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Structural investigations of Ni nanoclusters supported on Cr_2O_3

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The Ni nanoclusters supported on Cr_2O_3 were prepared using coprecipitation method. The heat treatment at different temperatures: 350, 650, 750 and 900°C was applied. The obtained samples were analyzed by X-ray Diffraction (XRD) and X-ray Absorption Spectroscopy (XAS) in order to determine their global and local structure. The average particle size, the mean squares of the microstrain, the particle size distribution and microstrain functions of the supported Ni nanoclusters were determined by XRD method using Generalized Fermi Function for the X-ray line profiles approximation. The present study has pointed out a strong deformation of the local structure of the active metal, due to small particle size effects. The recrystallization effect induced during the heat treatment process was analysed.

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1. Introduction

It is pointless to explain the importance of catalytic systems in our days. All the papers, reviews, books or even journals dedicated to catalysts stress about their growing importance and the multitude of their applications in chemical industry, environment protection, energy production from alternative sources or preparation of new materials. The synthesis methods and conditions are very important for their further characteristics (catalytic activity, stability, selectivity, etc) which are directly correlated with the catalysts structural properties.

In this paper we wanted to continue the series of the reports about the influence of manufacturing parameters (preparation methods, heat treatment temperature, relative concentration of active metal, etc) on structural properties of supported Ni catalysts. Average crystallites size, lattice microstrains and particle size distribution were obtained from XRD measurements using Warren-Averbach theory based on Fourier analysis of single X-ray diffraction line profile (XRDLP). X-ray absorption near edge structure (XANES) investigations were performed in order to obtain information about the electronic structure (Ni oxidation state), while extended X-ray absorption fine structure (EXAFS) measurements offered details about local structure (average coordination number and interatomic distances).

2. Experimental

The XRD and EXAFS measurements were carried out in 4W1B and 4W1C beamlines in Beijing Synchrotron Radiation Facilities (BSRF) operating at 30-50 mA and 2.2 GeV at room temperature. XAS measurements were performed in transmission mode using X-ray energy of incident flux between 8000 - 9400 eV. X-ray powder diffraction measurements were carried out using 1.54 Å wavelength radiation.

The Ni nanoclusters supported on Cr_2O_3 were prepared using coprecipitation method [1]. A mixture of nickel nitrate and chromium nitrate were precipitated in a solution of sodium carbonate/hydroxide. The ratio between the precursors salts were chosen in such a way to obtain the desired atomic percentage of nickel in the catalyst samples (70%). The concentration of active metal was defined by x=[at. Ni/(at. Ni+Cr)] x100%. Double distilled water was used to wash the sodium ions. In the next step the precipitate was dried at 105°C in stove, followed by the calcinations at 340°C in nitrogen flow. In order to obtain nickel in a metallic state a reduction process was carried out in a hydrogen flow at 350°C. Samples thus obtained are pyrophoric so that a passivation of the surface in a nitrogen flow with oxygen traces was performed, leading to the formation of o thin nickel oxide layer at the surface. In the following step the heat treatment in hydrogen flow was applied for three hours at different temperatures: 350 (Ni 1), 650 (Ni 2), 750 (Ni 3) and 900°C (Ni 4). In the final step the samples were passivated again in order to be handled in the upcoming investigations.

3. Results and discussions

3.1. XRD measurements

The XRD patterns of the investigated samples, presented in Fig. 1, showed the formation of Ni clusters having fcc crystallographic structure. Additional peaks belonging to Cr_2O_3 support appear. No peaks belonging to the NiO crystallographic phase are present although XAS measurements, that are presented in the next paragraph, indicate its presence for samples treated at low temperatures.

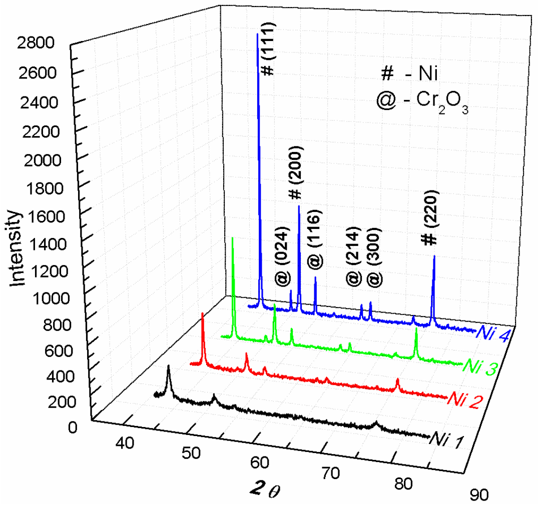

Fig. 1. X-ray diffraction patterns of the investigated samples

In order to obtain the global structure parameters XRLINE software product [2] was used. The (111), (200) and (220) peaks were investigated using classical Scherrer formula with Gauss approximation of XRDLPs, as well as Warren-Averbach method using generalized Fermi function for the approximation of XRDLPs. Lattice microstrains are consistent for small particle sizes; this is why Warren-Averbach method was involved not only the classical Scherrer one. Background correction together with instrumental one (using a standard SiO_2 sample) were performed. All parameters obtained are presented in Table 1. It is worth to mention that the uncertainty degree of the results obtained from Warren-Averbach method are around ±5% but for those obtained from Scherrer method are always higher and depend on the FWHM and diffraction angle. The well-known re-crystallization effect is responsible for the gradually increase of crystallite sizes (see Fig. 5) with the heat treatment temperature.

