

Fundamentals and Applications of Mechanochemical Processes

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Highlights

- Collisions in ball mills can create short-lived hot spots reaching up to 800 °C
- Ammonia synthesis benefits from different conditions for N₂ activation and NH₃ formation
- Shear forces allow for contacting solid feedstocks with solid reactants or catalysts
- PET can be depolymerized completely in less than 20 min by ball milling with NaOH

1. Introduction

Mechanochemical processes use mechanical collisions in a ball mill or similar device to drive chemical reactions. The collisions can create transient surface sites with extraordinary catalytic activity and hot spots that are characterized by rapid local temperature rises followed by dissipation of heat to the environment. Distortion of covalent bonds, mechanically induced charge separation (i.e., triboelectric effect), and mechanoradicals formed by homolytic cleavage of polymers can also initiate reactions. In addition, mechanical forces can create intimate contact between two solids through shearing, so that the conversion of a solid reactant over a solid catalyst becomes viable. Mechanochemistry has been used for synthesis of organic molecules and materials like MOFs and alloys as well as depolymerization of biomass and plastics.

2. Methods

Milling experiments were performed in a Retsch MM400 vibratory ball mill with stainless steel vessels and balls. Milling vessels were modified to allow for continuous gas flow through the vessel. Gas flows were regulated with mass flow controllers. CO₂ formation was monitored by online MS analysis using a Hidden HPR-20. NH₃ was detected by ion chromatography and mass spectrometry. Monomers from plastics depolymerization reactions were analyzed by GC or HPLC, whereas GPC was used to measure the molecular mass distributions of the residual polymers. Raman microscopy was performed using a Renishaw Reflex spectrometer.

3. Results and discussion

The formation of hot spots was analyzed in a fundamental study of the conversion of CaCO₃ to CaO [1]. Based on models for the impact of the milling ball and heat dissipation, each collision can be modeled as a transient batch reactor. The rates of CO₂ formation in a flow-through milling vessels were determined at different milling frequencies to validate the model. The impact of a 20 mm steel ball with a net velocity of 4 m/s results in a hot spot temperature of above 800 °C, which decays in 10s of ms.

These dynamic environments can be used for ammonia synthesis from the elements [2]. During milling in a mixture of N₂ and H₂, titanium metal was converted into TiN. SEM and TEM analysis showed the formation of agglomerates of TiN nanoparticles due to an equilibrium between fracturing and sintering of particles [3]. Once a TiN phase is formed, additional collisions lead to the formation of reactive nitride species (Figure 1). Under the conditions that allow for N₂ activation ammonia synthesis is likely thermodynamically limited, but the hotspots decay within milliseconds after the collision [2]. During the decay, the system passes through a regime in which hydrogenation of reactive nitrides to ammonia is thermodynamically and kinetically feasible.

The ability to shear different solids against each other opens new possibilities for converting solid feedstocks like biomass and waste plastics. The depolymerization of poly(ethylene terephthalate) (PET) occurred readily when the polymer was milled with NaOH [4]. After a short induction period in which particle size reduction dominated, monomers were produced at a constant rate up to a milling time of 12.5 min (Figure 2). At this point, the reaction mixture was converted from a powder into a wax that coated the milling balls or was pressed into the sites of the milling vessel (inserts in Figure 2). After wax formation, the remaining polymer was converted much faster. The molecular mass distribution of the residual polymer barely changed indicating that polymer domains are either entirely depolymerized or not affected at all. The reaction kinetics are consistent with a modified shrinking core model. To understand the reaction at impact sites in more detail, a 2.5 cm steel ball was dropped on a NaOH-coated PET film from a 1.07 m to have the same impact velocity as in a shaker mill at 30 Hz. Raman microscopy showed a gradient of PET depolymerization from 3% at the edge of the crater to 27% in the center.

Mechanocatalytic depolymerization of poly(styrene) (PS) follows a radical mechanism [5]. The presence of O₂ increased the formation of active radical species. When the concentration of monomeric styrene in the milling vessel reached a certain threshold repolymerization to a more stable polymer occurred. However, when styrene was continuously purged from the reactor in an inert gas stream the rate of styrene production remained approximately constant with respect to milling time.

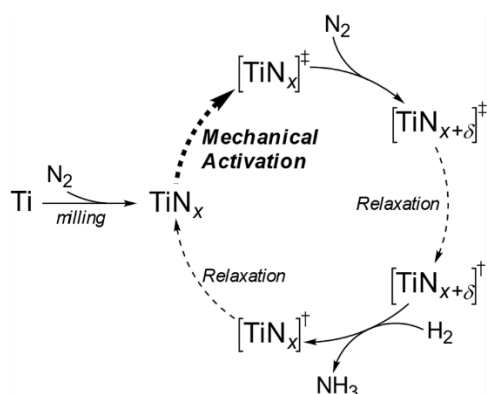


Figure 1. Reaction scheme for mechanocatalytic ammonia synthesis over in-situ synthesized TiN.

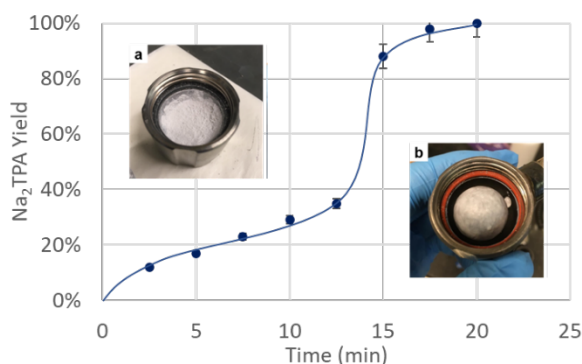


Figure 2. Monomer yield as a function of milling time during mechanochemical depolymerization of PET with NaOH with a stainless steel ball and vessel at 30 Hz.

4. Conclusions

Mechanocatalytic processes can provide unique transient reaction environments and intimate contact between several solids. In certain cases, this can overcome limitations of conventional thermochemical processes.

References

- [1] A.W. Tricker, G. Samaras, K.L. Hebisch, M.J. Realf, C. Sievers, *Chem. Eng. J.* 382 (2020) 122954.
- [2] A.W. Tricker, K.L. Hebisch, M. Buchmann, Y.-H. Liu, M. Rose, E. Stavitski, A.J. Medford, M.C. Hatzell, C. Sievers, *ACS Energy Letters* 5 (2020) 3362–3367.
- [3] J.A. DeWitt, E.V. Phillips, K.L. Hebisch, A.W. Tricker, C. Sievers, *Faraday Discuss.* 243 (2023) 65-76.
- [4] A.W. Tricker, A.A. Osibo, Y. Chang, J.X. Kang, A. Ganesan, E. Anglou, F. Boukouvala, S. Nair, C.W. Jones, C. Sievers, *ACS Sustainable Chem. Eng.* 10 (2022) 11338-11347.
- [5] Y. Chang, S.J. Blanton, R. Andraos, V.S. Nguyen, C.L. Liotta, F.J. Schork, C. Sievers, *ACS Sustainable Chem. Eng.* 12 (2024) 178-191.

Keywords

Ball mill, mechanochemistry, ammonia synthesis, plastics upcycling