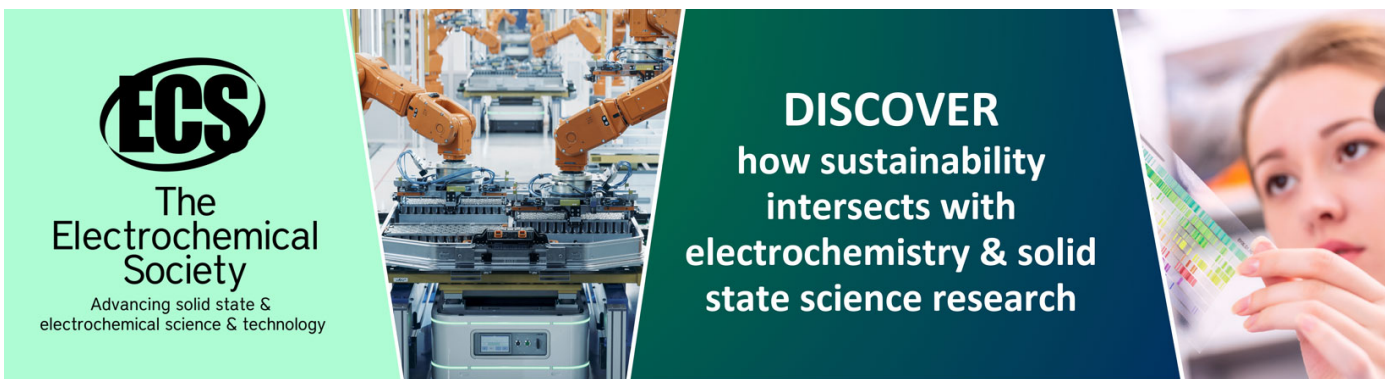# Temperature influence on the global and local structure of the chromia supported nickel catalysts

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Temperature influence on the global and local structure of the chromia supported nickel catalysts

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Abstract. The changes induced by the heat treatment on the global and the local structures of the supported nickel catalysts are investigated. The global structure parameters were obtained by processing the X-ray diffraction patterns of the samples using the Scherrer formula. The local structure parameters were determined by X-ray absorption spectra processing. Both types of measurements were carried out using synchrotron radiation. The nickel catalysts supported on chromia were prepared by coprecipitation method. The nickel/chromium atomic percent was 70/30. After preparation, the samples were thermally treated for three hours at 350, 650 and 950ºC. A strong correlation between previous catalytic activity information and the global and local structure is evidenced. Also the correlation between the nickel crystallite size and the active metal-oxide support interaction is discussed.

1. Introduction

Supported catalysts are widely used in chemical processes. Reactions like hydrogenation processes [1, 2], isotope separation [3] and production of the deuterium labelled compounds [4] requires supported metal catalysts that chemisorbs hydrogen dissociatively.

The mechanism of the heterogeneous catalysis is very complex, but one of the conditions to have a high catalytic activity is to have also a high metallic surface. In order to obtain a high metallic surface, the average crystallite size of the active metal must be as small as possible [5,6]. The present contribution contains the results for the calculations of the metallic nickel crystallite sizes. The calculations were processed by the Scherrer formula on X-ray diffraction (XRD) measurements using synchrotron radiation.

The presence of active metal-oxide support interaction is also a particularity of supported metal catalysts, also present at supported nickel catalysts. This interaction induces a deformation of the local vicinity of the active metal, evidenced in extended X-ray absorption fine structure

(EXAFS) as a decreasing in the coordination number of the first coordination shell for the central nickel atoms [7].

2. Sample preparation

For the preparation of the chromia supported nickel catalysts coprecipitation method [7] was used. This method involves the coprecipitation of the mixture of nickel nitrate and chromium nitrate with a solution of sodium carbonate/hydroxide. The precipitate was thoroughly washed with double distilled water in order to eliminate the sodium ions. Then the precipitate was dried at 105ºC in oven, calcined in nitrogen flow at 340ºC and reduced in flowing hydrogen at 350ºC. The catalyst samples obtained in this way are pyrophoric and they need passivation for handling them in air. The passivation was performed in nitrogen flow with low content of oxygen. By this process nickel ions with positive valence appear as a thin layer at the metal surface. The thermal treatments of the catalysts have been done in hydrogen flow at different temperatures for 3 h. In this way were prepared the nickel supported on chromium oxide catalysts samples thermally treated at 350, 650 and 950ºC with 70% atomic percent of nickel and 30% atomic percent of chromium.

