



Full multiple scattering approximation to K XANES of supported metal catalysts

N. Aldea^{a,*}, C. Tiuşan^b, A. Chezan^b

^a *Institute of Isotopic and Molecular Technology, P.O. Box 700, 3400 Cluj-Napoca, Romania*

^b *Department of Physics, "Babeş Bolyai" University, Cluj-Napoca, Romania*

Abstract

The paper presents a numerical model based on multiple scattering theory (MST) used in the investigation of electronic structure of the supported metal catalysts (SMC) employed in H/D exchange reaction and in the catalytic recombined process of hydrogen from the heavy water nuclear power reactors. Structural properties were investigated by X-ray diffraction technique (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Based on these information the model determines numerical K X-ray absorption near edge structure (XANES) spectra for supported Ni catalysts.

1. Introduction

It has been found that X-ray absorption spectroscopy can be a tool for determining the local structure around X-ray absorbing atom and the electronic structure of the materials. It is well-known that X-ray absorption spectra of materials are separated into two parts according to the spectral region. One is the structure expanding from the absorption threshold up to about 50 eV, the so-called XANES and the other is called EXAFS which appears in the higher-energy region following XANES. The absorption edge before the threshold of EXAFS oscillation is strongly influenced by multiple scattering effects. In this energy range, the photoelectron is strongly scattered by the surrounding atoms. We have adopted the short-range approach which was extended to the XANES range by including multiple scattering events.

Aldea et al. [1, 2] showed that the K or L₁ absorption edges arise mainly from transition of electrons initially in

the 1s or 2s core level to empty levels above the Fermi levels (s → p), and the L_{II} and L_{III} edges are due to electron transitions from 2p levels (p → d). For this reason, XANES contains more information on relative orientations and bond angle of atoms surrounding the absorption atom. The absorption coefficient is described in terms of XANES spectra. With it, we can estimate the density of states, the binding energy and the catalytic activity.

2. The theoretical background

The calculations were carried out following the formulation developed by Fujikawa et al. [3] and Kitamura et al. [4]. The absorption coefficient $\mu(E)$ is expressed in terms of the XANES χ , the Fermi distribution $f(E)$ and density of states $N(E)$ as follows:

$$\mu(E) = \sum_L |\langle L|z|L_0 \rangle|^2 N(E) [1 + \chi(E)] [1 - f(E)]. \quad (1)$$

* Corresponding author.

The XANES function is given as a sum of the following four equations:

$$\chi_1(E) = 2\Re\{S_{0,(10)}\}, \quad (2)$$

$$\chi_2(E) = 8\pi\Re$$

$$\times \left[\sum_{\alpha \neq 0} \sum_{L_1, L_2} i^{-L_2} j_{L_1}(kR_\alpha) Y_{L_2}(\hat{R}) \mathcal{G}(L_1, L_2|10) S_{\alpha L_1} \right], \quad (3)$$

$$\chi_3(E) = \sum_{\alpha} \sum_L |S_{\alpha L}|^2, \quad (4)$$

$$\chi_4(E) = 4\pi \sum_{\alpha \neq \beta} \sum_{L_1, L_2, L_3} i^{L_1} j_{L_1}(kR_{\alpha\beta}) \times Y_{L_3}(\hat{R}_{\beta,\alpha}) \mathcal{G}(L_3, L_1|L_2) S_{\beta L_2}^* S_{\alpha L_1}, \quad (5)$$

where $R_{\alpha\beta} = R_\alpha - R_\beta$, and the abbreviated notation $S_{\alpha L} \equiv [\tilde{T}(1 - \tilde{T})^{-1}]_{\alpha L; 0(10)}$ is used. The symbol \Re means the real part of the bracket. The supermatrix \tilde{T} describes the propagation of the photoelectron between atoms α and β sites and has the following elements:

$$[\tilde{T}]_{\alpha L; \beta L'} = t_l^\alpha(k) G_{LL'}(R_\alpha - R_\beta) (1 - \delta_{R_\alpha, R_\beta}). \quad (6)$$

Here t_l^α and $G_{L'L}(R)$ are the partial scattering amplitudes for the potential scattering at atom α and the angular momentum representation of the Green function, respectively,

$$t_l^\alpha(k) = -(e^{2i\delta_l^\alpha(k)} - 1)/2ik, \quad (7)$$

$$G_{L'L}(R) = -4\pi ik \sum_{l''} i^{-l''} (-1)^{l-l''+m} \times \mathcal{G}(L, l' - m'|l'') h_l^{(1)}(kR) Y_{l''}^*,_{m-m'}, \quad (8)$$

where $h_l^{(1)}$ is the spherical Hankel function of the first kind, Y^* is the conjugate of complex spherical harmonics and $\mathcal{G}(L_1, L_2|L_3)$ is the Gaunt coefficient defined by

$$\mathcal{G}(L_1, L_2|L_3) = \int Y_{L_3}^*(\hat{r}) Y_{L_1}(\hat{r}) Y_{L_2}(\hat{r}) d\hat{r}. \quad (9)$$

The quantity $\sum_L |\langle L|z|L_0 \rangle|^2$ reduces to $|\langle 10|z|00 \rangle|^2$ and its value was calculated by Müller et al. [5]. Fujikawa et al. and Kitamura et al. have employed this theory for determining Ge K-edge XANES of GeCl₄, respectively, Cl K-edge for SrCl₂ and CsCl [3, 4].

