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Synthesis of supported nickel catalysts in dynamic vacuum using nickel formate as precursor

Yurii N. Zhitnev, Boris S. Lunin, Evgeniya A. Tveritinova* and Valery V. Lunin

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
E-mail: eatver@mail.ru

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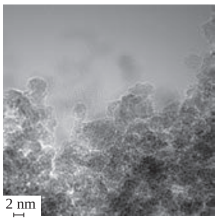
The innovative method of synthesis of supported nickel catalysts from nickel formate as a precursor is proposed. The conditions of dynamic vacuum allow one to reduce the temperature of nickel formate decomposition, to minimize the agglomeration of metal particles, and to exclude the high-temperature stage of hydrogen reduction. The derived catalysts demonstrate high catalytic activity and are easily regenerated.



Nickel-containing catalysts are widely used in chemical practices. Soluble salts of inorganic acids (chlorides, sulfates, and nitrates) commonly serve as precursors for synthesis of supported nickel catalysts. Those salts are deposited on the surface by impregnation, then come drying, degradation of the deposited salt at high temperatures and hydrogen reduction of nickel oxide thus obtained at even higher temperatures. The Cl^- and SO_4^{2-} ions may influence and even alter the surface properties. Nickel nitrate is used in conventional technology as a precursor due to its good solubility and commercial availability.[1–11] However, nitrogen oxides forming due to degradation of nickel nitrate in the air atmosphere are not only environmentally adverse products, but can also interact with surface functional groups of the support unless removed completely. The synthesis of Ni/SiO_2 catalyst from nickel nitrate was described stage by stage.[8] Both NiO nanosized particles and formation of agglomerates as the impregnated salt passed through the degradation in the air stage were observed. The latter was attributed to the impact of nickel nitrate degradation products, *viz*., O_2 and NO_x. It was found that, during the synthesis of Ni/SiO_2 catalyst from nickel nitrate, hydrogen reduction of NiO at 300 °C could also impair the catalyst activity due to a strong interaction of Ni with SiO_2 surface.[1] Nickel salts of organic acids are more suitable precursors as their degradation products are safer to the environment. The solubility of those salts was the only limitation to their choice. Nickel acetates and nickel formates are quite well-soluble; however, the thermal degradation of the former affords free nickel, nickel oxide and a few more by-products.[12–17] Coating of Ni particles on the surface of CdS nanocrystals was conducted by thermal decomposition of nickel acetylacetonate.[18]

Nickel formate (NF) stands out among the above nickels precursors because it yields free nickel and gaseous products (CO_2, CO and H_2O) upon degradation in the absence of air, while no nickel oxide is produced.[19] Sizes and structures of Ni particles formed depended on heating rate and pyrolysis temperature.[20] Increase in pyrolysis temperature enhanced aggregation of Ni particles, while raised heating rate resulted in the formation of particles with smaller size. Preparation of catalysts under static conditions and in the presence of air inevitably involved secondary processes with unwanted products, which had an adverse effect on the very course of the synthesis. Thus, the effect of dynamic vacuum and subsequent removal of gaseous products of NF pyrolysis on the degradation temperature of the latter and catalytic properties of nickel catalysts is of interest.

The aim of this work was to elaborate the synthesis of nickel catalysts from NF and to conduct the pyrolysis of impregnated NF in dynamic vacuum.† This method of preparing catalysts excluded the high-temperature stage at which NiO particles formed due to degradation of NF in air were reduced by hydrogen. A carbon material, detonation nanodiamond (ND), was used as a support. The choice of this support was due to its high specific surface area (284 $m^2\ g^{-1}$) and the presence of functional groups that acted as adsorption centers in catalysis. The standard method of saturating of the support with the water solution of nickel formate was used. In the absence of oxygen, NF degradation follows the equation:[19] $Ni(HCOO)_2 \rightarrow Ni + CO_2 + H_2O + CO$.

The TEM image of 5% Ni/ND catalyst is shown in Figure 1(*a*). The catalyst is a series of clusters composed of diamond structure carbon nanoparticles (sp^3 hybridization). The sizes of Ni particles apparently do not exceed 5 nm. The nickel is distributed over the

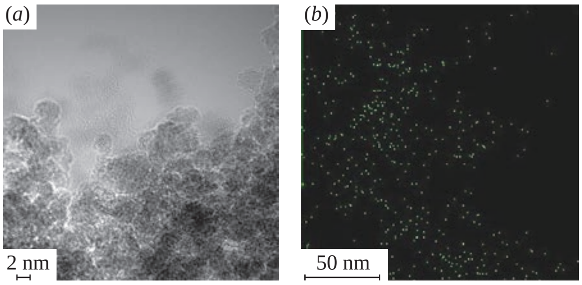


Figure 1 (*a*) TEM image of Ni/ND catalyst; (*b*) distribution of Ni particles over the surface of a nanodiamond.

