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One-step synthesis of H–β zeolite-enwrapped Co/Al_2O_3 Fischer–Tropsch catalyst with high spatial selectivity

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ABSTRACT

A tailor-made encapsulated catalyst with a H–β zeolite shell has been directly synthesized over Co/Al_2O_3 pellets to form a core–shell structure without pinholes and cracks by a hydrothermal synthesis method. Pretreatment of the Co/Al_2O_3 pellets with reflux of hot TEAOH solution can clean and corrode the pellet surface due to its strong basicity, and can enlarge the mean pore size of the pellets. Impregnation of the Co/Al_2O_3 pellets in EtOH is important to avoid the corrosion of the internal pores, to prevent the introduction of Co species into the zeolite coating, and to realize a pure and uniformed β-zeolite coating. For the catalytic reaction of direct isoparaffin synthesis from syngas, the molar ratio of $C_{\text{isoparaffin}}/C_{\text{normal-paraffin}}$ of the products obtained from the encapsulated catalyst increased about 64% than that of the products obtained from physical-mixed components. This concept of encapsulated catalyst can be useful to carry out various consecutive or multiple-step catalytic processes, where multiple reactions occur on different active centers.

1. Introduction

Because of the spatial selectivity offered by the unique pore and channel structure, zeolite membranes have been studied widely for separation. They can be supported onto inert materials, such as α-Al_2O_3, SiO_2, and stainless steel [1–4], to separate target molecules from mixtures, and can be incorporated in membrane reactors to separate products and overcome thermodynamic equilibrium limitations [5–7]. In almost all these cases, the zeolite membrane acts as an inert material without any catalytic activity.

The trapping of catalytic active species into a selective penetrable shell to form micro-encapsulated or nano-encapsulated catalysts with a core–shell structure has been reported, utilizing zeolite or carbon shells [8–15]. In most of these studies, the shell was only used for product or reactant separation. For example, the zeolite coating used was silicate-1, without acidic sites included [8,15].

On the other hand, physical-mixed catalysts with multiple functions are often used to carry out several catalytic reactions in one step in complex chemical processes. For example, Fischer–Tropsch synthesis (FTS) can produce synthetic diesel (normal paraffins) with Co-, Ru-, or Fe-based catalysts from syngas ($CO + H_2$), which can be obtained from resources such as coal, biomass, natural gas, and garbage [16]. After removing FTS by-products such as water and gaseous hydrocarbons, premier gasoline (branched paraffins) can be produced from FTS diesel in a separate reactor using solid acid catalysts, as in the Shell SMDS plant in Malaysia. It is well known that zeolites present good performance for hydrocracking and isomerization due to their acidic properties [17]. Accordingly, mixtures of H-type zeolite catalysts and FTS catalysts such as Co/SiO_2 [18,19] and iron-based catalyst [20] have been employed to produce isoparaffins directly from syngas. Long-chain normal paraffins including wax produced by the FTS catalyst are decomposed and transformed in situ to gasoline-range hydrocarbons by hydrocracking process and isomerization to isoparaffins with the aid of H_2 from syngas on the zeolite catalyst. This method can also treat FT wax, which generally deactivates FTS metallic catalysts, to form isoparaffins, the target products. It should be noted that loading of FTS active metals such as Co, Fe, or Ru directly onto zeolite supports to form metal-zeolite catalysts aiming at one-step isoparaffin synthesis from syngas is impractical because Co, Fe, or Ru on the zeolite surface cannot be easily reduced. Strong interactions between the zeolite and the precursors of these metals, generally oxides, make the extent of reduction of the supported metal quite low, resulting in a low FTS activity [21,22].

However, this kind of catalyst has no spatial relationship with component catalysts. For the physical-mixed H-ZSM-5 and Co/SiO_2 catalyst [18,19], syngas formed linear hydrocarbons on cobalt catalyst, and then these FTS hydrocarbons migrated to the

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neighboring H-ZSM-5 catalyst for hydrocracking and isomerization. Unfortunately, a part of FTS hydrocarbons desorbed directly and escaped without contact with the zeolite catalyst. This induced a high selectivity of the residual heavy FTS hydrocarbons (normal paraffins).

