CATALYST COMPOSITION FROM THEORETICAL MODEL OF RAMAN SPECTRA

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Introduction/background

Raman spectroscopy is optical resonance technique sensitive to atomic bonding. As such it is often used for catalyst characterization and for the investigation of the bulk and surface chemistry during catalyst activity. Method is of considerable interest in situations when catalyst is not single-phase material, but consists of a mixture of crystal phases. Ideally, in such situations Raman spectra supported by theoretical model would be indispensable tool for description of phase contacts. The Raman spectra modeling, however, even at the level of density-functional theory (DFT) proves to be rather computationally demanding. In the attempt to elucidate catalyst composition, and complement experimental findings (XRD, XPS, Raman spectroscopy) in our research of MnMOx catalysts, we begin by modeling separate crystal phases expected to be present in the multi-phase catalyst samples. Based on comparison of superposed theoretical spectra of several crystal phases and experimental Raman spectra of the catalyst we comment on the possibility to use such approach for determination of multi-phase catalyst composition.

To some extent, the boundary effects are taken into account by the finite size of the investigated crystallites. Our approach, however, at this point still lacks explicit description of specific modes that may be present at the crystal phase joints.

Methods

Preparation of the samples of MnMOx (M=Fe, Cu) catalysts is explained in detail in our previous works [1,2]. The X-ray diffraction (XRD) spectroscopy and the Raman spectroscopy techniques used for characterization of the catalysts were done and explained in course of these works also. XRD provides valuable information of the crystal composition of the complex catalysts, while Raman spectroscopy is used to further validate the importance of specific bond vibrations during catalytic activity. Here we rely to that experimental data and compare it to theoretical models of these complex catalyst multi-phase systems.

Model: MnFeOx – separate calculations of 3 unit cells of: $MnFeO_3$ and Fe_2O_3 (about 80 atom structures)

MnCuOx – separate calculations of 3 unit cells of $CuMn_2O_4$ and $CuMnO_4$

additional CuO, MnO_2 calculations

(choice of model based on XRD determined composition)

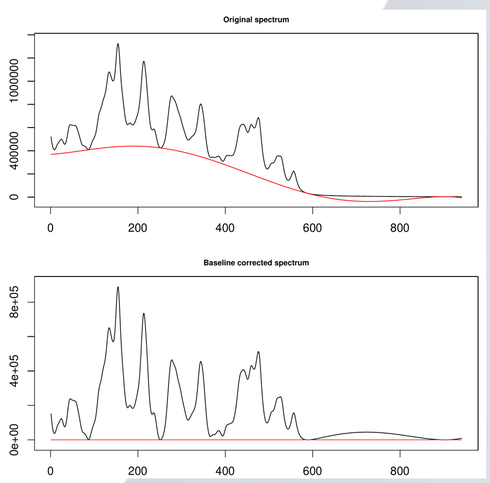
Calculations: *Gaussian 16* run on *Isabella cluster*, using *wB97XD* hybrid functional and *TZVP* and *lanl2dz* basis sets. Electric response of environment is somewhat included further by immersing the structure to polarizable continuum (*PCM* model of self-consistent reaction field.) Choice of dielectric constant is based on table values for similar compounds and is used

$\varepsilon_{(MnFeO3)} = \varepsilon_{(Fe2O3)} = \varepsilon_{(CuMn2O4)} = 14$

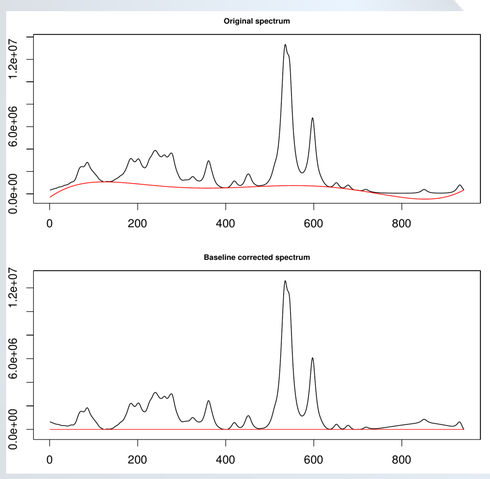
Processing of spectra is then performed using available routines in *R*, *Gnuplot* and *Python3*.

Results & Discussion

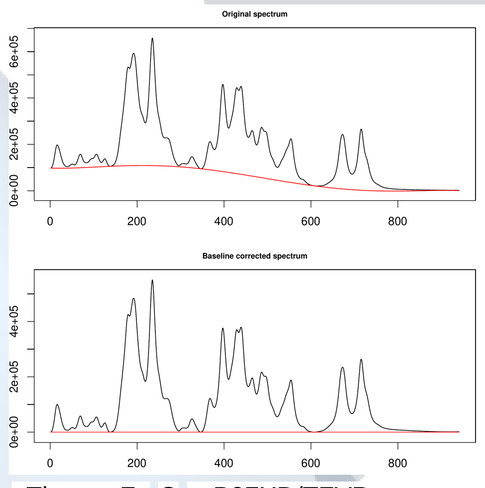
All spectra, experimental and theoretical was corrected for baseline using Lieber - Mahadevan-Jansen *baseline.modpolyfit* of rank 5 in *R*. Then, spectra was normalized using simple *min-max* normalization, and finally each spectrum fitted to sum of 7 or 8 Gaussians using least-squares minimization from *python.optimize* module.



