

MECHANO-CATALYTIC DEPOLYMERIZATION OF POLYOLEFINS

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Improving current recycling technology could help increase the currently low plastic recycling rate of 12% [1]. The aim of depolymerization is to produce monomers to make high-quality plastics again. However, the state-of-the-art for polypropylene (PP) is pyrolysis, which produces low-value product mixtures, due to the high temperature applied, which is required for thermal C–C bond cleavage.¹ The team of Vollmer investigates polymer conversion in a mechano-chemical ball mill reactor (Figure 1A), which enables conversion below 60 °C instead of the more than 500 °C used in pyrolysis.¹ Mechano-chemical bond scission is combined with heterogeneous catalysis by directly functionalizing the surface of ceramic grinding spheres to create catalytically active sites.² This led to the discovery of a new catalytic mechanism, where the activated surface of the grinding spheres can interact with the organic radicals formed by the mechano-chemical action of colliding grinding spheres to promote monomer formation. This is fundamentally different from thermal conversion using heterogeneous catalysts, such as solid acids, where the polymer backbone C–C bonds are activated via the formation of carbocations. The team developed a model based on the Zhurkov relation³ to predict the conversion rate based on ball milling parameters.

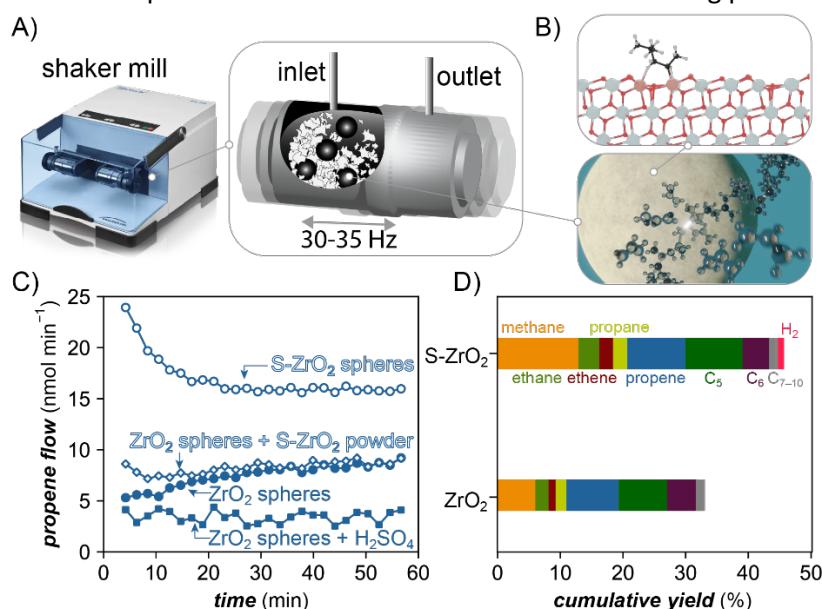


Figure 1. A) Milling container modified with gas in- and outlet to track gaseous products. B) Visualization of the mechano-chemical chain cleavage upon ball impact as well as density functional theory optimized structure of a radical interacting with the catalytic surface of the grinding sphere. C) Propene flow during milling of PP with untreated ZrO₂ spheres, sulfuric acid treated (S-ZrO₂) spheres, untreated spheres with sulfated ZrO₂ added as powder, and untreated spheres with sulfuric acid

added as liquid. C) Cumulative yields obtained from model PP after 1 h of milling with untreated and S-ZrO₂ spheres using optimized conditions.

¹ Vollmer, I., Jenks, M.J.F., Roelands, M.C.P., White, R.J., van Harmelen, T., de Wild, P., van der Laan, G.P., Meirer, F., Keurentjes, J.T.F., Weckhuysen, B.M. *Angew. Chem. Int. Ed.* **2020**, 59 (36), 15402–15423

² Hergesell, A. H., Baarslag, R. J., Seitzinger, C. L., Meena, R., Schara, P., Tomović, Z., Li, G., Weckhuysen, B. M., Vollmer, I.,* *J. Am. Chem. Soc.* **2024**, 146, 38, 26139–26147

³ Sakaguchi, M., Sohma, J. *J. Polym. Sci., Part B: Polym. Phys.* **1975**, 13, 6