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Synthesis of W/HZSM-5 catalyst for simultaneous octane enhancement-desulfurization process of gasoline production

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ABSTRACT

In this work, the effect of incorporating tungsten in HZSM-5 zeolites over the performance of desulfurization and octane enhancement processes of heavy naphtha was investigated. The physical and chemical characterization of the catalysts were analyzed by means of XRD, BET, NH_3-TPD, TPR and XRF. The catalytic properties were determined at 5 barg, 450 °C, H_2/Oil = 150 Nml/ml and WHSV = 1 h^{-1} inside a fixed bed reactor. The standard methods of detailed hydrocarbon analysis, gas chromatography, ASTM D-2699 and ASTM-D5453 were utilized to determine the liquid hydrocarbon compositions, detailed analyses of the off-gases, research octane number and the total amount of sulfur of the feed and products, respectively. The obtained results showed that the interaction between the Brönsted and Lewis acid sites for the W/HZSM-5 samples at low SiO_2/Al_2O_3 ratios and consequently high acidity in the specific operating condition led to the parallel aromatization-desulfurization reactions to proceed perfectly. The total amount of sulfur decreased by 71 wt% for the SiO_2/Al_2O_3 ratio of 20, and the aromatic component of the feed increased from 14.16 wt% to 72.82 wt% for the SiO_2/Al_2O_3 ratio of 40; hence, RON raised from 52 to 98. Overall, by comparing the performance of the catalysts, it can be concluded that the best performance of simultaneous octane enhancement-desulfurization process was observed for the catalyst No_3, in which the amount of sulfur compounds decreased by 67.5% and the octane increased by 90%.

1. Introduction

With respect to the new global strict rules concerning the air pollution in the world, refineries have to produce clean products nowadays. New standard values for sulfur components as well as octane number in gasoline have been established. Following the new established rules, industrial units have to reduce their sulfur yields to at most 10 mg/kg and increase their RON values to at least 90. Subsequently, there is an urgent need for the operating units to adapt their yields to new standards [1–3].

Prior to the octane number enrichment process, the sulfur component in gasoline is removed from the feed through hydrodesulfurization (HDS) process. Following HDS process, the output is passed from the catalytic reforming unit (CRU) in order to set the octane number of gasoline to the desired value [4]. To obtain the best yield, it would be ideal if the HDS process is conducted by using of a proper catalyst under high temperature and pressure. By taking advantage of the HDS operation, organic sulfuric compounds are converted to the sulfuric hydrogen (H_2S) component.

Two well-known catalysts for the HDS process are Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3. The performance of the aforementioned catalysts during the HDS process is influenced by the catalysts characteristics such as concentration of active sites, supports, paths and reactions conditions i.e. temperature and hydrogen partial pressure. These factors influence activity and selectivity of catalysts and subsequently the desulfurization operation. Also, parameters like the structure, entity and concentration of sulfuric compounds in the inlet and the types of reactor have direct effects on the HDS process [5, 6].

Bifunctional catalysts are usually applied to almost every industrial process to increase the octane number of naphtha in the reforming operation. Beside the platinum metal, other metals such as Re, Ir, Sn and Ge can be used for the Al_2O_3-Cl support, bimetallic and trimetallic catalysts to be applied to these fields. Several researchers have studied of enhancing aromatic production, adsorbing hydrogen component on the catalysts, sulfidation requirements and sulfidation impact on the catalytic sites. They made attempts to recognize the factors damaging the catalyst's sites, for example sulfur components [4].

The HDS process has been regarded as one of most expensive processes with high operating and capital costs. In addition to consuming H_2 component, it needs high pressure and temperature conditions for successful reactions. Moreover, as a result of their possible hydrogenation reactions, the aromatic and olefin compounds can be saturated, so

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a decrease in gasoline octane number during this process is expected [5–7]. Given this, after solving basic faults, introducing a new deep desulfurization process, whereby the octane number of gasoline could concomitantly be enhanced, could be designated for a cheap and favorable process in industrial fields.

ZSM-5 catalysts with medium porosity are regarded as leading catalysts in petroleum industry. The advantages are due to their morphology and specific properties, including crystalline structures, large numbers of uniform pores, thermal stabilities and high selectivities. There are many studies on the performances of zeolite catalysts, typically the ZSM-5 case (with and without metals), in the aromatization of different components [2, 8]. As mentioned in our previous studies [9–12], the application of this type of zeolite seems promising in the aromatization of linear alkanes and conversion of organic compounds. Moreover, ZSM-5 produces eye-catching results when applying to desulfurization of gasoline [13, 14].

We face two important types of reactions when analyzing the aromatization process to increase the octane number of gasoline. The first reaction is followed by the reformation of hydrocarbons' structures, such as oligomerization, isomerization, and cracking steps. The second type is the hydrogen-displacement reactions like hydrogenation/dehydrogenation. For catalysts with acid and metal agent, while the first group of reactions is accelerated by the acid agent, the second group of reactions proceeds with the metal agent. Needless to say that adding a metal agent to the catalysts increases the weak Lewis acid sites and decreases the strong Brönsted acid sites. Given this, the synergy effect between both Brönsted and Lewis acid sites could be a key parameter in promoting desulfurization and aromatization processes [15–17].

