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# HKP as a PM-process utilized for environmental applications in Mechano-Chemistry

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***Abstract*— Numerous wasteless solid-solid molecular reactions at laboratory scale up to 200 g batches have been published all across organic chemistry. Three reactions for further scaling with high energy ball mills to industrial scale are described here: the Knoevenagel condensation, a complexation reaction and a neutralization reaction. It is highly important to avoid local melting at and above the eutectic temperature in order to keep the solid state advantages and to ease the discharging process. Planetary ball mills are limited in volume. Therefore up-scaling by high energy ball mills is recommended for industrial scale applications. Wasteless and solvent-free quantitative stoichiometric and cost-effective reactions with short processing times are environmentally friendly. Because of the decreased activation energy no catalysts and due to the solid-solid reactions no solvents are necessary. The available equipment for high kinetic processing is described.**

**Keywords** – large scale high energy ball mills; industrial process; mechanochemistry; high kinetic processing; molecular solid-solid reactions

## I. INTRODUCTION

Solid state reactions at 100% yield such as gas-solid and solid-solid reactions as well as salt reaction without intermediate melting processes have been performed since the mid-1980s when the application of atomic force microscopy has risen [1,2]. Contrary to the common topochemistry hypothesis [3] molecules migrate anisotropically during chemical reactions in crystals along cleavage channels or plains or to voids, even in amorphous solids [4]. Characteristic surface features formed are face-specific. It has been shown that the reaction stops upon milling as the eutectic is reached and the melting starts. With mechanochemical reactions the reaction continues at this point as well. Melting reactions in mills do not lead to specific 100% yield reactions in contrast to mechanochemical solid-solid reactions. Here long milling times are necessary as well as high efforts for post-processing. Addition of solvents as process controlling agents or liquid assistant grinding are other techniques but they require catalysts and also high efforts for chemical treatment at non-quantitative yield and high amounts of dangerous wastes [5,6]. Correct solid-solid reactions by milling are sustainable and scalable, with adjusted impact, no local or intermediate melting, temperature control below eutectics and high yield with no added solvent [7].

## II. SOLID-SOLID REACTION AT SMALL SCALE

More than thousand gas-solid and solid-solid reactions are known [9].

The reduction of aldehydes and ketones with $NaBH_4$ in a temperature controlled ball mill is one example for the advantage of mechanochemical syntheses (Fig. 1). The resulting pure sodium borate is precursor for synthesis of $NaBH_4$ [10]. This also seems to be the only practicable way to synthesize tetraalkoxyborate salts because of the sensitivity to moisture and the insufficient reactivity of all B-H bonds in solid state. The intermediate can be used for alcohol synthesis.

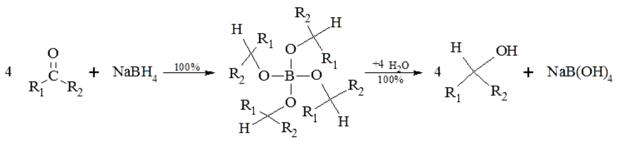

Fig. 1. Solid state reduction of carbonyls with $NaBH_4$.

There is a reaction leading to high excess of $NaBH_4$ and uncontrolled conditions at 65-70% yield of the resulting alcohols with dangerous wastes [11]. This process has been succeeded by mechanochemical synthesis.

Reduction of $NaBH_4$ by mechanochemical means can be up-scaled as well as other wasteless stoichiometric milling processes in organic and some inorganic chemistry, e.g. [7]. Evaluation of new systems by small scale milling by a 2L high energy ball mill Simoloyer® CM01-2lm (Fig. 2) [8] is preferable according to the milling conditions and the mill type in advance to the up-scaling, proofed in many experiments [7,12].

Fig. 2. Simoloyer® CM01-2lm (2 liters volume).

In batch processing mode without discharging cycle some product has to be left in the chamber as holdup in order to protect the milling tools and the product from contamination due to abrasion. Therefore discharging with application of a cyclone and a dust collector at lowered pressure has been performed. All process can be carried out without use of solvents.

## III. SCALING OF MOLECULAR SOLID-SOLID REACTIONS TO TECHNICAL SCALE WITH THE SIMOLOYER®

The possibility of synthesis at even 200 g scale can be of great interest for industrial applications. Fine chemicals which are synthesized at high expense can be obtained by mechanochemical synthesis at lower costs. Larger mills require improved temperature control facilities and a balanced temperature distribution because local melting has to be avoided. For discharging at larger scale a system of cyclone and vacuum unit has been applied.

Figure 3 shows the applied high energy ball mills, technical data of the devices are given in Table 1.

