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## The role of metal-support interaction in catalytic activity of nanodiamond-supported nickel in selective phenylacetylene hydrogenation



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#### ABSTRACT

Metal precursor coordination and its reduction mechanism in Ni catalysts supported on detonation nanodiamonds (ND) have been studied. TPR demonstrated multistage reduction of NiO supported on ND, which was explained by the presence of two types of Ni species on the ND surface. Weakly bonded Ni species are held on the ND surface by van der Waals forces, whereas strongly bonded ones are chemically bonded to the functional groups on the ND surface. Both Ni—Ni and Ni—O—C scattering paths were found in Ni/ND catalysts using Morlet wavelet analysis of EXAFS data. The ratio of weakly and strongly bonded Ni species in the catalyst was tailored either by removal of functional groups by annealing of ND support in Ar at 900 °C or by calcination of NiO/ND precursor in air at 300 °C. The former resulted primarily in weakly bonded Ni species in the catalyst, while the latter led to strongly bonded ones. These two catalysts demonstrated drastic differences in selective styrene formation upon phenylacetylene hydrogenation: weakly bonded Ni species gave rise mainly to ethylbenzene, while Ni species strongly bonded to the surface through the Ni—O—C bond afforded mainly styrene.

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### 1. Introduction

Metal-support interaction is one of the important factors controlling the catalytic activity of supported metal particles. The support type may affect the particle size, adsorption properties, electron density distribution, etc. The development of a convenient and affordable method of preparation of nanosized metal particles loaded onto a support with tailored properties is essential for the design of highly active metal catalysts. Nanodiamond (ND) materials have attracted significant attention as a promising catalyst support due to their high surface area, different types of carbonyl functional groups, a highly defective surface structure, extremely large number of unsaturated surface bonds, nanosize of particles, superhardness, and chemical stability [1]. Each primary ND unit consists of a diamond nanocrystal with a diameter of 4-5 nm coated with an onion-like carbon shell covered with a number of functional groups. Such primary units are combined into larger aggregates. The composition of the diamond core coating depends

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on the purification method used during ND synthesis [2]. On an industrial scale, detonation soot is purified using liquid oxidants (such as HNO<sub>3</sub>, a mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in H<sub>2</sub>SO<sub>4</sub>) or by air or ozone-enriched air at elevated temperatures. The type of purification technique greatly influences the composition of the functional groups [3]. NDs have a wide range of potential applications in tribology, catalysis, medicine, diamond–polymer composites, and coatings production [1,3] due to their excellent mechanical and optical properties, high specific surface areas, and tunable surface structure.

Previously we reported interesting results on the physicochemical and catalytic properties of Pd and Ni supported on ND [4,5]. ND was found to be a promising support material for heterogeneous catalysts for hydrodechlorination and CO oxidation. The investigation of metal nanoparticles supported on ND is a difficult task due to its small size, poor crystallinity, and diversity of surface functional groups, which hinder the application of standard techniques, such as XRD and IR. The understanding of the mechanism of active site formation opens ways for the tailored synthesis of catalytically active metal–ND systems. The involvement of ND surface functional groups in the coordination of metal precursors during impregnation was proposed on the base of FTIR data [6]. But the



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mechanism of precursor reduction and formation of the catalytically active sites on the surface of NDs is still missing in the literature.

Semihydrogenation of phenylacetylene to styrene is a process of great industrial importance, because phenylacetylene is a poisoning impurity in styrene feedstocks that causes deactivation of the styrene polymerization catalyst [7,8]. Styrene selectivity in this reaction is sensitive to catalysts' active site composition in bimetallic catalytic systems [9] and metal-support interaction [10]. Semihydrogenation of phenylacetylene is also a good model reaction for the evaluation of selective hydrogenation catalysts under very mild conditions.

Many technologically important solid materials are amorphous or poorly crystalline, and therefore their structure cannot be characterized by diffraction techniques. For example, heterogeneous catalysts comprising metal or metal oxide nanoparticles dispersed on a high-surface-area support commonly fall into this category. Even when a catalyst support is crystalline, active sites at the surface represent a very small atomic fraction of the material, and therefore have to be probed by a spectroscopic technique that offers selectivity to these particular sites. Variability in the active sites often increases with metal loading, while dilute systems pose challenges for spectroscopic sensitivity even when they are more uniform structurally.

Extended X-ray absorption fine structure (EXAFS) spectroscopy has proven to be a powerful technique for probing local structure in noncrystalline materials. EXAFS spectroscopy yields structural information within a sphere with a radius of about 5–7 Å around the central atom selected by the energy of the specific X-ray absorption edge. On the basis of EXASF data, adequate and reliable information about the environment of the atoms forming the active sites of heterogeneous catalysts can be obtained. Usually EXAFS measurements of the absorption spectrum  $\chi(k)$  are approximated by the function

$$\chi(k) = S_0^2 \sum_{i=1}^n \frac{N_i}{R_i^2} \frac{F_i(k)}{k} e^{-\frac{2R_i}{\lambda}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \Psi),$$
(1)

where  $N_i$  is the number of atoms in the *i*th coordination sphere,  $R_i$  is the distance from the central atom to the *i*th coordination sphere,  $\sigma^2_i$  is the Debye–Waller factor,  $F_i(k)$  is the photoelectron backscattering amplitude, and *k* is the photoelectron wavenumber.

