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Influence of Mo on catalytic activity of Ni-based catalysts in hydrodeoxygenation of esters

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ABSTRACT

The effect of molybdenum on activity of Ni-based catalysts in the hydrodeoxygenation of fatty acid esters was studied. Catalysts Ni-Cu/Al_2O_3, Ni-Mo/Al_2O_3, Cu-Mo/Al_2O_3, Mo/Al_2O_3, and Ni-Cu-Mo/Al_2O_3 with different ratios Ni/Mo were prepared and tested in the hydrodeoxygenation of methyl palmitate and ethyl caprate at 300 °C, 1 MPa. It was found that an increase in the Mo content (from 0.0% to 6.9%) in the Ni-Cu-Mo/Al_2O_3 catalysts leads to an increase in the yield of normal alkanes. The catalysts were characterized by X-ray photoelectron spectroscopy (XPS), temperature programmed reduction and X-ray diffraction techniques. The XPS data showed that the increase in the conversion of fatty acid esters is related to changes in the ratio between different oxidation states of molybdenum (Mo^0, Mo^{4+}, and Mo^{6+}) on the surface of the Ni-Cu-Mo/Al_2O_3 catalysts.

1. Introduction

Rising demand for energy, environmental issues and depletion of oil reserves create the need to develop alternative methods of energy production from renewable sources, including biomass. The use of biofuels can help to cope with the growing energy consumption and to solve a number of environmental problems [1]. Although the use of vegetable oils as a fuel is still considered today [2], they have certain drawbacks that lead to problems in the long-term operation of internal combustion engines [3]. Analogous drawbacks, but to a lesser extent, are inherent to biodiesel, as well. The higher viscosity, cloud point, and the higher acid number of biodiesel limit its use in conventional internal combustion engines. Removing oxygen from fatty oxygenates (triglycerides of fatty acids, free fatty acids, and their esters) is an alternative route for obtaining higher quality components of motor fuels—hydrocarbons [4]. In production of biofuels, the hydrodeoxygenation (a reaction of oxygen removal from an organic substrate via hydrogenolysis) is one of the main reactions for hydrotreatment of fatty oxygenates. Linear alkanes C_{15}–C_{18} that are formed after the hydrotreatment undergo further hydroisomerization to yield either kerosene or diesel fractions, depending on conditions [5].

To date, lipids of vegetable origin are hydrodeoxygenated mainly in the presence of catalysts of two major types: sulfided catalysts for desulfurization of petroleum (Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3) and catalysts based on noble metals (Pd/C, Pt/Al_2O_3) [6–8]. For example, Pd/C catalysts were shown to be highly effective in the selective hydrodeoxygenation of ethyl stearate into alkanes [4]. The hydrodeoxygenation of methyl esters of fatty acids in the presence of a Pt/Al_2O_3 catalyst also leads to a high yield of alkanes [7]. In general, the catalysts based on noble metals are more active, but more expensive. Therefore, catalysts with the active component based on less expensive metals are of greater interest. For example, the hydrodeoxygenation of various compounds, including fatty esters of carboxylic acids, has been tested in the presence of conventional sulfided catalysts for the desulfurization: Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 [9]. In recent studies [10], the catalyst Ni-Mo/Al_2O_3 was tested in the hydrodeoxygenation of rapeseed oil and, as in the case with the catalysts Pd/C and Pt/Al_2O_3, the major reaction products were alkanes. However, activity of sulfided catalysts in the hydrodeoxygenation reaction of esters could be lower in the absence of sulfiding agent [11–13]; to maintain catalytic activity, addition of sulfiding agent is necessary [11].

In this regard, an urgent task today is to design stable unsulfided catalysts containing no noble metals and exhibiting high activity in the hydrodeoxygenation of lipids of vegetable origin. A possible solution to this problem is the development of catalysts based on Ni. Monometallic nickel catalysts are known to be active in the hydrodeoxygenation of vegetable oils [14], while catalysts

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based on Ni–Cu alloys exhibit activity in the hydrodeoxygenation of biodiesel [15]. The addition of copper also reduces the production of methane, which is an undesired by-product formed during the hydrodeoxygenation of biodiesel [15]. Besides, the addition of copper can reduce carbonization of the catalyst surface [16,17] and increase the catalyst stability against sintering of the active component [17]. Unfortunately, the addition of copper does not solve the problem of leaching of the active component of the catalyst [18], and unsulfided nickel catalysts have to be additionally modified to improve their stability and resistance to leaching. For example, nickel–molybdenum alloys are known to have higher chemical resistance to acids as compared with monometallic nickel catalysts [19,20].

Nowadays, the study of the influence of molybdenum, as modifying metal, on activity and selectivity of nickel-based catalysts in the reaction of hydrogenation of esters is of interest. An additional challenge was determination of the main correlations between the nature of the active component of catalysts and their catalytic properties. For this purpose, we prepared a series of Ni-Cu-Mo/Al_2O_3 catalysts with different molybdenum contents and studied their chemistry, structure, and catalytic performance.

2. Experimental

2.1. Materials

Ethyl caprate (Acros organics, 99+%) and methyl palmitate (Alfa Aesar, 97%) were used as received. Spherical particles of Al_2O_3 with a diameter of 1.5 mm were obtained from Sasol (Hamburg, Germany).

