Fuel 210 (2017) 803–810

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Partial oxidation of vacuum residue over Al and Zr-doped α-Fe_2O_3 catalysts

Dechao Wang, Lijun Jin, Yang Li, Haoquan Hu*

State Key Laboratory of Fine Chemistry, Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Keywords:
Vacuum residue
Partial oxidation
α-Fe_2O_3
Doping

ABSTRACT

Partial oxidation presents a novel method to produce liquid fuels, such as gasoline, diesel and vacuum gas oil, from vacuum residue (VR). Al and Zr-doped α-Fe_2O_3 catalysts were prepared for partial oxidation of VR. The catalysts were characterized by N_2 adsorption/desorption, X-ray diffraction, H_2 temperature programmed reduction, Raman, and X-ray photoelectron spectroscopy. The results showed that the specific surface area and pore volume of doped α-Fe_2O_3 increase, and Al and Zr are incorporated into α-Fe_2O_3 structure. XPS analysis indicated that several oxygen species appear in α-Fe_2O_3 surface, in which lattice oxygen is the majority. The doped α-Fe_2O_3 catalysts show better catalytic performance than α-Fe_2O_3 alone in partial oxidation of VR at 550 °C. When an Al and Zr-doped α-Fe_2O_3 with Fe/Al/Zr atomic ratio being 16:1:1 (FeAlZr-1) was used as catalyst, the gasoline and diesel yields are 11.5 wt% and 43.8 wt%, respectively. Furthermore, FeAlZr-1 shows good regenerability in partial oxidation of VR.

1. Introduction

There is no doubt that the world will face formidable challenges in meeting energy demand as the conventional fossil reserves will not last forever [1], while the demand for light fuels is increasing. It is necessary to find alternative energy supplies from other natural resources. On the one hand, the oxygenated fuels produced from renewable resources have proposed as blends components in gasoline and diesel to reduce pollution and decrease the demand for fossil fuels [2,3]. Oxygenated fuels like furfural, vegetable oil, biodiesel, and alcohol can be produced from common biomass resources, which is environmental friendly, biodegradable and sustainable [3–5]. However, the addition of oxygenated fuels such as vegetable oil in conventional diesel engines will lead to some problems because the injection, atomization and combustion characteristics of vegetable oil in diesel engine are significant different from those of diesel fuel [3]. Another limitation on the content of oxygenated compounds in fuel blend is the heating values. For example, the heating vale of vegetable oil is in the range of 39–40 MJ/kg, which is lower than that of diesel fuel (about 45 MJ/kg) [3]. On the other hand, the unconventional heavy oil such as crude heavy and extra-heavy oil, bitumen, and petroleum residue (atmospheric residue AR, vacuum residue VR) was also paid great attention [6–11]. For example, VR, obtained from the bottom of vacuum distillation column, accounts for approximately 25 wt% of the feedstock. It is usually characterized by a high density, high molecular weight, high viscosity, and high content of asphaltene [3]. In this respect, upgrading technologies converting heavy oil into valuable light fuels are required [12–17].

Generally, upgrading of heavy oil is mainly achieved by thermal cracking, catalytic cracking, and hydrocracking, which are based on carbon rejection and hydrogen addition [12,16,17]. Among these methods, the catalytic cracking of heavy oil using lattice oxygen is an innovative technique, where hydrocarbon molecules can be converted into gas or light liquid products by using lattice oxygen in oxygen carrier instead of molecular oxygen in air [18–23]. The application of Fe-based materials is an alternative option for oxidation of heavy oil. Serrano et al.[19] proposed that Fe-based oxygen carrier can be used to convert low-value hydrocarbons from the refining of crude oil under chemical looping combustion (CLC) conditions. The integrated process can satisfy the demands of heat and steam of the refining process while reducing CO_2 emissions up to 50% in oil refineries [19]. Generally, the CLC process is conducted under higher temperature with the intention to convert hydrocarbon molecules into CO_2 and H_2O [24], while this process can be controlled for the production of light liquid fuels under mild reaction temperature, which can be considered as a partial oxidation technology. Golovko et al. [22] applied coal fly ash containing 85.20 wt% Fe_2O_3 for catalytic cracking of heavy oils (paraffin and asphaltenic oil) at 450 °C, and the selectivity of the formation of liquid products can be as high as 95–96% for paraffin oil and 72% for asphaltenic oil.

