

Reactive Milling with the Simoloyer®: environmentally benign quantitative reactions without solvents and wastes

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abstract

The pilot set-up of a horizontal high energy ball mill (Simoloyer®) that has been successful in reactive milling, mechanical alloying, and formation of ductile metal-flakes is used for semi-continuous processing of organic solid-solid reactions which proceed rapidly and without wastes in the absence of solvents. 200g batches were run in the exploratory investigation. Stoichiometric 1:1-mixtures of α -(D)-glucose and urea formed the 1:1-complex with quantitative yield after 5 min at a rotor frequency of 900 min⁻¹. Similarly the condensation reaction of solid p-hydroxybenzaldehyde with solid p-aminobenzaldehyde was complete after 15 min yielding the pure imine derivative in quantitative yield without waste producing work-up procedures. Further scale-up appears possible also with other solid-solid reactions.

1. Introduction

Chemical production continues to depend on environmentally benign techniques. The important aim of avoiding wastes is only obtained in 100% yield reactions that do not require workup for removal of catalysts, supports, solvents or other auxiliaries. Thus, the up-scaling of quantitative solid-state reactions in ball-mills [05] is of technical importance. We report here on the first semi-technical milling for the quantitative and waste-free production of an organic 1:1-complex **3** and a condensation product **6** in batches of 200 g that can be easily up-scaled further. The starting materials are commercially available and used as obtained.

2. Processing route

Since almost half a century scientists are using the mechanical alloying technique (MA) which can be used to produce powder-materials with new and insofar interesting properties [01]. The literature describes MA as repeated deformation, fracture and welding of powder particles by highly energetic ball collisions. This definition may be amplified in that MA stands out by the transfer of high levelled energy into powder and so Mechanical Alloying often leads to material transformation of the crystalline structure by solid state reactions. Atomic dislocations, a high defect structure of the lattice, the immense magnification of the boundary surface and a high diffusion rate leads to low activation energies for those reactions.

If the same technique is applied for particle size reduction and/or particle deformation of single-systems e.g. to receive a special particle geometry, this route is to be described as High Energy (ball) Milling (HEM) and is in particular very suitable for rapid particle size reduction of enamels, glass fluxes and glaze frits. On the contrary HEM has already been found to be very effective for the production of ductile metal-flakes for paint-pigments, electrical conductive pastes, anti-corrosives and many others [09].

The definition of Reactive Milling (RM) is suitable if during milling a chemical reaction is required and observed. The advantage here can be an ultra-fine dispersion of particles in a matrix (e.g. Ag-SnO₂ where the starting powder is AgO₂ + Ag₃Sn).

A major goal for high kinetic processing (HKP) is the possibility of producing large quantities in a short time at low cost. Therefore a project has been founded to explore the potential of a continuously route of HKP where the material is injected in a carrier gas flow and separated again after processing. The pilot plant is shown in Figure 1. A further use of the same set-up is in organic solid-state reactions where the necessity for repeated contacts between the micronized reacting crystals prevails for obtaining quantitative reactions without producing wastes.

3. Experimental

200 g quantities of stoichiometric 1:1-mixtures of the loosely premixed crystalline reaction partners (all starting materials were of 99% purity and purchased from Merck KGaA, Darmstadt) were fed to a stainless steel 2 l Simoloyer® horizontal rotary-ball-mill equipped with a hard metal rotor of standard geometry [08], 2 kg of steel balls (100Cr6) with 5 mm diameter, and water cooling. The rotor was run at 900 cm⁻¹ for 5 min in the case of **3** and 15 min in the case of **6** for quantitative reaction (m.p., IR spectra, chemical analyses and DSC experiments indicated 100% conversion) and the products were milled out for 10 min at the same rotor frequency. The yields of pure products **3** and **6** were quantitative from the second batch milled. For quantitative recovery of the material in one-batch runs and in the last batch, the Simoloyer® ball-mill can be connected to the air cycle for deposition in a cyclone (see Fig. 1).