The particle size diameters are different for different crystallographic orientations. This suggests that particles shape is not perfect spheres. Once the particle size increases due to the re-crystallization effect the difference in diameters obtained after the three investigated crystallographic directions decreases suggesting that the re-crystallization effect not only increases the particle sizes but also tends to form spherical shape particles. The lattice microstrains value strongly decreases with the increase of the particles size.

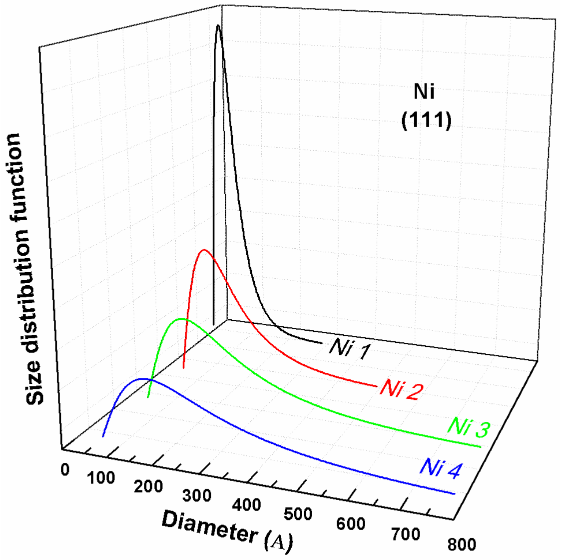

Fig. 2. Size distribution function of the investigated samples

The particle size distributions, shown in Fig. 2, were determined from the second derivative of the strain-corrected Fourier transform of true sample function [2] coming from (111) peak. It can be observed that the distribution width increases with the increase of the average particles size. Larger particle size distribution function means that there are more particles with closer diameters. This is another effect of applied heat treatment.

Table 1. Global structure parameters of the investigated samples

Sample	(111)			(200)			(220)		
	$D_{W\text{-}A}$ [Å]	$<\varepsilon^2_{hkl}>$ $\times 10^4$	D_{Sch} [Å]	$D_{W\text{-}A}$ [Å]	$<\varepsilon^2_{hkl}>$ $\times 10^4$	D_{Sch} [Å]	$D_{W\text{-}A}$ [Å]	$<\varepsilon^2_{hkl}>$ $\times 10^4$	D_{Sch} [Å]
Ni 1	131	0.2706	138	169	0.1214	174	132	0.0892	148
Ni 2	279	0.0491	308	213	0.0639	235	205	0.0210	267
Ni 3	362	0.0162	389	299	0.0258	364	251	0.0057	324
Ni 4	397	0.0097	443	361	0.0131	444	345	0.0018	420

$D_{W\text{-}A}$ - average crystallite diameters based on Warren-Averbach method; D_{Sch} - average crystallite diameters using Scherrer formula; $<\varepsilon^2_{hkl}>$ - lattice microstrains

3.2. XAS measurements

Fig. 3 shows the normalized absorption coefficients of all the investigated materials. The edge position of all investigated samples (see Table 2) is very close to that reported in the literature for Ni metal. The line that appears after the edge, called white line, indicates the existence of Ni in oxidation state [3]. Samples treated at 350 and 650°C seem to have small quantities of NiO even although the XRD showed only Ni in metallic state.

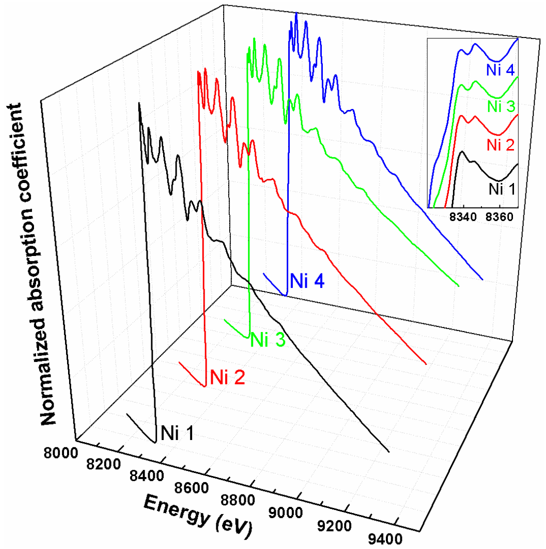

Fig. 3. Normalized absorption coefficient of the investigated samples. Inset: zoom on the region just after the edge

