Operando diffraction studies of mechanocatalytic reactions: challenges, technical developments and scientific insights

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During the last decades, mechanochemistry has become a very promising alternative to conventional syntheses, especially concerning sustainability and environmental friendliness. Further advantages are the option to obtain metastable products and/or enable the mechanical activations of solid catalysts. In previous studies, high catalytic activities were observed during ball milling under CO oxidation reaction conditions without any optimization of the catalysts [1]. Through collision between the catalysts and the milling media, reactive surfaces and defects are generated. In addition, crystallite sizes decrease and crystal morphologies of the catalysts may change. In situ X-ray powder diffraction is an appropriate tool to gain new insights into the processes taking place during mechanochemistry/mechanocatalysis. However, commercial milling vessels are solid and usually have thick walls made of stainless steel. This does not allow any diffraction experiments. As an alternative, vessels made of polymers can be used which allow the X-ray beam to penetrate. However, our studies show that polymer vessels are only suitable for the synthesis of soft matter such as MOFs or organic co-crystals but not for the synthesis of hard materials or catalytic reactions. In this contribution, we report on the technical challenges in developing milling equipment suitable for in situ diffraction experiments [2]. The setup was installed on the P02.1 beamline at PETRA III (DESY, Hamburg). The milling vessel has X-ray transparent windows and a gas supply system. The gas outlet of the vessel is connected to a mass spectrometer/gas chromatograph, which makes it possible to perform online gas analysis.

Three examples for the successful development and implementation of the in situ mechanochemical setup for synchrotron sources will be discussed:

(a) Phase transformation of boehmite (γ-AlOOH) into corundum (α-Al_2O_3) [2]

(b) The frequency-dependent direct synthesis of ZnS from its elements [3]

(c) The mechanochemical activation of Au@Fe_2O_3 for the oxidation of CO [4]

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