Magnetic resonance study of carbon encapsulated Ni nanoparticles

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Aim of the work

The aim of the work is to gain insight into the internal structure of two types of Ni/C nanoparticles obtained under CH_4 and C_2H_4 carburization. These nanopowders were already investigated by XRD, HRTEM, TGA and other chemical methods. It would be interesting to study the magnetic properties of these nanomaterials as they provide additional information about their magnetic component that is not available through other methods. Magnetic resonance study performed at room temperature on six different Ni/C nanopowders will enable modeling of a layered nanoparticle.

Sample designation	Amplitude [arb. units]			Resonance field [G]			Peak-to-peak linewidth [G]		
	A_1	A_2	A_3	B_{r1}	B_{r2}	B_{r3}	Δ_{B1}	Δ_{B2}	Δ_{B3}
CH_4/500	$4.92\cdot10^{16}$	$1.20\cdot10^{17}$	-	3595.5	3103.7	-	807.8	1402.3	-
CH_4/600	$9.72\cdot10^{16}$	$9.29\cdot10^{16}$	-	3443.9	2937.1	-	660.3	820.7	-
CH_4/700	$4.35\cdot10^{16}$	$3.96\cdot10^{16}$	-	3462.4	2969.7	-	584.4	771.4	-
C_2H_4/500	$1.09\cdot10^{14}$	$1.92\cdot10^{13}$	$3.3\cdot10^{12}$	3484.4	2335.2	3194.9	1952.4	920.8	445.9
C_2H_4/600	$1.15\cdot10^{15}$	$1.05\cdot10^{15}$	-	3357.5	2966.3	-	954.9	1285.6	-
C_2H_4/700	$1.51\cdot10^{15}$	$2.45\cdot10^{14}$	-	3167.3	2645.1	-	579.7	583.3	-

Table 1. Magnetic resonance parameters of the components lines.