This can be explained if we consider the different sensitivities of the two techniques. The presence of NiO comes from the surface passivation process. The absence of Ni oxide for samples treated at high temperatures (big crystallite sizes) confirms its presence only at the surface of crystallites (the ratio between the “surface” and “volume” Ni atoms decreases with the increase of the particles size). The spectra were further analyzed, based on EXAFS theory [4], using XAS computer code [5]. The Fourier transforms of the EXAFS function, for all the investigated samples, are shown in Fig. 4. The contributions for the first four coordination shells can be observed but each peak from is shifted from the true distance due to the phase shift function which is included in EXAFS function. The intensity of the FT magnitude corresponding to the first coordination shell is proportional to the average coordination number.

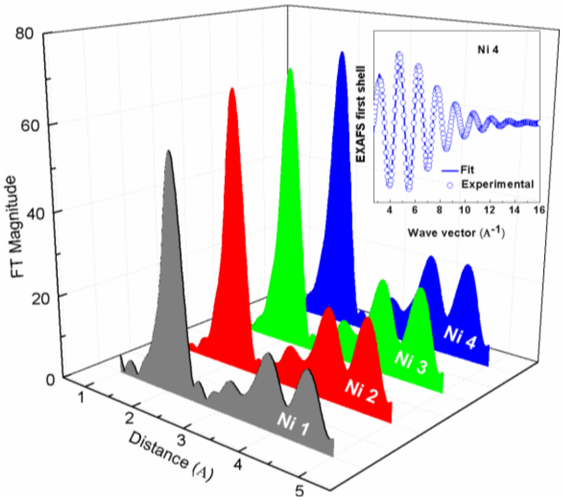

Fig. 4. Radial distribution functions of the investigated samples. Inset: the fit in k space corresponding to the first coordination shell of Ni 4 sample

The experimental results together with the fit corresponding to the first Ni-Ni distance are presented in Fig. 4 inset for Ni 4 sample. Based on the fit, the interatomic distances and the number of neighbours in the Ni first shell were evaluated. Table 2 contains the values of these local structure parameters.

Table 2. Local structure parameters of the investigated samples and Ni standard

Sample	Coordination number $N_1 \pm \Delta N_1$	Shell radius $R_1 \pm \Delta R_1$[Å]	Shift energy $E_0 \pm \Delta E_0$[eV]
Ni-Standard	12	2.49	8333
Ni 1	8.89±0.083	2.511±0.003	8334.334±0.0211
Ni 2	10.17±0.068	2.497±0.002	8333.986±0.0001
Ni 3	10.44±0.052	2.501±0.002	8333.772± 0.0110
Ni 4	11.07±0.046	2.489±0.001	8334.069±0.0033

The average coordination number (corresponding to the first coordination shell) for the investigated samples is smaller than that of Ni standard and increases with the heat treatment temperature (see Fig. 5). This reduction of coordination number is known as small particle size effect. Also, it was proved that metal-support interaction is another cause of reduced coordination numbers [6]. Even if the average coordination numbers are so different, the first Ni-Ni distances suffer minor changes with the re-crystallization process that appears during the heat treatments.

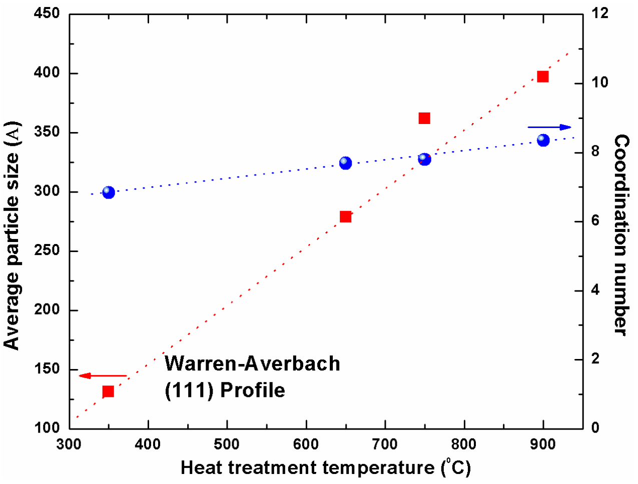

Fig. 5. Heat treatment influence on average particle size and first shell coordination number

4. Conclusions

The Ni average crystallite size gradually increases with the heat treatment temperature due to the re-crystallization effect.

There are two causes for the reduced average coordination number of the Ni nearest neighbours compared to Ni standard: small particle size effect and metal-support interaction. Ni-Ni distances seem to be less affected.

XAS investigation method revealed the presence NiO, at some of the samples surface, coming from the passivation process.

Acknowledgement

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