x-ray sources. Hence we have shown that such nanostructured materials can be characterized using standard powder diffraction sources. Results are published in [1].

[1] A. Cervellino, J. Schefer, L. Keller, Th. Woike, D. Schaniel, *J. Appl. Cryst.* **2010**, *43*, 1040-1045.

Keywords: debye approach, nanomaterial, powder diffraction

MS18.P03

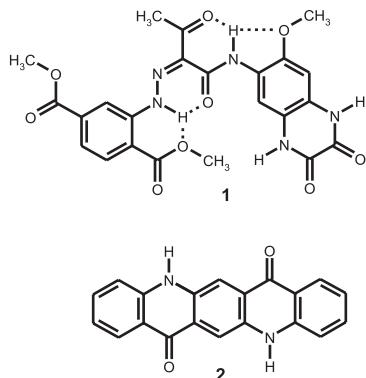**Pair-distribution function analyses of nanocrystalline organic pigments**

Martin Schmidt,[a] Lothar Fink,[a] Edith Alig,[a] Christian W. Lehmann,[b] Claudia Weidenthaler,[b] *[a]Institut für Anorganische und Analytische Chemie, Goethe-Universität, Frankfurt am Main (Germany). [b]Max-Planck-Institut für Kohlenforschung, Mülheim (Germany).* E-mail: m.schmidt@chemie.uni-frankfurt.de

The pair-distribution function (PDF), represents the probability to find two atoms with an interatomic distance r. The PDF is generally used to investigate local structures of disordered, nanocrystalline or amorphic inorganic compounds, liquids and glasses. Here, the PDF analysis is applied to nanocrystalline organic pigments, having domain sizes of 3 - 30 nm.

Pigment Yellow 213 (**1**) exists in two crystal phases. The structure of the yellow α-phase was solved from X-ray powder data with the help of electron diffraction. The brown β-phase shows only a few broad humps in the X-ray powder diagram. Its PDF analysis, based on synchrotron data, reveals, that the molecules are arranged in stacks. From the PDF curve, the domain size is determined to be about 3 nm in stack direction, and the local structure is found to be similar to the α-phase. [1]

The α^{II}-phase of quinacridone (Pigment Violet 19), **2**, is nanocrystalline, too. [2] Powder patterns of all four phases of **2** were recorded on laboratory STOE Stadi-P diffractometers in transmission mode, using Cu-$K\alpha_1$ and Mo-$K\alpha_1$ radiation, at temperatures from 100 K to 400 K. The PDF analyses proved that the local structures of the α^{I}, β and γ-phases are considerably different; in contrast the local structure of the α^{I} and α^{II}-phases have similarities, although their X-ray powder patterns are different.

[1] M.U. Schmidt, S. Brühne, A.K. Wolf, A. Rech, J. Brüning, E. Alig, L. Fink, C. Buchsbaum, J. Glinnemann, J. van de Streek, F. Gozzo, M. Brunelli, F. Stowasser, T. Gorelik, E. Mugnaioli, U. Kolb, *Acta Cryst* **2009**, *B 65*, 189-199. [2] E.F. Paulus, F.J.J. Leusen, M.U. Schmidt, *CrystEngComm* **2007**, *9*, 131-143.

Keywords: pair-distribution function analysis, pigment, local structure

MS18.P04

X-ray powder diffraction study of particle sizes of metastable Ru_xM_{1-x} (M = Ni, Cu)

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Transition metal alloys with ruthenium are efficient catalysts in Fischer-Tropsch synthesis. One way of preparing bimetal alloys as nanoparticles is thermal decomposition of appropriate binuclear complexes at 200-600°C. In this work, we studied thermal decomposition products of $[M(PyO_2)_2RuNO(NO_2)_4OH]$ M = Ni, Cu complexes at 300, 350, and 400°C.

Initial binuclear complexes were prepared by mixing equimolar amounts of $M(NO_3)_2$ M = Ni, Cu and $Na_2[RuNO(NO_2)_4OH]$ with pyridine-N-oxide (3 equivalents) in acetone.