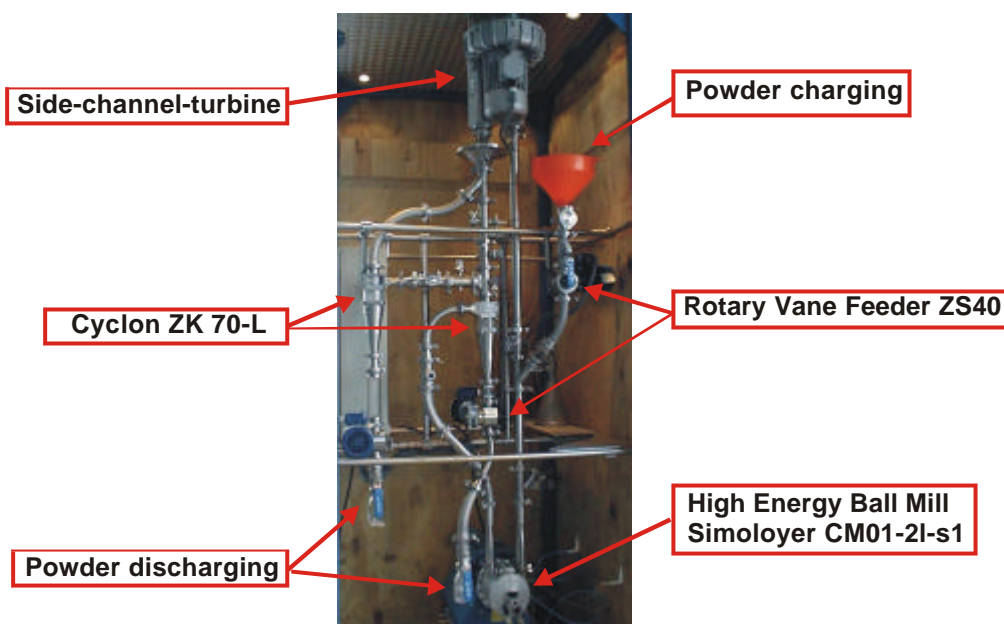
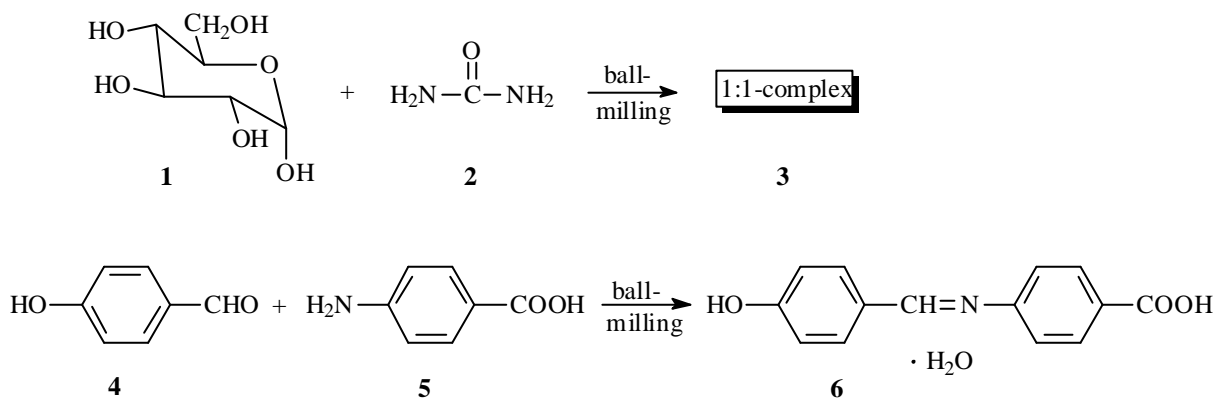


Fig. 1 pilot-set-up of a High Energy Ball Mill (Simoloyer) with air/inert carrier gas - cycle and separation/classification system

4. Results and Discussion

We chose formation of the 1:1-complex of α -D-glucose (**1**) (m.p. 153 - 156°C) with urea (**2**) (m.p. 132.5 - 134.5°C) and a condensation reaction of *p*-hydroxybenzaldehyde (**4**) (m.p. 114 - 117°C) with *p*-aminobenzoic acid (**5**) (m.p. 186 - 189°C) for this exploratory investigation, in order to demonstrate the application potential in very different fields of interest.



Short milling of compounds **1** and **2** quantitatively produces complex **3** (m.p. 115-120 °C). The α -configuration of the glucose part in **3** was shown by an initial rotation angle of $[\alpha]_D > 82^\circ$ (1% in water) when the usual mutarotation occurred. The same compound had been prepared from aqueous solution by inoculation with seed that was obtained after six months of crystallization [03] or from melts [07] and characterized by an X-ray structural analysis [06]. Interestingly, the chemical transformation proceeded rapidly without intervening liquid phases, despite the numerous hydrogen bonds in the crystal lattices of both starting materials.

Quantitative solid-state synthesis of compound **6** was initially tested at the gram scale in a 10 ml Retsch ball-mill MM 2000. **6** forms a crystalline hydrate. The water of reaction from the condensation reaction does not disturb the procedure by a liquid phase both in the small or large scale runs. Anyhow, the water of reaction can be removed from **6** in a vacuum at 80°C, if required. Importantly, the condensation reaction of **4** and **5** proceeds smoothly and efficiently at near ambient conditions without intervening liquid phase and further up-scaling in larger mills appears possible. This favorable waste-free technical procedure is remarkable, as the previous synthesis of **6** required 12 h boiling in ethanol and no yield was reported [02].

The semi-technical stoichiometric solid-state reactions run to completion by the ingenious kinetics involved in the solid-state mechanism [04]. Thus, the contact areas at the different touching crystals experience the well-established phase rebuilding, followed by phase transformation and disintegration with formation of fresh surface, etc.

5. Concluding Remarks

Precise stoichiometry of the reaction partners is crucial for 100% reactions yielding pure products without any necessity for purification. There is no trouble in this respect with batch runs in ball-milling. Continuous techniques will be more involved, because the stoichiometric ratio has to be maintained throughout. However, the number of batches can be kept low with larger ball-mills that are commercially available at sizes of up to 400 l and should be equipped with an internal air cycle cyclone (Fig. 1) for quantitative recovery at the last batch. The new technique has potential for resource saving environmentally benign up-scaling of numerous further solid-state syntheses.

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