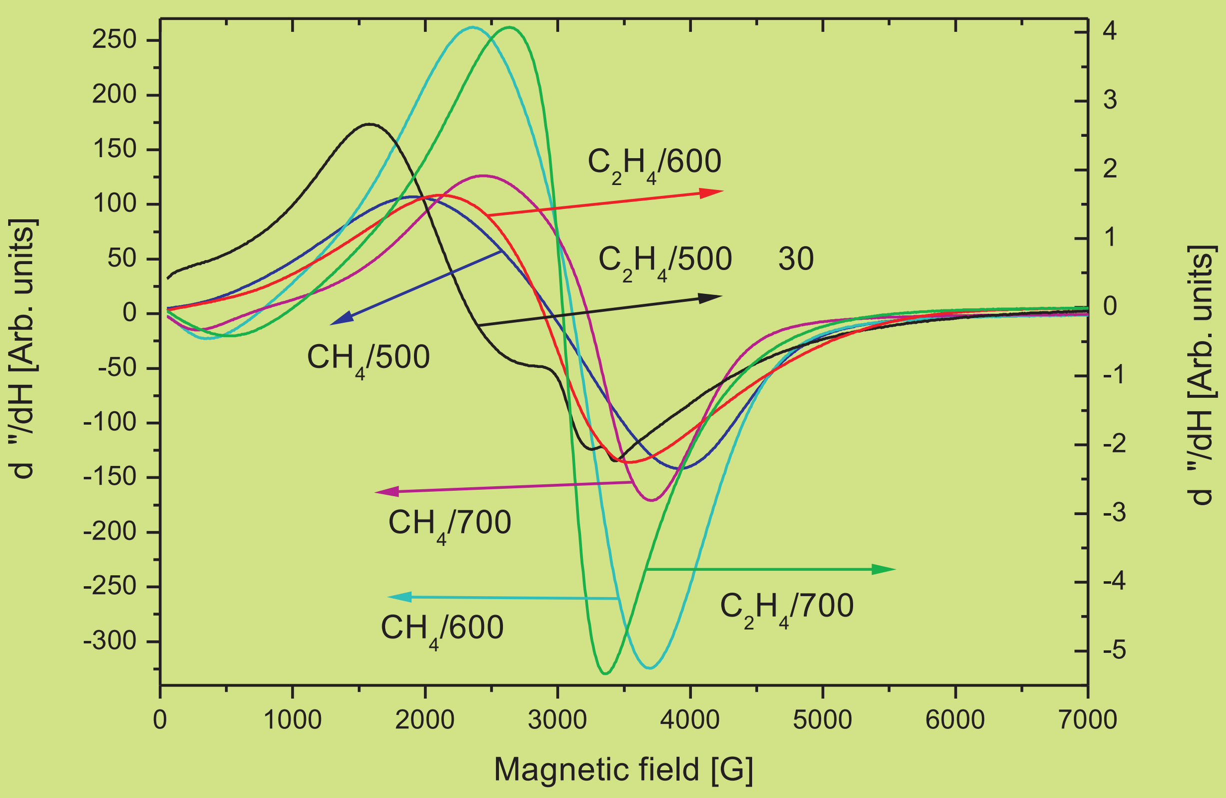

Figure 1. Magnetic resonance spectra of six investigated samples at room temperature rescaled to a unit mass. Due to a large difference in signals amplitudes the left and the right scales are used for three samples each.

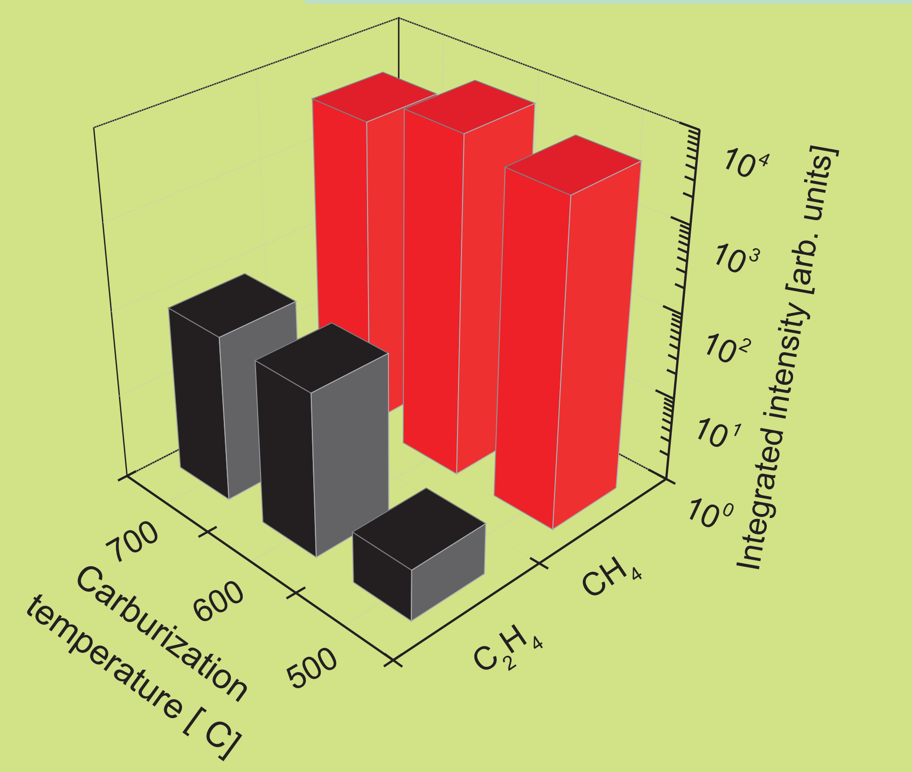

Figure 4. Comparison of the integrated intensities I_{int} calculated for a unit mass for six studied samples. Due to large differences in values of I_{int} a logarithmic scale is used.