As described above, iron oxide has a great potential to be used in partial oxidation of heavy oil; however, iron oxide often suffers from its low specific surface area due to the thermal sintering. It was reported that the specific surface area of iron oxide seemed to be an important factor for the catalytic tar decomposition [25]. The application of iron

---

* Corresponding author.
E-mail address: hhu@dlut.edu.cn (H. Hu).

http://dx.doi.org/10.1016/j.fuel.2017.09.008
Received 24 June 2017; Received in revised form 31 August 2017; Accepted 4 September 2017

oxide with high surface area would be a promising method to minimize sintering impact and improve activity. Doping can be used to increase specific surface area of metal oxide and modify their reactivity. Park et al. [26] studied Co, Cu and Ni-doped and codoped CeO_2, and the specific surface area increased compared with undoped CeO_2 due to a decrease in average particle sizes of doped CeO_2. Liang et al. [27] reported that a small amount of Fe_2O_3 doping can improve specific surface area of CeO_2, and the resulting solid solutions showed a higher surface area than that of pure Fe_2O_3 and CeO_2. The prepared solid solutions provided significant catalytic activity toward ethanol steam reforming with 64% selectivity of hydrogen [27]. Additionally, doping disrupts chemical bonding at surface of the host oxide, and the active centers in such system could be either the oxygen atoms near the dopant or the dopant itself [28]. Nolan [29] suggested that doping of metal oxides can modify their reactivity with respect to oxygen vacancy formation and molecular adsorption, and CO adsorbs much more strongly on the doped surfaces compared to undoped surface according to the density functional theory (DFT + *U*) calculations. Krcha et al. [30] indicated that doping transition metal on CeO_2 surface can alter the surface reducibility and catalytic activity for hydrocarbon conversion.

ZrO_2 and Al_2O_3, due to their thermal stability, were usually reported as support materials in heterogeneous reaction. Ge et al. [31] investigated the effect of preparation method on K-decorated Fe_2O_3/Al_2O_3 oxygen carrier in CLC of bituminous coal. Zhang et al. [32] synthesized a series of Al_2O_3-ZrO_2 composite supported NiMo catalysts with different ZrO_2 content. They found that the catalyst showed the highest hydro-desulfurization and hydro-denitrogenation activities for diesel oil when the ZrO_2 content were 15% and 5%, respectively [32].

In the present study, we proposed that the specific surface area of iron oxide could be enhanced and the physiochemical properties can be altered by doping Al_2O_3 and ZrO_2 (abbreviated as Al and Zr). A series of characterization methods including N_2 adsorption/desorption, XRD, H_2-TPR, Raman, and XPS were employed to understand the role of Al and Zr doping. The effect of Al and Zr doping on the activity of α-Fe_2O_3 in partial oxidation of VR was investigated.

2. Experimental

2.1. Catalyst preparation

Undoped and doped α-Fe_2O_3 catalysts were prepared by a conventional co-precipitation method using $Fe(NO_3)_3{\cdot}9H_2O$, $Al_2(SO_4)_3$, and $ZrOCl_2{\cdot}8H_2O$ (Sinopharm Chemical Reagent Co., Ltd, China) as precursors and ammonia solution (Tianjin Fuyu Fine Chemical Industry Co., Ltd, China) as precipitant. All the reagents are of analytical grade, and were purchased and used without further purification. $Fe(NO_3)_3{\cdot}9H_2O$ was mixed with $Al_2(SO_4)_3$ or/and $ZrOCl_2{\cdot}8H_2O$ according to the required atomic ratio of Fe/Al, Fe/Zr and Fe/Al/Zr, and dissolved in deionized water to obtain a solution. Ammonia solution was added continuously until the pH value of the resulting solution reached 9.0 ± 0.1. The mixed precipitation was aged at 60 °C for 3 h. After that, it was filtered and washed with deionized water. The resulting mixture was dried at 110 °C for 12 h, and calcined at 600 °C for 3 h. Finally, the calcined sample was crushed and sieved with an average size of 20–40 mesh for further tests. The synthesized catalysts are abbreviated as Fe_2O_3, FeAl, FeZr, FeAlZr-1 and FeAlZr-2, which represents the atomic ratio of Fe/Al, Fe/Zr and Fe/Al/Zr is 16:1, 16:1, 16:1:1 and 32:1:1, respectively.