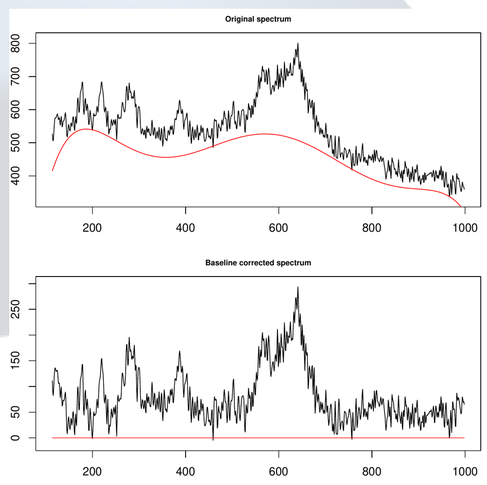
Theory, $MnFeO_3$ wB97XD/TZVP



Theory, $MnFeO_3$ wB97XD/lanl2dz



Theory, Fe_2O_3 wB97XD/TZVP

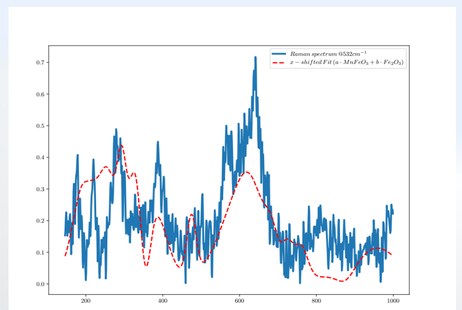


Experimental Raman spectrum of MnFeOx at 532 cm^{-1}

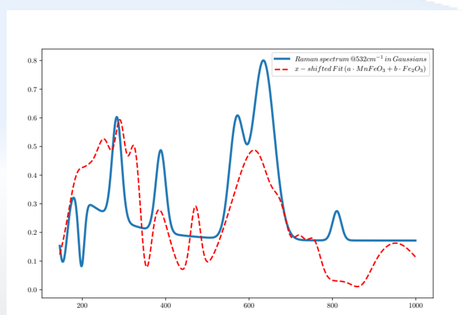
Least-squares minimization of experimental Raman spectrum $Y_{exp}(x)$ to the function of the shape:

$$Y_{theo}(x) = a \cdot Y_{MnFeO3}(x \cdot shift) + b \cdot Y_{Fe2O3}(x \cdot shift)$$

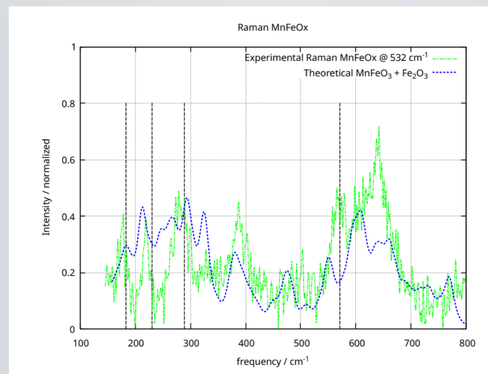
using *optimize.minimize* BFGS method as implemented in *python.scipy*



Raman spectrum (blue) compared to optimal superposition of $MnFeO_3$ and Fe_2O_3 theoretical spectra (red).



Raman spectrum (blue) deconvoluted to 8 gaussians compared to optimal superposition of $MnFeO_3$ and Fe_2O_3 theoretical spectra (red).



Optimized parameters:

shift = 0.721262

a = 0.401917

b = 0.345152

Approximate composition:

$n(MnFeO_3) : n(Fe_2O_3) \approx 1{,}18$

Final comparison of experimental and optimized superposition of constituents theoretical spectra. (Vertical lines show positions of experimentally determined peaks.)

Conclusions

Mostly ‘work-in-progress’ conclusions.

Modeling Raman spectra of complex phase catalysts very computationally intensive.

Dependence on basis set and approximate dielectric constant.

From deconvolution in several phase spectra, it is possible to estimate catalyst composition, but this requires prior calibration of theoretical method.

From comparison with experiment it is possible to improve initial theoretical model.

From deconvolution in single Gaussian peaks, it is possible to estimate hierarchy of vibrational modes contributing to the spectra of the complex.

References

[1] M. Duplančić, V. Gomzi, A. Pintar, S. Kurajica, V. Tomašić, (2020), Experimental and theoretical (ReaxFF) study of manganese-based catalysts for low-temperature toluene oxidation. Ceramics International, 47(3):3108-3121.

[2] F. Car, V. Gomzi, V. Tomašić, D. Vrsaljko, (2022) Development of novel monolithic catalysts for catalytic oxidation of BTEX compounds using 3D-printing technology. (under review)