2.2. Catalysts preparation

Before the catalyst preparation, Al_2O_3 was calcined in air at 1000 °C.

Monometallic catalysts Ni/Al_2O_3, Mo/Al_2O_3 and Cu/Al_2O_3 were prepared by incipient wetness impregnation of calcined Al_2O_3 with an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Cu(NO_3)_2\cdot 3H_2O$, respectively. Bimetallic catalysts Ni-Cu/Al_2O_3, Cu-Mo/Al_2O_3, and Ni-Mo/Al_2O_3 were prepared by impregnation of Al_2O_3 with mixtures of aqueous solutions of $Ni(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ taken in corresponding pairs.

All the impregnated catalysts were dried for 5 h at 120 °C and then calcined in a muffle furnace for 6 h at 520 °C. If necessary, the impregnation procedure followed by drying and calcination was repeated.

Trimetallic catalysts Ni-Cu-Mo/Al_2O_3 were prepared by the additional impregnation of the Ni-Cu/Al_2O_3 catalyst with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, also followed by drying and calcination.

2.3. Catalysts characterization

The specific surface area of samples were determined with the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption isotherms measured at liquid nitrogen temperatures with an automatic volumetric adsorption unit ASAP 2400 (Micromeritics Instrument. Corp., USA).

Temperature programmed reduction (H_2-TPR) of the catalysts was studied in a flow of a mixture of H_2 (10%) and Ar (90%) at the flow rate of 40 mL/min. The weight of a catalyst sample was varied depending on the metal content (m_{met} = 50 mg). Samples were placed in a U-shaped quartz reactor and heated in the reducing atmosphere at a constant heating rate of 5 °C/min up to 700 °C. Changes in the concentration of hydrogen at the reactor outlet were measured using a thermal conductivity detector (TCD).

X-ray diffraction (XRD) of the fresh catalysts was studied *ex situ* with a diffractometer X'tra (Thermo, Switzerland) using monochromatic Cu Kα radiation (λ = 154.18 pm). The diffraction patterns were recorded in steps of 0.05° with a count time of 3 s in the 2θ range of 15–70°. Before *ex situ* XRD analysis all the samples were reduced in a hydrogen flow at 520 °C and then passivated with alcohol to prevent the interaction with air. The reduction of the catalysts was studied *in situ* using synchrotron radiation facilities at the Siberian Synchrotron and Terahertz Radiation Center (Novosibirsk, Russia). The experiments were performed using a diffractometer equipped with a high-temperature reactor chamber XRK-900 (Anton Paar, Austria). The sample was loaded into the reactor on an open holder, allowing hydrogen to pass through the sample volume. The chamber was mounted to the diffractometer so that the monochromatic synchrotron radiation beam was incident on the sample surface at an angle of approximately 15°. The *in situ* X-ray diffraction patterns of the catalyst were recorded in the range of 32–61°.

The chemical composition of the catalysts was studied by X-ray photoelectron spectroscopy (XPS) using a photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Germany) equipped with a hemispherical analyzer PHOIBOS-150, an X-ray monochromator FOCUS-500, and an X-ray source XR-50M with a double Al/Ag anode. The spectrometer was also equipped with a high-pressure cell (HPC) that allowed us the heating of samples in gas mixtures at pressures up to 5 atm. The XPS spectra were recorded using monochromatic Al Kα radiation ($h\nu$ = 1486.74 eV). The binding energy (E_b) of the photoemission peaks were corrected to the Ni2$p_{3/2}$ peak (E_b = 852.70 eV) of nickel in the metallic state, which was a component of the catalysts.

Before XPS analysis all the samples were reduced in a hydrogen flow at 520 °C and then passivated with alcohol to prevent the interaction with air. Then, the samples were re-reduced at 350 °C at hydrogen pressure of 0.1 MPa for 1 h directly in HPC.

2.4. Catalysts performance

The catalyst performance was tested in a steel fixed-bed reactor at 1 MPa, 300 °C. The feed rates of the carrier gas (Ar) and hydrogen were 15 and 5 L/h, respectively. A mixture of methyl palmitate and ethyl caprate was used as a substrate. The substrate feed rate U was 3 mL/h, the LHSV was 3 h^{-1}, the catalyst volume was V_{cat} = 1 cm^3. Before the experiments, catalysts (fraction 0.2/0.5 mm) were reduced in the reactor at 520 °C in a hydrogen flow at 0.1 MPa for 1 h. After that, the reactor was cooled to a desired temperature and the substrate was added to the feed. The liquid phase was sampled not rarer than once per hour.

2.5. Analysis of reaction products

The product composition was analyzed in the liquid phase using a GC–MS spectrometer Agilent Technologies 7000B equipped with a quartz capillary column HP-5ms (stationary phase: 5% phenyl + 95% dimethylpolysiloxane, length 30 m, inner diameter 0.25 mm). The quantitative analysis of the liquid products was carried out using a chromatograph GC Chromos 1000 equipped with a capillary column Zebron ZB-5 (stationary phase: 5% phenyl + 95% dimethylpolysiloxane, length 30 m, internal diameter 0.32 mm, phase thickness 0.25 μm). The gas phase (H_2, CO, CO_2, and CH_4) was analyzed with a chromatograph GC Chromos 1000 equipped with a flame ionization detector and TCD and with a column packed with silochrome and activated charcoal (length 3 m, inner diameter 2 mm).