A traditional way to determine the interatomic distance *R* from EXAFS data utilizes the Fourier transform [11]. However, if two different atoms are located at similar distances from the absorber atom, their contributions in the *R*-space overlap and thus become indistinguishable. The wavelet transform (WT) is known to be useful for EXAFS signal extraction and for the discrimination of atoms by their atomic numbers in cases of heavily overlapping contributions. The WT has proven a valuable tool for EXAFS data analysis for structures, where two types of backscattering atoms, e.g., a heavy and a light one, are located at the same distance from the central atom [12–14].

This work focuses on the metal anchored to the ND surface. The effect of the nature of the ND surface on active site formation in supported Ni-containing catalysts, the mechanism of metal precursor coordination, and active sites evolution were investigated by in situ EXAFS combined with TPR. The influence of the surface structure characteristics of various types of NDs on the catalytic activity and stability in the selective phenylacetylene (PhA) hydrogenation was studied as well.

#### 2. Experimental

ND was obtained from "Sinta" JS Company (Belarus; sample was kindly donated by Dr. A. Korzhenevsky). Part of the ND sample

was treated under Ar flow (12 ml/min) at 900 °C for 3 h (designated as ND\_Ar).

Catalysts with 5 wt.% Ni loading were prepared by the wet impregnation of ND with nickel (II) nitrate solution. A suspension of raw or Ar-treated ND in distilled water was stirred for 10 min using a magnetic stirrer. A water solution of a required amount of Ni(NO<sub>3</sub>)<sub>2</sub> (Reachem, Russia) was slowly added to the ND suspension under continuous stirring. The solvent was slowly evaporated at 80 °C. The impregnated catalyst was then dried in air at room temperature for 12 h, heated to 150 °C, calcined at 150 °C for 2 h to decompose nitrates, and finally cooled to room temperature. The prepared samples were denoted as NiO/ND and NiO/ND\_Ar. Catalysts were reduced at 280 °C for 2 h by hydrogen (12 ml/min flow rate). Reduced catalysts were named Ni/ND and Ni/ND\_Ar, respectively.

Metal content in catalysts was measured by atomic absorption spectrometry (AAS) on a Thermo iCE 3000 spectrometer (Thermo Fisher Scientific Inc., USA). Metal was dissolved at 90 °C in a mixture of  $HNO_3/H_2SO_4$  (1:1 weight ratio). The relative error in the AAS measurements of metal concentration in solution was ±1%.

The BET surface area ( $S_{BET}$ ), pore diameter, and volume  $(V_{\text{pore}})$  were determined by low-temperature N<sub>2</sub> adsorption using an Autosorb-1 physisorption analyzer (Quantachrome, USA). High-resolution transmission electron microscopy (HRTEM) investigation was carried out with a JEOL JEM 2100F (Jeol, Japan) microscope operated at 200 kV. Energy-dispersive X-ray spectroscopy (EDX) was applied to assess the catalyst composition. The diffuse reflectance IR spectra were measured on a Bruker Equinox 55/S Fourier transform IR spectrometer (Bruker, USA). Quantitative X-ray fluorescence analysis was carried out on a "Re spect" X-ray spectrometer (LDC Tolokonnikov, Russia) equipped with two X-ray sources with Ag, Ti, Cu, Mo, and Re anodes. Zeta potential in a deionized water suspension was measured by a Malvern ZETASIZER nano-ZS instrument (Malvern, UK). Temperature-programmed reduction (TPR) was performed in a fixed-bed flow apparatus. The outlet of the reactor was connected directly to a thermal conductivity detector. A sample charge of 25 mg loaded into the reactor was heated from room temperature to 900 °C at a heating rate of 12 °C/min in a flow of 5%H<sub>2</sub>-95%Ar mixture.

The Ni K-edge EXAFS spectra were acquired at the "Structural Materials Science" beamline of the Kurchatov Synchrotron Radiation Source (NRC "Kurchatov Institute," Moscow, Russia) [15]. The electron storage ring operated at energy 2.5 GeV and current 120-150 mA was used as a source of radiation. The incident X-ray beam was monochromatized with a Si(111) channel-cut monochromator slightly detuned to suppress higher harmonics. All spectra were recorded in the transmission mode using a pair of ion chambers filled with the appropriate N<sub>2</sub>/Ar mixtures to provide 20% and 80% absorption. The radial pair distribution functions around Ni atoms were obtained by the Fourier transformation of  $k^2$ -weighted EXAFS functions over the range of photoelectron wave numbers 1.0–11.0 Å<sup>-1</sup>. The structural parameters were found by the nonlinear fit of theoretical spectra to experimental ones. Wavelet transform of EXAFS spectra was performed using an ad hoc routine programmed in the Math Lab software. In situ reduction of NiO/ND with H<sub>2</sub> (5% H<sub>2</sub> in Ar) was performed in the EXAFS spectrometer cell at 150, 300, and 900 °C.

