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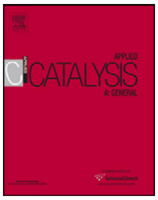

CoZr/H-ZSM-5 hybrid catalysts for synthesis of gasoline-range isoparaffins from syngas

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ABSTRACT

Different CoZr/H-ZSM-5 hybrid catalysts were prepared by a hydrothermal synthesis method, where H-ZSM-5 was enwrapped onto the Co-ZrO_2 Fischer–Tropsch synthesis (FTS) catalyst. The catalysts were characterized by BET, XRD, ^{27}Al NMR, SEM, TEM, XPS, H_2-TPR, NH_3-TPD and IR techniques. The catalytic performance for the direct conversion of syngas to high-octane gasoline-range (C_{5-11}) hydrocarbons was studied. Coke formation on the spent catalysts was measured by TGA. Compared with the base Co-ZrO_2 catalyst or the physically mixed catalyst of Co-ZrO_2 with H-ZSM-5, the reducibility of the hybrid catalyst was much lower due to the strong interactions of cobalt phase with zeolite and/or zirconia. The catalytic performance results showed that the as-prepared hybrid catalysts had high selectivity towards gasoline-range isoparaffins and relatively low methane selectivity in spite of the relatively low catalytic activity. The hybrid catalysts could effectively minimize the accumulation of carbonaceous deposits. The catalyst with aluminum isopropoxide as Al source exhibited excellent selectivity on the isoparaffin synthesis and relatively good stability.

1. Introduction

The Fischer–Tropsch synthesis (FTS) is a well-known process to produce high quality sulfur-free liquid fuels from alternative sources (e.g., coal, natural gas, and biomass) via the conversion of syngas over iron or cobalt based catalysts. The carbon number distribution of FT products (from methane to long-chain hydrocarbons) obeys a statistical model (Anderson–Schulz–Flory, ASF) with a chain-growth probability parameter α. Such a distribution caused a limitation to the maximum gasoline and diesel yield (i.e., 48 wt.% for gasoline and 40 wt.% for diesel) [1,2].

The FTS catalysts combined with acidic zeolite or other acidic supports had been proposed to produce more isoparaffins as the ideal synthetic gasoline [2,3], e.g., several groups tried to disperse FT active metal on the acidic zeolite [4–6]. However, due to the low reduction degree of the FT elements, the CO conversion was low and the methane selectivity was high. Recently, a novel zeolite membrane core-shell catalyst has been reported, over which both FTS and hydroprocessing reaction were combined [7–14]. The syngas (CO + H_2) diffused through zeolite shell and reached the core for FTS, then, the products of the FTS process might diffuse into zeolite channels where the hydrocarbons would be hydrocracked or isomerized over the acidic sites. Such capsule catalysts exhibited a quite high selectivity towards gasoline-range isoparaffins. Unfortunately, when H-ZSM-5 was used as the shell, the selectivity to methane over such core-shell catalyst was much higher than that of the FTS catalyst alone [7–11]. It might be because the different diffuse rates of H_2 and CO in the small pores or channels, e.g., the lower diffusion efficiency of CO cause a high H_2/CO ratio on the surface of the core catalyst, which might lead to high methane selectivity [15]. The methane selectivity was found to be remarkably reduced for H-β/Co/Al_2O_3 core-shell catalyst [12,13], which was ascribed to the hydrophilicity of the zeolite shell. According to the reference, there was a distribution gradient for the SiO_2/Al_2O_3 in the zeolite membrane, the part near the Al_2O_3 substrate that had a relatively higher Al content would be high hydrophilicity [12]. As a result of the solubility rule (like dissolves like) the presence of water could promote the accumulation of CO, which led to a lower H_2/CO ratio in the interior of the catalyst and then lower the methane selectivity [16]. It seems that the properties of the support of those FTS catalysts such as Co/SiO_2 or Co/Al_2O_3, which contained the important zeolite component of Si or Al element, might have an important impact on the performance of zeolite membrane core-shell catalysts.

