Mechanochemical Activation

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An Orders-of-Magnitude Increase in the Rate of the Solid-Catalyzed CO Oxidation by In Situ Ball Milling**

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Dedicated to Professor Manfred T. Reetz on the occasion of his 70th birthday

Heating to elevated temperatures is the typical form of energy input into heterogeneously catalyzed reactions, which are used for the majority of all chemical production processes. In contrast, other kinds of energy, such as mechanical forces, are rarely used to attain a reaction. Herein, we report the catalytic CO oxidation under in situ ball-milling conditions where the reaction rate was increased by three orders of magnitude by the milling. This finding could lead to new process options in the chemical industry; furthermore, such novel modes of catalytic action could improve our understanding of the nature of the catalytic effect.

Heterogeneous catalysis is one of the key technologies in chemical industry.[1] It has long been known that mechanochemical activation prior to use can lead to solid catalysts with an improved activity[2,3] that arises from an increased surface area,[4] the partial amorphization of the surface layer,[5] or the increased concentration of defects.[5,6] Transient defects, which might lead to even higher activities, however, will vanish after stopping the mill; moreover, the direct action of mechanical forces could lead to increased activity. Surprisingly, however, heterogeneously catalyzed gas-phase reactions under in situ milling conditions seem to be almost unexplored, with the exception of one study on CO_2 methanation in which moderate enhancement of the catalytic activity during milling was reported.[7] In general, the influence of mechanical forces on chemical reactions has been extensively studied,[8,9] both on the molecular and on the preparative scale. On the molecular scale, scanning probe methods are used to study bond breaking and bond formation under the influence of a mechanical load.[10,11] Mechanochemistry is also a viable synthetic method for bulk-scale synthesis.[9] It is well-known that solid-state reactions are accelerated by mechanochemical activation.[12] In the field of catalysis, for instance, Heck reactions[13] and organocatalytic reactions[14] have been carried out in the solid state under ball-milling conditions. The main advantage of such methods is the possibility to work without solvent. Mechanochemistry is also applicable to the depolymerization of cellulose under solvent-free conditions in the presence of a solid acid, as first described by Blair et al.;[15] subsequently, quantitative yields of water-soluble products from acid-impregnated cellulose were achieved by our group.[16] In all of these cases, however, the mechanical energy causes the reaction between solid reagents. We hypothesized that it should also be possible to activate a solid catalyst in situ to become more efficient in catalyzing the reaction between gas-phase molecules.[3] Aside from the case of CO_2 hydrogenation cited above,[7] and to the best of our knowledge, scattered observations of catalytic reactivity induced by the application of friction under high vacuum conditions[17,18] come closest to our observations, which are described in the following sections.

In an initial exploratory study to assess the potential of in situ milling in heterogeneous catalysis, a set of batch experiments with different metal oxides as catalysts (NiO, Cr_2O_3, Co_3O_4, Fe_2O_3, $Mg(OH)_2$, and 1 %Pt/γ-Al_2O_3) were carried out. A planetary ball mill (Fritsch Pulverisette 6) was filled with the solid (1 g) and three balls (12 g, $d = 10$ mm, hardened steel), and pressurized to 10 MPa with a mixture of reaction gas ($CO/O_2/He = 1{:}20{:}79$ v/v %). The gas/solid mixture was milled for 2–4 h at room temperature, and at the end of the experiment, the gas phase was analyzed. CO conversion was observed for NiO (22 % after 2 h), Cr_2O_3 (10 %), Pt/Al_2O_3 (48 %) and Co_3O_4 (7.3 % after 4 h). The use of Fe_2O_3 and $Mg(OH)_2$ did not lead to any conversion after 2 h.

After a clearly positive effect of the milling on the catalytic activity of the solid catalysts had been established, selected solids were studied in more detail in continuous experiments to provide closer insight into the process. For this purpose, a commercial shaker mill (Retsch MM200) was modified to allow the continuous operation of heterogeneously catalyzed gas-phase reactions. The milling capsule (Figure 1), which was made of stainless steel, was equipped with a gas inlet through a Swagelok fitting with a frit, and a small funnel at the gas outlet which acts in a similar fashion to a cyclone filter (for a detailed description, see the Supporting Information).

