

STRUCTURE AND PROPERTIES OF NANOSCALE AND MESOSCOPIC MATERIALS

PACS numbers: 82.20.-w, 82.30.-b, 82.30.Hk, 82.45.Jn, 82.65.+r

Graphite Nanoplatelets Modified with Bimetallic Ni–Fe Particles for Catalysis Purposes

A. G. Dyachenko, O. V. Ishchenko, L. Yu. Matzui, V. E. Diyuk,
A. V. Vakalyuk, A. V. Yatsymyrskiy, O. A. Syvolozhskiy,
O. S. Yakovenko, and O. V. Mischanchuk*

*Taras Shevchenko National University of Kyiv,
60 Volodymyrska Str.,
UA-01033 Kyiv, Ukraine*

**O. O. Chuiko Institute of Surface Chemistry, N.A.S. of Ukraine,
17 General Naumov Str.,
UA-03164 Kyiv, Ukraine*

The structure and surface morphology of graphite nanoplatelets (GNPs) modified by bimetallic Ni–Fe phase with 80% mass. Ni and 20% mass. Fe is investigated by the methods of scanning electron microscopy and X-ray analysis. The bimetallic active phase is applied onto GNPs surface with impregnation method using nitrate solutions of metals. The prepared Ni₈₀Fe₂₀/GNPs composite demonstrated high catalytic performance in the reaction of CO₂ methanation. At the temperature range of 350–450°C, it exhibited a high efficiency of CO₂ conversion compared to bulk Ni₈₀Fe₂₀. The thermoprogrammed desorption study of the surface condition of the Ni₈₀Fe₂₀/GNPs composite after exposition in the catalytic process showed that H₂O ($m/z = 18$), CO ($m/z = 28$) and CO₂ ($m/z = 44$) particles are desorbed from the surface.

Key words: graphite nanoplatelets, CO₂ methanation, bimetallic particles, supported catalysts.

Методами сканувальної електронної мікроскопії та рентгенофазового ана-

Corresponding author: Alla Grygorivna Dyachenko
E-mail: dyachenko.alla@yahoo.com

Citation: A. G. Dyachenko, O. V. Ishchenko, L. Yu. Matzui, V. E. Diyuk,
A. V. Vakalyuk, A. V. Yatsymyrskiy, O. A. Syvolozhskiy, O. S. Yakovenko, and
O. V. Mischanchuk, Graphite Nanoplatelets Modified with Bimetallic Ni–Fe
Particles for Catalysis Purposes, *Metallofiz. Noveishie Tekhnol.*, **42**, No. 8: 1055–1063 (2020),
DOI: [10.15407/mfint.42.08.1055](https://doi.org/10.15407/mfint.42.08.1055).

лізу досліджено структуру та морфологію поверхні графітових нанопластинок (ГНП), модифікованих біметалічною Ni–Fe фазою, що містить 80% мас. Ni та 20% мас. Fe. Одержаний Ni₈₀Fe₂₀/ГНП композит проявив високу каталітичну активність у реакції метанування CO₂, що сприяє повній конверсії диоксиду карбону на метан у температурному інтервалі 350–450°C за атмосферного тиску. Дослідження стану поверхні композиту Ni₈₀Fe₂₀/ГНП методом температурно-програмованої десорбційної мас-спектрометрії після роботи у каталітичному процесі показало, що з його поверхні десорбуються частинки H₂O ($m/z = 18$), CO ($m/z = 28$) та CO₂ ($m/z = 44$).

Ключові слова: графітові нанопластинки, метанування CO₂, нанесений каталізатор.

(Received December 5, 2019)

1. INTRODUCTION

The actual aim in the material science is finding and creation functional materials for sustainable energy technologies: energy generation, storage, transformation and transfer of energy. One of the priority areas of research in modern science is study the properties of nanosized carbon materials such as graphene, nanotubes, fullerenes, graphite nanoplatelets. The usage of exclusive properties of carbon particles surface opens the way to the creation of carbon-based composite materials [1–5].