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Addition of zirconia as promoter has been reported to improve the FTS activity of the Co-based catalysts [17–25] and the results also revealed that C_{5+} selectivity or chain growth probability of hydrocarbons could be promoted upon addition of zirconia [17,19,20,23,24]. Moreover, zirconia used as a catalyst support for FTS could be found in literatures [26–28] and high C_{5+} selectivity could be obtained. Our group had also make researches on Co-ZrO_2 catalysts for FTS [29–33].

Based on the above discussion, in this investigation we have designed a new hybrid catalyst combining FTS catalyst and acidic zeolite catalyst to improve the gasoline-range isoparaffin selectivity and decrease the methane selectivity. Herein, cobalt-zirconia (noted as CoZr) catalyst, prepared by co-precipitation as reported by our group [32], was adopted as the FTS catalyst due to its low methane selectivity and high C_{5+} selectivity, and H-ZSM-5 zeolite was enwrapped on the base CoZr catalyst by hydrothermal synthesis in the present work.

2. Experimental

2.1. Preparation of catalysts

The co-precipitated cobalt-zirconia (CoZr) catalyst (ca. 20 wt.% cobalt as active metal, molar ratio of Zr/Co was 1.74) was prepared in the usual batch-wise manner by adding ammonia solution (25.0 wt.%) to a solution containing $Co(NO_3)_2{\cdot}6H_2O$ and $ZrOCl_2{\cdot}8H_2O$ at 373 K. The precipitate was filtered until no Cl^- ion was detected by $AgNO_3$ aqueous solution. Then the precipitate was dried at 393 K and calcined in air at 673 K for 4 h. The CoZr catalyst was pressed at 40.0 MPa and then crushed to 200–400 mesh for further use. Co dispersion of the CoZr catalyst was 3.1% as determined by H_2 chemical adsorption.

For H-ZSM-5 zeolite precursor solution preparation, deionized water and ethanol (99.5%) were used as solvent. Tetrapropylammonium hydroxide (TPAOH, 25.0 wt.%) was used as the template, with aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, 99.5%) and tetraethyl orthosilicate (TEOS, 98.0%) as sources of aluminum and silicon, respectively. The composition of the H-ZSM-5 zeolite precursor solution was at a molar ratio of $1.0SiO_2$:0.25TPAOH:$0.025Al(NO_3)_3$:$60H_2O$:4EtOH. First, $Al(NO_3)_3{\cdot}9H_2O$, deionized water, absolute ethanol, TEOS, and 25.0 wt.% TPAOH in water were sealed in a stainless steel autoclave with a 150 mL Teflon inner tank, and then the autoclave was fixed in the hydrothermal synthesis equipment. Aging of the precursor solution was carried at 333 K for 2 h to form the lucid sol.

The CoZr/H-ZSM-5 hybrid catalysts were prepared by a hydrothermal synthesis method similar to the reference [13]. Two methods were used to pretreat the CoZr catalyst particles before they were added into the zeolite precursor solution: (1) heating under a reflux of a 25.0 wt.% TPAOH (Tetrapropylammonium hydroxide) solution at 383 K for 4 h, washing with deionized water, and then impregnating into absolute ethanol for 2 h, followed by filtration (denoted as method R); (2) only impregnating into absolute ethanol for 2 h, followed by filtration (denoted as method I).

For the hydrothermal synthesis process, the pretreated CoZr catalyst (particle size: 200–400 mesh) was added into the H-ZSM-5 zeolite precursor sol, then the autoclave was put into a hydrothermal synthesis equipment at 453 K and run at a rotation speed of 10 rpm for 5 days for crystallization. The obtained catalyst was poured into a large amount of deionized water, filtered and washed with deionized water until pH value of the filtrate was less than 8. Then, the sample was dried at 393 K for 12 h, followed by calcination at 773 K for 5 h in air to remove the organic template. The hybrid catalysts were noted as CoZr/Z-R, CoZr/Z-I, where the Z stands for H-ZSM-5 zeolite. The other two hybrid catalysts with aluminum isopropoxide ($((CH_3)_2CHO)_3Al$, 99.5%) as Al source were also prepared and named as CoZr/Z-I-P (crystallization of the zeolite for 5 days) and CoZr/Z-I-7 (crystallization of the zeolite for 7 days).

