



Stabilized Ni-based catalysts for bio-oil hydrotreatment: Reactivity studies using guaiacol



M.V. Bykova^{a,b,*}, D.Yu. Ermakov^a, S.A. Khromova^{a,b}, A.A. Smirnov^a,
M.Yu. Lebedev^a, V.A. Yakovlev^{a,c}

^a Borieskov Institute of Catalysis SB RAS, Pr. Akad. Lavrentieva, 5, Novosibirsk 630090, Russia

^b Novosibirsk State University, Pirogova Str. 2, 630090, Novosibirsk, Russia

^c UNICAT Ltd., Pr. Akad. Lavrentieva, 5, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:

Received 1 April 2013

Received in revised form 3 October 2013

Accepted 7 October 2013

Available online 1 November 2013

Keywords:

Bio-oil

Hydrotreatment

Hydrodeoxygenation

Guaiacol

Modified Ni-based catalyst

ABSTRACT

The development of catalysts possessing high activity and high stability in the catalytic hydrotreatment of pyrolysis oils (bio-oil) is of great interest. NiCu bimetallic catalytic systems are very attractive for use in hydrotreatment process due to their low price and high activity in hydrogenation, hydrodeoxygenation and hydrocracking reactions. In the present work P-/Mo-containing agents were used to modify bimetallic catalytic system NiCu/SiO₂-ZrO₂ to improve its mechanical strength and stability in acidic medium. The modified catalysts were tested in hydrodeoxygenation (HDO) of guaiacol—a well-known model compound of bio-oil. HDO process has been carried out in an autoclave at 320 °C, 17 MPa initial hydrogen pressure, reaction time 1 h. It was shown that phosphorus and molybdenum addition to the catalysts composition results in the decrease of guaiacol conversion and deoxygenation degree. The yield of undesirable gaseous reaction products (mainly methane) and coking of the catalyst were lower for the modified catalysts in contrast to the initial NiCu/SiO₂-ZrO₂ system. The catalysts treatment in glacial acetic acid at 118 °C showed that modification by P and Mo gives a significant improvement of catalysts stability in acidic medium (mass loss decreases from 53 wt.% to 1 wt.%). Also a significant improvement of bulk crushing strength has been observed for PMo-modified samples (from 0.5 MPa to 1.2 MPa).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Currently the problem of the limited fossil energy sources becomes more evident. Their rapid depletion is inevitable in future due to the constant growth of a human energy demand. Motor fuels production from plant biomass is a considerable alternative to fossil oils. Thermochemical treatment by pyrolysis is of great interest among the approaches used for the biomass conversion. The yield of a liquid pyrolysis products, so called bio-oil, can come up to 70–80 wt.% in special reaction conditions, when the elevated temperatures (450–550 °C) are combined with the extremely short residence time (< 1 s) under oxygen-free atmosphere [1,2]. The process being carried out at such conditions is called fast pyrolysis. However, thus obtained bio-oil is not suitable for the direct use as transport fuel due to the high water content and the presence of different oxygen-containing organic compounds in its composition (organic acids, aldehydes, ketons, sugars, aromatics, etc.) [3–5]. Because of the chemical complexity fast pyrolysis oils are corrosive, acidic (pH ≈ 2–3), and thermally and

chemically unstable [6]. Co-processing of bio-oil and conventional oil refinery products on the FCC units using traditional oil refinery equipment is of particular interest [7]. But before co-processing an upgrading of the crude bio-oil is required to reduce its polarity and increase its miscibility with non-polar petrochemicals. An attractive way for the improvement of the bio-oil quality is catalytic hydrotreatment (hydrodeoxygenation, HDO) [1,8–15]. Similarly to the hydrotreating of fossil oils (hydrodesulfurization) [16,17] HDO process is considered as an effective way for the selective oxygen removal from the biomass pyrolysis products. The main chemical reactions are hydrocracking, decarbonylation, decarboxylation, hydrodeoxygenation, cracking, and hydrogenation. However, the catalytic hydrotreatment of pyrolysis oils is far from the commercial scale in contrast to the conventional refining, and intensive research is required. The focus of this paper concerns the catalytic systems suitable for bio-oil hydrotreatment. The investigations in this field started in 1980's, and the first papers on the catalytic hydrotreatment of oxygen-containing feed were published [18,19]. The first catalytic systems used in HDO of bio-oil and its model compounds were conventional sulfided NiMo and CoMo alumina-supported desulfurization catalysts and noble metal based catalysts (Pt, Pd, Rh, Ru) [20]. These catalytic systems possessed high activity in target hydrodeoxygenation process, but some of