Catalytic tests were performed in the range 50–300 °C in a packed-bed reactor equipped with a hydrogen supply line at constant atmospheric pressure and a downstream trap for products accumulation cooled with ice water.  $H_2$  was fed through the top of the reactor. At each reaction temperature, phenylacetylene was injected by a syringe into a flow of hydrogen by pulses (0.23 mmol, 3 pulses at a given temperature at 10 min intervals). After three phenylacetylene pulses, the reactor was kept at a given

temperature for an additional 20 min. Then the trap was removed, 0.221 mmol of nonane (internal standard) and 1 ml of isooctane were added, and the products were analyzed by gas chromatography-mass spectrometry with a Thermo Trace DSQ II (Thermo, USA) GC/MS instrument (EI 70 eV, DB-5 column: 15 m, i.d. 0.25 mm). Careful scanning of mass spectra was performed to control all possible reaction products. No additional products except styrene and ethylbenzene were observed. Selectivity was calculated as

Selectivity (styrene) = 
$$\frac{S(styrene)}{S(styrene) + S(ethylbenzene)} \cdot 100\%$$
, (2)

where *S*(styrene) and *S*(ethylbenzene) are chromatographic peak areas of styrene and ethylbenzene, correspondingly. Sensitivity coefficients were not taken into account because these values for phenylacetylene and reaction products (styrene and ethylbenzene) are very close and equal to about 0.6 a.u./mmol.

#### 3. Results and discussion

#### 3.1. Characterization of ND and Ni/ND

To characterize pure ND, its textural properties, phase, and elemental composition and the presence of surface functional groups were determined. Nitrogen adsorption/desorption isotherms and the pore size distribution of ND are shown in Fig. 1. The adsorption isotherm (Fig. 1) is similar to a type IV isotherm according to the IUPAC classification [16], exhibiting a remarkable hysteresis loop, corresponding to the capillary condensation of nitrogen molecules in mesopores. The pore size distribution obtained from the desorption branch of the isotherm using the BJH method (Fig. 1) shows the presence of mesopores with diameter 2-30 nm. No predominance of any particular pore size was observed. The specific surface area and total pore volume of ND were found to be  $330 \pm 16 \text{ m}^2/\text{g}$ and  $0.9 \pm 0.1$  cm<sup>3</sup>/g, respectively. Trace amounts of Fe, Cr, and Ti were detected in ND by energy-dispersive X-ray fluorescence analysis. The presence of metal impurities is associated with the partial degradation of the surface of the reactor inner walls during the detonation synthesis. The composition and amount of impurities depend on the detonation conditions and purification procedure used during fabrication [17,18]. The starting ND sample was not active in catalytic phenylacetylene hydrogenation; therefore metal impurities showed no catalytic activity in this reaction.



**Fig. 1.** N<sub>2</sub> adsorption and desorption isotherms and pore size distribution of ND. (The pore size distribution was calculated from the desorption branch of the isotherm by the BJH method.)

Different types of ND are known to comprise diamond cores (about 4–10 nm in size) associated in aggregates (up to 200 nm) by amorphous carbon [18]. The microstructure of ND in this work was studied by XRD and transmission electron microscopy.

The identical diffraction patterns typical for the nanodiamond powder materials [18,19] were observed for both ND and Ni/ND samples (Fig. 2). The diffraction peaks at  $2\theta = 43.8^{\circ}$ , 75.5°, and 91.3° correspond to the (111), (220), and (311) cubic diamond reflections (JCPDS No: 00-006-0675). The broad peak at  $2\theta = 25^{\circ}$ corresponds to the (002) crystal graphite reflection. XRD data point to the presence of small particles with the cubic diamondlike lattice. The diffraction peaks were obviously broadened owing to the very small size of the nanodiamond crystallites, along with the abundance of strains and defects. No reflexes of Ni phases were observed in the XRD pattern of Ni/ND. The main reflexes of Ni face-centered cubic (fcc) structure are expected at  $2\theta = 44.45^{\circ}$ . 51.71°, and 76.41° (ICPDS No 00-004-0850). The absence of XRD peaks characteristic of Ni indicates that Ni particle size is less than 3-4 nm. Detonation nanodiamond is known to stabilize metal nanoparticles. In our previous study impregnation of ND with Pd  $(NO_3)_2$  with subsequent H<sub>2</sub> reduction provided the formation of Pd nanoparticles less than 8 nm in size on the ND surface, according to TEM data [20].

The presence of Ni nanoparticles in Ni/ND was confirmed by HRTEM study. TEM image of pristine ND (Fig. 3A) clearly demonstrates diamond nanocrystals 4–5 nm in size. The shape of ND particles is essentially spherical. Each ND particle is coated by a shell of differently hybridized carbon atoms. Our HRTEM images are typical for ND material described in [1,21].