Performing the catalytic CO oxidation over Cr_2O_3 during milling (one stainless steel ball of 15 mm diameter in the middle that separates two smaller balls of 10 mm each) led to

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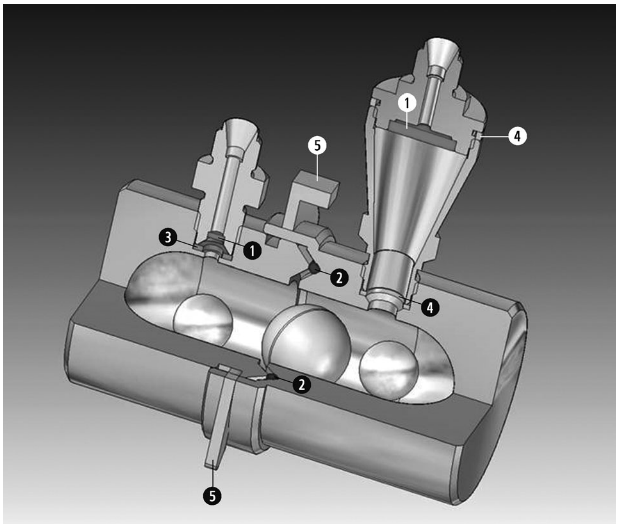

Figure 1. Diagram of the milling capsule with funnel and milling balls. (1: frit; 2: rubber sealing; 3: brass sealing; 4: plastic sealing; 5: clamp holding the milling capsule together).

a dramatic increase in the reaction rate. Without milling, no CO conversion to CO_2 was observed at room temperature over Cr_2O_3. After starting the mill, the reaction rate increased immediately, but required rather long milling times before a steady state was reached. A typical curve of conversion versus milling time is shown in Figure 2.

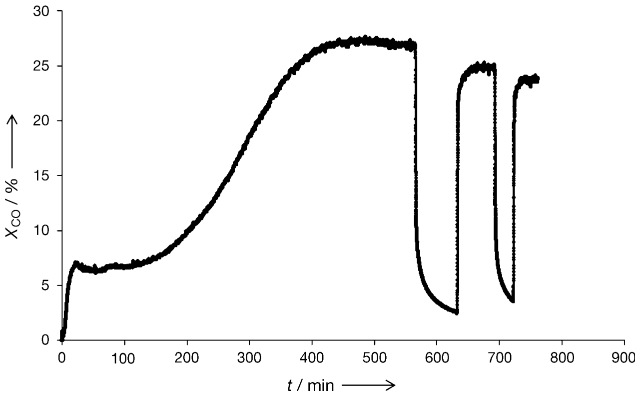

Figure 2. Typical conversion curve for an in situ milling experiment. The conversion drops immediately after stopping the mill and increases again after continuing the milling. $m(Cr_2O_3) = 1$ g, reaction-gas flow rate $= 50$ mL min^{-1}, $f = 25$ Hz, three balls (one ball with $d = 15$ mm in the middle, separating two balls with $d = 10$ mm).

When the milling was stopped, the rate rapidly dropped to almost zero, and it recovered after restarting the mill (Figure 2). The reproducibility of rates is not as good as for plug-flow reactors, and typically only within an error margin of ± 20%. This is due to the less-defined flow conditions in the milling vial, the fact that sometimes not all the catalyst separated in the funnel is directly fed back into the milling vessel but remains in the funnel, and some occasional loss of catalyst from the milling vial. These factors also explain the change in conversion over the course of the experiment, which is shown in Figure 2.

The crucial influence of the milling on the rate of the catalytic reaction is additionally confirmed by a number of observations. Using different balls to change the mechanical-energy input led to different conversions: With three balls as described above at a gas flow of 20 mL min^{-1} and a milling frequency of 25 Hz, a conversion of 25% was reached. With two balls of 15 mm the conversion was 55%, with five balls of 10 mm 10–15% conversion was achieved, and one ball of 15 mm led to a conversion that approached 10% over the course of several hours (Supporting Information, Figure S1). As expected, the performance is also strongly dependent on the milling frequency. Whereas at 10 Hz essentially no conversion was observed for a flow rate of 50 mL min^{-1}, the conversion increased to slightly over 18% at 30 Hz (Supporting Information, Figure S2). Several blank experiments were also carried out: 1) the reaction was carried out without balls, so that only the catalyst powder was shaken; 2) the gas was passed through the mill filled with catalyst and balls, but the mill was not operating; 3) premilled Cr_2O_3 was used as the catalyst, but there was no milling during the reaction itself; and 4) reaction gas was passed through the mill filled with balls, but not with catalyst, during mill operation. No CO conversion was observed in any of these reference experiments. This clearly shows that milling of the catalyst is crucial for rate enhancement.

