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

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A B S T R A C T

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

on the purification method used during ND synthesis [2]. On an industrial scale, detonation soot is purified using liquid oxidants (such as HNO_3, a mixture of H_2SO_4 and HNO_3, or $K_2Cr_2O_7$ in H_2SO_4) 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

mechanism of precursor reduction and formation of the catalyti-cally 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 char-acterized 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 sur-face 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 approx-imated by the function

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

where N_i is the number of atoms in the ith coordination sphere, R_i is the distance from the central atom to the ith coordination sphere, σ_i^2 is the Debye–Waller factor, $F_i(k)$ is the photoelectron backscat-tering 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 dif-ferent 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 use-ful for EXAFS signal extraction and for the discrimination of atoms by their atomic numbers in cases of heavily overlapping contribu-tions. 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 precur-sor 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) hydro-genation 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 (desig-nated 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 $Ni(NO_3)_2$ (Reachem, Russia) was slowly added to the ND suspen-sion 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 mix-ture 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_{pore}) were determined by low-temperature N_2 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 spec-troscopy (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_2–95%Ar mixture.

The Ni K-edge EXAFS spectra were acquired at the "Structural Materials Science" beamline of the Kurchatov Synchrotron Radia-tion 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_2/Ar mixtures to pro-vide 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^{-1}. 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 reduc-tion of NiO/ND with H_2 (5% H_2 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 con-stant 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