3. Experimental measurements

The XRD and EXAFS measurements were carried out on the 4W1B and 4W1C beamlines at the Beijing Synchrotron Radiation Facilities (BSRF).

The mentioned beamlines are operating at 30-50 mA and 2.2 GeV at room temperature [8]. The 4W1B beamline is an unfocussed monochromatic X-ray beam with 4 mrad of horizontal acceptance and has the following features: energy range of 3.5-22 keV; energy resolution of $\Delta E = $ 1-3 eV at E = 10 keV; the Bragg angle range of 5-70º.

The absorption coefficient of nickel K edge was determined using the Si(111) monochromator crystal on a transmission setup. The intensities of the incident and the transmitted beams were monitored by ionization chambers. As standard sample a nickel foil obtained by electrochemical method was used. Harmonics were rejected by detuning of the monochromator. For EXAFS analyses of the absorption coefficient different computer codes were used: EXAFS31 and EXAFS36 [9] from the library of the group and CDXAS [10].

XRD measurements were carried out using synchrotron radiation with 1.54 Å wavelength.

4. Results and discussion

4.1. XRD Results

The XRD patterns for the nickel supported on chromia catalysts are presented in figure 1. Notations (1), (2) and (3) correspond to the patterns of the Ni/Cr_2O_3 catalysts thermally treated at 350, 650 and respectively 950ºC. As standard sample a silicon crystal was used (see the XRD pattern of it in the inlet of the figure 1).

The most intense X-ray line profiles (XRLPs) present in these patterns corresponds to nickel in metallic state. One can see the (111), (200) and (220) XRPLs around the following values for the 2θ angle of incidence: 44.97º, 51.85º and 76.38º.

As a second conclusion one can evidence that all the nickel content of the sample is in metallic state as long as there are no evidences for any other type of nickel present in the samples. Small XRLPs corresponding to chromium oxide can be observed at the 54.95, 63.58 and 65.23º values in the 2θ.

In table 1 the crystallite sizes calculated with the Scherrer formula for the nickel nanoclusters are given. As we can see, with the increasing of the thermal treatment temperature, the crystallite size is increasing leading to the diminution of the nickel metallic surface. These results are in good agreement with previous catalytic activity results [11]. It is also important to mention that the crystallite sizes are different for different crystalline directions. This conclusion can determine

us to think about preferential orientations of the nickel clusters but the ratio between the intensities of the three peaks mentioned above are close to those for the pure nickel in the face centred cubic lattice so, preferential growth during the sample preparation or/and thermal treatment can be excluded. These different values for the crystallite sizes for different orientations can be useful information for further investigations regarding the shape of the crystallites.

Table 1. The crystallite sizes of the metallic nickel nanoclusters for different XRLPs calculated using the Scherrer formula.

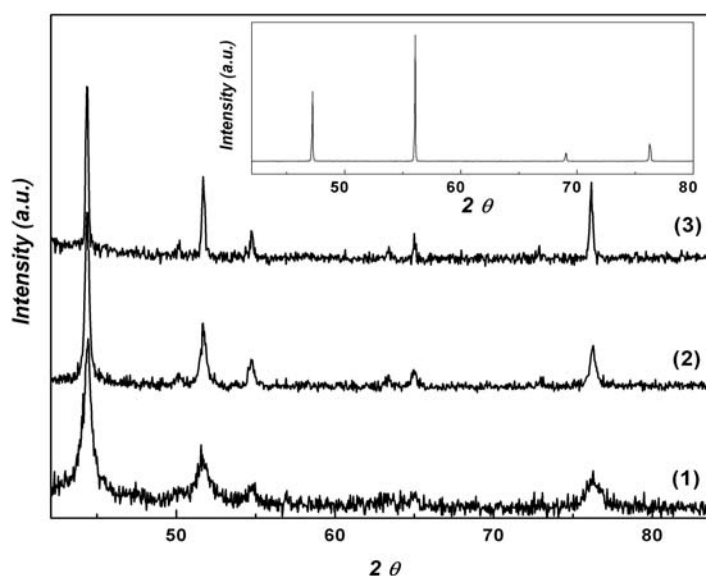| Sample		D [Å]		
	XRLP	**(111)**	**(200)**	**(220)**
Ni/Cr$_2$O$_3$ treated at 350ºC		138	174	148
Ni/Cr$_2$O$_3$ treated at 650ºC		308	235	267
Ni/Cr$_2$O$_3$ treated at 950ºC		800	571	800