HRTEM images of Ni/ND are presented in Figs. 3B and 4. The structure of the ND support is clearly seen in the TEM image (Fig. 3B). No large metal particles or metal aggregates were found in this sample. This result is in agreement with XRD data confirming the presence of only small Ni nanoparticles. A reliable metal particle size distribution could not be evaluated from HRTEM data because of low contrast between the Ni nanoparticles and the ND support. The presence of Ni particles a few nm in size is confirmed by the dark field HRTEM image (Fig. 4A and B). The bright areas in this image correspond to metal-containing areas of the sample. The Ni was also detected by EDX (Fig. 4C) and selected-area electron diffraction (Fig. 3B). The ring reflexes in the diffraction pattern correspond to the interplanar spacing of diamond. Additional reflections (marked by arrows in Fig. 3B) could be attributed to metallic Ni or nickel carbide.



Fig. 2. XRD patterns of ND and Ni/ND.



Fig. 3. HRTEM images of ND (A) and Ni/ND (B). (SAED pattern from the total image area is shown in the insert.)



Fig. 4. Bright (A) and dark (B) field HRTEM images of Ni/ND; (C) dark field HRTEM image and EDX spectra of Ni/ND.

Temperature-programmed reduction is a powerful method for studying metal-support interaction and formation of active sites in catalysts. The reduction temperature of the metal precursor registered during TPR is sensitive to minute changes in metal-support interaction strength. TPR profiles of ND and nonreduced NiO/ND are presented in Fig. 5A. Hydrogen consumption at temperatures higher than 400 °C corresponding to ND hydrogenation is observed for both samples. The ND contains amorphous carbon that can react with hydrogen, especially in the presence of Fe and Cr impurities, as well as supported Ni. The TPR profile of NiO/ND sample contains two hydrogen consumption peaks at 260 and 390 °C, both of which can be attributed to the reduction of NiO, and a shoulder at 550 °C, which is associated with ND hydrogenation.

The presence of several peaks of hydrogen consumption at different temperatures during TPR of a metal oxide may result from (1) the multistep metal oxide reduction reaction; (2) the presence



Fig. 5. TPR profiles (A) and infrared spectra (B) of ND and unreduced Ni/ND catalysts.

of metal oxide fractions with a significant difference in the crystallite size; (3) the presence of metal oxide particles with different interaction with the support. In the case of NiO the former two reasons are not significant, as it is known that the reduction of NiO proceeds as a one-step reaction [22] and the influence of NiO crystal size on the reduction temperature seems to make only a minor contribution. It was found that the NiO crystallite size in NiO/Al<sub>2</sub>O<sub>3</sub> exerts nearly no impact on the 50% reduction temperature, and the NiO obtained from different precursors exhibits the same reduction behavior [22]. For pure NiO the reduction temperature varies by only 30 °C when the particle size increases from 5 to 35 nm [23]. The second reason, namely, the bimodal or wide NiO particle size distribution, finds no proof in our TEM data. Therefore, the difference in NiO reduction temperature most probably corresponds to the coexistence of different NiO species, which interact with the support in a different way. The reduction peak at lower temperature (260 °C) can be attributed to the reduction of NiO weakly bonded to the support. This type of NiO species is formed by the physisorption of NiO on the surface. NiO species in this case are held only by van der Waals forces. The high-temperature (390 °C) reduction peak originates from the reduction of nickel species strongly attached to the ND surface. Such types of particles result from the chemical coordination of the nickel precursor to O-containing functional groups on the ND surface (Ni–O–C). The shift of the reduction temperature to a higher value due to the chemisorption of Ni<sup>2+</sup> by anchoring to O-containing functional groups was earlier observed for activated carbon-supported Ni catalysts [24,25]. The possible involvement of functional groups on the ND surface in metal salts coordination was found for ND material impregnated with Ni-acetylacetonate [6].

#### 3.2. Study of ND surface coverage by functional groups

The existence of oxygen and nitrogen-containing functional groups on the ND surface is well established. The composition of these groups depends on the purification technique utilized during the ND production and provides the unique properties of the ND surface. The FTIR spectra of ND are demonstrated in Fig. 5B. The wide absorption band at  $3400-3500 \text{ cm}^{-1}$  could be assigned to O–H vibrations, due to the presence of physisorbed water [26,27]. This band is usually accompanied by the peak at 1640 cm<sup>-1</sup> corresponding to the bending mode of water ( $\delta$ OH). In our case this band probably overlaps with more intense neighbors. Intense overlapping peaks at 2960 and 2870 cm<sup>-1</sup> are assigned to symmetric and asymmetric stretching vibrations of ali-

phatic CH<sub>2</sub> and CH<sub>3</sub> groups [26,27]. Absorption bands in the range 2100–2300 cm<sup>-1</sup> correspond to nitrile and alkyne groups.