In the both cases, thermal decomposition was performed on a TG 209 F1 Iris micro thermobalance (NETZSCH) in hydrogen atmosphere. Annealing was executed for 6 h at each temperature point with heating rate of 1 degree/min. The mass loss fits the calculated that within ± 2%.

X-ray diffraction study of thermolysis products was carried out on a Shimadzu XRD7000 diffractometer (CuKα-radiation, Ni-filter) at the ambient temperature. Upon decomposition of $[Cu(PyO_2)_2RuNO(NO_2)_4OH]$, two-phase material containing solid solutions based on the copper HCC and the ruthenium HCP cells was revealed to form. The particle sizes calculated by the Scherrer formula are ~ 4 nm for T = 300 and 350°C and 7 nm for 400°C. With decomposition of $[Ni(PyO_2)_2RuNO(NO_2)_4OH]$ at all temperatures mentioned, one-phase products formed, namely, solid solutions with the particle sizes of 4 nm and based on ruthenium HCP cell, Ru_xNi_{1-x} x = 0.68-0.75. The composition was estimated by the Retgers rule. Most likely a portion of nickel is amorphous, as further annealing of one sample at 850°C for 10 h resulted in two crystalline phases on the basis of ruthenium (60 % in mass) and nickel (40 % in mass). The compositions of the phases are near the corresponding boundaries of the two-phase range of the phase diagram.

Keywords: x-ray, ruthenium, nano

MS18.P05

Synthesis, structure and properties of nanosized titanium dioxide with η-TiO$_2$ modification

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In recent years, great attention has been focused on TiO$_2$ materials because they exhibit a variety of controllable electronic and optical properties and have extensive applications. TiO$_2$ is proved to be a good and perspective active component for different types of catalysts and photocatalysts. In comparison with other semiconductor catalysts, TiO$_2$ is biologically and chemically inert, stable to photodegradation, and also relatively cheap.

There are 12 polymorphic TiO$_2$ modifications in both bulk and nanoscale forms, but the η-TiO$_2$ phase was obtained only in the nanostate and rather scarcely characterized. One of the promising methods of its synthesis, a sulfate method, allows preparing nanosized

subjects with various parameters of their microstructure (sizes of microparticles, specific surface) and substructure (sizes of nanoparticles and crystallites) governing their working properties.

The purpose of the work is to find correlations between synthesis conditions of samples with nanosized η-TiO$_2$, their characteristics and structural, sorption, catalytic and photocatalytic properties.

The determination of η-TiO$_2$ cell parameters (a~3.8Å, c~19Å) has been made using sources of electrons, X-rays and synchrotron scattering. These parameters are associated with ones of anatase modification (a_0~3.8Å, c_0~9.5Å) by the relationship a~a_0, c~2c_0. Optimization of the sulfate method allowed increasing the yield of η-TiO$_2$ up to 95%. The samples were characterized by a set of methods showing variations in sizes of microparticles/ agglomerates (200/3000 nm; SEM, BET), nanoparticles (8÷24 nm, rarely 28÷55 nm; small angle X-ray scattering), crystallites, or coherent scattering regions (L=3÷6 nm; large angle X-ray scattering), as well as in sizes (~17 nm; BET) and capacities (0.02 cm^3/g; BET) of pores and specific surface (4.5÷16 m^2/g; BET). Dependence of some parameters (in particular, value L) on synthetic conditions (the initial concentration of TiOSO$_4$· xH$_2$SO$_4$·yH$_2$O reagent, the temperature and duration of hydrolysis, the heating speed of reaction mixture and so on) was found.

