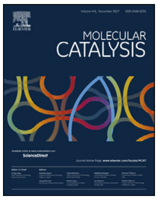
Molecular Catalysis 443 (2017) 253–261

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat



Research paper

Comparison of oxide, sulfide, carbide and nitride Ni-W catalysts supported USY-Al_2O_3 for ring opening of decalin

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ARTICLE INFO

Article history:
Received 28 June 2017
Received in revised form
21 September 2017
Accepted 4 October 2017
Available online 6 November 2017

Keywords:
Ni-W catalyst
Oxide
Sulfide
Carbide
Nitride
Deactivation
Decalin ring opening

ABSTRACT

The bimetallic Ni-W oxide catalyst supported on USY- Al_2O_3 has been prepared and converted into Ni-W sulfide, carbide and nitride catalysts. These four types of catalysts have been characterized by surface area measurements, pulsed CO chemisorption, thermogravimetric analysis, X-ray diffraction, temperature-programmed reduction and pyridine infrared spectroscopy. The initial decalin reaction activity of the catalysts decreases in the order of carbide catalyst > oxide catalyst > sulfide catalyst » nitride catalysts. The catalysts deactivation decreases in the order of: sulfide catalyst > carbide catalyst » nitride catalyst > oxide catalyst. The initial ring-opening activity decreases in the order of carbide catalyst > oxide catalyst $\sim$sulfide catalyst » nitride catalyst. The catalyst activity has relation with the metal sites, the amount of the strong Brönsted acid sites and the surface area on the catalyst. Besides these, the catalyst deactivation also has the close relation with the coke produced on the catalyst during the reaction.

1. Introduction

With increasingly strict regulations of the environment, the fuel with low sulfur and aromatics and high cetane number (CN) is much needed [1–3]. As technology advances, the reduction of sulfur and aromatics in fuel can be achieved by hydrotreatment and hydrocracking process [4]. Although the CN of fuel also can be improved with the reduction of sulfur and aromatics, the CN of naphthenes in fuel cannot be further increased because of the ring of naphthenes [5,6]. Especially for highly aromatic fractions, such as light cycle oil (LCO) from fluid catalytic cracking (FCC) [3]. Therefore, opening the ring of the naphthenes is necessary to improve the CN value of fuel [7].

Recently, some catalysts have been studied on ring opening of naphthenes including monofunctional acid catalyst [1,3,8–10], monofunctional metallic catalysts [3,6,11,12] and bifunctional catalysts [5,6,9,12–32]. It has been found that the ring opening of naphthenes mainly occurred on the Brönsted acid sites on the monofunctional acid catalysts. The strength of the Brönsted acid sites played a more important role than the density of the Brönsted acid sites [33,34]. The monofunctional acid catalysts showed some advantages such as easy recovery, high recyclability and low amount catalyst in heterogeneous phase [35,36]. The metal sites also played a crucial role on the monofunctional metal catalysts. In summary, at least three mechanisms have been put forward [5,37], including the metallocyclobutane mechanism, multiplet mechanism and the dicarbene mechanism.

Among all the catalysts studied in literatures, the noble bifunctional catalysts showed good potential for the ring opening of naphthenes [5,6,9,12–14,16–27,29,30] due to the high hydrogenation activity on the metal sites as well as the suitable acidy for isomerization provided by the Brönsted acid sites. But the noble bifunctional catalysts are easier sulfur poisoning [6,38,39].

In this respect, typical industry Ni-W/Al_2O_3 sulfide catalyst is an alternative for ring opening reaction due to the high sulfur resistance [40]. However, the hydrogenation activity of the catalyst is not efficient for the reaction [40–42]. According to Moraes's report [3], WO_3 supported on Al_2O_3 catalysts as monofunctional acid catalysts showed low selectivity for one-ring opening products. It is also found that the yield of the ring opening products with the Ni-Mo

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http://dx.doi.org/10.1016/j.mcat.2017.10.008
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Table 1
The S_{BET} (m^2/g), average pore size (nm), coke content (wt.%), CO uptakes and W/A molar ratio of Ni-W sulfide, carbide and nitride catalysts.

Catalyst	Oxide	Sulfide	Carbide	Nitride
Surface area (passivated catalyst).	302.5	91.1	291.6	270.2
Surface area (spent catalyst)	180.9 [a]	133.5 [b]	178.8 [b]	159.3 [a]
Pore size (passivated catalyst)	3.8	4.4	3.5	4.0
Pore size (spent catalyst)	4.4	4.1 [b]	5.2 [b]	4.9
Coke content	4.2[a]	0.7 [b]	2.4 [b]	2.5 [a]
CO uptakes (activated catalyst)	–	34.0	44.0	30.4
CO uptakes (spent catalyst)	–	26.1 [b]	30.6 [b]	20.6[a]
W/A ratio	–	0.4	2.3	2.1

[a] 58 h later.
[b] 96 h later.

carbide catalysts were comparable with that of the noble catalysts [6], while few studies focused on the metal nitride catalysts.

It is reported that the same catalyst with different treatment process such as sulfide process or carbide process, possibly present different activity and stability [41,43]. In our previous paper, the activity of the oxide and carbide catalyst was investigated and they showed different performance on the ring opening reaction [34]. However, there are few systematic reports of the comparison of supported Ni-W oxide, sulfide, carbide and nitride catalysts. In order to find the difference of the four types of catalysts for ring opening reaction and provide the meaningful information for choosing catalysts, this work focused on the study to compare the performance of the Ni-W oxide, sulfide, carbide and nitride catalysts. The composite support of USY-Al_2O_3 was used, which can provide suitable acidity and mechanical property for the catalysts [44,45]. The decalin is chosen as the model reactant for ring opening of naphthenes which is more representative for the LCO fraction.

