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Chemical Selectivity in Diffraction by Statistical Analysis of in situ XRPD Data

M. Milanesio[1], L. Palin[1], D. Viterbo[1], R. Caliandro[2], A. Urakawa[3], W. van Beek[4], D. Chernyshov[4]

[1]Università del Piemonte Orientale, DiSIT, Alessandria, Italy, [2]Institute of Crystallography, CNR, Bari, Italy, [3]Institute of Chemical Research of Catalonia, ICIQ, Tarragona, Spain, [4]Swiss-Norwegian Beamlines, ESRF, Grenoble, France

X-ray diffraction methods in general allow only a limited chemical selectivity. Structural information on a subset of atoms can be obtained by a modulation enhanced diffraction (MED) experiment, using a periodic stimulus supplied in situ on a crystal, while diffraction data are collected several times within a stimulus period. The data are then treated by statistical methods such as phase sensitive detection (PSD) and Principal component analysis (PCA) techniques. The application of PSD to diffraction has been proposed as a tool to extract crystallographic information on a subset of atoms [1], thus allowing to introduce selectivity in diffraction. Simulated and experimental PSD-MED powder data were produced by using a TS-1 zeolite as spectator, in which Xe, acting as active species, is adsorbed and desorbed in a periodically modulated mode. By first demodulating these data, MED allowed to obtain the powder diffraction pattern of the active subset, i.e. to obtain selectively the crystallographic information on Xe, by solving the crystal structure of the active species out of the zeolite framework. The "real world" experiments indicated that the PSD-MED approach has some limitations related to its theoretical assumptions. PCA is widely used in spectroscopic analyses and was recently applied to XRPD data by some of us [2]. PCA was exploited to evaluate the in situ XRPD data quality, to speed up the data analysis and data pre-treatment required by PSD and improve the extraction of the substructure information from MED data. It resulted that the first two components obtained by PCA are related to the 1- and 2-omega patterns from PSD. The two approaches (PCA and PSD) are finally compared from the viewpoint of their capacity of gathering information on the Xe substructure inside the zeolite channels and used in a synergic way to obtain the optimal data analysis efficiency.

[1] *D. Chernyshov, W. van Beek, H. Emerich, M. Milanesio, A. Urakawa, D. Viterbo, L. Palin, R. Caliandro, Acta Crystallographica Section A 2011, A67, 327-335.,* ***[2]*** *R. Caliandro, G. Di Profio, O. Nicolotti, J. Pharm. Biomed. Anal., 2013, 78.*

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