To assess the effect of temperature on the catalytic activity, the milling vessel was equipped with a heating tape and a thermocouple (for a detailed description, see the Supporting Information). Without external heating the temperature of the vessel increased to 34 °C owing to the milling-energy input (18.7% conversion). The temperature was then raised stepwise to 50 °C (21.7%), 65 °C (23.7%), 80 °C (25.3%), 100 °C (26.9%), and 120 °C (28.2%) (Supporting Information, Figure S3).

For comparison, the activity of the Cr_2O_3 catalyst in CO oxidation was also measured in a conventional plug-flow reactor (Supporting Information, Figures S4, S5). At an identical space velocity as in the shaker mill (although with lower catalyst mass and gas flow rate owing to limitations of the set-up), and with pre-milled Cr_2O_3, CO conversion was first observed slightly above 100 °C, and reached essentially full conversion at 230 °C. The rates over Cr_2O_3 that had not been milled before were approximately six times lower, which scales moderately well with the surface area of the materials. The BET surface area of the fresh sample was 2.4 m^{2}g^{-1}, whereas the milled sample had a surface area of 17.7 m^{2}g^{-1}. Because of the considerably different activities of the catalyst during milling and in the plug-flow reactor, the activities cannot be directly compared at identical temperatures. However, extrapolating the Arrhenius plot (Figure 3) for the plug-flow reactor, an activity difference can be estimated of approximately one order of magnitude at temperatures of around 100 °C, and of more than three orders of magnitude at room temperature. The comparison experiment in the plug-flow reactor also incidentally shows that abrasion of steel from the balls and the milling vessel, which is observed as an additional phase in XRD (Supporting Information, Fig-

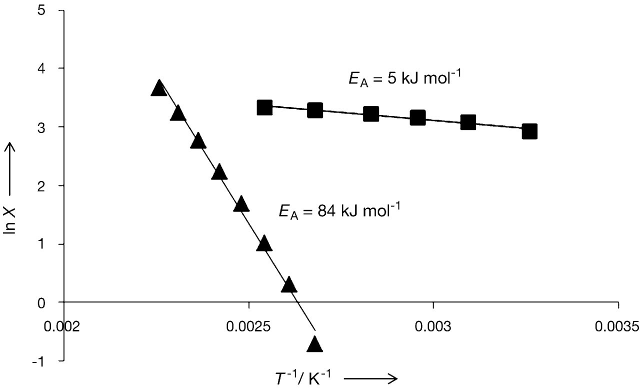

Figure 3. Comparison of the activation energy (E_A). Arrhenius plots for the CO oxidation in the shaker mill (■) and the plug-flow reactor (▲). The natural logarithm of conversion is plotted, which is approximately proportional to the rate constant at low conversions and thus gives a good approximation for the activation energy.

ure S6), is not responsible for the increased rate during milling, because a milled catalyst containing this contamination was used for the plug-flow experiments.

Milling leads to an increased surface area and to the presence of microstrain as well as to smaller crystalline domain sizes (Supporting Information, Figures S7, S8). This accounts for the higher activity of the pre-milled sample in the plug-flow reactor. The increase in rate correlates reasonably well with the increase in surface area. The persistent defects in the Cr_2O_3 or possible surface contamination that is due to abrasion from the mill thus only have a minor influence on activity.

A number of different explanations have been put forward for the effect of mechanical energy input on solid-state inorganic or organic reactions. A relevant hypothesis in the context of catalyzed gas-phase reactions, as investigated here, is based on the formation of hot spots in the impact zone between balls and between balls and wall.[19]An estimation of the number of molecules present in the impact zone between balls and between balls and walls (for calculations, see the Supporting Information) reveals that this explanation could account for a substantial increase in conversion. However, if this was the only and crucial reason, then the rate should rapidly increase directly after starting the mill, and the reaction should immediately cease after stopping the mill, which has not been observed. An activation period, as shown in Figure 2, was observed for all reactions carried out under milling.