H-ZSM-5 powder was directly synthesized with H-ZSM-5 zeolite precursor solution under the same preparation condition that was used for the hybrid catalyst. The physical mixture catalyst was prepared by well mechanically mixing CoZr FTS catalyst and H-ZSM-5 zeolite in which the H-ZSM-5 zeolite was loaded 30.6 wt.%, the same as that for the hybrid catalyst. The obtained physical mixture catalyst was denoted as CoZr/Z-M.

2.2. Catalysts characterization

Measurements of the surface area and pore volume of catalysts were performed in a Micromeritics ASAP-2000 instrument by N_2 adsorption–desorption. Before analysis, the samples were degassed at 473 K overnight.

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-A X-ray diffractometer using a Cu K_α radiation. The spectra were scanned at a rate of $2^\circ\,min^{-1}$ in the range $2\theta = 5$–80°.

^{27}Al solid-state NMR experiments were carried out at $B_0 = 9.4\,T$ on a Bruker AVANCE III 400 WB spectrometer. The corresponding resonance frequency of ^{27}Al was 104.3 MHz. Samples were packed in a 4 mm ZrO_2 rotor and spun at the magic angle (54.7°), and the spin rate was 15 kHz. Single pulse magic angle spinning spectra were acquired using a high power 0.5 μs pulse, corresponding to a tip angle of 18° and a recycle delay of 0.5 s. The ^{27}Al chemical shift was externally referenced to a 1.0 M aqueous solution of $Al(NO_3)_3$.

Scanning electronic micrographs (SEM) images were obtained on LEO 1530VP.

Transmission electron microscopy (TEM) images were recorded using a JEOL-2011 microscope operated at 200 kV.

X-ray photoelectron spectroscopy spectra (XPS) were recorded on a XSAM-800 spectrometer using an Al K_α (1486.7 eV) X-ray source. To remove charging shifts and deal with Fermi edge coupling problems, binding energies (BE) were scaled against the peak of the C–(C, H) component coming from contamination carbon (set to 284.6 eV). The pressure of the analysis chamber was less than 2×10^{-8} Pa.

Hydrogen temperature-programmed reduction (H_2-TPR) was carried out with a mixture of 5% H_2/N_2 as the reductive gas. The sample (0.025 g) was reduced in a flow of H_2/N_2 at a rate of $10\,K\,min^{-1}$. The effluent gas was detected by TCD after removal of the product water using 5 Å molecular sieves.

Temperature programmed NH_3 desorption (NH_3-TPD) was performed in a quartz micro-reactor. 0.10 g of each sample was freshly heated in argon at 873 K for 30 min. NH_3 was then introduced to the sample after it was cooled down to 373 K. To remove the weakly adsorbed NH_3, the sample was swept using argon at 373 K for 2 h. The TPD experiments were then carried out with a carrier-gas flowing rate of $40\,mL\,min^{-1}$ argon from 373 K to 873 K using a linear heating rate of $10\,K\,min^{-1}$. Desorption of NH_3 was detected by Shanghai GC-920 equipped with a thermal conductivity detector (TCD).

Infrared (IR) spectroscopy of adsorbed pyridine was applied to determine the surface acid properties of the selected catalysts. The measurements were performed in a Nicolet Magna 550 spectrophotometer. Wafers of $15\,mg\,cm^{-2}$ were degassed overnight under vacuum (10^{-3} Pa) at 673 K. The transmission spectra were recorded, and then pyridine (6×10^{-2} Pa) was admitted. After equilibration, the samples were degassed for 1 h at 533 K. After desorption, the spectrum was recorded at room temperature and the background was subtracted. The amount of Brønsted and Lewis acid sites was derived from the intensities of the IR bands at ca. 1450 and $1550\,cm^{-1}$, respectively.