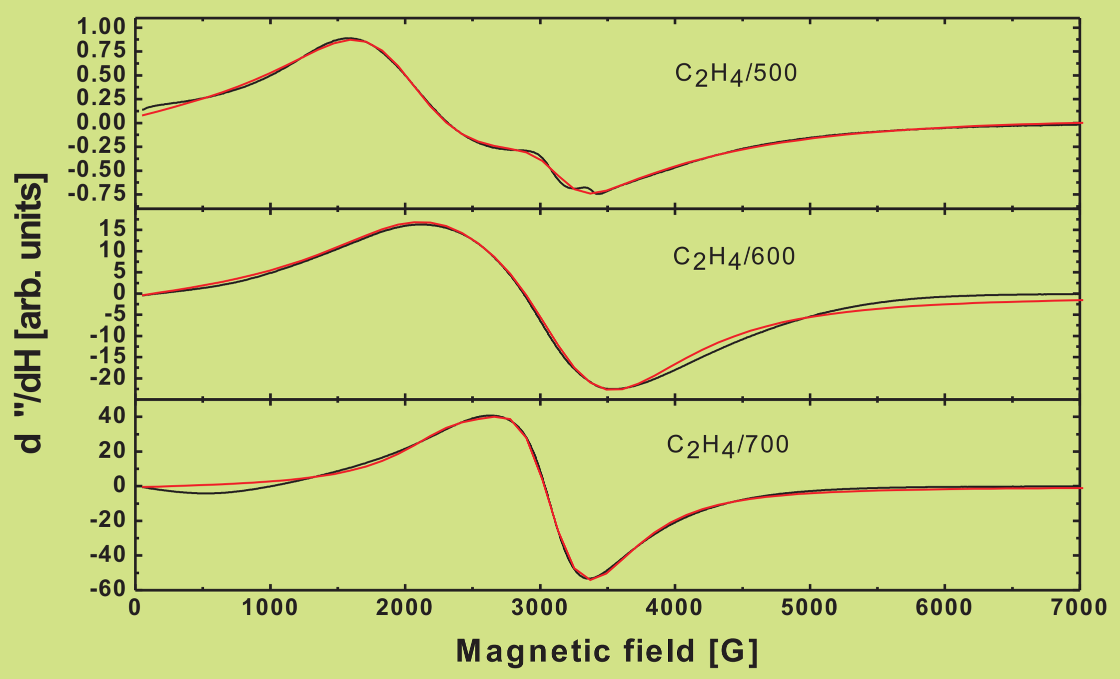

Figure 2. Experimental (black) and fitted (red) spectra of three samples carburized in ethylene.

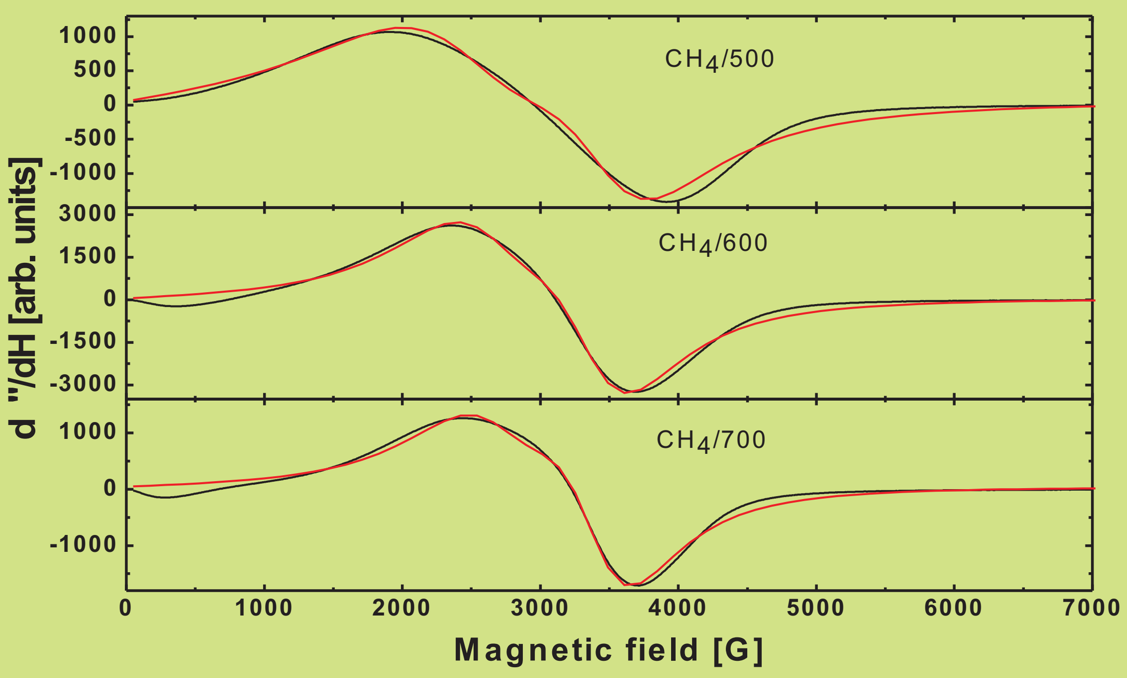

Figure 3. Experimental (black) and fitted (red) spectra of three samples carburized in methane