2. Experimental

2.1. Catalyst preparation

The supports were used by mixing pseudo-boehmite (70 wt.%) and USY zeolites (Si/Al = 42, 30 wt.%). The physically mixed compounds were dried at 100 °C for overnight in the drier and then calcined at 550 °C for 2 h in the muffle. The supports contained γ-Al_2O_3 (51 wt.%) and USY zeolites (49 wt.%) after calcination. The Ni/W phases (4.5 wt.% NiO and 18 wt.% WO_3) were deposited by incipient wetness impregnation method with co-impregnation method of nickel nitrate and ammonium metatungstate. The oxide catalysts were dried for 10 h at 100 °C in the dryer and calcined for 4 h at 550 °C in the muffle. Different pretreatment of oxide catalyst was performed to prepare the sulfide, carbide and nitride catalysts.

For the preparation of the sulfide catalyst, the oxide catalyst loaded into the stainless steel tube was treated with hydrogen at a flow rate of 80 cm^3/min with a 4 ml/h feed of 5% CS_2 in cyclohexane. The sample was heated at 2 °C/min to 370 °C and held for 4 h, then cooled down to the 320 °C for reaction.

For the preparation of the carbide catalyst, the oxide catalyst loaded into the stainless steel tube was treated with a gas mixture (H_2/CH_4 volumetric ratio of 4) with a total flow rate of 80 cm^3/min, the catalyst was heated from room temperature to 700 °C and hold for 2 h until no carbon oxides were detected by a gas chromatography (GC 9560).

The nitride catalyst was prepared under a gas mixture (H_2/N_2 volumetric ratio of 4) flow of 80 cm^3/ min. The same temperature program was used on the nitride catalyst.

All the samples for characterization were passivated by using 2% O_2 in He (v/v) for 5 h before they were exposed to air to avoid the bulk oxidation.

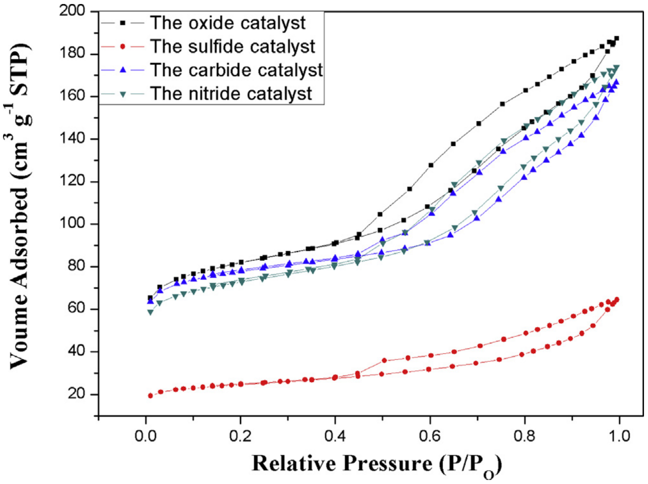

Fig. 1. N_2 adsorption-desorption isotherms of the Ni-W catalysts.

2.2. Catalyst characterization

The specific surface areas and average pore size of all the fresh and spent catalysts were measured by the BET method.

The powdered catalyst samples were analyzed by the X-ray powder diffraction (XRD) using a Rigaku D/max-2500 diffractometer, using the Cu K_α.

According to the previous studies [6,46–48], CO uptakes was measured by Quantachrome Instruments (Chem BET Pulsar) to titrate the number of accessible surface metal atoms on alumina-supported sulfide, tungsten carbides and nitride. 0.2 g sample (20–40 mush) was used for titration by U-shaped vessel. They were obtained by pulsing calibrated volumes of CO into a He carrier and measuring the decrease in the peak size caused by adsorption. The carbide and nitride catalysts were activated in flowing gas mixture (H_2/He volumetric ratio of 4, 30 cm^3/min) at 500 °C for 2 h, while the sulfide catalyst was activated at 375 °C for 2 h, then quenched at 30 °C and purged in He flow for 1 h, CO uptakes were obtained after the reduction of samples.

Thermogravimetric (TG) profiles in oxidation mode for the fresh and spent catalysts were obtained to calculate the amount of coke content during the reaction. The analysis was started with argon flow under 30 °C for 30 min. Next, the samples were heated to 1000 °C at a 10 °C/min heating rate under a 100 ml/min synthetic air flow.

Sulfide, carbide and nitride contents of the corresponding catalysts were analyzed by element analysis (Varion EL).

The Brönsted and Lewis acidities of the fresh and spent catalysts samples were analyzed by Thermo scientific (Nicolet 380) with pyridine as a probe molecule. The strengths of the Brönsted acid sites and Lewis acid sites were identified by the different desorbed temperature (250 °C, 350 °C and 450 °C).

The dispersion and size of the samples were analyzed by high-resolution transmission electron microscopy (HRTEM).

Hydrogen temperature programmed reduction (H_2-TPR) analysis was analyzed by Quantachrome Instruments (Chem BET Pulsar). 0.1 g sample (20–40 mush) was placed in an electric furnace and heated from 100 °C to 900 °C at a 10 °C/min heating rate.

2.3. Catalytic evaluation

Decalin ring opening was carried out in a continuous flow fixed-bed microreactor under a total pressure of 5 MPa at 320 °C. 3 g catalyst with catalyst size of 10–20 mesh was loaded. The feed flow was 4 ml/h with the H_2/oil = 1000(v/v). The constant flow pump