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Water as a cosolvent – Effective tool to avoid phase separation in bimetallic Ni-Cu catalysts obtained via supercritical antisolvent approach

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ABSTRACT

A series of Ni-Cu metal catalysts were synthesized using supercritical antisolvent (SAS) approach under conditions of controlled water content in the initial solution of precursors. It is shown that low content of water in methanol (up to 9 vol.%) helps to adjust the structure, texture and morphology of the obtained materials. The water additives promote the formation of carbonate phase that during further decomposition and reduction steps allows obtaining the solid $Ni_{1-x}Cu_x$ solution without phase separation. In particular the addition of 7 and more vol.% of water leads to the complete introduction of Cu into the Ni crystal lattice without formation of separate enriched phases of Ni or Cu.

1. Introduction

Heterogeneous catalysts based on the nanosized Ni-Cu bimetal particles are used in a great number of chemical processes: fast oil pyrolysis [1], steam hydrodeoxygenation [2], decomposition of methane [3,4], synthesis of carbon nanofibers [5], catalytic hydrodechlorination [6], CO_2-reforming of methane [7], etc. Introduction of a small amount of copper into the nickel particles results in noticeable changes in their structure and physicochemical properties. The heterogeneous catalysts based on bimetal Ni-Cu containing particles demonstrate a higher activity and stability, leading to the increase in selectivity of the target process. Thus, more than 40 years ago it was shown that the catalytic activity of Ni-Cu solid solution nanoparticles in the reaction of dehydration of, for example, cyclohexane is higher than the activity of the metal nanosized particles of Ni [8]. Later it was demonstrated that the introduction of copper into the nickel particles prevents methanation during upgrading bio-fuels production [9], and introduction of 3 wt.% of Ni into Cu leads to a significant growth in activity of the catalysts of glycerin steam hydrogenolysis [10]. In the reaction of partial methane oxidation the introduction of copper in the nickel particles hinders the coke formation [11] and in the reaction of methane decomposition copper prevents sintering of the active phase [12]. Increase in the Cu content in the Ni-Cu system allows decreasing the temperature of reduction of bimetal particles [13,14].

The mixed Ni-Cu catalysts are often subject to phase separation into formation Ni- or Cu-rich solid solutions under synthesis or operating conditions, for example, during synthesis of nitrogen-containing carbon nanofibers or during the reaction of hydrodeoxigenation of anisole [14,15]. In both cases the active phase of the catalyst is the Ni-rich solid solution $Ni_{1-x}Cu_x$ with $x < 0.5$, whereas with $x > 0.5$ this system does not show any significant activity in both reactions. Thus, the development of the methods of reproducible synthesis of nanosized bimetal particles based on solid solution $Ni_{1-x}Cu_x$ with the desired structure and morphology without the phase separation is a relevant challenge.

Today the methods for synthesis of functional materials with the use of supercritical (SC) media are being actively developed [16–23]. One of the promising approaches to the synthesis of heterogeneous catalysts is based on the precipitation of solid phase in the medium of supercritical anti-solvent (for instance, SC CO_2), which is known as SAS method (Supercritical Anti-Solvent) [24]. This method is used for production of pharmaceuticals [25], polymers [26], dyes [27], polymer coatings [28], explosives [29], etc.

SAS method is distinctive for the fast formation of supersaturated solution of precursors, which occurs as they are precipitated in the medium of supercritical fluid. This method allows ones to produce nanosized heterogeneous catalysts without nitrates as precursors. The supercritical CO_2 as a reaction media also excludes the formation of water wastes that meets the basic principles of green chemistry [30]. Under supercritical conditions the formation of well-crystallized particles is difficult, which often results in the deposition of X-ray amorphous powder [31]. In the case of multicomponent systems as several precursors are being precipitated simultaneously, the components mix more homogeneously. Thus, in [32–34] the mixed Cu-, Mn-oxide catalysts of low-temperature oxidation of CO with hopcalite phase without

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other polymorphs were synthesized, whereas the traditional synthesis method leads to the phase separation into Mn_2O_3 and CuO phases [35].

Similar approaches were used for synthesis of the supports of the heterogeneous catalysts. In particular, it was shown that CeO_2 and TiO_2 obtained by SAS can be used as the supports for efficient Au-containing catalysts of the low-temperature oxidation of CO [36] and Au-Pd-catalysts of oxidation of benzalcohol [37]. The distinction of the obtained catalysts is the homogeneous application of the noble metals on the support, which, in the opinion of the authors, happens due to the defective nature of the obtained oxides.

In work [38] it is first proposed to use the SAS method for the synthesis of multicomponent metal catalysts. We proposed a novel approach, when introduction of SiO_2 sol into the solution in the course of the following dispersion by SAS results in a high dispersion of metal particles. The bimetal Ni-Cu-containing catalysts were used to show that silica addition (≥30 wt.%) prevents the sintering of metal particles and increases the dispersion, specific surface area, and accessibility of Ni-Cu solid solution particles. The suggested approach allowed us to stabilize a high amount of metal nanoparticles (up to 70 wt.%) with < 10 nm in size.

The structure and properties of the dispersed systems obtained by SAS depend on a high number of parameters of synthesis, which are hard to control. As a result, the researchers often face the fact that even insignificant changes in the conditions of dispersion process (pressure, temperature, etc.) or in the solution composition (addition of surfactants or co-solvents) can lead to dramatic changes in the properties of the obtained dispersed systems. Thus, in [33,39] the authors showed that addition of 5 vol.% of water as co-solvent leads to significant changes in the properties of the oxide Cu-, Mn-containing and Co-containing systems. At the same time there are no published examples where water was used as tool to control phase composition of not oxide but bimetal systems.