The asymmetric band at 1740–1800 cm<sup>-1</sup> is attributed to cyclic anhydrides -C(O)-O-C(O) and surface carboxyl and carbonyl groups. The peak at 1750 cm<sup>-1</sup> is caused by the -C=O and -COOHstretching vibrations [28]. The band in the range 1840–1850 cm<sup>-1</sup> could be attributed to C=C species and C=O in carboxylic (COOH), lactone (COO), or cyclic ketone (-CO-) structures on the surface. It seems difficult to reveal the dominance of certain types of carbonyl groups on the surface of ND on the basis only of the IR spectra. Weak bands, which are observed at 1257 and 1192 cm<sup>-1</sup>, may be explained by the presence of C-O-C stretching vibrations of cyclic ethers or esters [26,28]. The band at 1257 cm<sup>-1</sup> could be also attributed to the presence of nitrogen A-centers formed by two adjacent nitrogen atoms in the diamond lattice [29].

Functional groups on the ND surface are assumed to play an important role in the formation of supported metal particles. In this work, FTIR study of the Ni/ND catalyst was performed as well. The FTIR spectra of ND and Ni/ND are presented in Fig. 5B. There is only one small distinction between ND and Ni/ND spectra, in the region 1100-1300 cm<sup>-1</sup>. The low-intensity absorption bands at 1192 and 1257 cm<sup>-1</sup> disappeared after Ni supporting, possibly as a result of Ni coordination with O-containing functional groups. Stabilization of Ni nanoparticles by surface oxygenates was demonstrated in work [6]. It is believed that the direct formation of NiO coordinated to cyclic anhydrides takes place and ensures good dispersion of metal species. The disappearance of the absorption band characteristic for a particular type of surface groups after metal deposition indirectly points to the possibility of involvement of these groups in the coordination of the metal precursor. Such coordination provides the uniform metal precursor distribution that results in the formation of tiny nickel particles in the prepared catalyst.

The set of functional groups on the surface of a particular ND material defines the integral value of the surface charge in colloidal solution, which is known as the zeta potential ( $\zeta$  potential). The sign and value of surface charge are very important for sorption and electrophoretic applications of ND. Remarkably, the  $\zeta$  potentials of different commercial and modified NDs vary from highly positive to highly negative values. In this work the  $\zeta$  potential was measured for ND and Ni/ND dispersed in deionized water. The pristine ND showed a negative charge of about -4 mV (Table 1). The negative value of the  $\zeta$  potential is caused by the dissociation of acidic groups in water. Carboxyl groups, lactones, and phenol and lactol groups contribute to the acidic character of the

**Table 1** *ζ* potential of ND and Ni/ND dispersed in deionized water.

| Sample    | Sample description                   | ζ potential, mV |
|-----------|--------------------------------------|-----------------|
| ND        | Pristine ND                          | -4.3            |
| ND_air320 | ND, treated in air at 320 °C for 3 h | -17.5           |
| ND_Ar     | ND, treated in Ar at 900 °C for 2 h  | 23.8            |
| Ni/ND     | Ni supported on ND                   | 0.5             |

carbon materials [30]. This result agrees with the IR data, which demonstrate the intense absorption bands of carboxyl groups. Additional air treatment of ND at 320 °C leads to an increase of negative charge to -17.5 mV. This change of  $\zeta$  potential is associated with the oxidation of the ND surface, which increases the content of carboxyl groups. For Ni/ND catalysts, the  $\zeta$  potential is 0.5 mV. The origin of the positive values of  $\zeta$  potential is still debated in the literature. The basicity of carboxyl groups on the ND surface could be caused by chromene structures, diketone or quinone groups, pyrone-like groups, or electrostatic interaction of protons with the  $\pi$ -electron system of the graphene structures [31]. It is known that an sp<sup>2</sup>-like carbon shell exists on the surface of ND, providing sites for pyrone formation. The change of  $\zeta$  potential from negative to positive values points to the binding of carboxyl groups by the metal precursor.

#### 3.3. EXAFS study

To study the mechanism of the Ni precursor anchoring to the ND surface and the reduction of NiO/ND, in situ EXASF combined with TPR was performed. In the present work, WT was used to reveal the presence of Ni-O-C bonds characteristic of Ni species strongly anchored to the ND surface. Application of WT to the experimental data provides a valuable tool to distinguish metal and carbon atoms, due to the large difference in their atomic numbers (6 for C and 28 for Ni). However, carbon and oxygen atoms are very close in the Periodic Table (6 for C, 8 for O), so the possibility of their separation in the spectrum is vaguer. From this point of view, EXAFS data were analyzed by the application of WT with the modified Morlet function. The approach using this function is not novel, but it has not yet become widely used. The development of a wavelet basis function in this work was based on the literature data [14]. The proposed function provides a good resolution of experimental data:

$$w(a,b) = \sqrt{a} \int_{-\infty}^{+\infty} \chi(k) \exp(-ica^{2}(k-b)) \exp(-a^{2}(k-b)^{2}) dk.$$
(3)

In this work an additional parameter, *q*, was included in the final equation to control the deviation of the Morlet function from the exact quantum–mechanical solution. The relevance of the used function was verified by comparison of the calculated and experimental data for model compounds. The final basis function used for EXAFS data analysis is

$$w(a,b) = \int_{-\infty}^{+\infty} \chi(k) \cdot \exp(-i2a(k-b)) \cdot \exp(-2a^q(k-b)^2/c)dk.$$
(4)

All obtained EXAFS results are represented as WT image (center),  $\chi(k)$  signal (running horizontally below the WT image), and Fourier transform  $FT\chi(k) * k^n$  (running vertically to the left from the WT image). The RGB palette from blue (minimum) to red (maximum) was used for the visualization of WT depending on the distance from the Ni as a central atom and the wavevector (*k*) of neighboring atoms.

