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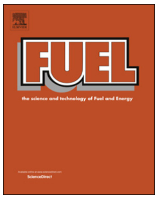

Full Length Article

Direct synthesis of liquid fuels and aromatics from syngas over mesoporous FeZrOx catalyst mixed with Mo/ferrierite

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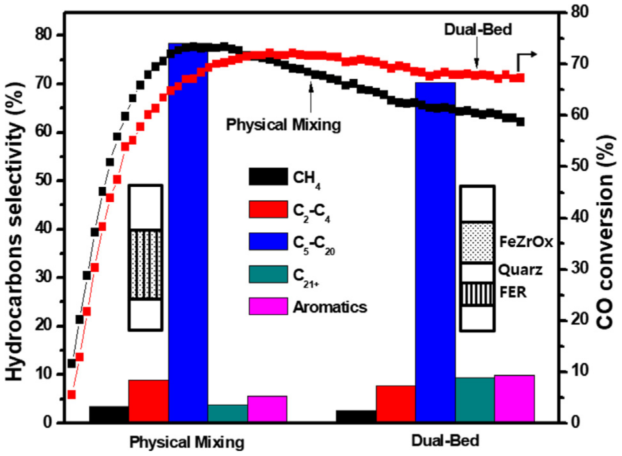
GRAPHICAL ABSTRACT



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ABSTRACT

Fischer–Tropsch synthesis (FTS) reaction on the hybrid catalysts containing a highly ordered mesoporous FeZrOx bimetal oxide physically mixed with Mo-modified ferrierite (Mo/HFER) were carried out to directly produce environmentally benign middle distillates and aromatics (BTXs) from syngas. Compared to the pristine FeZrOx itself, the simply mixed hybrid catalyst largely enhanced the selectivity to middle distillates and aromatics (BTXs) through direct CO hydrogenation by preserving its original ordered structures in the forms of partially reduced iron oxides due to their stronger interactions. At an optimal Mo content (~6 wt%) on the HFER frameworks, the hybrid FeZr-Mo(6)/HFER showed the synergistic effects such as higher CO conversion (59.7%) to liquid hydrocarbons (78.4% for C_5–C_{20}, 3.7% for C_{21+} and 5.7% for aromatics including BTXs) with a smaller CO_2 formation due to the less accumulation of carbonaceous deposits, optimum hydrophilicity, lower water-gas shift (WGS) reaction activity and larger number of weak acid sites. However, an excessive amount of Mo promoter (> 6 wt%) on the acidic HFER surfaces accelerated the formation of the graphitic carbons leading to the decrease of catalytic activity, which were attributed to its excess hydrophobicity and small amounts of acidic sites.

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1. Introduction

Fossil fuels have allowed a remarkable prosperity and advancement of human life, and vast multitude of essential petrochemical and fuel derivatives are currently originated from oil [1], and the majority (92%) of global energies in the area of transportation has been covered by fossil fuels [2]. Because of depleting fossil fuels reserves and rising atmospheric CO_2 concentration by an increasing energy demands, renewable energy resources such as biomass, wind, solar, and tidal have been largely attracted to generate alternative power sources [3]. With those context, chemical conversion of syngas ($CO + H_2$), which can be produced from carbon-based feedstock (biomass, petroleum coke, hydrocarbons, coal), into value-added fuel products (e.g., gasoline and diesel) and commodity petrochemicals (e.g., alcohols, olefins and aromatics) can be promising solutions to produce renewable energies. One of the essential driving forces for a revived interest in the syngas conversion processes is to produce liquid fuels through a typical Fischer-Tropsch synthesis (FTS) reaction [4,5]. It has played a remarkable role as gas-to-liquid (GTL) technology for producing synthetic lubricants and fuels, which can produce sulfur-free environmentally friendly fuels compared to conventional petroleum-based liquid fuels [6,7]. In comparison with a traditional coal-to-liquid (CTL) and GTL processes, biomass-to-liquid (BTL) process has been developed as the core technology by FTS reaction having the natures of wide-range hydrocarbon distribution [8,9], which can be generally described by a chain growth probability (α) with Anderson–Schulz–Flory (ASF) distribution [10]. However, the statistical ASF distribution of the hydrocarbons reveals two main obstacles for a direct synthesis of liquid hydrocarbon fuels with the limitation of maximum selectivity to fuels, 45% for gasoline (C_5–C_{10}) and 30% for diesel (C_{11}–C_{20}) [11].