* Corresponding author. Tel.: +7 383 326 96 52; fax: +7 383 330 62 54.

E-mail address: bykova@catalysis.ru (M.V. Bykova).

Table 1
Catalysts composition (measured by ICP-OES) and texture characteristics (BET method) after the reduction at 0.1 MPa H₂, H₂ flow rate–200 cm³/min (the reduction temperature was selected according to the TPR analysis).

No.	T _{red} (°C)	Active component (wt.%)				Stabilizing component ZrO ₂ -SiO ₂ , wt.%	A _{BET} (m ² /g)	V _Σ (cm ³ /g)	<d> (Å)
		Ni	Cu	Mo	P				
1	400	52	5.6			12–27	188	0.19	41
2	500	48	5.2	8.8		11–25	115	0.12	42
3	500	48	5.1		4.9	11–25	139	0.17	47
4	500	42	4.5	10.1	4.7	9.7–22	135	0.16	46
5	500	39	4.2	9.7	7.1	8.9–20	113	0.15	53

their disadvantages were also revealed [20–23]. Conventional sulfided catalysts deactivated due to sulfur removal from the catalysts composition and oxidation of the active sulfide phase. Addition of sulfur-containing agents (H₂S, CS₂) to maintain catalyst activity resulted in products contamination with sulfur [24,25]. The main disadvantage of noble metal based catalysts is high cost that makes their use in hydroprocessing of bio-oils economically unprofitable. Thus, an important task is the development of the catalysts meeting all the necessary requirements for use in bio-oil hydrotreatment. They are the low cost, non-sulfided nature, high activity and stability to coking, stability in corrosive media (against leaching) at high temperatures and pressures, high thermal stability (e.g. against agglomeration) and ability for multiple regeneration by coke combustion. As an alternative for the sulfided catalysts and noble metal based catalysts mentioned above, non-sulfided systems based on transition metals (Ni, Fe, Co, Mo, etc.) were considered [8]: systems with the metallic state of the active component [26–29], transition metal oxides [8,27,30,31], transition metal phosphides [32–35] and amorphous boron-containing catalysts [36–39], etc. They catalyze hydrogenation and hydrodeoxygenation reactions and are cheaper than noble metal based ones.

Recent works have shown that Ni–Cu bimetallic supported catalysts are highly active in catalytic hydrotreatment of bio-oil and its model compounds [26,29]. In terms of activity in the target process these catalysts were comparable with the noble metal based systems and better than commercial sulfided hydrotreating catalysts [26]. The role of copper in these systems is to decrease the reduction temperature of nickel oxide species followed by the formation of Ni_xCu_{1-x} solid solution. Moreover Cu addition results in the decrease of undesirable products yield (mainly CH₄) during hydrotreatment of oxygen-containing compounds [26]. However, despite high activity of supported NiCu catalysts, they had a number of disadvantages: low stability in acidic medium (active component leaching), low thermal stability (active component particles agglomeration) and tendency to coking [29]. Thus, one of the prospective directions for further research is the development of new Ni-based catalysts possessing high activity and improved stability in hydrodeoxygenation of oxy-organic compounds including bio-oil. A possible way to improve catalysts is the use of modifying additives.