One of the ways for applications of such composite materials is heterogeneous catalysis. Thermally expanded graphite and carbon nanotubes are widely used to create supported catalysts for various catalytic processes: ammonia synthesis, CO oxidation [6–11] *etc.* One of the important processes of heterogeneous catalysis is the reaction of CO₂ methanation. It is interaction of carbon dioxide and hydrogen with methane formation. Among the wide variety of catalysts studied in this process the most attention is to Ni–Fe bulk and supported compositions [12–16]. Certainly, the nature of the support significantly affects to an interaction with the active metal, thereby determining the effect on the activity and selectivity of the catalysts in the CO₂ methanation process.

Oxides (Al₂O₃, SiO₂, TiO₂, CeO₂, ZrO₂) with high specific surface area traditionally are used as a support for creation high dispersion catalysts. Carbon nanotubes also could be applied as perspectives supports for obtaining active catalysts [17, 18]. In our opinion graphite nanoplatelets can be an alternative oxide supports for metal catalysts of the CO₂ methanation reaction, and therefore the purpose of this work is preparation and investigation the physicochemical properties of graphite nanoplatelets modified with bimetallic Ni–Fe nanoparticles for catalysis purposes.

2. EXPERIMENTAL

2.1. Samples Preparation

The graphite nanoplatelets are prepared by ultrasonic treatment of thermoexpanded graphite (TEG) dispersion in acetone. The treatment procedure is provided for 3 hours in the ultrasonic bath 'Baku-9050' with a maximum output power of 50 W and an ultrasound frequency of 40 kHz. Then the dispersed GNPs are dried at room temperature until complete evaporation of the dispersing liquid. The modification of GNPs with the metal phase is carried out by the method of impregnation with a concentrated solution of metal nitrates, followed by drying in a sand bath and reduction in a hydrogen-helium flow (50% vol. H₂ - 50% vol. He). The temperature of reduction is determined by the thermogravimetry (TG) method. As the result, the active mass of metals (80% wt. Ni and 20% wt. Fe) is supported to the GNPs surface. The amount of supported metals is 60% by weight of the mass of carrier.

2.2. Methods

Thermogravimetric analysis is used to study the process of reduction of the oxide phase of the catalysts and to determine the temperature dependence of the weight loss of the sample. This analysis allows determining the optimal conditions for the reduction of oxides to the metallic state. The catalyst samples are heated in a mixture of 50% vol. Ar + 50% vol. H₂ at a temperature range 30–600°C.

X-ray diffraction pattern of the sample is registered on the DRON-4-07 diffractometer with CoK_α radiation ($\lambda = 1.7902 \text{ \AA}$) with pyrolytic graphite monochromator. The data are collected in the angle range of 10–110° with the step of 0.05°.

The morphology of sample is determined by scanning electron microscopy (SEM) using Vega-3 Tescan Scanning Electron Microscope (SEM) equipped with Energy-dispersive X-ray (EDX) detector (Oxford INCA).

The surface state of Ni₈₀Fe₂₀/GNPs catalyst is studied after explorer in the process of CO₂ methanation by means of thermoprogrammed desorption mass spectrometry (TPD MS) method. Measurements are carried out on a quadrupole MX 7304A mass spectrometer, as a detector of particles desorbed from the surface of catalysts. The TPD MS measurements are performed between 30 and 800°C at a heating rate of 14°C/min.

2.3. Catalytic Performance

Catalytic activity of the sample is studied in 2% vol. CO₂ + 55% vol. H₂ gaseous mixture (balanced with He), at GSV = 100 ml/min and sample

mass of 1 g. The reactor with inner diameter of 8 mm contained a 1 mm glass tube with a thermocouple inside, put in the catalyst bed. The gaseous mixture is analyzed by gas chromatograph with a thermal conductivity detector (Shimadzu GC-2014, 1 m-length packed column, molecular sieves 5A).

3. RESULTS AND DISCUSSION

The ability of the catalyst to recover affects its effectiveness in the CO₂ methanation reaction. This parameter often depends on the formation of chemical compounds between the support and the catalyst, as well as on the physico-chemical properties of the support, such as dispersion, porosity. Since the process of reduction from the oxide form to the metallic state is one of the steps of catalyst synthesis, it is important to clearly define the temperature at which the metal phase is formed to avoid the thermal degradation of the catalyst [19].

Figure 1 presents the results of thermoprogrammed reduction of Ni₈₀Fe₂₀ sample supported to the surface of graphite nanoplatelets.

