

New Heterogeneous Nanostructured Catalysts Based on Transition Metal Nanoparticles and Hexagonal Boron Nitride

A. S. Konopatskii^{a*}, K. L. Firestein^b, I. N. Volkov^a, D. V. Leibo^a, V. V. Kalinina^a,
D. V. Golberg^b, and D. V. Shtanskii^a

^a National University of Science and Technology "MISiS," Moscow, 119049 Russia

^b Queensland University of Technology, Brisbane, Australia

*e-mail: konopatskiy@misis.ru

Received April 16, 2021; revised May 1, 2021; accepted May 7, 2021

Abstract—The structure of new heterogeneous FePt/*h*-BN nanomaterials and their catalytic activity in the model reaction of carbon monoxide oxidation have been studied. The structure and surface composition were analyzed by methods of transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. It is established that the new materials exhibit pronounced catalytic activity and can provide complete CO conversion at a temperature of 250°C. The process of thermal activation involves ordering of the structure of FePt nanoparticles.

Keywords: nanomaterials, heterogeneous catalysis, hexagonal boron nitride, thermal treatment.

DOI: 10.1134/S1063785021080186

In recent years, much research attention has been devoted to heterogeneous catalysts based on hexagonal boron nitride (*h*-BN) playing the role of a substrate for catalytically active particles [1]. Nanoparticles of transition metals such as silver, palladium, platinum, etc., are known to exhibit pronounced catalytic activity in a number of commercially important reactions [2]. However, increasing attention is now given to bimetallic catalysis systems [3], the properties of which can be controlled by changing their chemical composition [4]. New catalytic nanosystems are conveniently verified using model (but still commercially important) chemical reactions, in particular, carbon monoxide (CO) oxidation.

The present work was aimed at synthesis of new heterogeneous FePt/BN catalysts and the study of their structure and catalytic activity in the reaction of CO oxidation. Special attention was devoted to analysis of the structure and chemical state of the material surface after thermal treatment, which is a necessary stage in catalyst preparation.

The heterogeneous FePt/BN catalysts were obtained using a polyol process. According to this, 200 mg *h*-BN powder was dispersed in 100 mL ethylene glycol and treated on a magnetic stirrer with ultrasonic processing for 5 min. The obtained homogenized suspension (synthesis medium) was transferred into a laboratory oven and heated to 180°C. The agglomeration of particles was prevented by ultrasonic

processing (at 15% power) with the aid of an immersed sonicator. When the indicated temperature was reached, H₂PtCl₄ and FeCl₃ · 3H₂O were added to the synthesis medium in a molar ratio of 1 : 40. This was followed by adding 3.6 g NaOH, and the exposure was continued for 3 min, after which the reaction mixture was allowed to cool in a vent hood. Upon attaining room temperature, the mixture was centrifuged at 8500 rpm for 30 min and rinsed with distilled water. The solid residue was collected and used for subsequent analyses.

The catalytic activity with respect to CO oxidation reaction was studied in a flow-type quartz reactor. Each test was performed using 25 mg catalyst mixed with silica granules. The activity was measured in a gas flow with a composition of 5.6% CO, 11.1% O₂, 83.3% He (43200 mL/(g_{cat}⁻¹ h⁻¹)) at a flow rate of 36 mL/min and atmospheric pressure. The reaction products were studied on a ThermoStar mass spectrometer. Prior to testing, the catalyst was annealed in a hydrogen atmosphere at 500°C for 8 h, which is a conventional scheme of thermal activation for heterogeneous catalysts based on metal particles. After annealing, the furnace was allowed to cool down to room temperature and the catalyst was used for test-

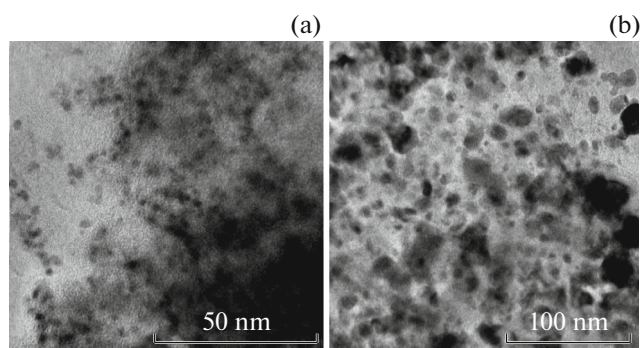


Fig. 1. Electron-microscopic images of FePt/BN catalyst (a) before and (b) after activation.

ing. The conversion of carbon monoxide was calculated by the formula

$$X = 1 - \frac{Q_{CO}^f}{Q_{CO}^s},$$

where Q_{CO}^s is the initial CO flow and Q_{CO}^f is the final CO flow at the reactor output.

Since the activation pretreatment can lead to significant structural changes in the material, the catalyst structure was studied in two states: prior to activation (as synthesized) and after activation (as used in the catalytic process). The chemical and phase compositions and the surface structure of obtained materials were studied by the methods of transmission electron microscopy (TEM) on a JEM 2100 microscope, X-ray photoelectron spectroscopy (XPS) on an AXIS Supra surface analysis system, and X-ray diffraction (XRD) on a DRON-3 diffractometer.

