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Ultra-deep desulfurization of gasoline through aqueous phase in-situ hydrogenation and photocatalytic oxidation

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ABSTRACT

ZSM-5 zeolite was comodified with zirconium oxide, nickel oxide and titanium oxide. A fixed-bed reactor and a photocatalytic reactor were used to investigate the performance of the resulting catalysts in the desulfurization of fluid catalytic cracking (FCC) gasoline through coupling in-situ hydrogenation with photocatalytic oxidation desulfurization (HPODS). The resultant samples were characterized using the nitrogen adsorption-desorption, X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. X-ray diffraction analysis indicated the coexistence of ZrO_2, NiO and TiO_2 in the catalysts. The desulfurization rate, the refined oil yield and the increase in the research octane number reached 100%, 99.9% and 2 units, respectively, under suitable conditions of a hydrogenation catalyst weight of 3 g, a catalyst ratio of 1.8, a pressure of 2.0 MPa, a hydrogenation reaction time of 60 min, a hydrogenation temperature of 453 K, an oxidation temperature of 323 K, and an oxidation reaction time of 40 min.

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1. Introduction

Ultra-deep desulfurization of fluid catalytic cracking (FCC) gasoline has attracted much attention because of strict government regulations on sulfur discharge considering clean environment and human health. According to these regulations, the upper limit of sulfur content in gasoline is 10 μg/g [1,2].

Hydrodesulfurization (HDS) for the transformation of organic sulfides to sulfur-free organic compounds and hydrogen sulfide represent a valuable and timely technology. However, HDS operates under the conditions of the high temperature, the high pressure and in the presence of hydrogen. Severe conditions make HDS a costly alternative for ultra-deep desulfurization and lead to a decrease in the research octane number of FCC gasoline because of the hydrogenation of aromatic and olefin in the feedstock. Besides, HDS is not effective in the removal of thiophene and its derivatives, especially 4,6-dimethyldibenzothiophene because of its steric hindrance [3–6]. Some important progresses have also been achieved with mild conditions of HDS by applying active catalysts [7].

Owing to the inherent difficulties of HDS for removing thiophenic compounds, many alternative technologies have been studied, for example: biodesulfurization [8,9], selective adsorption [10–13], physical extraction [14–17], oxidative desulfurization (ODS) [18–21], complexation, pervaporation [22–27], and their combinations. Among these desulfurization processes, ODS might be the most feasible route for the desulfurization of FCC gasoline. ODS has received attention because the operating conditions were mild, the desulfurization rate was high, and the research octane number was no loss. Photocatalytic oxidation was regarded as a promising desulfurization process due to the high selectivity and the high desulfurization rate of thiophene and its derivatives. However, according to previous studies [28,29], a certain part of carbons and hydrogens were also removed by oxidants leading to a decrease in refined oil yield when organic sulfides were oxidized to the corresponding sulfoxides and sulfones. Therefore, further increasing the desulfurization rate is still a challenging goal, because a decrease in the refined oil yield and the research octane number is inevitable in the desulfurization of FCC gasoline. However, ODS seems to be more feasible as a subsequent process of HDS because oxidation and hydrogenation are complementary [30]. The hydrogenation activity of the sulfur compounds is thiophenes > BTs > DBTs, while their oxidation activity is just the opposite [31]. Organic sulfides, which was difficult to be removed by HDS, can be easily removed by ODS. Therefore, ultra-deep desulfurization of FCC gasoline would be achieved through the combination of HDS and ODS.

Hydrogen of the liquid phase in-situ hydrogenation is produced from methanol aqueous-phase reforming over catalysts. The production, preservation and transportation of H_2 in the traditional

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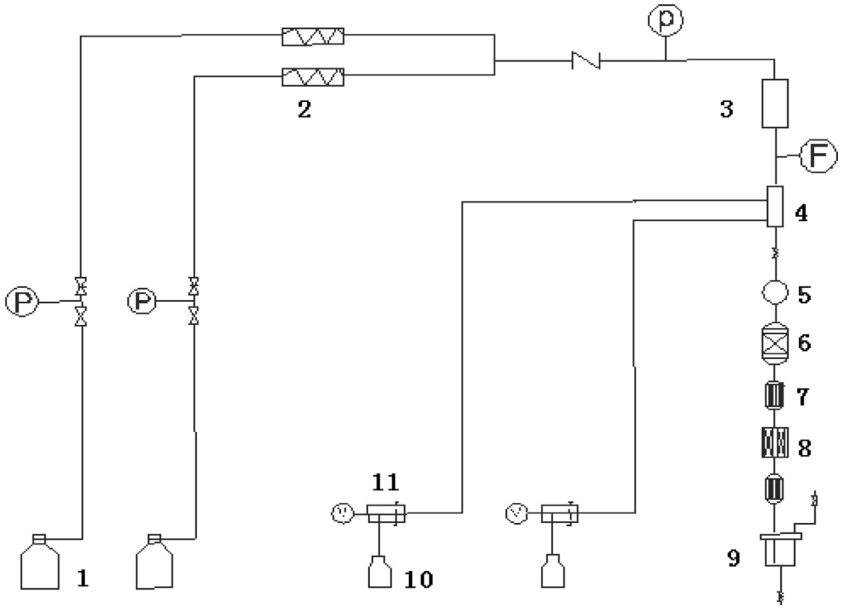