Analysis of the obtained data indicates the several loss mass extremes. In the temperature ranges of 30–200°C desorption of physisorbed water and decomposition of a leftover nitrate group are observed. The intense peak with a maximum at $T = 250^\circ\text{C}$ in the temperature range of 200–300°C corresponds to the process of reduction of the metal oxides. It can be claimed that before applying in the methanation process the catalyst precursor must be heated in a hydrogen stream at the temperature of 300°C, preventing sintering of the active sites of the catalyst surface.

CO₂ methanation reaction is investigated over the Ni₈₀Fe₂₀/GNPs

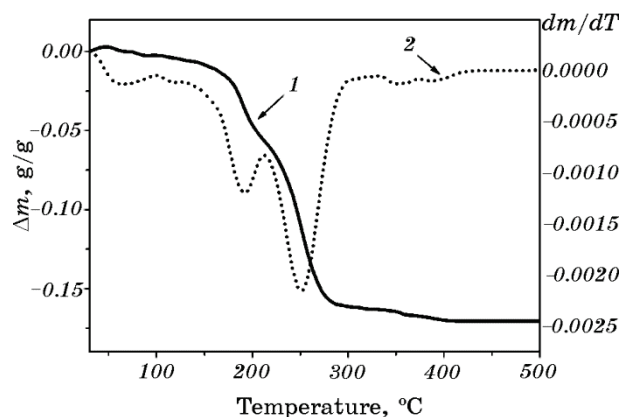


Fig. 1. Representative TG/DTG analysis of Ni₈₀Fe₂₀/GNPs in argon–hydrogen atmosphere. Weight loss: 1—TG, 2—DTG.

catalyst under the atmospheric pressure. Catalytic activity of $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ composite in the methanation process is presented in the Fig. 2 as amount (W, % vol.) of component in reaction mixture vs temperature.

It can be seen that CO_2 conversion started at 225°C with the simultaneous formation of two products: carbon monoxide and methane. Complete conversion of CO_2 occurs at 375°C and remains constant up to 450°C . A sharp increase of methane amount is observed since 275°C and achieved a maximum (100%) at 375°C . The maximum amount of CO (5% vol.) is registered at 300°C and with the temperature increase up to 375°C the production of carbon monoxide is stopped.

The thermodesorption spectra recorded from the catalyst surface $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ after exploring of them in the methanation reaction contains the profiles of H_2O ($m/z = 18$), CO ($m/z = 28$) and CO_2 ($m/z = 44$) (Fig. 3).

In the temperature range of $50\text{--}150^\circ\text{C}$, there are TD peaks of physisorbed H_2O with a temperature maximum (T_m) at 60°C , CO with $T_m = 70^\circ\text{C}$, and CO_2 with $T_m = 65, 115^\circ\text{C}$. Intense peaks in the temperature range from 200 to 350°C can be attributed to the process of desorption of chemically adsorbed H_2O ($T_m = 280^\circ\text{C}$), CO ($T_m = 275, 305^\circ\text{C}$) and CO_2 ($T_m = 285, 295^\circ\text{C}$) on the catalyst surface involved in the methanation reaction. The CO emission of about $500\text{--}550^\circ\text{C}$ is probably due to the decomposition of the phenolic groups at the graphite boundary defects. It should be noted that the TD profiles of all particles have a symmetrical shape. It indicates to desorption of species from the surface of the catalysts in the second order [20]. This means that CO, CO_2 and H_2O

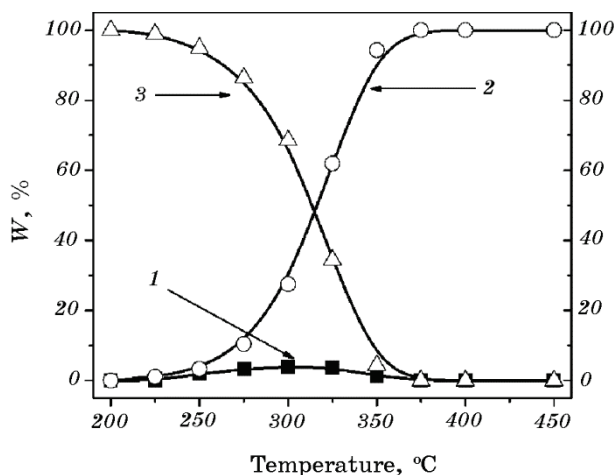


Fig. 2. Content of CO (1), CH_4 (2), and CO_2 (3) presented in the reaction mixture against the reactor temperature over $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$.

molecules are formed in the surface layer of the catalyst by recombination of the corresponding atoms similarly to bulk catalysts [12].