Figure 1. XRD patterns of the supported nickel catalysts thermally treated at: (1) 350ºC, (2) 650ºC and (3) 950ºC. As inlet appears the XRD pattern of the Si standard sample.

4.2. EXAFS Results
The local structure of the nickel catalysts samples were investigated by X-ray absorption spectroscopy (XAS) and the resulted local parameters were extracted using a computer package program dedicated to EXAFS spectra processing developed in our working group.

In figure 2 the absorption coefficient of standard nickel sample obtained by electrochemical processes is represented.

Figure 3 includes the (XAS) spectra for the thermally treated samples. There are no evidences of the nickel oxides, as a proof that all the nickel oxide was reduced during the reduction step of the catalysts preparation process.

After data processing, the EXAFS functions of the first coordination shells corresponding to the catalysts samples were obtained. These first coordination shells are represented in figure 4.
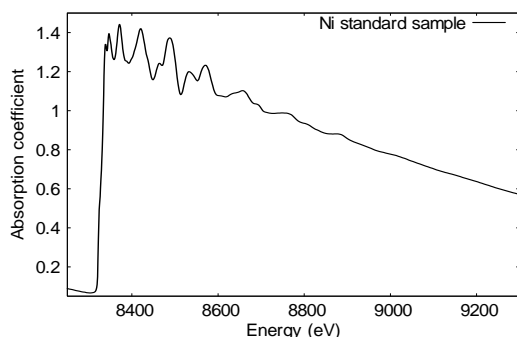
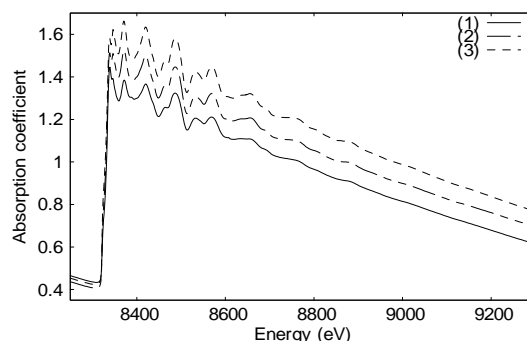**Figure 2.** The X-ray absorption coefficient of the nickel standard sample.

Figure 3. The X-ray absorption coefficient of the nickel catalysts thermally treated at: (1) 350ºC, (2) 650ºC and (3) 950ºC.
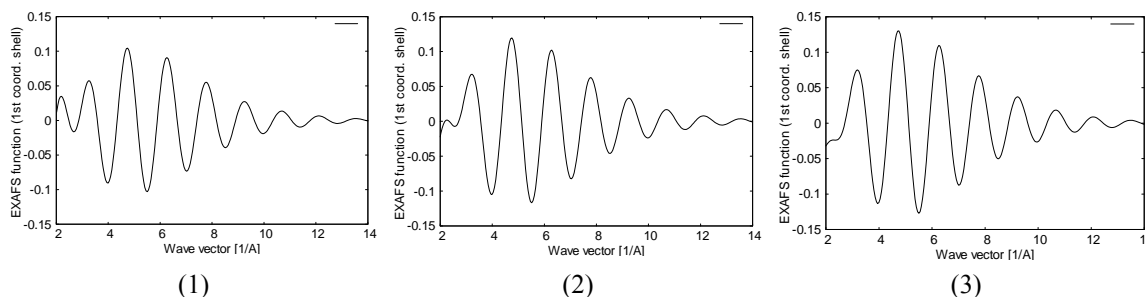

(1)   (2)   (3)

Figure 4. The EXAFS function of the first coordination shell for the samples thermally treated at: (1) 350ºC, (2) 650ºC and (3) 950ºC.