Table 1 Technical data of different types of applied high energy Simoloyer® ball mills.

| **Simoloyer®** | **CM01** | **CM08** | **CM20** |
|---|---|---|---|
| motor power (max.) [kW] | 2,7 | 11 | 22 |
| max. rotor speed [min$^{-1}$] | 1800 | 1000 | 750 |
| max. relative velocity [m/s] | 10.9 | 10 | 11.2 |
| grinding unit (type) | W01-2lm | W08-8lm-s2 | W20-20lm-s2 |
| volume grinding unit (standard) [L] | 2 | 8 | 20 |
| spec. power, max. (stand. grind. unit) [kW/l] | 1.35 | | 1.1 |
| cooling grinding unit | standard, water | | |

Figure 3. Simoloyer® CM08-8lm (left) and CM20-20lm high energy ball mill (right).

The Simoloyer® high energy ball mills are used for high kinetic processing (HKP) and following reactive milling (RM) with temperature control. There is also the possibility of mechanical alloying (MA) and high energy milling (HEM) all leading to nanostructures within amorphous and crystalline materials. The processes are scalable up to 900L volume as industrial scale and the charging and discharging can be performed under controlled atmosphere (air, inert gas or vacuum) due to patented air-lock systems. The grinding unit can be changed and replaced quickly providing no internal dead zones. There is versatile adaptive measuring equipment and automatic software control with documentation of parameter and process history. The milling chamber can be coated or lined with ceramics instead of hard metal, as well as ceramic balls can be used allowing processes without contamination. Processes can be run in batch, auto-batch and semi-continuous mode with defined temperatures due to the cooling/heating jacket as well as under high or low pressure. Wet milling is also possible.

### A. *Knoevenagel condensation*

The test solid-solid molecular reaction for up-scaling to technical scale was chosen from already known reactions. The Knoevenagel condensation of vanillin and barbituric acid has already been performed in 2 mmol batches (Fig. 3, c). 100% yield was confirmed.

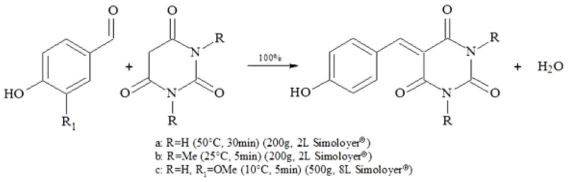

Fig. 3. Knoevenagel condensation.

The melting point of the desired product c is 313°C [12] and the reaction has been carried out in planetary ball mills with and without auxiliaries. There has been the problem of melting of the starting mixture which led to incomplete reactions due to kneading of the high viscous mixture. Process controlling agents (PCA) such as silica did not improve the reaction.

The efficiency of the Simoloyer has been demonstrated by up-scaling of this reaction up to 500 g batches with the CM08-8lm unit at ~10°C without melting (Fig. 4) and without hard coating on the chamber walls or the rotor.

Fig. 4. Provisional open cyclone equipment, collected powder in discharging container after the cyclone.

This leads to the conclusion that the Simoloyer® technique is favorable for industrial continuous processing at 100% yield without wastes or solvents.

## B. Complexation

The technical use of large scale high energy ball mills has been demonstrated by the up-scaling of the complexation reaction of glucose and urea (Fig. 5) [7,9,13] from 200 g to 2 kg scale in a Simoloyer® CM20 with 20 Liters volume (Fig. 3).

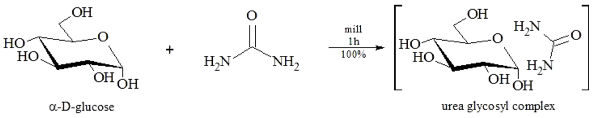

Fig. 5. Complexation of α-D-glucose and urea.

It happens that this complex cannot be synthesized in solution but only by solid-state reactions. The mechanochemical synthesis leads to the possibility of advanced, cost-effective and solvent-free production of ureido glucoses of pharmaceutical interest (e.g. [14]). The complexation in a 1:1 ratio provides 100% yield at no waste and easy temperature control. With this technique the complexation product has been synthesized and the discharging result is excellent with no hard coating at the inner walls or grinding unit or rotor (Fig. 6).

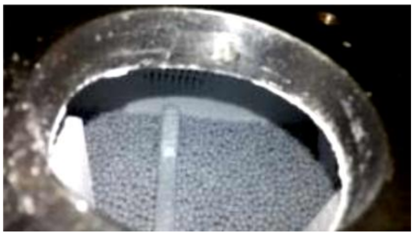

Fig. 6. Holdup of the glucose-urea complex.

Processing times can be estimated to 5 min up to quantitative conversion because IR spectra showed no further changes afterwards.

## C. Neutralizsation

A gas-forming solid-solid neutralization reaction of tartaric acid and sodium carbonate has been performed in the Simoloyer® CM20 as well to demonstrate the scalability (Fig. 6). $CO_2$ and crystal water are byproducts [7].

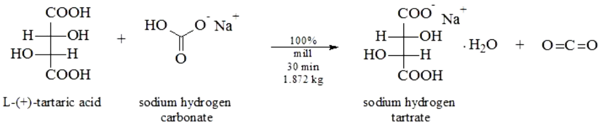

Fig. 6. Neutralization reaction.