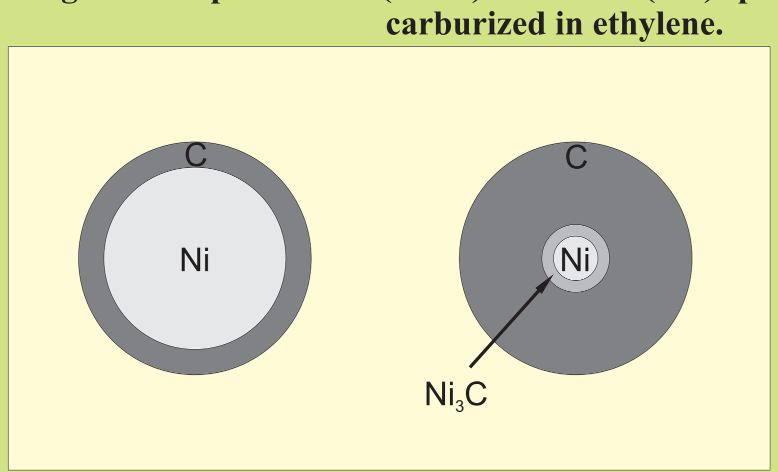

Figure 5. Simplified model of the Ni/C nanoparticles obtained in carburization in (left) methane, (right) ethylene. The thickness of all layers is drawn to scale.

Sample designation	Nanoparticle radius r_0 [nm]	Radius of Ni layer r_1 [nm]	Outer radius of Ni_3C layer [nm]	Thickness of C layer [nm]	Thickness of Ni_3C layer [nm]
CH_4/500, CH_4/600, CH_4/700	27.5	21.5	-	6	-
C_2H_4/500, C_2H_4/600, C_2H_4/700	27.5	5.25	8.0	19.5	2.75

Table 2. Dimensions of different layers in Ni/C nanoparticles.

Experimental

Samples of Ni/C nanomaterial were prepared by carburization of nanocrystalline nickel with methane and ethylene. At first, a solution containing nickel (II), calcium and aluminum nitrates was used to obtain nanocrystalline nickel. The salts were dissolved in water. A solution with 25% NH_4OH was added to obtain pH=8. Metal hydroxides were precipitated from the solution. The obtained deposit was washed with water, filtered and dried at 70ºC. The next preparation step was the calcination at 500ºC for 1 hour to get the precursor of nanocrystalline nickel oxide (with a small amount of structural promoters - CaO and Al_2O_3). Nickel precursor samples containing 0.8 % CaO, 3.6 % Al_2O_3 were received. Nickel oxide powder was next pressed, crushed and sieved to get a grain size fraction in the range 1.2-1.5 mm. 1 g of this material was put into a quartz crucible. The carburization process was performed under pure methane (99.5%) or ethylene (99.99%) flow of 20 dm^3/h at different temperatures: 500oC, 600ºC, 700ºC. Next the samples were cooled with helium (99.99 %) flow. The six obtained samples will be designated as CH_4/500, CH_4/600, CH_4/700, C_2H_4/500, C_2H_4/600 and C_2H_4/700, were the first part indicates on the used carburization gas and the second on the decomposition temperature.

The average crystallite size of Ni/C nanoparticles obtained after methane and ethylene decomposition was 53 nm and 56 nm, respectively. The spread in crystallite sizes was rather large and ranged from 25 to 100 nm.

Magnetic resonance spectra were recorded using a standard X-band spectrometer, Bruker E 500 (υ=9.45 GHz) with a magnetic field modulation of 100 kHz. The measurements were performed at room temperature. The registered spectra are the first derivative of the absorption curve with respect to the sweeping external magnetic field.