As well-known [21], the CO_2 methanation reaction can proceed by one of the mechanisms: associative or dissociative. The associative mechanism of methanation process involves the formation of CH_4 and H_2O through intermediates formyl compounds (CHO^* , CHHO^* etc). The dissociative mechanism passed through the CO_2 dissociation on the catalysts surface up to individual carbon and oxygen atoms with following formation of CH_4 and H_2O molecules respectively. The presented TPD MS results showed no intermediate compounds are formed on the surface of $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ catalyst. It can be involved that the reaction over $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ proceeded by a dissociative mechanism similar to the $\text{Ni}_{80}\text{Fe}_{20}$ bulk catalyst [12, 13].

The surface morphology of the carrier and graphite nanoplatelets with deposited metallic phase is presented in Fig. 4.

In the process of synthesis of graphite nanoplatelets, thermally expanded graphite loss of sponge structure and takes the form of randomly arranged plates (Fig. 4, *a, b*).

The SEM images of GNPs modified with $\text{Ni}_{80}\text{Fe}_{20}$ particles show that the metal phase is located on the surface of the carrier as a round shaped single particles with size of 40–60 nm, as well as in the agglomerated form, which are layered on graphite nanoplatelets and cover a large part of GNPs surface (Fig. 4, *c, d*). In this case significantly decreasing of catalysts dispersion could be expected. However, the specific surface of $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ composite ($S_{sp} = 20 \text{ m}^2/\text{g}$) is very close to the one of pristine support ($S_{sp} = 18,6 \text{ m}^2/\text{g}$). This fact indicates that

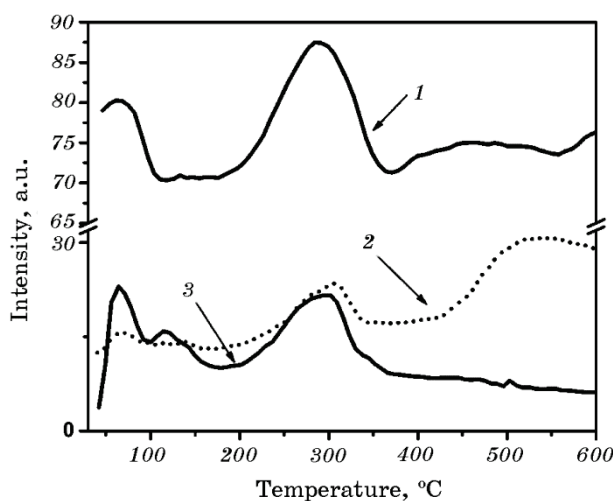


Fig. 3. TPD profile of 1— H_2O ($m/z = 18$), 2— CO ($m/z = 28$), 3— CO_2 ($m/z = 44$) species for $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ composite.

the structure of the support is not changed during the synthesis.

Figure 5 shows the XRD pattern of the synthesized Ni₈₀Fe₂₀/GNPs composite registered after catalytic test.

The sharp diffraction peak at $2\Theta = 30.92^\circ$ in the XRD spectrum (Fig. 5) corresponds to (002) reflection of graphite. The other most intense signals are located at $2\Theta = 52.25^\circ$, $2\Theta = 64.43^\circ$ and are identified as (101) and (004) reflections of graphite, respectively. The peaks at about 50.16° , 52.88° , and 81.75° can be respectively indexed to (111), (200) and (220) planes of the cubic (f.c.c.) crystalline phase with cell parameters of 3.54–3.56 Å what are intermediate between that for pure f.c.c. Ni (3.520 Å) and for pure f.c.c. Fe (3.568 Å) [12]. Thus, the analysis of XRD data confirms predomination of the graphite phase in the investigated nanopowder and existence of different f.c.c. phases Ni and/or solid Fe–Ni solutions. The calculated crystallite sizes for

