Fuel 105 (2013) 353–357

Contents lists available at SciVerse ScienceDirect

Fuel

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

Nickel-heteropolyacids supported on silica gel for ultra-deep desulfurization assisted by Ultrasound and Ultraviolet

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HIGHLIGHTS

- Ultra-deep desulfurization assisted by ultraviolet and Ultrasound was studied.
- Up to 100% of sulfur removal were achieved for model compounds.
- Nickel-heteropolyacids supported on silica gel was used as the desulfurization catalyst.

ARTICLE INFO

Article history:
Received 14 February 2012
Received in revised form 21 April 2012
Accepted 4 June 2012
Available online 19 June 2012

Keywords:
Desulfurization
Ultrasound and Ultraviolet
Fuel
Nickel
Heteropolyacids

ABSTRACT

Heteropolyacids used as active phase precursors, a kind of desulfurization catalysts which was promoted by nickel and supported on silica gel was prepared. The prepared catalysts were then characterized by XRD and N_2 physisorption, and evaluated in terms of the removal of sulfur compounds (thiophene, alkyl thiophene, BT and DBT) under the condition of Ultrasound and Ultraviolet irradiation (ODSUU). The effect of the catalyst amount on the desulfurization rate for fuel, as well as that of the reaction time, the oxidant dose, the reaction temperature and the Ultrasound and Ultraviolet irradiation time, was investigated. Under the optimized conditions for ODSUU, sulfur removal rate, up to 100% for model compounds and 99.5% for fuel, was achieved. However, sulfur removal rate under the same conditions without Ultrasound and Ultraviolet irradiation was lower than 100% for model compounds and 99.5% for fuel, which represented that catalysts assisted by Ultrasound and Ultraviolet showed better performance in the highly efficient deep removal of sulfur compounds than those of the traditional ODS procedure.

1. Introduction

Presence of high level of sulfides in FCC gasoline is still a major source of SO_X emission, which contributes to air pollution. For this reason, more stringent environmental regulations are established to reduce the sulfur concentration limits in gasoline, so the reduction of sulfur content in fuel has received much attention in recent years in many countries for a sulfur level less than 10 μg/g. To reach this low level, complete removal of highly refractory S-containing compounds, such as alkyl thiophene, BT, DBT, is inevitable [1–3]. To remove these undesirable sulfur compounds, various alternative or complementary processes different from traditional HDS have been proposed to produce ultra-low sulfur gasoline. Among them, the prominent ones are as follows: physical extraction with liquid, catalytic oxidation, selective adsorption on suitable materials and oxidative microbial transformations.

Specifically, the catalytic oxidation removal of sulfur compounds has attracted much attention due to some advantages, such as no need of hydrogen and mild operation conditions. Many studies have been undertaken to develop oxidative catalyst for desulfurization of gasoline with heteropolyacids. Many factors, such as catalyst type, feedstock quality and process parameters, can have significant influence on the degree of desulfurization of gasoline. The oxidative process, with nickel-heteropolyacids as catalysts, supported on silica gel and assisted by Ultrasound and Ultraviolet (ODSUU), is one of the most promising processes for producing ultra clean gasoline. The greatest advantage of ODSUU, compared with the other conventional oxidative desulfurization processes discussed in Refs. [4–6], is that nickel modification heteropolyacids catalysts supported on silica gel in H_2O_2 oxidation system have higher catalytic activity and selectivity for sulfides in the gasoline under the synergy of Ultrasound and Ultraviolet at near room temperature and atmospheric pressure. Therefore, the product yield of ODSUU procedure is higher than that of the other ODS process, and sulfur content inversely.

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0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.06.021

In this context, we have studied the ODSUU process, catalyzed by the nickel-heteropolyacids and supported on silica gel in H_2O_2 oxidation system. The operational parameters for the ODSUU procedure were investigated, such as the effect of the reaction temperature, reaction time, Ultrasound and Ultraviolet irradiation time etc. The results reported here provide basic information about the applicability of the ODSUU process with hydrogen peroxide as an oxidant and catalyzed by the nickel-heteropolyacids supported on silica gel for the removal of S-containing compounds in fuel.

2. Experimental

2.1. Apparatus

Experiments of the ODSUU procedure were performed with an ultrasonic processor and a mercury vapour lamp with quartz double tube. For all experiments an ultrasonic probe and a mercury vapour lamp were dipped directly into the oil–reagent mixture. Experiments were carried out in a batch reactor with a temperature controller. For comparison tests were performed with a high speed mechanical stirrer without Ultrasound and Ultraviolet.

Total sulfur concentration in fuel was determined by a sulfur–nitrogen analyzer (Atnek2000).

2.2. Reagents and materials

Oxidizing reagents used for ODSUU procedure were hydrogen peroxide (Sinopharm Chemical Reagent Co. Ltd.). Model sulfur compounds, produced by Shanghai Aladdin reagent Co. Ltd., were added to *n*-octane, which were used as process parameters optimization. The fuel samples used for experiments were from Sinopec Shanghai Petrochemical Company.

