Structural and Electronic Characterization of Supported Ni and Au Catalysts used in Environment Protection Determined by XRD, XAS and XPS methods

N. Aldea, V. Rednic, F. Matei, Tiandou Hu and M. Neumann

Abstract—The nickel and gold nanoclusters as supported catalysts were analyzed by XAS, XRD and XPS in order to determine their local, global and electronic structure. The present study has pointed out a strong deformation of the local structure of the metal, due to its interaction with oxide supports. The average particle size, the mean squares of the microstrain, the particle size distribution and microstrain functions of the supported Ni and Au catalysts were determined by XRD method using Generalized Fermi Function for the X-ray line profiles approximation. Based on EXAFS analysis we consider that the local structure of the investigated systems is strongly distorted concerning the atomic number pairs. Metal-support interaction is confirmed by the shape changes of the probability densities of electron transitions: Ni K edge (1s → continuum and 2p), Au L_III-edge (2p_3/2 → continuum, 6s, 6d_5/2 and 6d_3/2). XPS investigations confirm the metal-support interaction at their interface.

Keywords—local and global structure, metal-support interaction, supported metal catalysts, synchrotron radiation, X-ray absorption spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy.

I. INTRODUCTION

Electronic and structural information about the local vicinity around a specific atomic constituent in the amorphous materials [1, 2], the location and chemical state of any catalytic atom on different oxide supports [3] and nanoparticle of transition metal oxides [4-6] can be obtained through X-ray absorption spectroscopy (XAS) technique.

X-ray absorption near edge structure (XANES) is sensitive to local geometries and electronic structure of atoms that constitute the nanoparticles. The changes of the coordination geometry and the oxidation state upon decreasing the crystallite size and the interaction with supports on metal nanoparticles surface can be extracted from XANES spectrum.

Extended X-ray absorption fine structure (EXAFS) is a specific element of the scattering technique in which a core electron ejected by an X-ray photon probes the local environment of the absorbing atom. The ejected photoelectron backscattered by the neighbouring atoms around the absorbing atom interferes constructively with the outgoing electron wave, depending on the energy of the photoelectron.

X-ray diffraction (XRD) line broadening investigations of nanostructured materials is limited to find the average crystallite size from the integral breadth or the full width at half maximum (FWHM) of a diffraction profile. In the case of nanostructured materials due to the difficulty of performing satisfactory intensity measurements on the higher order reflections, it is impossible to obtain two orders of (hkl) profile. Consequently, it is not possible to apply the classical method of Warren and Averbach [7] or the subsequent developed method of Balzar at al., based on Voigt approximation [8]. In this paper we developed a rigorous analysis of the X-ray line profile (XRLP) in terms of Fourier transform where zero strains assumption is not required. The apparatus employed in a measurement generally affects the obtained data and a considerable amount of work has been done to make resolution corrections. In the case of XRLP, the convolution of true data function by the instrumental function produced by a well-annealed sample is described by Fredholm integral equation of the first kind [9]. A rigorous way for solving this equation is Stokes method based on Voigt approximation [8]. In this paper we developed a rigorous method of Balzar at al., based on Voigt approximation [8].

The following catalyst samples were investigated: Ni/Cr_2O_3 treated at 420 and 650 °C temperatures, Au/MnO_x/Al_2O_3 and Au/Al_2O_3. The Ni/Cr_2O_3 catalysts are applied for H/D reaction between hydrogen and water vapour [10]. The supported gold catalysts are used in reduction or oxidation of NO applied in the environment protection [11, 12].
II. EXPERIMENTAL AND DATA PROCESSING

A. Samples preparation

The Ni/Cr2O3 systems treated at 420 and 650 °C temperatures were prepared by coprecipitation method [13]. The precursor materials used for preparation of the supported gold catalysts were HAuCl4, 3H2O, urea (NH2)2CO p.a. and γ-Al2O3. Atomic ratio Au:Al was 1:75. The nanosized Au/Al2O3 was prepared by homogeneous deposition-precipitation (HDP) using excess urea as precipitating agent [14]. The Au/MnOx/Al2O3 has been prepared by impregnation under vacuum conditions where atomic ratio Mn:Al was 1:15 [15].