Experimental EXAFS spectra were acquired under nominally identical conditions both for the catalysts and for a set of model

compounds. EXAFS data for Ni/ND produced by in situ reduction of NiO/ND with  $H_2$  in the EXAFS spectrometer cell at 150, 300, and 900 °C were compared with the experimental EXAFS data for Ni, NiO, Ni(CH<sub>3</sub>COO)<sub>2</sub>, and NiCO<sub>3</sub>. The last two salts were chosen as model references to simulate the coordination of the metal precursor by carboxyl groups. In situ reduction of NiO/ND in the EXAFS spectrometer cell provides reliable information on the active site structure, eliminating the possible influence of ambient gases. The obtained WT plots were compared to confirm the possible existence of Ni–O–C bonds between Ni and nanodiamond.

Wavelet transform plots for model compounds are presented in Fig. 6. For metallic nickel (Fig. 6A), two maxima at R = 2.1 and 4.3 Å at similar *k*-values correspond to the Ni–Ni bonds for the first and second coordination spheres, correspondingly. The WT plot for NiO (Fig. 6B) contains three peaks at R = 1.56, 2.63.1, and 4.45 Å. The peak at R = 1.56 Å corresponds to O from the first coordination sphere, the foothill at R = 2.63 Å originates from the Ni–O–Ni scattering contribution, and the last peak at R = 4.45 Å corresponds to the Ni atom. The maximum at R = 1.5 Å in WT plots for Ni(CH<sub>3</sub>-COO)<sub>2</sub> (Fig. 6C) can be associated with the Ni–O scattering path. The second maximum at R = 3.2 Å results from the Ni–O–C path. The location of the second peak at lower values of the wavevector number points to the contribution of the C atom. NiCO<sub>3</sub> (Fig. 6D) demonstrates WT with two maxima at R = 1.6 Å (from the O atom in the first coordination sphere) and R = 2.6 Å (from the Ni–O–C path). Again, the maxima are at different ordinate positions because k(C) < k(O).

NiO/ND reduction temperatures in the EXAFS cell (150, 300, and 900 °C) were chosen on the base of TPR results. Reduction at 150 °C corresponds to the beginning of NiO reduction. The value of 300 °C was chosen because this temperature was used during Ni/ND catalyst preparation and therefore the material reduced in situ at this temperature was the most similar to the catalyst tested in the reaction. Deep NiO reduction was achieved at 900 °C. It is important to note that in contrast to traditional TPR study, where hydrogen consumption is measured during continuous heating, during EXAFS investigation the catalyst was heated to a given temperature and maintained at this temperature for several hours for chemical equilibration and spectra acquisition. Then the sample was heated to the next temperature. The isothermal heating in  $H_2/Ar$  flow may result in a lower reduction temperature than in the TPR profile. Wavelet transform plots for Ni/ND reduced at 150, 300, and 900 °C are presented in Fig. 7. In Ni/ND reduced at 150 °C (Fig. 7A), the predominant metal state is Ni<sup>2+</sup>. The Ni–O scattering path is evidenced by an intense peak at R = 1.56 Å. It is necessary to note that the Ni atom from the second coordination sphere of NiO  $(R = 2.6 \text{ Å and } k \sim 6)$  is not clearly visible in WT. This fact points to a small size of the NiO particle, in agreement with XRD and TEM data. The strong broadening of the main peak in the region of  $k \sim 2$  results from the presence of the Ni–O–C scattering path, originating from the anchoring of Ni on O-containing surface functional groups. The low-intensity peak at R = 2.3 Å corresponds to the Ni-Ni scattering path; it is associated with the beginning of the NiO reduction process, which leads to Ni(0) formation.

The reduction at 300 °C leads to an increase of the intensity of the peak at R = 2.3 Å ( $k \sim 6.4$ ) as a result of Ni(0) formation by NiO reduction (Fig. 7B). A new peak also appears at R = 2.1 Å ( $k \sim 3.8$ ), which most likely is associated with the Ni—C scattering path in nickel carbide, according to the modeling of Ni<sub>3</sub>C (IEFFIT8 software). NiO is present in this sample as well, probably because of the insufficient retention of the sample at 300 °C and incomplete NiO reduction. Only reduction at 900 °C provides complete reduction of the NiO precursor to form Ni(0). WT of Ni/ND reduced at 900 °C (Fig. 7C) is identical to the WT of metallic Ni (Fig. 6A) and contains two peaks at R = 2.03 and 4.15 Å, which correspond to Ni—Ni scattering paths in the first and second coordination



Fig. 6. Wavelet transform plots of the EXAFS experimental data for model compounds: Ni (A); NiO (B); NiAc (C); NiCO<sub>3</sub> (D).

spheres. Under  $H_2$ ,  $Ni_3C$  can be converted into Ni(0) at temperatures above 350 °C [32].