Figure 1 shows TEM images of the catalyst material before and after the activation pretreatment. The surface of as-synthesized *h*-BN particles is uniformly covered by metal nanoparticles with an average size of 3.4 nm and with the largest particles being up to 5 nm (Fig. 1a). Thermal activation leads to the agglomeration of metal particles and results in their average size increasing to 8.6 nm and the coarsest particle diameter reaching 20 nm (Fig. 1b). In addition, the morphology of nanoparticles also changes, so that many of them acquire irregular shapes due to agglomeration. In any case, both samples represent powdered materials comprising heterogeneous FePt/BN particles with bimetallic nanoparticles occurring on the surface of *h*-BN.

Figure 2 presents the results of studying surface features and phase compositions of catalyst materials by the XPS and XRD techniques. The Fe 2*p* and Pt 4*d* X-ray photoelectron spectra of as-synthesized FePt/BN particles display no sharply pronounced peaks. However, the signals of iron and platinum from activated samples become well distinguished, as is manifested by doublets in the regions of 710–730 eV (Fe 2*p*) and 310–340 eV (Pt 4*d*). The increase in peak intensities can be related to the removal of residual polymeric and side products from the surface of particles in the course of thermal activation. This result emphasizes the importance of the stage of catalyst activation, since its properties in chemical reactions directly depend on the surface composition and structure.

The content of iron and platinum calculated from the results of XPS measurements of FePt/BN samples after annealing amounted to 5.2 and 2.8 at %. Decomposition of the Fe 2*p*_{3/2} signal into components of Gaussian function revealed the presence of iron in the oxidation states Fe³⁺ (711.0 eV) and Fe²⁺ (712.6 eV) in the catalyst upon activation, which is indicative of the presence of some oxygen bound to iron ions on the

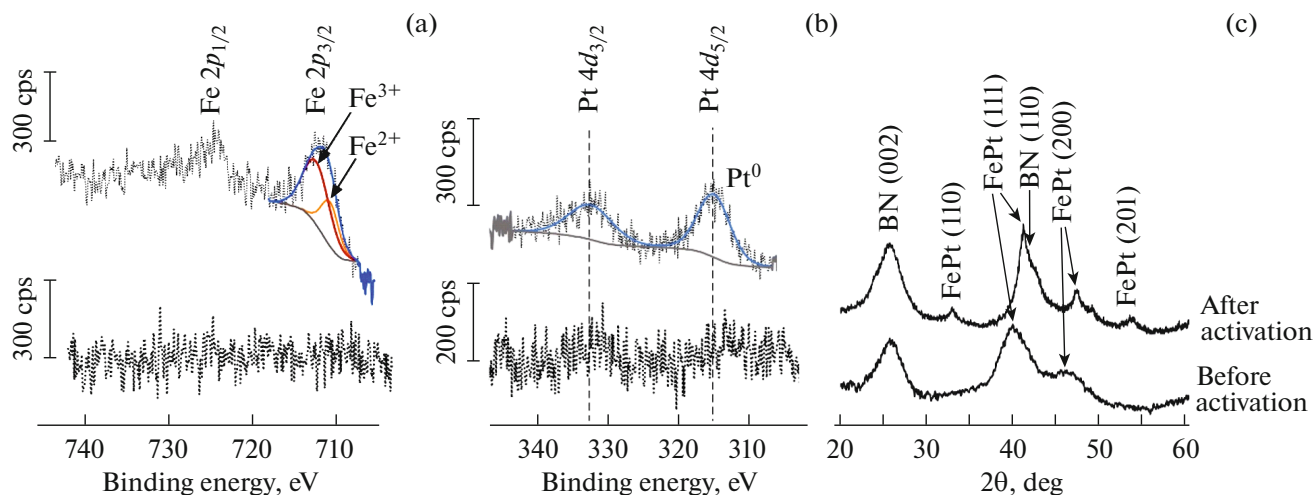


Fig. 2. Results of (a, b) XPS and (c) XRD measurements of FePt/BN catalysts before activation (lower curves) and after activation (upper curves).

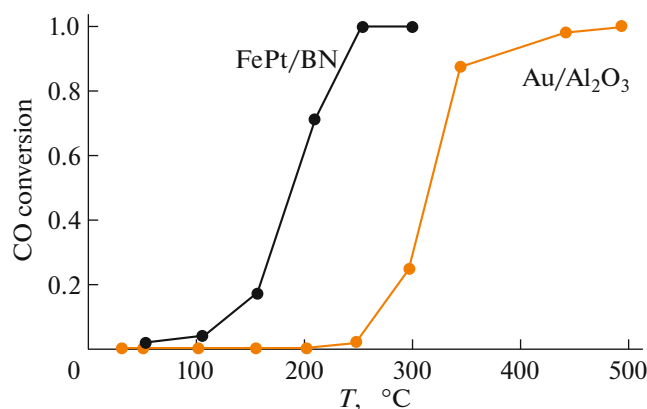


Fig. 3. Catalytic activity of FePt/BN and Au/Al₂O₃ in the reaction of CO oxidation.

surface of FePt nanoparticles. The binding energies of Pt 4d_{5/2} (315.3 eV) and Pt 4d_{3/2} (332.8 eV) peaks and their possible approximation by single Gaussian components are indicative of the metallic state of platinum. In comparison to the well-known published data [5], there is a small shift of the Pt 4d signal toward higher binding energies. This shift is frequently explained in the framework of a charge transfer model [6] which well describes changes in the XPS spectra related to the formation of ionic or covalent bonds. However, in the case of metal bonds, such as contacts in the two-component FePt system under consideration, the observed shift may be caused by the process of ordering in the FePt structure during thermal treatment and related changes in the electron structure of this intermetallic compound.