2.2. Catalyst characterization

Nitrogen adsorption-desorption isotherms were obtained by N_2 adsorption at −196 °C on JK-BK 122 W. Specific surface area and pore size distribution were determined by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods [33,34], respectively.

X-ray diffraction (XRD) patterns were recorded on a D/Max 2400 diffractometer using Cu Kα radical source ($\lambda = 0.15406$ nm) operated at a voltage of 40 kV and a current of 100 mA. The samples were scanned in a 2θ range from 10 to 70° with steps of 0.02°. The average crystal size was calculated by Scherrer formula according to the face (1 0 4) at 33°, which has the highest intensity in all diffraction peaks.

H_2 temperature programmed reduction (H_2-TPR) profiles were achieved on self-build apparatus equipped with thermal conductivity detector. About 0.1 g sample was placed in a quartz U-tube and preheated to 400 °C for 30 min to remove water adsorbed on samples. After that, it was cooled down to 120 °C and heated to 850 °C with a heating rate of 5 °C/min under H_2 atmosphere.

Raman spectra were obtained on a Thermo Fisher DXR Microscope using an excitation wavelength of 532 nm. Raman scanning range was recorded in a spectral range of 150–900 cm^{-1} with a spectral resolution of 2 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) spectra were collected with a Thermo Scientific™ ESCALAB 250Xi spectrometer using Al Kα X-rays source ($h\nu = 1486.6$ eV), operated at a power of 150 W. The binding energy step size of 0.05 eV was employed and the binding energies were referenced to C1s peak at 284.8 eV to account for charging effects.

2.3. Partial oxidation of VR

VR sample was provided by Petrochina Fushun Petrochemical Company, and was used as feedstock in this work. Some properties of VR are shown in Table 1. The VR has high molecular weight and heavy oil (with boiling point higher than 500 °C) content. The carbon content of VR is more than 85 wt%, and the content of heteroatom atom (including S, N, and O) is below 1 wt%.

The partial oxidation of VR was conducted in a fixed bed reactor at 550 °C under ambient pressure for 1 h, as shown in Fig. 1. For each experiment, about 1.25 g sample (undoped or doped α-Fe_2O_3) was placed in the vertical stainless steel reactor. VR was diluted with toluene (20 wt% VR) to reduce the viscosity, and the solution was pumped into the reactor with a mass flow rate of 5.0 g/h. Blank tests confirmed that all the catalysts are inactive to toluene. Nitrogen was used as carrier gas with a constant flow rate of 25 mL/min. The weight hourly space velocity (*WHSV*) without toluene is 0.8 h^{-1}. The liquid and gas products were collected through ice trap and gas bag, respectively. To ensure the reproducibility, all the tests were conducted at least two replicates. The standard variance for each products are within ± 2.0%, indicating the good reproducibility.

The non-condensable gases were analyzed by GC 7890 II equipped with a thermal conductivity detector (5 A molecular sieve packed column) and a flame ionization detector (GDX502 packed column), respectively.

In analysis the yield of liquid product, because toluene was unchanged after reaction, we can calculate the weight of liquid product through eliminating the weight of toluene. Therefore, the weight of liquid product was calculated by the difference of collected liquid from ice trap to the toluene in the feedstock. The liquid yield was calculated based on the Eq. (1):

$$\text{Liquid yield (wt\%)} = \frac{\text{Weight of liquid product}}{\text{VR weight}} \times 100 \tag{1}$$

Table 1
Some properties of VR.

Mn[a]	> 500 °C fraction (wt%)	Elemental analysis (wt%)				
		C	H	N	S + O[b]	H/C
1061	86.5	86.34	12.92	0.57	0.17	1.80

[a] Number-average molecular weight.
[b] By difference.