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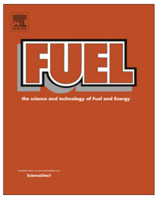

Catalytic cracking of heavy oil over TiO_2–ZrO_2 catalysts under superheated steam conditions

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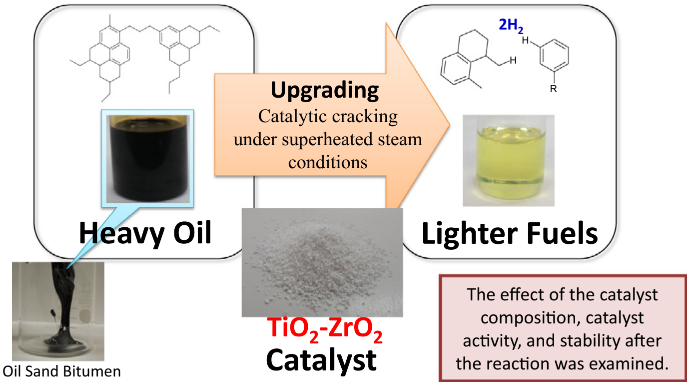
HIGHLIGHTS

- Upgrading of heavy oil was examined over TiO_2–ZrO_2 mixed catalysts.
- Heavy oil could be converted to lighter fuels over TiO_2–ZrO_2 mixed catalyst.
- Carbonaceous residue was suppressed upon catalyst cracking by using TiO_2–ZrO_2 catalyst.
- TiO_2–ZrO_2 comprising TiO_2 and ZrO_2 in equimolar showed the most effective to upgrade.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy oil upgrading was examined over titania–zirconia mixed oxide (TiO_2–ZrO_2) catalysts using fixed-bed flow-type reactors. Catalytic cracking of atmospheric residual oil (AR) and oil sand bitumen into lighter fuels such as gas oil and vacuum gas oil (VGO) was carried out in a superheated steam. The upgrading mechanisms were found to occur by carbon–carbon bond cleavage and naphthalene-ring opening caused by cracking, oxidation, or hydrogenolysis. The carbon–carbon bond cleavage reaction over acid sites is a well-known FCC (Fluid Catalytic Cracker) process, whereas coke formation on catalysts is a serious problem. Hence, repetition of the sequence of reactions over a short period of time and immediate regeneration of the catalyst is required. We previously developed a CeO_2–ZrO_2–Al_2O_3–FeO_X iron oxide catalyst for heavy oil conversion into lighter fuels (Funai *et al.*, 2010a,b; Kondoh *et al.*, 2015). When this catalyst was applied to the degradation of heavy oil, the lattice oxygen in the catalyst was the main active site, and it decomposed the heavy oil through partial oxidative cracking. Although the catalyst showed a high upgrading activity, it was gradually deactivated due to carbon deposition. In contrast, we found TiO_2–ZrO_2 catalysts exhibited acidic cracking activity for heavy oil cracking under superheated steam conditions. In this study, we conducted experiments with TiO_2–ZrO_2 catalysts for upgrading heavy oil. The effect of the catalyst composition on the yield of the lighter fuels, catalyst activity, and stability after the reaction was examined. As a result, the yield of light fractions from AR decomposition reached 71 mol%-C when using a TiO_2–ZrO_2 catalyst comprising TiO_2 and ZrO_2 in equimolar amounts and the catalyst structure remained intact after the reaction.

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1. Introduction

Crude petroleum is one of the main global sources of energy, and the demand for useful fuels such as gasoline and kerosene has grown year by year. There are, however, some serious problems, such as unstable petroleum prices, a decline in the demand of low-grade fuels, and a lack of diversification of energy resources. The BP Statistical Review of World Energy suggests that about half of the Earth's primitive petroleum deposits have already been consumed [1]. Hence, unconventional oil resources must now be used, e.g., atmospheric or vacuum distilled oils, oil sand, and Orinoco tar. Moreover, the demand for useful fuels such as gasoline, kerosene, and gas oil has grown. To meet these demands, new techniques to produce fuels from unused heavy oil are required.

Upgrading methods for heavy oil by thermal cracking [2], hydrocracking, and catalytic cracking [3,4] have been reported. With these methods, the deposition of carbonaceous residue formed on catalysts and in reactors is a serious problem [5,6].

In this study, catalytic cracking of heavy oil into lighter fuels such as gas oil or VGO was carried out under superheated steam conditions. Upgrading mechanisms were found to occur by carbon–carbon bond cleavage and naphthalene-ring opening caused by cracking, oxidation, or hydrogenolysis [5,7]. To improve the H/C ratio in hydrogenation and hydrogenolysis, it is necessary to add H_2 as a hydrogen source. However, because a large amount of energy is required in a H_2 production system, an alternative hydrogen source would be indispensable. Therefore, superheated steam with feedstock was fed into the reactor as the hydrogen source instead of H_2 gas.

We have previously reported that iron oxide catalysts show high activity for the cracking of heavy oil [7–10]. In contrast, since the concentration of poly-aromatic material, called asphaltene, in heavy oils such as AR (atmosphere residual oil) and oil sand bitumen is high, some solid products (carbonaceous residue) will be formed during the decomposition reaction of heavy oil.