Photocatalitic activity (in model reactions of decomposing methyl-orange, methylene-blue and xylenol-orange indicators under UV radiation), sorption properties (extraction of various ions from aqueous media) and catalytic properties (oxidation of CO to CO$_2$ in air at room temperature) depend on sample characteristics. Efficiency of CO conversion to CO$_2$ correlates with specific surface. For bismuth, arsenic and vanadium ions, degree of sorption equal to maximal permissible concentration was achieved. A relation between the degree of metal-ion sorption and the coherent scattering regions (value L) has been established. Degree of metal-ion sorption and rate constant for photocatalytic reactions are maximal for L ~ 4.5 nm. Photocatalytic activity (pH < 3) for the samples with η-TiO$_2$ is considerably higher than for commercial photocatalysts Degussa P25 (anatase–rutile mixture) tested in comparable conditions. The photocatalytic and catalytic activities obtained confirm unique surface properties of η-TiO$_2$.

From the X-ray diffraction study data by means of crystallochemical approach, the structure of η-TiO$_2$ was proposed. The quasi-layered structure model provides a very fit to the experimental data (in particular, the sorption properties).

MS18.P06

(Micro)structure determination of ferrite nanoparticles using multiple techniques

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We report results of systematic studies utilizing multiple techniques on series of two nanoparticle ferrite systems, ZnFe$_2$O$_4$ and Li$_{0.5}$Fe$_{2.5}$O$_4$, obtained using variable thermal annealing protocols. Details of structure and microstructure changes of ferrite nanoparticles are assessed using synchrotron X-ray and TOF neutron diffraction data by combining Rietveld method in reciprocal space with the atomic pair distribution function (PDF) method in direct space. Such obtained (micro)structural parameters were correlated with physical properties revealed by HRTEM, Mössbauer spectroscopy and DC magnetization.

Small discrepancies between Rietveld and PDF results were found for the values of lattice parameters of ZnFe$_2$O$_4$, in which case those derived from PDF can be considered as more reliable. Refined occupation number of Zn ions, as determined by Rietveld refinement, reveals change of occupation ratio over tetrahedral and octahedral sites within the space group Fd-3m. The results show that bulk sample resembles a normal uninverted spinel structure, while there is about 25% of inversion found in as-prepared sample (S1) and annealed sample at 300 ºC (S2). This is in good agreement with results obtained from Mössbauer spectroscopy, where degree of inversion was found to be 27%. With further annealing at 400 ºC (S3) inversion drops to 16%.

Particle size and microstrain were determined using isotropic (spherical) particle shape model and isotropic microstrain (random defects distribution). This resulted in crystallite size values of 3.4 nm (S1), 7.7 nm (S2), and 13 nm (S3), in good agreement with those obtained from PDF and HRTEM analyses. These results further indicate a tiny shell, in agreement with DC magnetization data that suggest negligible interaction between magnetic moments in nanoparticle core and shell. The coercivity and blocking temperature were found to increase with increasing crystallite size.

Crystal structure and microstructure evolution of Li$_{0.5}$Fe$_{2.5}$O$_4$ nanoparticles obtained after annealing at 180, 300 and 400 ºC were also studied. The 5-10 nm particles exhibit similar crystal structure, on average, with a partial ordering of Li$^+$ and Fe^{3+} ions between octahedral 4b and 12d sites on the spinel crystal lattice (space group P4$_3$32). PDF analysis reveals an anomalous increase of the oxygen O1 isotropic atomic displacement parameters to unphysical values, suggesting significant disordering within the O1 network. Since the nearest neighbor coordination of the iron in tetrahedral sites is much more influenced by the oxygen O1 anions than the octahedral sites in spinel structure, it can be concluded that thermal annealing of lithium ferrite powder mainly activated relaxations of the oxygen sublattice and does not change significantly the cation distribution up to 400 ºC.

MS18.P07

NiO/Ni nanocomposite (micro)structure evolution induced by thermal annealing and milling

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There is an increasing interest in the last few years for studies of ferromagnetic (FM) - antiferromagnetic (AFM) systems because of exchange coupling between FM and AFM phases that influence on physical properties as well as unresolved scientific issues. Therefore, there is a challenge to find a simple and controlled procedure for preparation of FM-AFM nano systems with technological impact. Although, the process of thermal decomposition of nickel(II) acetate tetrahydrate was described in literature, we performed an integrated study of it by different techniques.