

MECHANOCHEMICAL AND MECHANOCATALYTIC REACTIONS IN BALL MILLS

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Mechanochemical reactions are being used routinely for the synthesis of metal hydrides and complex hydrides, as well as for the doping of hydrides with catalytic additives to improve the kinetics of hydrogen absorption and release. Mechanochemical synthesis allowed in various cases the synthesis of materials which are otherwise difficult to access, such as complex rare earth aluminum hydrides.¹ For such studies, milling vessels were equipped with various additional features, such as cryo-capabilities and remote sensors for pressure and temperature to follow the processes in the mill in more detail.

Based on this experience, the milling was extended to catalytic processes. A breakthrough was achieved with the discovery, that cellulose and also native lignocellulose biomass can be depolymerized into fully water-soluble products after impregnation with an acid and milling in a ball mill for two hours.² This process results in the formation of sugar oligomers with 1-10 sugar units and small lignin fragments. The process does not only lead to depolymerization, but also repolymerization takes place under the conditions of the catalytic milling, so that also linkages other than the 1,4-glycosidic bonds between sugar molecules are formed.

The mechanocatalytic treatment is not only useful for depolymerization, but can also be used for the fractionation of native biomass. Simple heating of the aqueous solution obtained after milling leads to precipitation of the lignin fraction, while the sugars remain dissolved in the aqueous phase and can be processed to further products.³ While milling in the laboratory is possible in planetary ball mills, scale-up requires different types of mills. Experiments in this direction, using so-called Simoloyer[®] mills, allowed the processing of kilogram amounts of native biomass, and the results suggest that the process is scalable. At the laboratory scale, the energy required for milling exceeds by far the energy content of the depolymerized biomass, but on the kilogram scale, energy input and energy content of the products are already in a similar range, so that viability on large scale seems possible.⁴

Mechanocatalysis, however, is not only suitable for solid substrates. Even the rate of gas phase reactions catalyzed by a solid can be accelerated, if the solid catalyst is ball milled during the catalytic reaction. For the oxidation of CO a rate increase by three orders of magnitude was observed in a continuous ball milling reactor compared to the reaction in a conventional plug flow reactor.⁵ Rate enhancements during ball milling were also observed in the preferential oxidation of CO in hydrogen-rich gas streams or during propene oxidation, where, in additionally rate oscillations during ball milling occurred.

The presentation will give a survey of status and perspectives of mechanocatalytic reactions.

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³ M. Kaeldstrom, N. Meine, C. Fares, R. Rinalid, F. Schüth, *Green Chemistry* **2014**, *16*, 2454-2462.

⁴ M.D. Kaufmann Rechulski, M. Kaeldstrom, U. Richter, F. Schüth, R. Rinaldi, *Ind.Eng.Chem.Res.* **2015**, *54*, 4581-4592.

⁵ S. Immohr, M. Felderhoff, C. Weidenthaler, F. Schüth, *Angew.Chem.Int.Ed.* **2013**, *52*, 12688-12691.