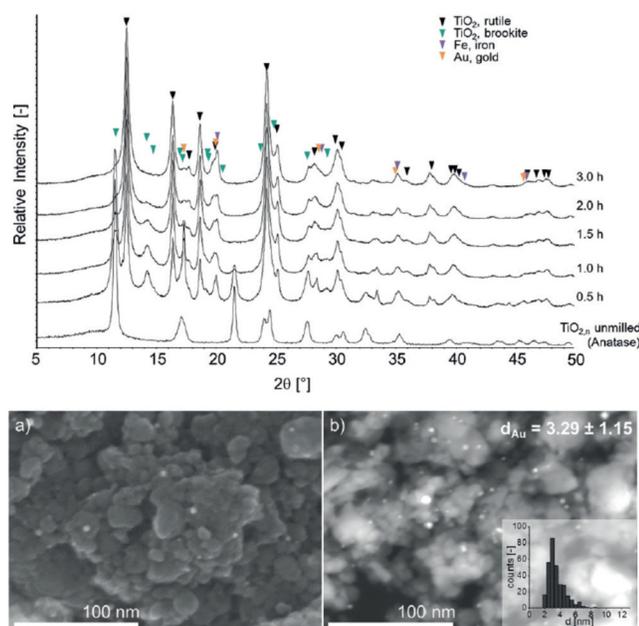
**Figure 4.** Mechanistic proposal for the selective mechanocatalytic formation of chloromethane from methane and TCCA over solid Lewis acids (in this case CeO<sub>2</sub>).

Gold powder consisting of micrometer-sized particles was first milled with different types of titania, and after 3 h of milling, gold particles with sizes of approximately 3 nm supported on titania are obtained (Fig. 5). The method is versatile, since alumina, cobalt oxide as well as iron oxide could be used as supports with similar results. Also the supported metals could be varied: with platinum, silver, copper, and cobalt metal nanoparticles with sizes on the order of 5 nm - with some variation for the different metals - were dispersed on the support oxides. Finally, if two different metal powders were used as starting material, together with a support oxide, bimetallic alloy nanoparticles were synthesized.

As can be seen in the XRD pattern in Fig. 5, the anatase phase of the support transforms via brookite to rutile. A more interesting transformation was observed when starting with  $\gamma$ -alumina: during milling,  $\alpha$ -alumina (corundum) with high surface area was obtained. Since corundum is a technologically extremely interesting material, which can hardly be obtained with surface areas exceeding a few m<sup>2</sup>/g, and since there are several interesting, but partly contradictory studies concerning the stability of high surface area corundum, it was attempted to mechanochemically synthesize high surface area corundum. These attempts were successful. Starting from boehmite, an aluminium oxide hydroxide ( $\gamma$ -AlOOH), corundum with surface areas of up to 140 m<sup>2</sup>/g was synthesized (Fig. 6).<sup>10</sup> Structural water

in the boehmite precursor was identified to play crucial role: Firstly, it acts as a process control agent to assist the fragmentation of agglomerates formed during milling into corundum nanoparticles, and secondly, it stabilizes the formed corundum nanoparticles *via* hydroxylation. These observations were supported by quantum chemical calculations suggesting that only with hydroxylated surfaces the energetics of the process are favourable for nano-corundum formation. Thus, the water content of the precursors has to be controlled within certain limits for optimum conversion of the boehmite to corundum. The process is rather robust: similar results were obtained with different types of boehmite and also pseudoboehmite as starting materials, and the transformation takes places in different types of milling vessels with different milling materials, although the exact conditions may have to be adapted. The results have been reproduced in an industrial laboratory, and work to scale-up the process to industrial dimensions is under way.

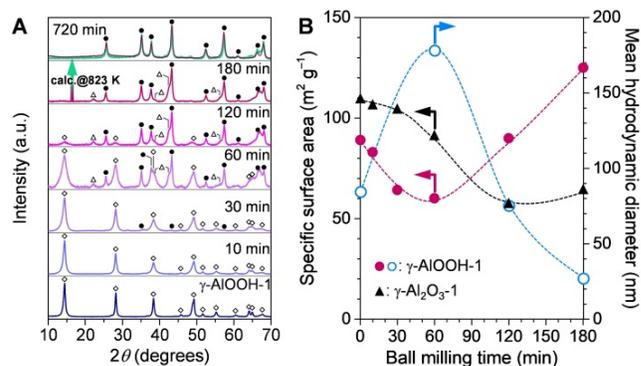
Finally, milling techniques can also be used to modify catalytic materials: The hydrophobicity of oxides can be adjusted by surface modification with, for instance, functional silanes. Carrying out such reactions in ball mills requires only very little energy input and proceeds to a high degree of surface modification in only a few minutes. Also the intercalation of layered materials by milling is easily achieved, as has been demonstrated for several clay types, into which different guest species were intercalated. It is expected, that mechanochemical methods can be extended also further beyond these first examples to result in even further modified catalytic materials.



**Figure 5.** Development of XRD pattern with milling time during milling of gold powder with titania (top). SEM (a) and STEM (b) of microtomed sections of the sample after 3h milling (bottom).

As the previous results and discussion have shown, mechanochemical methods are extremely interesting in heterogeneous catal-

ysis. Yet, the processes are little understood. Thus, mechanochemical approaches in heterogeneous catalysis will be explored in two directions in the future: On the one hand, the potential of these methods for further catalytic reactions of high relevance, such as methane activation and ammonia synthesis, will be elucidated. On the other hand, the scope of the studies will be expanded to obtain a molecular level understanding of the relevant processes. Synchrotron beamtime for in-situ XRD studies during milling has already been granted and a suitable milling vial has been constructed, first tests at BESSY have been carried out. Also microscopic, both electron microscopic methods and probe microscopies, will be employed to lay a sound foundation for the understanding of mechanochemical processes in catalysis.



**Figure 6.** Development of XRD pattern with milling time during milling of boehmite (A) and development of surface area and particle size with milling time for boehmite and  $\gamma$ -alumina as precursor (B). Identified crystalline phases:  $\diamond$ :  $\gamma$ -AlOOH,  $\bullet$ :  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and  $\Delta$ :  $\alpha$ -AlOOH. Milling conditions: WC jar (25 cm<sup>3</sup>), 3×12 mm WC balls, 1 g powder charge,  $\kappa_{\text{mill}} = 25$  Hz,  $t = 10$ -720 min.

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