Temporary milling-induced defects with high catalytic activity would also be a plausible explanation for the observed high rates. If such defects do not heal instantaneously, residual and decreasing activity should be observed over time after the mill was stopped. As seen in Figure 2, the rate considerably drops immediately after stopping the mill, but some residual activity decays much more slowly over several ten minutes (Supporting Information, Figure S9). The immediate drop in activity could be due to the lack of a direct impact that induces reactivity, or the rapid vanishing of some defects. Other types of defects could be more stable and heal over time periods of the order of minutes. This explanation would also be in line with the observed influence of temperature on the reaction. Close inspection of the Arrhenius plot in Figure 3 reveals that the behavior does not fully correlate with the Arrhenius law, which would be expected if different factors with different time scales contributed to the overall behavior. A non-Arrhenius-type behavior has previously been observed for the mechanically assisted formation of $[Ni(CO)_4]$ from nickel and CO under milling.[20]

The slower decay of some of the milling-induced active sites is even more clearly seen for another system studied, namely gold powder. Whereas supported gold nanoparticles, with sizes of approximately 5 nm, are highly active at room temperature for CO oxidation, this does not hold for bulk gold, which is essentially inactive.[21] Nevertheless, when exposed to the conditions of ball milling, gold powder with large particle sizes in the micrometer range (for a TEM image, see the Supporting Information, Figure S10) also exhibits high activity in CO oxidation (Figure 4).

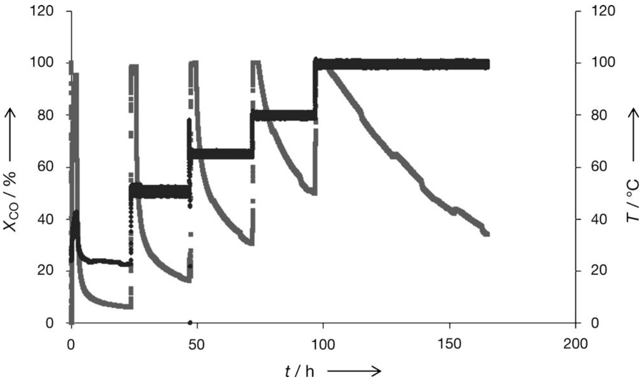

Figure 4. CO oxidation in the shaker mill over gold powder. An increase in conversion (——) indicates start of the milling at each temperature (——), the decrease in conversion starts after stopping the mill (gas flow rate = 50 mL min^{-1}, f = 25 Hz, m(Au powder) = 1 g).

During milling, full conversion is reached, but the catalytic activity decays much more slowly after stopping the mill than in the case of Cr_2O_3 as the catalyst. This decay is even slower at higher temperatures, probably because the base activity from which the decay starts is much higher. The milled gold catalysts were also studied in a conventional plug-flow reactor, and extrapolating the curve to room temperature gives a difference for the logarithm of conversion of 9.3 between the plug-flow reactor and the conversion under milling (Supporting Information, Figure S11), which translates to a rate approximately three orders of magnitude larger considering the space–velocity difference, which had to be adjusted to be ten times higher in the plug-flow reactor for technical reasons. The true rate difference is even greater, as in the milling reactor full conversion was reached at any of the temperatures studied, which is a highly surprising observation.

Overall, we have shown that the activity of solid catalysts for CO oxidation can be increased by several orders of magnitude, when the reaction is performed during ball milling of the catalysts. We expect that this finding can be applied to other reactions, where selectivity issues are also important.

The results presented are of high relevance for the fundamentals of catalysis; after all, this is an almost unexplored method to dramatically improve catalyst effectiveness. Currently, the nature of the highly active sites is not clear, although defects induced by the high mechanical-energy input are probably strongly contributing. Although it is very difficult to obtain insight in the processes during milling, a recent study introduced a method for in situ XRD experiments during ball milling,[22] which could be a suitable method for studying the catalytic reaction during milling. Beyond their fundamental importance, these results may have substantial practical implications. Ball milling is possible on a production scale (in the cement industry mills with volumes of 100 m^3 are in use), and if improvements in catalytic effectiveness outweigh the more complex process and potentially high running costs that are due to the milling energy requirements, then such processes could even become suitable for industrial applications.

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