Summarizing the EXAFS data, the following reduction mechanism can be proposed. The metallic nickel appears at 150 °C due to H<sub>2</sub> reduction of Ni in NiO/ND. The fraction of Ni(0) increases significantly with the reduction temperature and at 900 °C nearly all NiO is reduced to Ni(0). The reduction of weakly bonded NiO proceeds at lower temperatures and results in the formation of Ni(0) particles. The observed Ni-O-C scattering path in EXAFS data for Ni/ND (150  $^{\circ}$ C) indicates the presence of Ni<sup>2+</sup> species strongly bonded to ND through the oxygen-containing surface groups. The reduction of nickel species strongly bonded with the ND surface proceeds at higher temperatures to form both Ni<sub>3</sub>C and Ni. The nickel carbide phase can be described as an interstitial solid solution of carbon in metallic Ni. The formation of the Ni<sub>3</sub>C phase in the Ni/C catalyst was also observed during the hydrodechlorination of chlorinated hydrocarbons [33,34] and led to catalyst deactivation. Nickel carbide formation was detected during metal vapor synthesis under hydrocarbons [35], as well as at thermal decomposition of nickel acetylacetonate in oleylamine under inert atmosphere [36]. It was proposed that during Ni salt thermolysis, metallic nickel is formed at the first stage, and Ni carbidization proceeds only then under reaction with CO resulting from the decomposition of acetylacetonate ions. If Ni in Ni/ND coordinates with the ND surface through the oxygen-containing functional groups, the structure of such coordination complexes is similar to that of Ni in nickel acetylacetonate or nickel acetate, depending on the particular type of surface groups. So a similar mechanism of Ni<sub>3</sub>C formation is possible for the studied samples. Our EXAFS study confirms the Ni coordination with the functional groups proposed on the base of IR results [6]. Indeed, the presence of the Ni–O–C scattering path found by EXAFS proves the chemical bonding of Ni to the carbon surface through O-containing surface functional groups. It needs to be emphasized that the presence of the nickel carbide phase could strongly affect the catalytic performance of the material.

# 3.4. Separation of Ni forms in active sites and catalytic activity in PhA hydrogenation

According to physicochemical study, the two forms of supported Ni were found in Ni/ND. The first form of Ni, weakly bonded to the ND surface, is most likely associated with physical adsorption through van der Waals interaction. The second form



Fig. 7. Wavelet transform plots of the EXAFS experimental data for NiO/ND reduced at 150 (A), 300 (B), and 900 °C (C).

of Ni is characterized by the species chemically bonded to the ND surface via oxygen atoms (Ni–O–C bond), as shown by EXAFS, which also confirms the different mechanisms of the reduction of weakly and strongly bonded Ni species. The reduction of strongly bonded species is accompanied by nickel carbide formation. The catalytic activity of the two forms of Ni in reduced catalysts may be different.

In an attempt to distinguish the role of each Ni form in catalytic performance, two additional samples of Ni supported on ND were prepared, comprising mostly weakly or strongly bonded Ni. The presence of these forms of Ni was monitored by TPR. To prepare the catalyst containing mostly the strongly bonded Ni species, the sample after impregnation with Ni salt was calcined in air at 300 °C instead of 150 °C. This sample was designated as Ni/ND\_300. The increase of calcination temperature was assumed to favor Ni–O–C bonding during Ni(NO<sub>3</sub>)<sub>2</sub> decomposition. Since the studied Ni/ND catalyst was reduced at 300 °C and no Ni sintering was found by TEM, the treatment of the precursor in air at this temperature was expected to affect only the decomposition of the precursor without the aggregation of Ni particles.

To prepare the sample with a predominance of weakly bonded Ni species, we had to completely eliminate chemical bonding of nickel to the ND surface, which is a complicated task. Since the surface groups are involved in metal–precursor bonding, we attempted to remove carboxylic groups from the ND surface before the metal deposition. According to [37], the treatment of ND under an inert atmosphere (N<sub>2</sub>) at temperature above 700 °C leads to the decomposition of the carbonyl and carboxyl groups. In our work, to remove O-containing functionalities from the surface, ND was treated in Ar flow at 900 °C (sample ND\_Ar). The removal of carboxyl groups was confirmed by  $\zeta$  – potential measurements: the ND\_Ar surface charge becomes positive, namely 23.8 mV. The catalyst was prepared by the impregnation of ND\_Ar with Ni(NO<sub>3</sub>)<sub>2</sub> using the same procedure as for Ni/ND.

The presence of Ni weakly or strongly bonded to ND was monitored by TPR of nonreduced NiO/ND\_300 and NiO/ND\_Ar samples. The TPR of NiO/ND\_300 (Fig. 5A) confirms the removal of most of the weakly bonded metal: the hydrogen consumption at 260 °C significantly decreases. The TPR profile for NiO/ND\_Ar is shown in Fig. 5A as well. Hydrogen consumption at 570 °C corresponds to ND hydrogenation. One intense hydrogen consumption peak at 260 °C and two less intense peaks at 330 and 420 °C are attributed to the reduction of various types of NiO surface species. The hydrogen consumption peak at 260 °C is attributed to the reduction of weakly bonded NiO. As expected, the pretreatment of ND with Ar has no effect on the low-temperature hydrogen consumption peak.