Among the active metals such as Fe, Co and Ru nanoparticles [12,13], Ru or Co-based FTS catalysts haven been considered as the most effective ones to selectively produce long-chain hydrocarbons by CO hydrogenation [14]. However, their higher costs and limited reserves, especially for Ru metal, seem not to be proper for an industrial-scale application. In addition, the Co-based FTS catalysts seem to be less suitable for the synthesis of liquid fuels from CO-rich syngas derived from biomass or coal feedstock, which makes it less favorable for the BTL and CTL application [8]. On the other hand, the Fe-based FTS catalysts are economically attractive due to its flexibility with wide operation conditions as well as due to less significant formation of CH_4 and paraffins. Moreover, the Fe-based catalysts compared to the Co or Ru-based ones can offer a significantly higher activity for WGS reaction, which can be useful for the conversion of syngas with a lower H_2/CO ratio derived from biomass or coal to directly produce alkenes from syngas [15,16]. However, the widely distributed hydrocarbon products (C_1–C_{80}) obtained from conventional FTS catalysts are generally required to further treat to produce high-quality liquid fuels such as gasoline, jet fuel, and diesel [10]. To produce those liquid fuels directly from syngas, it is necessary to decrease the selectivity to gaseous light hydrocarbons (CH_4 and C_2–C_4 paraffin) as well as to increase that of C_{5+} hydrocarbons on the well-designed hybrid catalysts consisting of active metals for CO hydrogenation and solid-acid components for hydrotreating reactions. For more details, in-situ conversion of α-olefins and long-chain *n*-paraffins (primary FTS products) takes place into useful gasoline and diesel fuels on Brønsted acid sites of zeolites by oligomerization, cracking or isomerization reaction. Based on the perspective of many solid-acid zeolites in the hybrid catalysts, it has to possess enough active sites to be incorporated with Fe-based FTS catalysts working at higher temperatures (250–350 °C) than that of the Co-based FTS catalysts (200–240 °C) [12,13,17] such as ZSM-5 [18], Y zeolite [19], L zeolite [20] and Beta zeolite [21]. In general, the higher selectivity to CH_4 and light (C_2–C_4) alkanes have been reported on the acidic ZSM-5 and Beta zeolite mixed with Co/SiO_2, CoZr and Ru metals as the FTS catalysts [18,22,23]. In addition, the deactivation behaviors occurring on the solid-acid catalysts depend on the relative spatial locations of the active metals and zeolite components on the hybrid catalysts [5,24]. Therefore, FER zeolite seems to be a good candidate for a liquid product synthesis because of its relatively planar pore structures consisting of the 8 and 10-membered rings (MR) channels with larger moderate acidic sites than other zeolites, which can produce less amount of heavy coke precursors as well [25–27]. In addition, Mo species plays a key role in accelerating CO hydrogenation with moderate H_2 activation ability as well as in promoting zeolites activity, which can increase the selectivity of middle distillates with enhanced nonlinear hydrocarbons by isomerization [28,29].

Based on our previous work [30], the highly ordered bimetal oxides of Fe_2O_3-ZrO_2 without any promoters showed a dramatically increased activity for CO hydrogenation to value-added C_{5+} products. The mesoporous Fe_2O_3-ZrO_2 structures effectively promoted the mass transport rate of hydrocarbons formed, which was responsible for more stable mesopore structures with a small amount of inactive coke precursors formations. In the present study, we demonstrate a highly efficient and simple hybrid catalysts comprised of the ordered mesoporous Fe_2O_3-ZrO_2 with Mo(x)-modified H-form FER (denoted as FeZr-Mo(x)/HFER), wherein the Mo(x)/HFER played crucial roles in tuning the hydrocarbon distributions. However, to date, there has been little reports on the utilization of the FER for the direct conversion of CO to gasoline and diesel-range hydrocarbons. We found that the addition of optimal amount of Mo species to the H-form FER leads to a significant increase of CO conversion with an improved selectivity to C_5–C_{20} hydrocarbons (78%) as well as to suppresses CH_4 and light paraffinic C_2–C_4 selectivity on the optimal FeZr-Mo(x)/HFER hybrid catalyst.

2. Experimental section

2.1. Catalyst preparations

The highly ordered mesoporous Fe_2O_3-ZrO_2 bimetal oxides were prepared by the well-known nano casting replica method with a hard template of a well-ordered mesoporous KIT-6 [30,31], by using two different metal precursors as reported in our previous work [31,32]. Briefly, two metal precursors such as 8 mmol of iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Samchun Chem.) and 1 mmol of zirconium nitrate oxide dihydrate ($ZrO(NO_3)_2 \cdot 2H_2O$, Kanto Chem.) were dissolved simultaneously in deionized water, and the solution was completely impregnated into the mesopores of the KIT-6 using an incipient wetness impregnation method. Then, the powder was dried overnight at room temperature and subsequently calcined at 500 °C for 6 h under a heating rate of 1 °C/min. The as-prepared bimetal oxides embedded into three dimensional mesoporous channels of the KIT-6 were washed with an aqueous basic NaOH solution at 80 °C to extract the mesoporous KIT-6 template, followed by washing with deionized water for several times. Finally, the template-free ordered mesoporous Fe_2O_3-ZrO_2 oxides (molar ratio of $Fe_2O_3/ZrO_2 = 1/0.12$) was dried again at 80 °C, and the final bimetal oxides were denoted as FeZrOx. In addition, an ammonium-form ferrierite zeolite with a SiO_2/Al_2O_3 molar ratio of 12 (Zeolyst International Inc.) was calcined at 550 °C under air environment to prepare solid-acid H-form ferrierite (HFER). An aqueous solution of Mo precursor ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Alfa Aesar) was impregnated on the surfaces of the HFER, which was dried overnight at 80 °C and calcined at 550 °C for 4 h. The Mo-modified HFERs with different Mo loading are denoted as Mo(x)/HFER, where x digit represents a nominal Mo content in wt%. For the preparation of the hybrid catalysts, the mesoporous FeZrOx and Mo(x)/HFER were physically mixed, and subsequently grinded manually at a fixed weight ratio of the FeZrOx bimetal oxides to HFER at 1:1, and the final hybridized catalysts are denoted as the FeZr-Mo(x)/HFER.

2.2. Catalytic activity measurements

The catalytic activity of the fresh hybrid FeZr-Mo/HFER was