Fig. 1. Schematic diagram of ultra-deep desulfurization of gasoline ((1) air and N_2 cylinders; (2) filters; (3) buffer vessel; (4) mixer; (5) preheater; (6) reactor; (7) cooler; (8) reactor; (9) gas-liquid separator; (10) material tank; (11) bump).

Table 1
Physical properties of FCC gasoline and refined oil.

Items	Properties										
	Distillation range/°C				Octane number		The type of Sulfur content/$\mu g\, g^{-1}$				Total content/$\mu g\, g^{-1}$
	IBP	10%	50%	90%	EP		Thiophene	BT	DBT	Others	
FCC gasoline	48	62	110	182	200	93	478	223	150	349	1200
Refined oil	46	66	116	180	204	95	4	2	0	2	8

hydrogenation process could be eliminated, which leads to the decrease in cost and enhancement of safety significantly. In this process, methanol is the raw material of the aqueous-phase reforming reaction. The active hydrogen generated from the aqueous-phase reforming of methanol could be quickly removed from the active sites of the catalyst, which is superior to the traditional HDS. In this work, ultra-deep desulfurization of FCC gasoline through the aqueous phase in-situ hydrogenation and photocatalytic oxidation desulfurizatoin (HPODS) were investigated with catalysts of ZSM-5 comodified with zirconium, nickel and titanium oxide. This technique could be promising for improving the economic output of refineries.

2. Experimental

2.1. Materials and chemicals

Thiophene, benzothiophene (BT) and dibenzothiophene (DBT) were purchased from Sigma-Aldrich. FCC gasoline (Table 1) was obtained from PetroChina Urumqi Petrochemical Company. Kaolin and zeolite were purchased from Kaolin Co., SINOPEC Catalyst Co., respectively. Pseudo-boehmite powder, diatomite and silica sol were purchased from Shandong Aluminum Industry. Others were bought from the Sinopharm Chemical Reagents Co., Ltd. The model oil was prepared by dissolving thiophene, BT, and DBT in the mixture of *n*-octane, benzene and butylethylene with a sulfur content of 1200 μg/g.

2.2. Preparation and characterization of catalysts

Typical preparation process is described as following.

Seven grams of ZSM zeolite (Si/Al = 180) and 50 mL of deionized water were introduced into a 100 mL flask to form a slurry. The slurry was adjusted with 31 wt% HCl until the pH was 1.5. The mixture was washed with deionized water and filtrated. The filter cake obtained was impregnated with a mixture of hydrochloric acid solution, titanium tetrachloride (5 g), Zirconium oxychloride (2.8 g) and nickel nitrate (3.4 g) at 313 K for 2 h; dried at 403 K for 5 h; and calcined at 673 K for 3 h to obtained ZrO_2/NiO-TiO_2-ZSM-5.

The crystallinity of the catalysts was characterized by X-ray diffraction (XRD; D/Max 2500X; worked at 40 kV and 100 mA, CuKα source). The valence states of active metals of samples were characterized by Fourier Translation Infrared Spectroscopy (FT-IR). The morphology and size were characterized with scanning electron microscopy (SEM; JEOL, JSM-6480A). The pore size and volume distribution were measured with nitrogen adsorption-desorption (Quantarome NOVA 4000) at 77 K. The surface areas of the samples were determined according to the Brunauer-Emmett-Teller (BET) equation. The acidity was characterized by the temperature programmed desorption of ammonia (NH_3-TPD) in a dynamic chemisorption analyzer (Micromeritics ASAP 2920).Pyridine-adsorbed infrared (Py-FTIR) spectra were used to discriminate acid type of samples by EQUINOX 70 (Buker, Germany).

2.3. Desulfurization testing

The desulfurization of gasoline was carried out in a fixed bed reactor and a photocatalytic reactor equipped with mercury lamps (100 w; a main peak 254 nm). A scheme of the reaction setup is shown in Fig. 1. First, ZrO_2/NiO-TiO_2-ZSM-5 in the hydrogenation reactor (3 g) and photocatalytic reactor (1.6 g) was

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