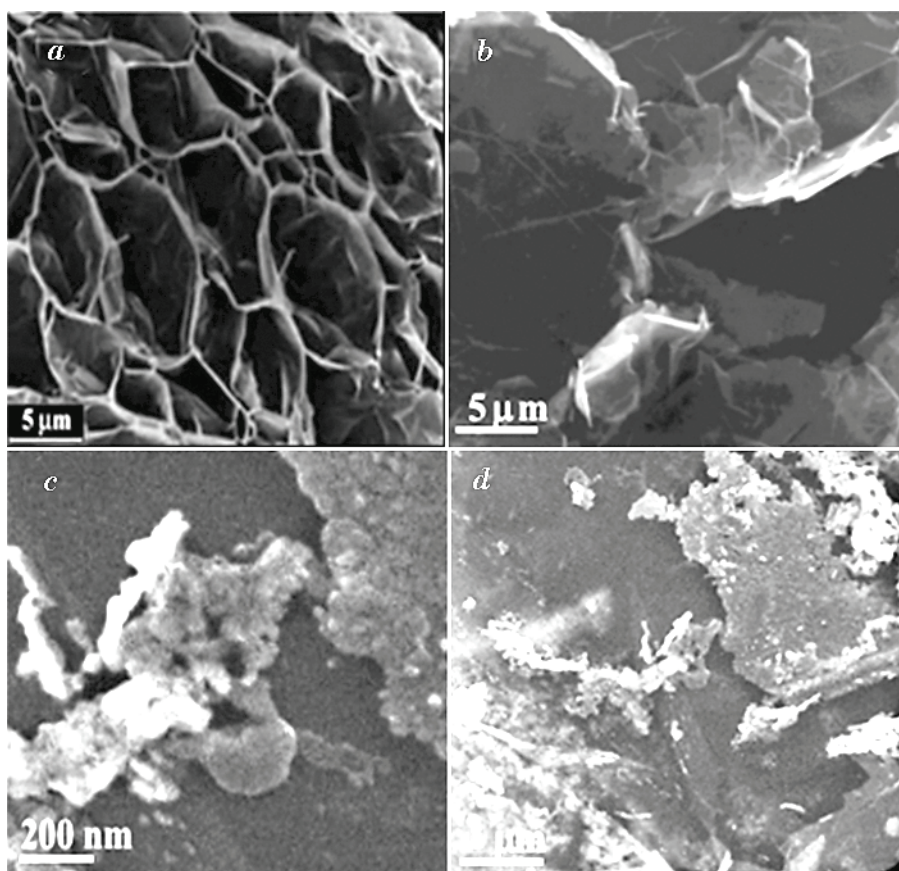


Fig. 4. SEM images of initial TEG (*a*), prepared GNPs (*b*), and GNPs modified with Ni₈₀Fe₂₀ (*c*, *d*).

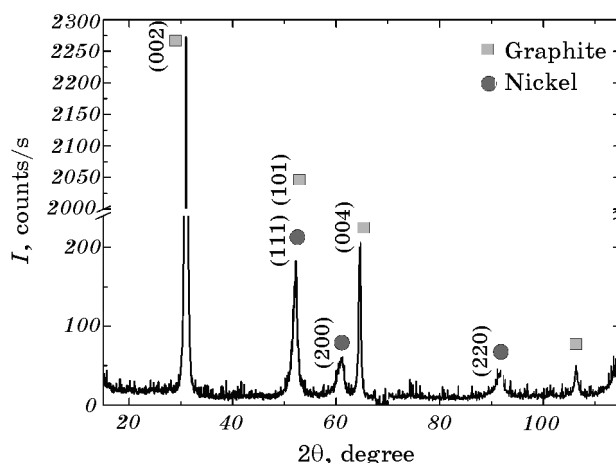


Fig. 5. XRD pattern of $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ composite.

graphite are 24 nm and 7 nm for nickel which is half the size of a bulk catalyst. The absence of an oxide phase in the diffraction pattern indicates the stabilization of the metal phase of the catalyst by the GNP matrix, different to a bulk catalyst of the same composition.

4. CONCLUSION

It can be concluded that the deposition of a metal phase consisting of 80% wt. Ni and 20% wt. Fe on the surface of graphite nanoplatelets allows to achieve complete conversion of CO_2 with the formation of methane at atmospheric pressure at the temperature of 375°C , compare to the bulk bimetallic catalyst of the same composition for which no 100% conversion of CO_2 to CH_4 is obtained. The state of the particles desorbed from the surface of the $\text{Ni}_{80}\text{Fe}_{20}/\text{GNPs}$ nanocomposite indicates that the process of CO_2 methanation carried out by the dissociative mechanism the dissociation of the carbon dioxide molecule into carbon and oxygen atoms and their subsequent interaction with hydrogen to form methane and water molecules. The metal phase consists of agglomerated particles located on the surface of the GNPs in a uniform layer.