B. Measurement methods

The transmission and fluorescence EXAFS measurements on Ni K and Au LIII edges were carried out on 4W1B beamline in Beijing Synchrotron Radiation Facilities operating at 30-50 mA and 2.2 GeV [16]. The beamline 4W1B is an unfocussed monochromatic X-ray beam with 4 mrad of horizontal acceptance. The X-rays are monochromatized by a fixed exit Si double crystal monochromator. The features of 4W1B beamline are: energy range of 3.5-22 KeV, energy resolution of ∆E = 0.5-2 eV at E = 10KeV, Bragg angle range of 5-70°, the crystals Si(111), Si(220) and Si(311) can be alternatively used. A Ni and Au foils were used as a standard samples. The absorption coefficients of Ni K and Au LIII edges were determined using a Si (111) double-crystal monochromator. The absorption coefficients were measured in an energy scale from 8186 to 9331 eV for Ni and 11500 to 12808 eV for Au, respectively. Harmonics were rejected by detuning of the monochromator. Special care was taken in preparation of the samples for measurements, especially for thickness and homogeneity of samples to obtain absorption spectra of good quality. All samples were ground to fine powder and homogeneously dusted on scotch tape. The EXAFS analysis of the absorption coefficient was processed by computer codes EXAFS51 to EXAFS56 [17] from our library.

The XRD measurements for supported nickel catalysts were realized on beamline 4W1C that is a time-sharing branch with beamline 4W1B. The energy resolution is 0.5 eV at 0.154 nm. A NaI(Tl) detector was used, signals were amplified and fed to a single channel analyser (ORTEC 850) and read out by a computer. A silicon powder was used as standard sample for instrumental correction. The XRD measurements range, 2θ, was from 28° to 70°. The X-ray diffraction data for supported gold catalysts were collected using a Rigaku rotating anode setup in Bragg-Brentano geometry with Ni filtered Cu Kα radiation, λ = 1.5406 Å at room temperature. The Fourier transform of the supported nickel and gold catalysts XRLP (111), (200) and (220) as well as (111), (200), (220) and (311), respectively were processed by computer code SIZE developed with Maple software. This computer code is improved version of XRLINE [9] and XRLINE1 [18] computer programs, respectively. Its purpose is to show intermediate processing results in a graphic manner.

The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monochromatic Al Kα X-ray radiation (1486.6 eV) at room temperature. The pressure in the ultra-high vacuum chamber was within the 10^-10 mbar range during the measurements. A neutralizer was used in every case due to a charge effect which occurs for non-conducting samples. The binding energy was determined by reference to the C 1s line at 284.8 eV. SimPeak and Unifit computer packages programs were used for data analysis of the XPS spectra. They are globally approximated by the asymmetric Donjac-Sunjic distribution using Levenberg Marquardt algorithm. For background correction we used Shirley and Tougaard algorithm based on mathematical description of the electron transport.

III. RESULTS AND DISCUSSION

A. XANES results

The electronic properties of supported nickel and gold catalysts are evidenced by the XANES analysis of the following electronic transitions: Ni K edge (1s → continuum and 2p), Au LIII-edge (2p3/2 → continuum, 6s, 6d5/2 and 6d3/2). Fig. 1 shows XANES spectra for investigated nanostructured Ni/Cr2O3 sample in the range of -40 up 30 eV as well as the electron transition probability approximations.

![XANES spectrum](image)

The white line, which is due to a mixing process of the electrons of central metal atom with neighbouring oxygen electrons, is not present. This suggests that both Ni and Au active metals are not oxidized. Based on classical theory these electron transition probabilities have been approximated by Cauchy, and arctan distributions [19]. The main parameters are: the threshold energies, the amplitude, the position and the full width at half maximum and their values are also presented in Table I.
TABLE I
PARAMETERS OF THE ELECTRON TRANSITION PROBABILITIES(*)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aretan distribution</th>
<th>Cauchy distributions</th>
<th>K edge 1s → continuum</th>
<th>Dipole 1s → 2p</th>
<th>EXAFS region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₀ [eV]</td>
<td>Γ₀ [eV]</td>
<td>E₁-E₀ [eV]</td>
<td>Γ₁ [eV]</td>
<td>E₂-E₀ [eV]</td>
</tr>
<tr>
<td>Ni foil</td>
<td>8333.91</td>
<td>30.62</td>
<td>-8.39</td>
<td>8.72</td>
<td>2.68</td>
</tr>
<tr>
<td>Ni/Cr₂O₃ 420 C</td>
<td>8334.06</td>
<td>17.23</td>
<td>-8.38</td>
<td>7.73</td>
<td>2.69</td>
</tr>
<tr>
<td>Ni/Cr₂O₃ 650 C</td>
<td>8334.12</td>
<td>17.68</td>
<td>-8.49</td>
<td>8.52</td>
<td>2.34</td>
</tr>
<tr>
<td>Au foil</td>
<td>11918.0</td>
<td>5.42</td>
<td>2.22</td>
<td>18.84</td>
<td>26.86</td>
</tr>
<tr>
<td>Au/MnOₓ/Al₂O₃</td>
<td>11913.7</td>
<td>5.89</td>
<td>-1.55</td>
<td>13.28</td>
<td>27.86</td>
</tr>
<tr>
<td>Au/Al₂O₃</td>
<td>11909.7</td>
<td>10.44</td>
<td>-0.32</td>
<td>10.32</td>
<td>26.28</td>
</tr>
</tbody>
</table>

