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Effects of composition and production route on structure and catalytic activity for ammonia decomposition reaction of ternary Ni–Mo nitride catalysts

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ABSTRACT

Ternary Ni–Mo–N systems with high (up to 82 wt. %) content of Ni₂Mo₃N phase were produced by means of hydrogen reduction of different complex metal containing precursors. The precursors were obtained by two production routes, viz. evaporation and coprecipitation, with using of different initial Ni-containing salts. The samples were characterized by x-ray diffraction analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, low-temperature nitrogen adsorption, evolved gas analysis by mass spectrometry. Catalytic activity of ternary Ni–Mo nitride catalysts for ammonia decomposition reaction at atmospheric pressure and different temperatures was determined. It was established that the composition of the precursor and its production route notably influenced the relative yield of the nitride phase and specific surface area of the products. The ammonia conversion vs. temperature plot was similar for nitride catalysts with onset at 400 °C and full conversion at 650 °C. It differed only at moderate temperatures in the range from 500 °C to 600 °C with the highest conversion rate for the sample obtained by evaporation route with using of nickel acetate as precursor. It was shown that the relative catalytic activity of all obtained nitride samples were substantially higher than the activity of iron containing catalyst used as the reference material.

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Introduction

Ternary Ni–Mo nitrides have attracted attention of scientists due to their catalytic properties in different reactions such as

ammonia synthesis [1,2], hydrodesulphurization and hydrodenitrogenation [3], oil hydrotreating [4] and others. The usual routes for synthesis of Ni–Mo nitride catalysts used by various research groups were ammonolysis of metal oxide precursors by means of heat treatment under NH₃ atmosphere [1,5,6] or

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decomposition of organometallic nitrogen containing complexes under inert gas atmosphere [7,8]. The nitration of oxide precursor requires calcination step in order to transform metal containing salts into mixed oxide as well as long heat treatment at high temperature in a flow of corrosive ammonia gas. This route results in high energy consumption during production process and implication of corrosion resistant equipment. The utilization of organometallic complexes leads to the contamination of the product by carbon which negatively affects catalytic activity. Wang et al. suggested method which allows to avoid these disadvantages [9]. The key point of the method is the utilization of NH_4^+ contained in the inorganic salt as the N source for Ni–Mo nitride. The reduction of precursor is performed under hydrogen atmosphere. However the parameters of the process are not optimized and there is no information about influence of Ni containing salt and precursor production method on final product properties.

The choice of the precursor synthesis method largely determines the physicochemical and catalytic properties of final nitride product. Fan et al. investigated the influence of oxide precursor preparation method on activity of Ni–Mo nitride catalysts in propane ammoxidation reaction [10]. Among the methods considered by the authors were sol–gel, rotary evaporation-microwave drying, co-precipitation, impregnation and mechanical mixing. It was shown that the activity and selectivity of nitride catalysts strongly depend on preparation method being highest for co-precipitation method. The initial salt for precursor synthesis also influences properties of catalysts. It was shown [11] that in case of binary molybdenum nitride synthesis the different precursors (MoO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{MoO}_4$, H_xMoO_3) can lead to the production of either Mo_2N or MoN with various specific surface area values differing up to 13 times. Chouzier et al. studied the effect of initial salt composition on final Co–Mo samples properties [8]. The samples were produced by decomposition of hexamethylenetetramine (HMTA) complexes under inert atmosphere. It was established that the using of cobalt nitrate leads to the formation of bimetallic carbides, while acetylacetonates are more suitable for production of carbonitrides and nitrides.

The ammonia decomposition reaction is of great interest for production of high purity CO_x free hydrogen for fuel cells as well as for off-gas treatment [12]. The possible applications and catalysts studied for this reaction is widely covered in the review article by Schuth et al. [13]. The most active metallic catalyst found so far is ruthenium. However its limited availability and high price promotes the development of new catalytic systems.

The aim of this work was to elucidate the influence of initial salt composition and precursor obtaining route on composition, morphology and catalytic activity of ternary Ni–Mo nitride based catalysts for ammonia decomposition reaction.

Experimental

Catalyst preparation and characterization

In this work ternary Ni–Mo nitride catalysts were prepared according to the route described previously [9]. In

details, the mixture of Ni- $(\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$) and Mo-containing salts ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) with Ni/Mo molar ratio of 2/3 were dissolved in ammonia water (25 wt.% of NH_3 in H_2O). The solutions were transformed into solid with using of two different methods: (1) evaporation of solvent at 95 °C; (2) co-precipitation by addition of acetone with subsequent filtering of precipitate. After precipitation the solids were dried at 50 °C overnight. By means of these methods four precursors of catalysts differing in Ni-containing initial salt and precipitation method were obtained.

The reduction of the precursors was performed in a tube furnace under the flow of 700 ml/min of hydrogen. 4 g of sample was placed in a quartz tube and the temperature was linearly increased from 25 °C to 650 °C at 5 °C/min and held at that temperature until the relative humidity of the off-gases was less than 5% for ca. 1 h. To prevent self-ignition a cooling of samples under hydrogen flow to room temperature was followed by passivation under the flow of 1% O_2/N_2 gas mixture during 12 h.

Low-temperature N_2 physical adsorption isotherms were determined with using of Nova 1200e analyzer (Quantachrome Instruments, USA) at 77 K. Specific surface area was calculated by Brunauer–Emmett–Teller method.

X-ray diffraction (XRD) patterns were measured on Diffractometer (Scientific Instruments, Russia) equipped with position sensitive detector capable of simultaneous spectrum collection in the $\Delta 2\theta$ range of 58°. Spectra was measured at room temperature with $\text{Cr-K}\alpha$ radiation ($\lambda = 2.2909 \text{ \AA}$) in the 2θ range of 20–140° with 300 s exposition at each detector position. The phase content was estimated using reference intensity ratio method.

The Fourier transform infrared (FTIR) spectra of the precursors were obtained on Nicolet 380 FT-IR spectrometer (Thermo Scientific, USA) at room temperature. Spectral range was 4000–650 cm^{-1} .

The morphology of samples before and after catalytic tests was investigated on JEOL JSM-6610LV (Jeol Ltd., Japan) scanning electron microscope operating at 10 kV accelerating voltage. The elemental analysis was done by energy dispersive X-ray spectroscopy (EDXS) with INCA SDD X-MAX detector (Oxford Instruments, UK) installed on SEM. EDXS data for each sample were collected from several regions with area of ca. 160 $\mu\text{m} \times 160 \mu\text{m}$. The results obtained from various regions differed by ± 1 at. %. The Ni:Mo ratios presented in the paper are average values calculated from elemental composition of these regions.

Evolved gas analysis during reduction was performed for all precursors using ThermoStar mass-spectrometer (Pfeiffer Vacuum, Germany). In typical experiment approximately 100 mg of sample was placed in U-tube and linearly heated at 10 °C/min to 800 °C in a flow of 15 ml/min 30% H_2/Ar gas mixture. Mass spectra during the treatment was continuously scanned over the m/q range from 0 to 50 a.m.u with exposition of 200 ms/a.m.u. After the treatment qualitative analysis of evolved gases composition was performed using spectral library included in mass-spectrometer software. The results presented here are temperature dependencies of selected m/q ion currents: 18 for H_2O , 16 for NH_3 , 28 for N_2 or CO , 30 for N_2O and NO , and 44 for CO_2 .

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