



Selective synthesis of gasoline from syngas in near-critical phase



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ABSTRACT

The conversion of syngas ($\text{CO} + \text{H}_2$) to hydrocarbons in gasoline fraction over a hybrid catalyst composed of Cu-ZnO and Pd/ZSM-5 in a near-critical *n*-hexane solvent was investigated. Methanol was synthesized from syngas over Cu-ZnO; subsequently, was converted to hydrocarbons through the formation of dimethyl ether (DME) over Pd/ZSM-5. The yield of hydrocarbons increased from ca. 29% to ca. 54% with increasing the partial pressure of *n*-hexane from 0 MPa to 1.5 MPa. By contrast, the yields of CO_2 and DME decreased with increasing the partial pressure of *n*-hexane. A decrease in the particle size of ZSM-5 as well as an increase in a Pd loading led to the selective production of hydrocarbons in the gasoline fraction. The hybrid catalyst containing 0.5 wt% Pd/ZSM-5 with ca. 100 nm in size exhibited 51% gasoline fraction yield with 75% CO conversion. The catalyst stability was also improved by increasing the Pd loading during the reaction.

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1. Introduction

Because of a drastic increase in worldwide energy consumption, the development of hydrocarbon production processes with carbon resources alternative to crude oil has been highly desirable. Syngas ($\text{CO} + \text{H}_2$), which can be produced from a variety of carbon resources such as natural gas, biomass, and coal, has been focused on as a raw material for the production of fuels and chemicals. Syngas can be converted directly to hydrocarbons through the Fischer-Tropsch synthesis (FTS) [1–7]. Another way of uses of syngas is the production of methanol. Methanol can be utilized for the production of hydrocarbons through the methanol-to-hydrocarbons (MTH) reaction using zeolites or zeolite-type catalysts. In the MTH reaction, hydrocarbon distribution is strongly dependent on the micropore size of zeolites, and the production of heavy hydrocarbons such as diesel fraction hydrocarbons are strictly inhibited [8–12]. Thus, a process of the methanol synthesis from syngas following the MTH reaction would be effective on the selective production of light hydrocarbons with the efficient utilization of the alternative carbon resources.

By employing hybrid catalysts composed of a methanol synthesis catalyst, e.g. Pd/SiO₂, Cu-ZnO and Cr-ZnO, and a zeolite catalyst, e.g. ultra-stable Y zeolite (USY) and beta zeolite, the direct synthesis of light hydrocarbons in liquefied petroleum gas (LPG) fraction from syngas has been developed [13–17]. In these LPG synthesis processes, syngas can be primarily converted to methanol over the metal-based catalyst. Subsequent conversion of methanol to hydrocarbons readily takes place over the zeolite which neighbors the metal-based catalyst in the hybrid catalyst. The rapid consumption of methanol gives the methanol synthesis from syngas an advantage over the reverse reaction of methanol to syngas over the metal-based catalysts, leading to higher yield of hydrocarbons than the calculated value based on the thermodynamic equilibrium [13].

ZSM-5, a MFI-type aluminosilicate material, is well known as a zeolite catalyst having the pore size and acid properties suitable for the production of gasoline-range hydrocarbons in the MTH reaction [8–10]. Considering the selective production of specified fuel hydrocarbons, the employment of a hybrid catalyst containing ZSM-5 would be suitable for the hydrocarbon production from syngas. Furthermore, since olefins are primarily produced in the MTH reaction, metal catalysts with high hydrogenation ability are required for obtaining paraffins as a final product. It was reported that Pd supported on zeolite efficiently converts olefins to paraffins during the conversion of syngas to hydrocarbons [15]. Thus,

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Pd/ZSM-5 is expected to efficiently produce paraffins in gasoline fraction from methanol that is generated from syngas.

Reaction processes using solid catalysts in near- and supercritical solvents have received considerable attention in the fields of organic synthesis [18–21] and biomass conversion [22–26] in the recent decades because a reaction rate can be significantly improved in the solvents. Supercritical hydrocarbon fluids have been applied to the FTS to increase the hydrocarbon yield and to suppress the generation of undesired products due to the efficient extraction of products from catalysts [27–31]. In a manner similar to the FTS reaction in the supercritical phase, the LPG synthesis from syngas using a hybrid catalyst in a near-critical solvent of *n*-hexane has been studied [32]. Efficient removal of heat generated during the reaction by the near-critical fluid leads to improvements in the stability of the catalyst as well as the selectivity for light hydrocarbons. In this paper, the term “near-critical” is used to connote the region close to the critical temperature and pressure of *n*-hexane.

In this study we investigated the catalytic activity of a hybrid catalyst composed of Cu-ZnO and Pd/ZSM-5 in a near-critical *n*-hexane solvent in the conversion of syngas to hydrocarbons via methanol. During the experimental trials, the reaction in the near-critical phase was compared with those in conventional phases to clarify the effect of the near-critical solvent on the catalytic activity and product distribution. We also investigated the effects of the acid amount and particle size of ZSM-5 as well as Pd loading on the hydrocarbon yield.