2.3. Catalyst preparation and characterization

The modified heteropolyacids have been prepared with supersaturation and impregnation. An aqueous solution of the tungstophosphoric acid, acetic acid and nickel nitrate in appropriate proportions was made and then mixed with the silica gel. The solid was then dried and calcined under vacuum for 5 h at 60 °C and then for 3 h at 350 °C respectively. And the final catalysts were gained after a pretreatment under the condition of air stream at different temperatures.

The catalysts were characterized by N_2 physisorption (ASAP2020M+C, USA) and XRD (PW 3040/60X′PertPRO, Holland).

2.4. Procedure

Reactions for sulfur removal were carried out in a batch reactor with a mixture of the given amount of hydrogen peroxide, supported catalyst and 100 mL of oil samples. The Ultrasound probe (amplitude control was set at 60%) and a mercury vapour lamp with quartz double tube were immersed into the reaction mixture. In the first step, the effect of the different catalysts on the sulfur removal rate was studied. After the catalyst and its amount were selected, the effect of H_2O_2 amount and the temperature on the desulfurization was evaluated. Under the selected temperature conditions, the reaction time was investigated from 20 to 90 min. Finally, under the above selected conditions, the influence of Ultrasound and Ultraviolet irradiation time on the sulfur removal was investigated, as well as the influence done without Ultrasound and Ultraviolet irradiation. All the tests were performed at atmospheric pressure.

3. Results and discussion

Oxidation desulfurization schemes, which are based on the use of hydrogen peroxide and heteropoly acids, have been reported in literature [7–9]. In the present work, initial studies were carried out in view of increasing the desulfurization efficiencies by nickel modification supported heteropolyacids under the conditions of Ultrasound and Ultraviolet irradiation.

3.1. Characterization and evaluation of catalyst

It is well known that the catalytic activity of supported heteropolyacides depends greatly on the preparation methods. Thus, for the nickel modification supported heteropolyacids, the calcination temperature during the catalyst preparation has a great influence on the highest sulfur removal rate in fuel. The catalyst characterization and experiment results are shown in Figs. 1 and 2 and Table 1.

Fig. 1 shows the effect of calcination temperature on the removal of sulfur compounds in model compound and fuel. The NWS catalysts calcined at five different temperatures show significantly different catalytic activities. The desulfurization rates increase as calcination temperatures increase from 250 °C to 350 °C. However, further increases in calcination temperatures result in a decrease in desulfurization rates. Therefore, the catalytic activity can be described in the order of NWS450 < NWS400 < NWS250 < NWS300 < NWS350. Hence, it is clear that NWS350 has the highest catalytic activity in the desulfurization of sulfur compounds from the fuel.

It is not easy to explain the reason why the NWS-350 shows the best performance among the catalysts. Hence, the physicochemical properties of the catalysts were analyzed with several characterization methods. According to the literature analyzed data shows the X-ray diffraction patterns of NWS catalysts [10–17] in different calcination temperature. The X-ray diffraction patterns of NWS250, NWS300, and NWS350 are similar to that of phosphotungstic acid, which illustrates that catalyst structures are still Keggin structures. The diffraction peaks of NWS350 catalyst did not move, but the intensity increased, indicating that the catalyst maintains the original structure with more perfect crystal. As the calcination temperature increased up to 400 °C, crystalline WO_3 gradually appeared. Moreover, the intensity of crystalline WO_3 increased with an increase in calcination temperature up to 450 °C. Nevertheless, the surface area of the NWS catalysts gradually decreased with an increase in the calcination temperature [18]. The high

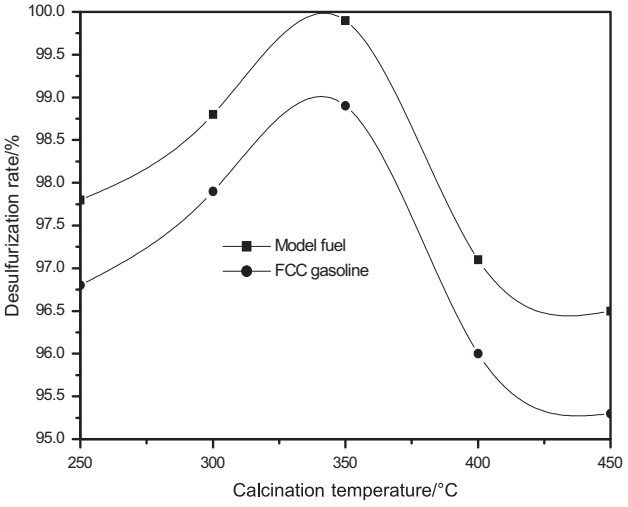

Fig. 1. Effect of calcination temperature on the desulfurization rate.