3. The description of the programs

This program package consists of four programs which may be run interactively between the user and a batch command file in sequential or selective mode,

depending on the user's needs. The programs package has the following tasks:

(i) The muffin tin potential for Ni crystallites is calculated by Löwdin and Mattheiss approximation [6]. The necessary structural parameters have been obtained by processing the XRD and EXAFS experimental spectrum and electronic densities were calculated by Herman et al. [7]. The muffin tin potential V_{mt} is characterized by muffin tin radius R_0 and muffin tin zero V_0 . The imaginary part values of optical potential V_{oi} for transition metals have been calculated by Pendry [8].

(ii) The calculation of the logarithmic derivatives is based on the muffin tin potential elaborated in the previous step. The integration of the radial Schrödinger equation has been done by the Numerov procedure.

(iii) The phase shift function is given by relation

$$\delta_l(k) = \text{atan} \left[\frac{kj_l'(x) - L_l(x)j_l(x)}{kn_l'(x) - L_l(x)n_l(x)} \right], \quad (10)$$

where $x = kR_0$, $j_l(x)$ and $n_l(x)$ are spherical Bessel and Neumann functions, $L_l(x)$ are logarithmic derivatives and R_0 is the muffin tin radius which is taken to be half the minimum distance between the nearest atoms. This task can also calculate the complex phase shift function by using Pendry's expression

$$\delta_l(E - V_0 - iV_{oi}) \simeq \delta_l(E - V_0) - iV_{oi} \frac{d\delta_l(E - V_0)}{dE}. \quad (11)$$

In order to see the contribution of partial wave scattering to K XANES signal, we calculated the total cross-section $\Sigma(k)$ for the muffin tin potential constructed by the first code, using the relation

$$\Sigma(k) = \frac{2\pi}{k^2} \sum_l (2l+1) (1 - e^{-2\Im\delta_l(k)} \cos(2\Re\delta_l(k))), \quad (12)$$

where $\Im\delta_l(k)$ means imaginary part of the phase shift function.

(iv) The main part of this programs package consists in determining the K XANES function by the short-range-order multiple scattering theory. Input data are formed by the following information:

- the phase shift function, the real part and the imaginary part;
- the geometrical data cartesian coordinates for each atom from cluster must be expressed in fractions of lattice parameter;
- the maximum number of coordinate shells;
- the range of energy, E_{min} , ΔE , E_{max} ;
- the Debye–Waller factor;
- the dumping factor.

4. Results

In the calculation of $\chi(E)$, the size of the supermatrix \tilde{T} should be truncated at a certain finite size N , which is given by $(l_{\max} + 1)^2 N_{\text{atom}}$ where N_{atom} is the total number of the atoms from cluster. Here we calculated the K XANES of Ni crystallites based on structural parameters determined by EXAFS spectroscopy, for $l_{\max} = 2$, and the maximum cluster size S_{\max} to the third coordination shell; thus $N_{\text{atom}} = 43$, $(S_{\max}, l_{\max}) = (3, 2)$ and the supermatrix dimension is 387. Based on these numerical results and the experimental K XANES spectra we can calculate the density of states of the crystallites used in determining the binding energy and the catalytic activity.

The calculations were made on SUN SPARC Station at International Centre for Theoretical Physics from Trieste, high speed storage required is 1.4 Mbytes and running time in the batch queue system was about 10 h for hundred values of the energy.

References

- [1] N. Aldea, in: *Physics Computing '92*, eds. R. A. de Groot and J. Nadrchal (Word Scientific, Singapore, 1992) p. 229.
- [2] N. Aldea and E. Indrea, *Comput. Phys. Commun.* 60 (1990) 145; 60 (1990) 155.
- [3] T. Fujikawa, M. Matsuura and H. Kuroda, *J. Phys. Soc. Japan* 52 (1983) 1983.
- [4] T. Kitamura, M. Muramatsu and C. Sugiura, *Phys. Rev. B* 33 (1986) 8.
- [5] J. E. Müller and J. W. Willkins, *Phys. Rev. B* 29 (1984) 4331.
- [6] L. F. Mattheiss, Wood J. H. and A. C. Switendick, in: *Methods in Computational Physics*, eds. B. Alder, S. Fernbach and M. Rotenberg (Academic Press, London, 1968) p. 63–145.
- [7] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
- [8] J. B. Pendry, *Low Energy Electron Diffraction* (Academic Press, London and New York, 1974) p. 57.