2. Experimental

2.1. Catalyst preparation

A hybrid catalyst was prepared by physically mixing the 355–710 μm pellets of a Cu-ZnO methanol synthesis catalyst of 0.5 g with those of a Pd/ZSM-5 catalyst of 0.5 g. Cu-ZnO was a commercial catalyst (MK-121, TOPSØE). Pd/ZSM-5 was prepared by impregnation method with a 4.557 wt% $\text{Pd}(\text{NH}_3)_2(\text{NO}_3)_2$ aqueous solution and commercial ZSM-5 with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 23 (CBV2314, Zeolyst) or 80 (CBV8014, Zeolyst). Commercial NH_4^+ -type ZSM-5 was calcined at 823 K for 3 h to become proton-type ZSM-5. Proton-type ZSM-5 was immersed in the $\text{Pd}(\text{NH}_3)_2(\text{NO}_3)_2$ aqueous solution with a supported Pd weight at room temperature overnight. The resultant was evaporated at 333 K, dried at 393 K for 3 h, and calcined at 823 K for 3 h. In addition, a MFI zeolite was hydrothermally synthesized by using an aluminosilicate gel with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 23 and tetrapropylammonium hydroxide (TPAOH) as a structure-directing agent (SDA) at 443 K for 24 h, according to the previous report [33]. The obtained Na^+ -type MFI zeolite was transformed to a proton-type MFI zeolite by ion-exchange treatment with 2.2 M NH_4NO_3 aqueous solution followed by calcination at 823 K for 3 h.

2.2. Characterization

The structure of the catalysts was examined by X-ray diffraction (XRD, Rigaku XRD-DSC-XII). The diffractometer was operated at 40 kV and 20 mA using Cu-K α radiation source. XRD patterns were recorded at 6 degree/min over the angular range of 5–50°. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the samples were determined by X-ray fluorescence analysis (XRF, Rigaku ZSX101E). The BET surface area and micropore volume were estimated from nitrogen adsorption isotherms at 77 K with a Micromeritics ASAP 2010 instrument. Prior to the analyses, the sample was treated at 573 K for 3 h under nitrogen flow in order to remove adsorbed compounds. External surface area (S_{EXT}) was estimated by the *t*-plot method. Field-emission scanning electron microscopic (FE-SEM) images of the catalysts

were obtained on an S-5200 microscope (Hitachi) operating at 10–15 kV.

Temperature programmed ammonia desorption (NH_3 -TPD) profiles were recorded on BELCAT-B (BEL Japan). The sample was pretreated under a He flow at 723 K for 1 h, and then cooled down to 373 K. Ammonia was allowed to make contact with the sample at 373 K for 1 h. Subsequently, the sample was evacuated to remove weakly adsorbed ammonia at 373 K for 30 min. Finally, the sample was heated from 373 K to 883 K at a raising rate of 10 K/min in a He flow. The desorbed ammonia was monitored on a TCD.

Temperature programmed hydrogen desorption (H_2 -TPD) profiles were recorded on BELCAT-B (BEL Japan). The sample was pretreated under a He flow at 473 K for 5 h, and then reduced under 10 vol% H_2 balanced by He at 573 K for 10 h. After cooling down to 323 K, a mixed gas composed of 10 vol% H_2 and He balance flowed into the sample for 1 h. Finally, the sample was heated from 323 K to 923 K at raising rate of 10 K/min in a He flow. A mass spectrometer was used to monitor the desorbed hydrogen ($m/e=2$).

2.3. Catalytic reaction test

A pressurized flow type of reaction apparatus with a fixed-bed reactor was used for this study. The experimental set-up scheme is shown in Fig. 1. The apparatus was equipped with an electronic temperature controller for a furnace, a vaporizer of a solvent, a stainless tubular reactor with an inner diameter of 6 mm, thermal mass flow controllers for gas flows and a back-pressure regulator. A solvent was pumped into the reactor by a high-pressure pump. 1 g of a hybrid catalyst was loaded in the reactor, and inert glass sand was placed above and below the catalyst. The length of the catalyst bed was about 6.0–6.5 cm. The catalyst was reduced in a flow of a mixture of 5% hydrogen and 95% nitrogen with 100 mL min^{-1} at 573 K for 3 h. After the reduction of the catalyst, the catalyst was cooled down to 473 K. Syngas (60% H_2 , 32% CO , 5% CO_2 , and 3% Ar) and *n*-hexane as a solvent were introduced into the catalyst to make the total pressure inside reach to 4.0 MPa in a He flow, and then the catalyst was heated up to 553 K. The partial pressure of syngas, P_{syngas} , of 2.5 MPa was retained, and the partial pressure of *n*-hexane, $P_{n\text{-hexane}}$, was varied from 0 MPa to 1.5 MPa. The catalyst weight to the flow rate ratio (W/F_{syngas}) was 9.7 g-cat h/mol-syngas. CO , CO_2 and CH_4 of the reaction products were analyzed with an on-line gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and a packed column of activated charcoal. The light hydrocarbon products were analyzed with another on-line gas chromatograph (Shimadzu GC-2014) equipped

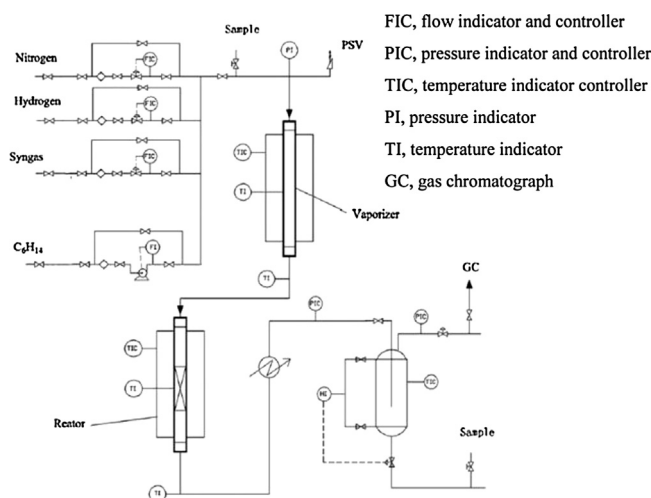


Fig. 1. Scheme of experimental set-up.

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