Fig. 8. PhA conversion (A) and ST selectivity (B) at different reaction temperatures for Ni/ND, Ni/ND\_Ar, and Ni/ND\_300.

The TPR profile of NiO/ND\_Ar shows the decrease of the intensity of the high-temperature peak of hydrogen consumption. According to the change in  $\zeta$ -potential value, the Ar treatment leads to the elimination of carboxyl groups from the ND surface. It is natural that after Ar treatment the fraction of strongly bonded NiO decreases significantly in NiO/ND\_Ar, which confirms that the Ni/ND-Ar sample contains mainly weakly bonded Ni.

To compare the catalytic properties of the catalyst with different bonding of Ni species, Ni/ND, Ni/ND\_300, and Ni/ND\_Ar were tested toward gas phase phenylacetylene (PhA) partial hydrogenation. The hydrogenation reaction can yield either styrene (ST) or ethylbenzene (EB). ST is a valuable industrial semiproduct and thus it is desirable to make the hydrogenation proceed selectively along the partial hydrogenation path. The reaction was performed in the temperature range 50–300 °C. ST and EB were the only products. Other possible hydrogenation products (ethylcyclohexane, ethane, cyclohexane, benzene, etc.) and condensed products (1.3-diphenylpropane, 1.4 diphenyl-butane, etc.) were not detected by GC/MS. The deposition of polymerization products on the catalyst surface seems to be unlikely, because no decrease of PhA conversion was observed at each tested reaction temperature, and the mass balance was closed. The steady state PhA conversion and styrene selectivity were measured at each reaction temperature (Fig. 8). The PhA conversion was slightly higher over Ni/ND\_Ar than over Ni/ND at 100 and 150 °C; at higher temperatures PhA conversion achieved 100% over both catalysts (Fig. 8A). At 50 °C, Ni/ND provided somewhat increased PhA conversion in comparison with Ni/ND\_Ar, and at this point styrene selectivity over Ni/ND\_Ar was significantly higher than over Ni/ND (80 vs. 20%). In contrast, Ni/ND yielded ST with 50% selectivity at 150 °C, whereas Ni/ND\_Ar afforded only EB. The Ni/ND\_300 was less efficient; PhA hydrogenation started only at 150 °C, and even at 300 °C PhA conversion was as low as 60%. The difference in bonding of Ni species to ND surface results in a difference in ST selectivity of Ni/ND\_300 and Ni/ND\_Ar (Fig. 8B). The catalyst comprising weakly bonded Ni (Ni/ND\_Ar) provides PhA hydrogenation to EB. The ST selectivity of this catalyst was high only at 50 °C, where PhA conversion is extremely low (2%). At higher reaction temperatures, ST selectivity does not exceed 15%. The predominance of strongly bonded Ni in Ni/ND\_300 promotes a high ST selectivity at all studied temperatures. In this case ST selectivity does not drop below 75% even at 300 °C. The ST selectivity over the Ni/ND catalyst comprising an intrinsic mixture of weakly and strongly bonded Ni species is higher at 100 and 150 °C than that over Ni/ND\_Ar comprising mainly Ni species weakly bonded to the ND surface. For Ni/ND at higher reaction temperatures, EB becomes the main product. Therefore, catalytic tests show that the anchoring of the metal precursor by Ni—O—C bonds during the preparation steps leads to the formation of active sites that are highly selective toward PhA partial hydrogenation to ST.

#### 4. Conclusions

On the base of IR and  $\zeta$ -potential measurements as well as literature data, the presence of various oxygen-containing groups on the ND surface was confirmed. Nickel precursor coordination with oxygen-containing functional groups on the ND surface was studied by in situ EXAFS combined with TPR. The wavelet transform analysis of EXAFS spectra confirmed the presence of Ni-O-C bonds. It seems that two types of NiO species are formed on the ND surface during catalyst preparation: the weakly bonded species are physically adsorbed on the ND surface and the strongly bonded ones are chemically bonded to the ND surface through the Ni-O-C bonds. In situ reduction of NiO in the EXAFS cell in combination with TPR evidenced that weakly bonded NiO species started to reduce to Ni(0) even at 150 °C. At 300 °C a significant part of NiO is reduced, but not all. Nickel carbide and Ni(0) are formed at a higher reduction temperature (900 °C). Variation of the ratio of weakly and strongly bonded Ni species in the catalyst resulted in different ST selectivity in phenylacetylene hydrogenation. The catalyst containing mainly Ni species strongly bonded to the ND surface provides high selectivity in the PhA partial hydrogenation to ST, whereas the catalyst containing mainly weakly bonded Ni species produces predominantly the total hydrogenation product (EB). The catalyst containing both types of Ni species showed intermediate ST selectivity.

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