The approach suggested here based on the water addition allowed us for the first time to demonstrate, using Ni-Cu bimetallic system as an example, that SAS can be used for the preparation of a stable solid bimetallic solution without phase separation. In this work we studied in detail the influence of water as co-solvent in the initial solution of precursors on the phase composition and morphology of Ni-, Cu-containing metal systems obtained by the SAS approach. It is shown that a low content of water in methanol (up to 9 vol.%) helps to regulate the structure, texture and morphology of the obtained materials. The addition of 7 vol.% of water leads to the formation of the mixed oxide $Ni_{1-x}Cu_xO$ in the course of calcination, and its reduction provides a stable solid solution $Ni_{1-x}Cu_x$ without phase separation.

2. Experimental

2.1. Materials

In our study, we used nickel acetate ($Ni(OAc)_2*4H_2O$, 99%, extra), copper acetate ($Cu(OAc)_2*H_2O$, ACS reagent) from Acros Organics Company, and methanol (J.T. Barker, HPLC Gradient Grade) as a solvent. CO_2 (Promgazservis, Russia, 99.8% purity) was used as the antisolvent. Distilled water was used as an addition to the solvent. All substances were used without further purification.

2.2. Ni-Cu- systems synthesis

The synthesis of Ni-Cu-containing systems was performed using a specially designed SAS-50 (Thar Technologies Co., USA). The liquid CO_2 was input via preheater (5 Fig. 1) by a high-pressure pump (4 Fig. 1) into a precipitation vessel (9 Fig. 1). After reaching temperature, pressure and CO_2 flow required for the certain experiment a pure solvent (about 10 ml of methanol) was passed through a nozzle (8 Fig. 1) by a high-pressure pump (7 Fig. 1) into the precipitation vessel (9 Fig. 1) followed by the injection of the solution of Ni, Cu acetates in methanol. Due to the very fast diffusion of SC−CO_2 into the methanol, the solvent power of the methanol-CO_2 system was dropped fast and the precipitation of Ni, Cu acetates occurred on metal filter (11 Fig. 1). Afterwards the methanol-CO_2 mixture was transferred into a separator (14 Fig. 1), where the pressure was decreased to separate gas and liquid. The pressure was controlled by an automatic back-pressure regulator (13 Fig. 1). After the precipitation pure CO_2 was passed through the powder for 20 min to remove residual solvent. The apparatus used in our work allowed us to obtain ~2 g of acetates during one run that implies the mass content of the metal particles in the sample after annealing procedure was around 0.5 g.

Experimental parameters: CO_2 flow 80 g/min, solution flow 2 ml/min, temperature 40°C, nozzle 0.004” (0.1016 mm), pressure 150 bar. The $Ni(OAc)_2*4H_2O$ and $Cu(OAc)_2*H_2O$ concentrations were 13.0 mg/ml and 2.6 mg/ml, respectively.

Different amount of distilled water was added to the methanol to obtain the samples with different water concentration in the system. The obtained species were designated as $Ni_{79}Cu_{21}W\_x$, where x is the volume water percent in the solution. We chose this composition because it is close enough to the optimal Ni/Cu ratio observed in highly active catalysts for hydrodeoxygenation reaction which do not display the phase separation phenomenon [14]. The samples obtained after the SAS dispersion procedure were calcined at 300 °C for 3 h with ramp rate of 3 °C/min in static air to get the oxide phase. Reduction was performed in H_2 atmosphere at 350 °C for 3 h with ramp rate of 3 °C/min and the flow rate of H_2 60 ml/min.

2.3. Ni-Cu characterization

Powder XRD patterns were obtained using a Bruker D8 Advance diffractometer (Cu K_α radiation, $\lambda = 0.15418$ nm) equipped with a LynxEye position-sensitive detector. Measurements were performed in the 2θ range of 10° − 85° with a step of 0.05° and a collection time of 3 s. The average sizes of the coherently scattering domain (CSD) D_{XRD} were calculated by the line broadening analysis according to the Scherrer equation. The ICDD PDF-2 database (Powder Diffraction File database PDF-2, International Centre for Diffraction Data, USA, 2009) was used for phase identification. Rietveld refinement was performed using TOPAS software (TOPAS 2009 Bruker AXS, 4.2 edn, 1999).

SEM images were obtained using a JSM-6460 LV (Jeol, Japan) microscope to study the morphology of solids with a magnification from 8 x to 300 000x. The samples were fixed on the object table, which was able to move in three mutually orthogonal directions, with allowable slope of the sample to the electron-optical axis up to 90° and rotation around the axis from 0 to 360°. TEM studies were conducted using a JEM-2010 electron microscope (Jeol, Japan) with 1.4 Å lattice resolution at an accelerating potential of 200 kV.

The specific surface areas of the samples (S_{BET}) were determined by the BET method from Ar adsorption isotherm data obtained with a Sorbi N.4.1 apparatus (META, Russia). The samples were pre-calcined at T = 250°C.

The FTIR spectroscopic analysis was done using Bruker Vertex 70 v spectrometer equipped with a diamond ATR accessory (Specac Ltd., UK) and a DLaTGS detector. A total of 100 scans were taken for each sample recorded from 4000 to 370 cm^{-1} at a resolution of 4 cm^{-1} and the spectra were transformed by the ATR correction function of the OPUS software using a refractive index (n = 1.5).

3. Results and discussion

Fig. 2 shows SEM microphotographs of the samples obtained after dispersion by SAS with different water content in the solution for dispersion. It is seen that the samples $Ni_{79}Cu_{21}W\_0$ (see Fig. 2(a)) and $Ni_{79}Cu_{21}W\_3$ (see Fig. 2 (b)) obtained, respectively, from waterless solution or solution containing 3 vol.% H_2O have similar structure. The spherical particles with size of ≤400 nm form aggregates with a