Tungsten has been used as a conventional metal in the industrial catalysts of the HDS process for many years [5, 6]. The application of carbon-supported tungsten catalysts for hydrodesulfurization of thiophene was also investigated in some other studies [18]. There are some reports that the ZSM-5 catalyst has a very high efficiency in the aromatization of and upgrading of gasoline [1, 2, 19]. Based on these reports, one could expect that the mutual cooperation between acid zeolite catalysts, such as ZSM-5, and tungsten as a promoter could tangibly enhance the efficiency of the parallel desulfurization-aromatization process.

FCC naphtha as a product with high olefin components is produced by many refineries. According to available data, in some cases, the percentage of olefin in the products is higher than 50 Vol%. Generally, if the feed containing high olefin components is mixed with hydrogen, it is possible to saturate the olefins and then convert them to paraffin and consequently reduce the octane number of products [1]. Unlike to FCC naphtha, heavy straight run naphtha (HSRG) has a very low amount of olefinic compounds. By selecting proper catalyst and maintaining ideal operating conditions, it is possible to develop a process containing desulfurization and aromatization simultaneously. In fact, it provides a chance for engineers to apply both conventional processes of HDS and CUR together in oil refineries.

In this study W/HZSM-5 catalysts were synthesized for various SiO_2/Al_2O_3 ratios. In continuation, the effects of changes in catalyst acidity, and eventually, the effects of Brönsted and Lewis acid sites on the process of the parallel desulfurization-aromatization were studied to find out the ratios which could lead to production of high quality of gasoline.

2. Experiment

2.1. Catalyst preparation

The hydrothermal method was used to synthesize five ZSM-5 zeolites with the SiO_2/Al_2O_3 ratios of 20, 40, 60, 80, and 200. For this purpose, aluminum nitrate (ANN; $Al(NO_3)_3.9H_2O$, 98.5 wt%), tetra ethyl ortho silicate (TEOS; $Si(OC_2H_5)_4$, 98 wt%) and tetra-propyl ammonium hydroxide solution (TPAOH; $C_{12}H_{29}NO$, 40 wt% aqueous solution) were used. The HZSM-5 catalysts were synthesized by ion-exchanging ZSM-5 using one molar NH_4NO_3 occurred four times, each of which took 4 h. Tungsten (VI) chloride was used to incorporation W metal in 5 wt% into HZSM-5 by the wet impregnation method. Next step was drying the products overnight in an oven at 110 °C followed by heating in furnace at 550 °C for 3 h.

2.2. Catalyst characterization

1. X-ray diffraction (XRD). To recognize the crystal structure, the X-ray analyses were conducted through XRD by using a D5000 Siemens instrument (scan speed 0.04 s^{-1}, range 2, between 5 and 50° with Cu-ka radiation and 0.154056 nm wavelengths in 30 kV and 40 mA). The quality of each product was perceived through comparison between XRD analyses and the reference XRD diagrams.
2. X-ray fluorescence (XRF) spectroscopy. By using a PHILIPS PW 1480 spectrometer and X-ray fluorescence (XRF), the concentrations of Si, Al, W and O were detected.
3. Temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) were measured by An American Micrometrics TPD/TPR 2900.
4. The temperature-programmed reduction (TPR) was operated under a reducing gas containing 10% H_2 in Ar with a thermal conductivity detector. The temperature raised from 30 to 800 °C with a heating rate of 10 °C/min.
5. Porosity and surface area. BET method was used for obtaining the specific surface area of the samples. To detect the Brunauer-Emmett-Teller surface area, the nitrogen adsorption/desorption isotherms with a micromeritics ASAP 2010 analyzer at 77 K were applied to the system.

2.3. Catalytic reaction

Fig. 1 shows a Catatest reactor system which was used in this study. To determine the performance of the produced catalysts at different conditions, the catatest system was used. This system was made up of a bed reactor with three separate zones to measure and to set the temperature of the media. The feed of the reactor was supplied through the entrance located at the top of the reactor, where the components of N_2 and H_2 could be injected. The products were also discharged from the bottom. The products downstream could be cooled in two separate steps and gathered as a liquid phase. The components of the outlet gas collected in a sampling bomb were measured by the GC bed. The feed to be considered is Iranian heavy straight run naphtha. According to the aim of the present work, the naphtha was applied to the reactor under the pressure of 5 barg, 450 °C temperature, H_2/Oil = 150 Nml/ml, WHSV = 1 h-1 to get familiar with the abilities of the synthesized catalysts. The following procedure was used in order to distinguish the exact amount of each component of the liquid product, such as i-paraffin, n-paraffin, olefin, naphthalene and aromatics (PIONA); and the fraction of outlet gas; and the octane number of the feed and product; and the total amount of sulfur element.

1. Detailed hydrocarbon analysis (DHA) of paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) in samples has been conducted by gas chromatographic (GC) tests, which is based on the PIONA concept reported in the literature [20]. The GC test was carried out on a Varian 3800 gas chromatograph, with a split injector (at split ratio 100, 280 °C) and a FID (280 °C), equipped with a flexible Petrocol DH capillary column (100 m, 0.25 mm internal diameters; 1.0 μm film thickness). About 0.3 μL of 10% CS_2 diluted sample was injected; the oven temperature was programmed from 35 (15 min) to 60 °C (1 °C/1 min) and then to 240 °C (2 °C/1 min), and maintained at 240 °C for 20 min, using helium career gas at the flow rate