The pure nickel has a face centered cubic lattice. In this configuration, the number of atoms in the first coordination shell is 12. In the catalysts a metal-support interaction could appear. This interaction leads to the diminution of the coordination number. The metal-support interaction is as big as the coordination number decreases. As one can see in table 2, the coordination number of the nickel atoms, N_1, increases when the thermal treatment temperature increases and this value tends to the value for the pure nickel. The coordination number increases as a sign of the recrystalization processes that occur during the heat treatment. In the same time, the coordination shell radius, R_1, does not change significantly. Only a small variation of this parameter is observed, as we can conclude looking in the table 2.

Table 2. The local structure parameters obtained by EXAFS spectra processing.

Sample	$N_1 \pm \Delta N_1$	$R_1 \pm \Delta R_1$ [Å]	$E_0 \pm \Delta E_0$ [eV]
Nickel standard	12	2.49	8333.915
Ni/Cr$_2$O$_3$ treated at 350ºC	8.89 ± 0.083	2.511 ± 0.003	8334.334 ± 0.0211
Ni/Cr$_2$O$_3$ treated at 650ºC	10.17 ± 0.068	2.497 ± 0.002	8333.986 ± 0.0001
Ni/Cr$_2$O$_3$ treated at 950ºC	11.09 ± 0.058	2.499 ± 0.002	8333.983 ± 0.0003

The investigated samples from table 2 have about the same value of threshold energy as the K edge of pure nickel, but their positions are shifted to higher energy compared with the binding energy, $E_0 = 8333$ eV, of the standard nickel sample. This feature is due to the strong electronic interaction of the nickel nanocrystallites surrounded by oxide supports.

5. Conclusions

The local and the global structure are playing an important role in the catalytic activity. Variations of both of them with the thermal treatment were evidenced.

The strong dependence of the crystallite size on the treatment temperature was evidenced. The different values for the crystallite size corresponding to different orientations of the crystallites could be important information for further studies regarding the crystallites shape.

As long as in the XRD and XAS spectra of the supported nickel catalysts are no evidences of nickel oxides but only nickel in metallic state, we can consider the preparation method as an efficient one from the nickel consumption point of view.

The decrease in the number of atoms corresponding to the first coordination shell points out the existence of an electronic interaction between the nickel nanoclusters and the surrounding oxides. This interaction is evidenced also by the shift in the edge energies of the supported nickel catalysts investigated in the present contribution.

References

[1]   Pajonk G M and Teichner S J 1986 *Catalytic Hydrogenation* ed I Cerveny (Amsterdam: Elsevier) p 277
[2]   Ponec V and Bond G C 1995 *Catalysis by Metals and Alloys* (Amsterdam: Elsevier)
[3]   Shimizu M, Kioto S and Ninomiya R 1992 *Proc. Int. Symp. on Isotope Separation and Chemical Exchange Uranium Enrichment* eds Y Fujii *et al* (Tokyo) p 560
[4]   Allen J and Voges R 1995 *Synthesis and Applications of Isotopically Labelled Compounds* (New York: John Wiley and Sons)
[5]   Niemantsverdriet J W 2007 *Spectroscopy in Catalysis* (Weinheim: Wiley-VCH)
[6]   Roduner E 2006 *Nanoscopic Materials. Size-dependent Phenomena* (Stuttgart: RSC Publishing)
[7]   Aldea N, Gluhoi A, Marginean P, Cosma C and Yaning X 2000 *Spectrochim. Acta* B **55** 997
[8]   BSRF *Activity Report 1991-1998* Beijing Electron Positron Collider National Laboratory, China
[9]   Aldea N and Indrea E 1990 *Comput. Phys. Comm.* **60** 145
[10]   San-Miguel A 1995 *Phys.* B **208-209** 177
[11]   Gluhoi A, Marginean P and Stanescu U 2005 *Appl. Catal*, A: *General* **294** 208-14.