(*) E₀ – energy binding of K and LIII edges, Γ₀, Γ₁, Γ₂ – full widths at half maximum

The extraction of EXAFS signal is based on the determination of the threshold energy for Ni K and Au L III edges followed by pre-edge and after-edge background removal with base line fitting using different modelling functions and by absorption coefficients evaluation with 3rd order bell spline functions [17]. The EXAFS signals of supported Ni and Au catalysts were performed in the ranges 15-160 nm⁻¹ and 25-120 nm⁻¹, respectively. In order to obtain the distribution of the atomic distances we calculated the radial distribution function using the classical method [2, 20]. The mean Ni-Ni and Au-Au distances of the first and the second coordination shell for standard sample, at room temperature have values close to R₉Ni₁=0.249 nm, R₉Au₁=0.352 nm, Rₙ₁=0.287 nm and Rₙ₂=0.407 nm. Based on the Fourier transform of EXAFS contribution, performed in the range 0.02-0.5 nm, we obtained the magnitude of the atomic radial distribution for investigated samples as well as for standard Ni and Au foils. In order to reduce the spurious errors due to limited interval in the wave vector space we have taken into consideration the Kaiser window function [17, 21]. Fig. 3 shows the Fourier transform magnitude of the investigated samples.

The parameters values are reliable because they differ with about one order of magnitude from the value of the experimental resolution. The different values of FWHM, ¾, compared to the standard one confirm the specific strong electronic interaction between the metal and the oxide supports. The threshold energy of XANES spectra of supported gold nanoparticles are moved to lower energy, compared to Au standard sample, with about 4 and 7 eV. The presence of the supports Al₂O₃ and MnOₓ can explain this behaviour. These features are due to strong electron interaction of gold nanocrystallites with surrounded supports. The supported Ni catalysts have also shift the threshold energy of the K edge, but the parameters of the electron transition probabilities are close to those of Ni standard. This is a measure of lower electron interaction of nickel metal nanocrystallites with chromium oxide compared to the supported gold catalysts.

B. EXAFS results

The EXAFS experimental spectra for Au/MnOₓ/Al₂O₃, Au/Al₂O₃ and the gold foil are given in Fig. 2.

The Fourier transform magnitudes are diminished as a result of the reduced average co-ordination number and their peaks are shifted from the true distance due to the phase shift function that is included in the EXAFS signal. The backscattering amplitude and the phase shift functions were obtained by analysing the Ni and Au standard samples using “small perturbation limit” method [21]. Table 2 contains the best fitting values of the local structure parameters: N, R and E₀ of the investigated samples and their uncertainties: ΔN, ΔR and ΔE₀.
The average interatomic distances obtained for the first coordination shell have practically the same values as those of the standard sample. Fig. 4 shows for the supported gold catalysts calculated and experimental EXAFS signal of the first shell coordination. The relative difference of the average nearest coordination number, between the standard sample and investigated catalysts, were about 16% for Ni-Ni and 58-64% for Au-Au. We have considered that these diminutions of the average nearest-neighbour coordination numbers are due to various degrees of the electron interactions between the active metal and oxide supports [22-24].

### C. XRD results

The Fourier analysis of XRLP validity depends strongly on the magnitude and nature of the errors propagated in the data analysis. Young et al treated three systematic errors: uncorrected constant background, truncation and the effect of the sampling for the observed profile at a finite number of points that appear in discrete Fourier analysis [25]. In order to minimize propagation of these systematic errors, a global approximation of the XRLP is adopted instead of the discrete calculus. Therefore, herein the analysis of the diffraction line broadening in X-ray powder pattern was analytically calculated using the generalized Fermi function (GFF) which can have asymmetrical feature [13]. The atomic scattering factor, included in the XRLP, is asymmetric versus diffraction angle and this is why the broad peaks are best fitted by asymmetric GFF distribution. The robustness of the GFF approximation for the XRLP arises from possibility of using the analytical form of Fourier transform instead of a numerical fast Fourier transform (FFT). It is well known that validity of numerical FFT depends on the filtering technique adopted [26]. In this way validity of the microstructural parameters are closely related to accuracy of the Fourier transform magnitude of the true XRLP.