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† NF concentration and minimum amount of the impregnation solution were calculated based on the targeted Ni-percentage in the prepared catalysts. After drying in air atmosphere, the samples were placed inside the cell of a vacuum chamber with thermocouple vacuum gauge, the air was pumped from the chamber until the residual pressure inside the chamber reached 5 Pa. The samples were heated up to 255 °C at the continuously pumping. The heating rate was 30 K min^{-1}. Duration of thermal vacuum treatment depended on mass of NF in the sample of catalyst. To prepare 10 g of catalyst containing 5% Ni, this time was ~90 s. Completion of decomposition of NF was monitored using a vacuum gauge.

surface quite evenly [Figure 1(*b*)]. At the same time, a conventional nickel catalyst was obtained *via* saturating the support by nickel nitrate solution with subsequent decomposition in the air atmosphere and reduction in the hydrogen flow at 300 °C.

The catalytic properties of the obtained catalysts were investigated by a pulse microcatalytic method.[21] A catalyst sample was loaded into a quartz reactor (15 cm long and 0.5 cm in diameter). The reactor was then placed inside a metal core shroud heated by a controlled temperature furnace. We compared catalytic activities of nickel catalyst samples obtained by conventional method from nickel nitrate precursor and those obtained from NF in dynamic vacuum during the 1,2-dichloroethane (DCE) dechlorination. The DCE (3.3×10^{-2} mmol) vapor was entered in a catalytic reactor with the sample of catalyst (0.07 g) by means of syringe. The products were entered using gas-carrier (nitrogen) into a chromatograph for analysis. Ethylene was the basic reaction product for both catalytic samples. The negligible amount of acetylene (< 1%) indicated that the contribution of the dehydrochlorination reaction was insignificant. Catalytic activity observed was equally high in all fresh samples; however, complete activity renewal was only observed in the catalysts obtained in dynamic vacuum. Figure 2 shows the temperature dependence of DCE conversion over hydrogen-regenerated catalysts containing 5% of Ni and prepared *via* one of two ways: either degradation of impregnated NF in dynamic vacuum (Catalyst 1) or the conventional method of degradation of impregnated nickel nitrate in the air atmosphere, followed by NiO reduction stage at 300 °C (Catalyst 2). Hydrogen treatment at 300 °C completely restored the activity of Catalyst 1 and only partially that of Catalyst 2. While fresh Catalyst 2 reached DCE conversion of 100% within the temperature range between 250 and 300 °C, the regenerated catalyst failed to reach this level even at 300 °C. The different nature of the precursor can be considered as the underlying cause. First, degradation of NF does not release oxygen or any other gaseous products contributing to agglomeration of the metallic phase in the catalyst. Second, the synthesis method, involving removal of degradation products of impregnated precursor salt, prevents interaction between degradation products and surface groups of the support, which means that the support retains its original nature. It is fair to assume that differences between catalytic activities of hydrogen-regenerated nickel catalysts may be attributed to difference between their regeneration mechanisms. In turn, the latter is caused by both methods of catalyst preparation and the various chemical nature of their precursors.

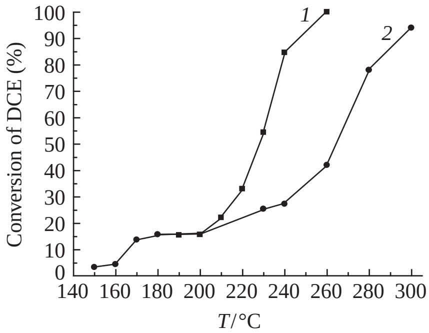

Figure 2 DCE conversion *vs*. temperature over hydrogen-regenerated catalysts containing 5% Ni at 300 °C: (*1*) Catalyst 1 and (*2*) Catalyst 2.

Thus, an innovative method was proposed for synthesis of supported nickel catalysts from nickel formate as precursor in dynamic vacuum. The advantages of the method are as follows: (1) the pyrolysis temperature of impregnated salt NF decreases under the conditions of dynamic vacuum, which inhibits agglomeration of metallic particles; (2) the high-temperature stage of hydrogen reduction of nickel oxide is excluded, as pyrolysis of NF in an anoxic environment leads to formation of metallic Ni only; and (3) catalysts obtained in this way have high catalytic activity. As distinct from catalysts prepared from nickel nitrate by conventional method, hydrogen regeneration of spent catalysts obtained by the method described above completely restores their catalytic activity.

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The morphology of nickel catalysts, their shapes, and sizes were studied by a JEOL SEM6390 LA scanning electron microscope (SEM) and a JEOL JEM-2100 F/CS ultrahigh resolution transmission electron microscope (TEM). The elemental compositions of the catalysts prepared and distribution of nickel over the surface were established by luminescence-based imaging. A DRON-4 diffractometer fitted with a CuKα emitter was used for X-ray phase analysis of the catalysts. An ASAP 2010 V2.00 unit was used to find the specific surface area after vacuum heating at the pressure ~10^{-5} Pa and at T = 120 °C from low-temperature nitrogen absorption by the BET method with a 1 m^2 g^{-1} accuracy. The differential thermal analysis (DTA) of the precursor was accompanied with vacuum pumping down to a residual pressure value of 350 Pa and conducted by a NETZSCH STA 449C thermal analyzer. It was found that the NF degradation temperature was reduced by 20 °C, while pyrolysis accompanied with vacuum pumping down to 5 Pa reduced it by ~40–45 °C.