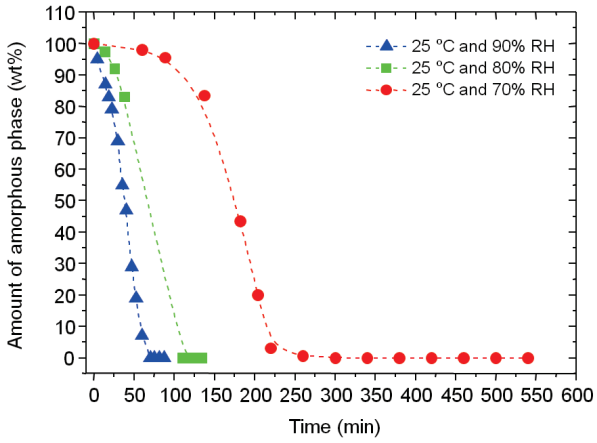

Figure 1. Amorphous-to-crystalline ratio for spray dried salbutamol plotted as a function of time at relative humidity of 70 %, 80 % and 90 %.

Keywords: Pharmaceutics, crystallization process, X-ray diffraction, partial least square regression

MS17-P10 In situ XRD study of reduction of $Mn_xZr_{1-x}O_2$ solid solutions

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Solid solutions based on ZrO_2 exhibit high catalytic activity in a number of practically important reactions. Mn-Zn mixed oxides can effectively catalyze the gas-phase oxidation of hydrocarbons or chlorcarbons. Mn cations can enter the lattice of ZrO_2 with the formation of solid solutions $Mn_xZr_{1-x}O_2$, in which lattice oxygen possesses sufficiently high mobility and hence high reactivity.

A series of mixed Mn-Zr oxides with different molar ratios Mn/Zr (0.1-9) have been prepared by coprecipitation of manganese and zirconium nitrates and characterized by XRD and N_2 adsorption techniques. It has been found that at low Mn/Zr ratios, when the Mn content is below 30 atom %, the catalysts are single-phase solid solutions ($Mn_xZr_{1-x}O_{2-\delta}$) based on a ZrO_2 structure. According to XPS data, manganese in these solutions exists mainly in the Mn^{4+} state. An increase in the Mn content mostly leads to an increase in the number of Mn cations in the structure of the solid solutions, but a part of manganese form Mn_2O_3 and Mn_3O_4 in crystalline and amorphous states.

Reduction of solid solutions in hydrogen was studied by a TPR, in situ XPS and XRD, at temperature range 100 to 700 °C. Figure 1 shows a series of diffraction patterns recorded during the reduction of the sample with Mn/Zr=1. At room temperature, the sample contains two phases: a solid solution $Mn_xZr_{1-x}O_4$ and Mn_2O_3. The reduction of this sample leads to a change in the lattice parameter of the solid solution $Mn_xZr_{1-x}O_4$, which is indicated by the shift of corresponding peaks to larger angles. Besides, the reduction leads to transformations of manganese oxides. The reduction of the solid solutions proceeds in a wide temperature range 100-700 °C via two steps. In the first stage, at temperatures of 100-500°C, manganese cations undergo partial reduction to Mn^{2+}, whose presence is confirmed by XPS measurements. The lattice parameter of $Mn_xZr_{1-x}O_2$ in this case varies because of changes in the oxidation state of manganese cations in the bulk of solid solution. In the second stage, at temperatures of 500-700°C, manganese cations exit from the bulk of the solid solution and segregate on its surface. The lattice parameter at this stage increases because of the decrease in the number of Mn cations in the oxide.

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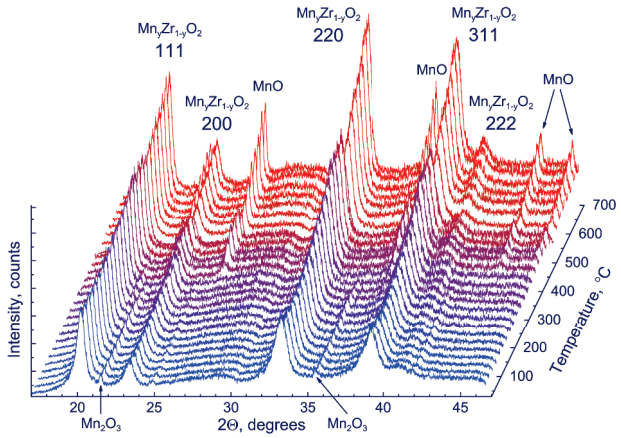

Figure 1. Series of diffraction patterns (λ = 1.0157 Å) recorded in situ during reduction with hydrogen in the temperature ranges from 30 to 700 °C

Keywords: in situ XRD, solid solution, reduction

MS17-P11 A new micro-furnace for "in situ" high-temperature single crystal X-ray diffraction measurements

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Elastic properties reflect the nature of atomic bonding and allow the retrieval of crucial information about physical, chemical and mechanical behavior of materials. This explains the strong and increasing interest in quantifying elastic properties of materials in several scientific fields. To this aim several devices and methods have been developed so far. In particular, for high temperature devices for "in-situ" measurements, even if the small isothermal volume required for single-crystal X-ray diffraction experiments, the design of a furnace should also aim to reduce thermal gradients by including a large thermal mass that encloses the sample. However, this solution often leads to complex design that results in a restricted access to reciprocal space or attenuation of the incident or diffracted intensity.

Here we present a newly-developed H-shaped Pt-Pt/Rh resistance micro-furnace for in-situ high-temperature single-crystal X-ray diffraction measurements. The compact design of the furnace together with the long collimator-sample-detector distance allows us to perform measurements up to 2θ = 70°. The microfurnace is equipped with a water cooling system that allows a constant thermal gradient to be maintained that in turn guarantees thermal stability with oscillations smaller than 5°C in the whole range of operating T of room-T to 1200°C. The furnace has been built for use with a conventional 4-circle Eulerian geometry diffractometer equipped with point detector and automated with the SINGLE software (Angel and Finger 2011) that allows the effects of crystal offsets and diffractometer aberrations to be eliminated from the refined peak positions by the 8-position method (King and Finger 1979), and thus maximize precision in unit-cell measurements. The software has been modified to reduce chimney effects in the furnace and thus improve the stability by (i) restricting the χ circle movements to between -90° and +90°; (ii) optimizing the order of measurements to minimize χ circle movements (iii) imposing a waiting time after large angular movements on χ.

Temperature calibration has been performed iteratively by combining measurements with a standard small diameter thermocouple mounted in the same conditions as the sample together with the lattice parameter determination of materials with known thermal expansion behavior (i.e. quartz and pure silicon).

References

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Keywords: X-Ray diffaraction, single crystal, high temeprature, thermal expansion