REFERENCES

1. E. T. Thostenson, C. Li, and T.-W. Chou, *Compos. Sci. Technol.*, **65**: 491 (2005).
2. M. Alberts, K. Kalaitzidou, and S. Melkote, *Int. J. Mach. Tool Manuf.*, **49**: 966 (2009).
3. I. Sulym, A. Kubiak, K. Jankowska, D. Sternik, K. Terpilowski,

- Yu. Sementsov, M. Borysenko, A. Derylo-Marczewska, and T. Jesionowski, *Physicochem. Probl. Miner. Process.*, **55**: 1394 (2019).
4. A. K. Geim and K. S. Novoselov, *Nat. Mater.*, **6**: 183 (2007).
 5. A. Yu, P. Ramesh, M. E. Itkis, E. Bekyarova, and R. C. Haddon, *J. Phys. Chem. C*, **111**: 7565 (2007).
 6. E. V. Ishchenko, S. V. Gaidai, A. A. Byeda, T. M. Zakharova, A. G. Dyachenko, and E. V. Prilutskiy, *J. Superhard Mater.*, **39**: 336 (2017).
 7. Raquel P. Rocha, Olívia S.G.P. Soares, José L. Figueiredo, and Manuel Fernando R. Pereira, *J. Carbon Res.*, **2**: 17 (2016).
 8. V. K. Yatsimirsky, V. L. Budarin, V. Y. Diyuk, L. Y. Matzui, and M. I. Zacharenko, *Ads. Sci. Tech.*, **18**: 609 (2000).
 9. V. L. Budarin, V. Diyuk, L. Matzui, L. Vovchenko, T. Tsvetkova, and M. Zakharenko, *J. Therm. Anal. Calorim.*, **62**: 345 (2000).
 10. V. A. Zazhigalov, E. A. Diyuk, and V. V. Sidorchuk, *Kinetics and Catalysis*, **55**: 399 (2014).
 11. V. K. Yatsymyrs'kyi, G. G. Tsapyuk, O. V. Ishchenko, V. Ye. Diyuk, T. V. Kartashova, and L. M. Grishchenko, *J. Superhard Mater.*, **32**: 263 (2010).
 12. R. Meshkini-Far, A. Dyachenko, S. Gaidai, O. Bieda, M. Filonenko, and O. Ishchenko, *Acta Phys. Pol. A*, **133**: 1088 (2018).
 13. R. Meshkini Far, O. V. Ischenko, A.G. Dyachenko, O. Bieda, S. V. Gaidai, and V. V. Lisnyak, *Func. Mat. Lett.*, **11**: 1850057 (2018).
 14. P. A. Ussa Aldana, F. Ocampo, K. Kobl, B. Louis, F. Thibault-Starzyk, M. Daturi, P. Bazin, S. Thomas, and A. C. Roger, *Catal. Today*, **215**: 201 (2013).
 15. O. Linnik, N. Chorna, and N. Smirnova, *Nanoscale Res. Lett.*, **12**: 249 (2017).
 16. N. Chorna, N. Smirnova, V. Vorobets, G. Kolbasov, and O. Linnik, *Appl. Surf. Sci.*, **473**: 343 (2019).
 17. Patrizia Frontera, Anastasia Macario, Marco Ferraro, and PierLuigi Antonucci, *Catalysts*, **7**: 59 (2017).
 18. Wei Wang, Wei Chu, Ning Wang, Wen Yang, and Chengfa Jiang, *Int. J. Hydrogen Energy*, **41**: 967 (2016).
 19. V. L. Budarin, V. E. Diyuk, N. V. Zakharenko, B. A. Eichis, and V. K. Yatsimirskii, *Theor. Exp. Chem.*, **34**: 283 (1998).
 20. M. W. Roberts and C. S. McKee, *Chemistry of the Metal-Gas Interface* (UK: Clarendon Press: 1978).
 21. Bin Miao, Su Su Khine Ma, Xin Wang, Haibin Su, and Siew Hwa Chan, *Catal. Sci. Technol.*, **6**: 4048 (2016).