The mechanochemical synthesis at 200 g scale avoids highly caustic sodium hydroxide in aqueous solution and subsequent cost-intensive evaporation of water. This solid state synthesis of a food additive is therefore of technical interest, and the reaction has been performed at 2 kg scale with the Simoloyer® CM20. The conversion control has been monitored by frequent release of gas pressure. After no more gas was released, the mill was discharged using an external cyclone.

The application of cooling cycles during the process also prevents the formation of hard coatings (Fig. 6).

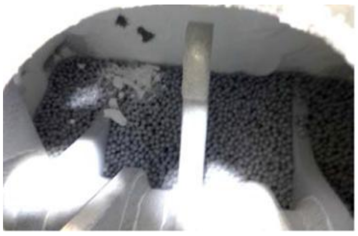

Fig. 6. Holdup in the grinding unit after neutralization.

Temperature in the grinding unit was kept low by decrease of rotation speed and the reaction was completed in 30 min. Thus 100% yield in the follow-up batches of a (semi)continuous technical processing with internal cycle discharging can be achieved.

## IV. MECHANOCHEMICAL REACTIONS

Mechanochemical bond-breaking means counter-thermodynamic initiation of reactions [18]. For example, quartz sand as a tribomaterial. forms local surface plasma on broken surfaces during milling that sparks, or mineralizes any organic materials in the presence to graphitic carbon, e.g. dioxin has been completely carbonized in the Simoloyer® CM01-2lm with excessive sand or glass [15]. Stoichiometric reactions between infinite 3D-covalent materials that form local surface plasma by sudden breakage of numerous metal-oxygen bonds are tribo-chemical reactions. The finally obtained double oxides are not tribomaterials, because the formed surfaces do not form surface plasma (Eq. 1) [7,20].

$$\begin{aligned} &PbO + CrO_3 \rightarrow PbCrO_4 \\ &ZnO + \alpha - Fe_2O_3 \rightarrow ZnFe_2O_4 \end{aligned} \tag{1}$$

These successful syntheses and others are basis for a continuous industrial production.

## V. CONCLUSION

Three wasteless solid-solid reaction types have been successfully up-scaled and it has been proofed that mechanochemical syntheses are possible and of industrial relevance. There are hundreds of possible reaction types for the application of large Simoloyer® high energy ball mills in the technical, medicinal, and life sector [4,7,9,12-13,15-18]. The equipment for an industrial wasteless production by mechano-chemical milling is already available. Tempera-ture control is highly important and very efficient with the Simoloyer® CM20-20lm.

## ACKNOWLEDGMENT

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## REFERENCES

[1] G. Kaupp and D. Matthies, *Chem. Ber.* vol. 119, 1986, pp. 2387-2392;
[2] G. Kaupp, C. Seep, *Angew. Chem. Int. Ed.*, vol. 27, 1988, pp. 1511-1512.
[3] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, pp. 1996-2000.
[4] G. Kaupp, in *Atomic force microscopy, scanning nearfield optical microscopy and nanoscratching − application to rough and natural surfaces*, 2006, pp. 177-227.
[5] D. Braga, F. Grepioni and G. I. Lampronti, *CrystEngComm*, vol. 13, 2011, pp. 3122-3124.
[6] T. Friscic, *Chem. Soc. Rev.* 2012, vol. 41, pp. 3493-3510.
[7] G. Kaupp, *CrystEngComm*, vol. 8, 2006, pp. 794-804.
[8] Zoz Group, Simoloyer®: http://www.zoz.de
[9] G. Kaupp, *Top. Curr. Chem.* 2005, vol. 254, pp. 95-183.
[10] M. R. Naimi-Jamal, J. Mokhtari, M. C. Dekamin, and G. Kaupp, *Eur. J. Org. Chem.* 2009, pp. 3567-3572.
[11] J. Mack, D. Fulmer, S. Stofel and N. Santos, *Green Chem.*, vol. 9, 2007, pp. 1041-1043.
[12] G. Kaupp, M. R. Naimi-Jamal and J. Schmeyers, *Tetrahedron*, vol. 59, 2003, pp. 3753-3760.
[13] G. Kaupp, J. Schmeyers, and J. Boy, *Chemosphere*, vol. 43, 2001, pp. 55-61.
[14] M. J. McKay, and H. M. Nguyen, *Carbohydrate Res.*, vol. 385, 2014, pp. 18-44.
[15] G. Kaupp, 2004, DE 10261204 to Zoz GmbH
[16] G. Kaupp, *CrystEngComm*, vol. 11, 2009, pp. 388-403.
[17] G. Kaupp, *CrystEngComm*, vol. 13, 2011, pp. 3108-3121;
[18] G. Kaupp, in *Mechanochemistry - mechanical breaking of chemical bonds, in Encyclopedia of Life Support Systems (EOLSS) of UNESCO*, 2012.
[19] G. Kaupp, in *Organic solid state reactions, in Physical Organic Chemistry Encyclopedia*, vol. 2, 2016.
[20] G. Kaupp, M. R. Naimi-Jamal, H. Ren and H. Zoz, Process Worldwide, vol. 4, 2003, pp. 24-27.