The XRLP for Ni and Au catalysts were analysed. The XRD patterns of the Ni catalysts together with standard sample used for instrumental correction are shown in Fig 5.

The next steps consist in background correction of XRLP by polynomial procedure especially in the tails domain of the profiles. The polynomial approximation is more adequate for small crystallite size determination than a constant background correction because it can avoid the “hook” effect contained in true sample function [27]. The best parameters of GFF distributions were determined by nonlinear least squares fit.

In order to determine the global nanostructure parameters of the investigated samples we computed the Fourier transforms of the true XRLP and integral width [6]. In terms of the classical Scherrer equation [28] the crystallite size is proportional with wavelength, inverse proportional with the product from cosine of gravity centre of the true sample function and its full width at half maximum.
and other methods could also be used to determine grain size of particles by taking into account a prior spherical form for the grains. By XRD method one can obtain the crystallite size that has different values for the different crystallographic planes. There is a large difference between the grain size and crystallite size due to the physical meaning of the two concepts. It is possible that the grains of the active metal are built up of many metal crystallites.

The global structural parameters obtained for the investigated samples are summarized in Table 3.

**TABLE III**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(111)</th>
<th>(200)</th>
<th>(220)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D_{hkl}</td>
<td>ε_{hkl}</td>
<td>D_{hkl}</td>
</tr>
<tr>
<td>Ni85Cr15 at%</td>
<td>10.5</td>
<td>0.2863</td>
<td>11.4</td>
</tr>
<tr>
<td>420°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni85Cr15 at%</td>
<td>36.4</td>
<td>0.0158</td>
<td>47.1</td>
</tr>
<tr>
<td>650°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au/MnOx/Al2O3</td>
<td>5.2</td>
<td>3.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Au/Al2O3</td>
<td>5.5</td>
<td>3.4</td>
<td>6</td>
</tr>
</tbody>
</table>

The microstrain parameter, $\varepsilon_{hkl}$, of the lattice can also be correlated with effective crystallite size, $D_{\text{eff}}$, in the following way: $D_{\text{eff}}$ increases when $\varepsilon_{hkl}$ value decreases. The nanocrystallites sizes determined by Scherrer method $D_{\text{Sch}}$ are greater than $D_{\text{eff}}$ because Scherrer equation do not consider the lattice microstrains. Therefore, the values from Scherrer relation of Table 3 are less reliable than the results from general formula.

**D. XPS results**

The survey photoemission spectrum of Au/MnOx/Al2O3 catalyst with the identification of the main XPS core level lines is presented in Fig. 6. Besides the spectral features related to the constituent elements of the supported gold catalysts only a weak C 1s peak has been detected. The presence of the C element is due to hydrocarbons absorbed on the surface of the sample powder.

In Fig. 7 the XPS O 1s line is presented. The two contributions from oxide supports MnOx and Al2O3 can be observed.

The Au 4f XPS spectra of the active metal, after background removal, are shown in Fig. 8.
In the present paper it has been shown how, in addition to EXAFS experiments with their specific advantages, XRD analysis can add more information for understanding nanostructure of the supported nickel and gold catalysts. Also, the XPS method provides information on the electronic structure from the surfaces of gold nanoclusters and their oxide supports. The conclusions that can be drawn from these studies are:

(i) The reduction of Au-Au and Ni-Ni coordination number from the first coordination shell of the investigated samples point out the existence of a more or less electronic interaction between the metal nanoparticles and the oxide supports.

(ii) For XRLP analysis, a global approximation is applied rather than a numerical Fourier analysis. The former analysis is better than a numerical calculation because it can minimise the systematic errors that can appear in the numerical Fourier analysis and GFF approximation of XRLP describe more accurate the broad asymmetric peaks.

(iii) Our numerical results have showed that by using the GFF distribution we have successfully obtained reliable global nanostructural parameters.

(iv) The XPS measurements confirm the presence, on the surface, of gold metallic states while Ni is in both metallic and oxidized states.

(v) The EXAFS and XPS results of Au supported catalysts are good agreement concerning the strong metal-support interaction.

ACKNOWLEDGMENT

The authors are grateful to BSRF for the beam time and to Dr. Xie Yaning and Dr. Zhonghua Wu for their technical assistance in EXAFS and XRD measurements. The author (N. A.) is also indebted to Professor Hu Tiandou, Director of Institute of High Energy Physics for his hospitality during the stage. This work is the result of the Scientific Cooperation Agreement between our institutes. The authors thank Dr. C. A. Gluhoi for providing the samples used in this work. This work was supported by the research programmers of Romanian Ministry of Education and Research (PN II projects nr. 22098/2008 and 32119/2008).

REFERENCES