The XRD patterns presented in Fig. 2c show that the main components of the as-synthesized catalyst are *h*-BN and FePt nanoparticles. Significant broadening of the FePt (111) reflection is indicative of a small size of particles. After annealing, the width of the most intense FePt (111) peak decreases, which is related to the coarsening of FePt nanoparticles during activation. The average size of crystallites calculated by the Debye–Scherrer formula was 2.2 nm before activation and 6.5 nm after this thermal treatment, in good agreement with the TEM data. Activation leads to the shift of FePt 111) and (200) peaks toward greater 2θ angles and to the appearance of a new FePt (110) peak. These changes are characteristic of the ordering of an equiatomic FePt phase with an A1 structure and the appearance of an L1₀-FePt “superstructure” [7], in agreement with the XPS analysis. The positive influence of the FePt structure ordering on the catalytic activity (e.g., in the reaction of oxygen reduction) was recently noted in [7].

Figure 3 presents the results of studying the catalytic activity of heterogeneous FePt/BN nanomaterial in comparison to the well-known heterogeneous Au/Al₂O₃ system also prepared by the polyol method.

The average size of Al₂O₃ supporting particles was about 100 nm, and the calculated Au content was 10 mass %. As can be seen from these data, the new heterogeneous material manifested a pronounced catalytic activity in the reaction under consideration. Complete conversion of carbon monoxide was achieved at 250°C. The maximum growth rate of conversion (from 20 to 80%) is observed in the temperature interval from 150 to 250°C. At the same time, the reference catalyst exhibited a much higher (about 440°C) temperature of complete conversion.

The adsorption and dissociation of molecular oxygen on active centers of the catalyst are an important stage in the catalytic process of CO conversion. High thermal stability and the energy barrier for molecular oxygen dissociation hinder the reaction of CO oxidation. However, it has been demonstrated [8] that bimetallic systems favor a decrease in this energy barrier and activate oxygen via increased adsorption energy, which accounts for the increase in the CO conversion.

In conclusion, the results of our catalytic experiments have showed that the heterogeneous FePt/BN system represents a new and promising catalyst for the reaction of carbon monoxide oxidation. Using XRD and XPS data, it was established that the stage of thermal activation not only increases the average size of catalytically active nanoparticles, but also leads to ordering of their structure, which improves the functional properties of catalysts.

FUNDING

This work was supported in part by the Russian Science Foundation, project no. 20-79-10286.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Y. Chen, J. Cai, P. Li, G. Zhao, G. Wang, Y. Jiang, J. Chen, S. X. Dou, H. Pan, and W. Sun, *Nano Lett.* **20**, 6807 (2020). <https://doi.org/0.1021/acs.nanolett.0c02782>
2. L. Liu and A. Corma, *Chem. Rev.* **118**, 4981 (2018). <https://doi.org/10.1021/acs.chemrev.7b00776>
3. A. Verlee, T. Heugebaert, T. van der Meer, P. Kerchev, K. van Hecke, F. van Breusegem, and C. V. Stevens, *ACS Catal.* **9**, 7862 (2019). <https://doi.org/10.1021/acscatal.9b02275>
4. A. M. Kovalskii, A. T. Matveev, Z. I. Popov, I. N. Volkov, E. V. Sukhanova, A. A. Lytkina, A. B. Yaroslavl'tsev, A. S. Konopatsky, D. V. Leybo, A. V. Bondarev, I. V. Shchetinin, K. L. Firestein, D. V. Shtansky, and

- D. V. Golberg, Chem. Eng. J. **395**, 125109 (2020).
<https://doi.org/10.1016/j.cej.2020.125109>
5. W. D. Schneider and C. Laubschat, Phys. Rev. B **23**, 997 (1981).
<https://doi.org/10.1103/PhysRevB.23.997>
6. L. Chen and A. Yelon, J. Phys. Chem. C **116**, 6902 (2012).
<https://doi.org/10.1021/jp301372j>
7. R. Sandström, E. Gracia-Espino, A. Annamalai, P. O. Persson, I. Persson, J. Ekspong, H. R. Barzegar, and T. Wågberg, Energy Mater. **3**, 9785 (2020).
<https://doi.org/10.1021/acsaem.0c01368>
8. M. A. Dar and S. Krishnamurty, ACS Omega **4**, 12687 (2019).
<https://doi.org/10.1021/acsomega.9b01581>

Translated by P. Pozdeev