According to the data available from the literature [32,40–43], P-modified hydrotreating catalysts and catalysts based on transition metal phosphides were intensively studied in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of crude oil and certain sulfur- and nitrogen-containing compounds. The use of these catalysts in hydrodeoxygenation processes is much less reported [32–35]. According to [44], transition metal-rich phosphides have physical properties similar to those of ordinary metallic compounds like the carbides, nitrides, borides and silicides. They combine the properties of metals and ceramics, and thus are good conductors of heat and electricity, are hard and strong, and have high thermal and chemical stability. On the other hand according to [45], Ni–Mo alloys with the Mo content of 15 wt.% (in relation to nickel) possess high stability in acids. When Mo content is higher than 20 wt.% the

stability of these alloys to corrosion is particularly high. Therefore the aim of the present study was to investigate the effect of phosphorus and molybdenum as modifying additives on the stability and activity of Ni-based catalysts. The initial catalytic system used was sol–gel catalyst NiCu/SiO₂–ZrO₂. This catalyst was similar to NiCu/SiO₂ and NiCu/SiO₂–ZrO₂–La₂O₃ previously studied in HDO of guaiacol, and their high activity was reported in [46].

2. Experimental

2.1. Catalyst preparation

At the first stage catalytic system NiCu/SiO₂ was prepared using sol–gel method described elsewhere [47]. The appropriate amounts of commercial NiCO₃·mNi(OH)₂·nH₂O, CuCO₃·mCu(OH)₂ were mixed with required amount of aqueous ammonia solution (25% NH₃) in ball mill. Afterwards, the suspension was filtered out, dried in air at 120 °C for 12 h and calcined at 400 °C for 4 h. Thus obtained nickel–copper mixed oxide system was crushed and sieved (fraction 2–5 mm). After that the granules were impregnated by commercial ethyl silicate-32 (ES) comprising SiO₂ in amount of 32%, which was used as the silica precursor without any additional treatment. The desired NiCu/SiO₂ ratio was provided by diluting ES with ethyl alcohol. Samples were dried at room temperature, then at 120 °C for 12 h and calcined at 400 °C for 4 h. The granules of NiCu/SiO₂ catalyst thus prepared were impregnated by ZrO(NO₃)₂ salt solution of required concentration to improve catalyst mechanical strength and thermal stability [48]. Then the catalysts was dried at 120 °C for 12 h and calcined at 400 °C for 4 h. Thus obtained catalytic system was modified by molybdenum- and/or phosphorus-containing agents. The modification procedure was performed by impregnating of NiCu/SiO₂–ZrO₂ system with (NH₄)₆Mo₇O₂₄·4H₂O and/or H₃PO₄ aqueous solution of required concentration. After each impregnation stage the catalyst was dried at 120 °C for 12 h followed by the calcination at 500 °C (4 h). At the final stage the modified catalysts were reduced in a quartz reactor in a hydrogen flow. The reduction temperature was chosen according to the TPR analysis of the catalysts (see Section 3.1): 500 °C in the case of Mo- and P-modified systems, 400 °C–non-modified catalyst NiCu/SiO₂–ZrO₂. After 2 h of the reductive treatment the catalyst was cooled down in a hydrogen flow. Upon reaching room temperature hydrogen was switched to argon and the catalyst was passivated by ethanol and dried at the room temperature.

Table 1 presents the chemical composition (measured by ICP-OES) and texture characteristics (BET method) of catalysts used in the present study. The catalysts were characterized in their reduced form.

2.2. Catalytic hydrotreatment of guaiacol

The catalysts were tested in HDO of guaiacol on a high-pressure set up (Autoclave Engineers, USA) in a sealed 300 mL stainless steel batch reactor (EZE Seal type). Before the reaction, the catalysts (1 g, 0.05–0.1 mm fraction) were activated inside the reactor in a flow

Download English Version:

<https://daneshyari.com/en/article/54384>

Download Persian Version:

<https://daneshyari.com/article/54384>

[Daneshyari.com](https://daneshyari.com)