Each spectrum (except for sample C_2H_4/500) consists of one broad, asymmetrical line. For sample C_2H_4/500 an additional weaker line could be recognized. It is reasonable to assume that the registered signal is the FMR line from magnetic nanoparticles in the superparamagnetic phase. In literature devoted to that subject several different FMR lineshapes were considered and applied. Very often the Landau-Lifshitz lineshape is used that follows from the Landau-Lifshitz equation of motion of the total magnetization that contains one damping term proportional to precessional component of magnetization. In case of a perfect soft ferromagnet characterized by a stepwise dependence of magnetization on applied field the folowing normalized Landau-Lifshitz (LL) lineshape is obtained

$$I(B) \quad \frac{1}{} \quad \frac{B_r^2 \quad _B \quad B_r^2 \qquad {}^2_0 \, B^2 \quad B_r^4}{B \quad B_r \; {}^2 B_r^2 \qquad {}^2_B B^2 \quad B \quad B_r \; {}^2 B_r^2 \qquad {}^2_B B^2}$$

where B_r is the true resonance field and Δ_B is true linewidth parameter.

Knowing the carbon yield C_y it would be possible to calculate the radius of an inner Ni layer. For the radius r_1 of the central Ni sphere the following equation could be easily obtained

$$r_1(Ni) \quad r_0 \quad \frac{(Ni)}{(C)} C_y \quad 1 \quad ^{1/3}$$

where r_0 is the radius of a nanoparticle, C_y is the carbon yield, ρ is the density. For Ni/C nanoparticles obtained under CH_4 carburization r_1(Ni)=21.5 nm is calculated from Eq. (2) for r_0=27.5 nm. Thus the thickness of carbon layer is 6 nm. As the integrated intensity of CH_4 carburized samples is on average 69 times stronger than in C_2H_4 carburized samples thus the radius of Ni sphere in these Ni/C nanoparticles should be $69^{1/3}$ times smaller. Hence r_1(Ni)=5.25 nm in Ni/C nanoparticles synthesized in C_2H_4 carburization.

For the outer radius of the Ni_3C layer the following expression could be obtained

$$r^{out}(Ni_3C) \quad \frac{r_0^3 \quad (C) \quad r_1^3 \quad (Ni_3C) \; C_y \quad \frac{(Ni)}{(Ni_3C)} \quad \frac{(Ni)}{(Ni_3C} \quad \frac{(C)}{(Ni_3C)}}{(C) \qquad (Ni_3C) \; C_y \quad \frac{(Ni)}{(Ni_3C)} \quad \frac{(C)}{(Ni_3C)}} \quad ^{1/3}$$

where r_0 is the radius of a nanoparticle, r_1 is the radius of Ni sphere, ρ is the density, C_y is carbon yield, μ is molar mass. Substitution of the following numbers: r_0=27.5 nm, r_1=5.25 nm, ρ(C)=2.27 g/cm^3, ρ(Ni)=8.91 g/cm^3, ρ(Ni_3C)=15.8 g/cm^3, C_y=6.77, μ(Ni)=58.7, μ(C)=12, μ(Ni_3C)=188.1 in Eq. (3) yields r^{out}(Ni_3C)=8.0 nm. Thus the thickness of the Ni_3C layer is 2.75 nm. The dimensions of different layers in both types of samples are collected in Table 2. In Fig. 5 the calculated dimension of different layers in both types of Ni/C nanoparticles were used to present them graphically in a common scale.

Conclusions

FMR lines attributed to Ni/C nanoparticles were registered and fitted by two (three for sample C_2H_4/500) LL lineshapes. There was no correlation of magnetic anisotropy of the nanoparticles (determined from the separation of the two components lines) on the decomposition temepratute and the type of used carburization gas, but strong correlation between the components linewidths and the decomomposition temperaure has been observed. Study of the FMR integrated intensity revealed the the presence of a nonmagnetic layer (Ni_3C) between the inner Ni nucleus and the outer graphite layer. Combination of the FMR results with carbon yields values allowed calculation of layers dimensions.