Titanium oxide (TiO_2) is widely used in various fields for practical purposes due to its unique properties. TiO_2 is known to have several natural multiforms, e.g., anatase has structural metastability at low temperature, but rutile is thermodynamically stable and brookite is made only under hydrothermal conditions [11]. Furthermore, it is widely known that using zirconium oxide (ZrO_2) inhibits some sintering of the active components, due to its high mechanical strength and good thermal resistance [12].

There has been some research on oxide catalysts such as TiO_2 and ZrO_2 nanoparticles, which are very promising materials for use in industrial applications. These oxide catalysts are expected to be applied in new decomposition reactions of heavy oil because metal oxides have been utilized to decompose glycerol [13] and cacao pod husks [14] into useful materials. Therefore, we selected titanium and zirconium as catalyst components for the catalytic upgrading of heavy oil.

The main objective of this work was to develop TiO_2–ZrO_2 catalysts for upgrading heavy oil. First, a series of TiO_2–ZrO_2 catalysts with different compositions was prepared. Then, the heavy oil was upgraded using these catalysts in a superheated steam atmosphere to verify their abilities.

2. Experimental

2.1. Preparation and characterization of TiO_2, ZrO_2, and TiO_2–ZrO_2 catalysts

TiO_2, ZrO_2, and TiO_2–ZrO_2 catalysts were prepared by the sol–gel method, a process for producing solid materials from small molecules, using $Ti[OCH(CH_3)_2]_4$ and $Zr[OCH(CH_3)_2]_4$. Each reagent was purchased from Wako Pure Chemical Industries in Japan. The obtained catalysts were calcined at 600 °C for 2 h in an air atmosphere. The TiO_2 and ZrO_2 compositions of the catalysts were 100:0, 20:80, 40:60, 50:50, 67:33, and 0:100 mol%. The catalysts are referred to as Ti(X)Zr(Y), where X and Y indicate the content in molar percent.

The gaseous and liquid products were analyzed by gas chromatography (GC; GC-8A, Shimadzu Co., Ltd.) and high-performance liquid chromatography (HPLC; CTO-10A, Shimadzu Co., Ltd.). The crystallinity of the catalyst was amorphous. The catalysts were analyzed with an X-ray diffractometer (XRD; JDX-8020, JEOL Co. Ltd.). The coke amount on the catalyst after reaction and the surface acidity of the catalysts were measured by an elemental analyzer and a NH_3-TPD apparatus, respectively. Pyridine adsorption on the obtained samples was observed using a diffuse reflectance infrared Fourier transform (DRIFT) spectrometer equipped with a mercury cadmium telluride (MCT) detector (FT/IR-4100, JASCO Co., Ltd.). The surface areas of the obtained samples were calculated by the Brunauer–Emmett–Teller (BET) method based on N_2 adsorption isotherms (Belsorp mini, BEL JAPAN Co., Ltd.).

2.2. Experimental procedure

AR and oil sand bitumen were diluted with toluene and benzene at 10 wt% to reduce the viscosity. TiO_2–ZrO_2 catalysts were confirmed in advance to be inactive to toluene and benzene. There was no change with benzene and toluene under superheated steam conditions. Therefore, the solvents produced by this reaction could be ignored. The catalytic reaction using TiO_2–ZrO_2 catalyst was carried out in a fixed-bed flow-type reactor. Fig. 1 shows a schematic illustration of the fixed-bed flow reactor.

The experimental procedure was carried out on the fixed-bed flow reactor according to previous reports [3,4] under atmospheric pressure. The reactants, which consisted of solvent solutions of heavy oil and water, were fed to the reactor with a syringe pump. A mixture of steam and diluted solvent was introduced into the stainless steel reactor over 2 h. The time factor W_{cat}/F_{Feed} (W_{cat}: catalyst weight/g; F_{Feed}: feedstock flow rate/g h^{-1}) and F_{H2O}/F_{Feed} (F_{H2O}: water rate/g h^{-1}; F_{Feed}: feedstock flow rate/g h^{-1}) were 0.4 h and 2, respectively. The reaction temperature was set to 470 °C, which was established by previous experimentation. After optimizing the catalyst composition, because heavy oil decomposition occurs on the catalyst surface, the modified time factor

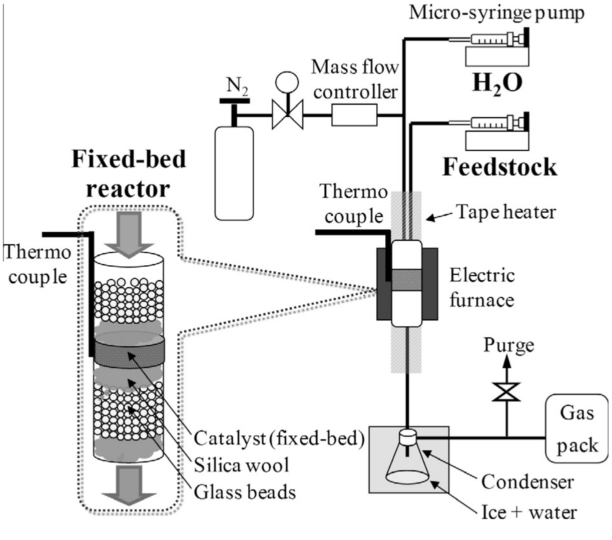

Fig. 1. Experimental apparatus of the reactor for catalytic cracking of heavy oil.