Due to the drawback of the hybrid catalyst, a two-stage reactor was designed, i.e. FTS catalyst in the first one, and H-type zeolite in the second one, in our previous study [23]. It was found that the distribution of carbon number of the hydrocarbons was extremely confined after the gas passed through the second reactor. To save energy and improve economic efficiency, our group firstly proposed one kind of encapsulated catalyst by coating H-ZSM-5 zeolite onto Co/SiO_2 pellet for one-step synthesis of isoparaffins from syngas [24,25]. It was found that the encapsulated H-ZSM-5/Co/SiO_2 catalyst could remove all the C_{11+} hydrocarbons, while the physical-mixed catalyst with the same composition still had a lot of C_{11}–C_{25} products. Recently, a tailor-made encapsulated catalyst, i.e. H–β zeolite shell directly enwrapped Co/Al_2O_3 FTS catalyst pellet [26] by one step, was designed through a hydrothermal synthesis process. This novel H–β/Co/Al_2O_3 encapsulated catalyst presented not only a much higher isoparaffin selectivity but also a more perfect zeolite coating formation than the previous H-ZSM-5/Co/SiO_2 encapsulated catalyst [24,25]. The conventional H–β zeolite preparation method by ion-exchange from Na-β zeolite [27–29] is not applicable to our study since Na is considered to be a poison for FTS process [30,31].

In this paper, the preparation method and synthesis mechanism are elucidated and discussed in detail. The structure of the encapsulated catalyst was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and energy-diffusive X-ray spectroscopy (EDX) analysis, and the catalytic activity of the encapsulated catalyst for isoparaffin synthesis directly from syngas was also investigated and compared with that of the physical-mixed catalyst.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation of Co/Al_2O_3 FTS catalyst

Co/Al_2O_3 FTS catalyst was prepared by a conventional incipient wetness impregnation method. An aqueous solution of $Co(NO_3)_2$ was added to γ-Al_2O_3 (JRC-ALO-6, JGC Universal Ltd.; specific surface area: 180 $m^2\,g^{-1}$ and pore volume: 0.93 $cm^3\,g^{-1}$) pellets, which had been heated at 400 °C for 2 h in air before the impregnation. The catalyst precursor was evaporated for 1 h, dried at 120 °C for 12 h, and was then calcined in air at 400 °C for 2 h. The size of catalyst pellet was 0.85 to 1.7 mm. The cobalt loading in the samples was 7 wt%.

2.1.2. Preparation of H–β zeolites and H–β/Co/Al_2O_3 encapsulated catalysts

For H–β zeolite precursor solution preparation, 4.1 g of SiO_2 (Aerosil 200, fumed, Silica content: 99.8%, particle: 0.014 μm, surface area: 200 $m^2\,g^{-1}$, Sigma–Aldrich, Inc.), 14.4 g of 25 wt% TEAOH in water, 0.3 g of $((CH_3)_2CHO)_3Al$ (Aluminum iso-propoxide, Sigma–Aldrich, Inc.), and 3.6 g of deionized water were mixed under continuous stirring at room temperature for 2 h. The composition of the H–β zeolite precursor solution was at a molar ratio of $96.53SiO_2$:34.55TEAOH:$1.0Al_2O_3$:$1130H_2O$.

The H–β/Co/Al_2O_3 encapsulated catalysts were prepared by a hydrothermal synthesis method. A H–β zeolite coating was directly constructed onto the pretreated Co/Al_2O_3. Three methods were used to pretreat the Co/Al_2O_3 FTS catalyst pellets before they were added into the zeolite precursor solution: (1) vacuuming for 1 h, soaking in a 25 wt% TEAOH (tetraethylammonium hydroxide) solution, treating by ultrasonication (38 W) for 15 min, followed by filtration (denoted as method T1); (2) heating under a reflux of a 25 wt% TEAOH solution at 114 °C for 4 h, followed by filtration (denoted as method T2); and (3) heating under a reflux of a 25 wt% TEAOH solution at 114 °C for 4 h, washing with distilled water thrice, and then immersing into an absolute ethanol liquid (purity > 99.5%) for 24 h, followed by filtration. This method is denoted as T3.

For the hydrothermal synthesis process, 2.0 g of pretreated Co/Al_2O_3 catalyst (pellet sizes: 0.85 to 1.7 mm) and 22.4 g of H–β zeolite precursor solution were added into a hydrothermal synthesis equipment (DRM-420DA, Hiro Company). Crystallization of the zeolite was carried out at 155 °C and at a rotation speed of 2 rpm for 3 days. The obtained catalyst was filtered from the solution and was washed with distilled water until its pH value was less than 8. It was then dried at 120 °C for 12 h and was calcined at 550 °C for 8 h in air. The synthesized catalyst, distinguished from the catalysts prepared by the different Co/Al_2O_3 pellet pretreatment methods, was denoted as H–β/Co/Al_2O_3-T1, H–β/Co/Al_2O_3-T2, or H–β/Co/Al_2O_3-T3. The weight of H–β zeolite coating on the H–β/Co/Al_2O_3-T3 catalyst was found to be 23.2 wt%.

Moreover, direct synthesis of H–β zeolite was also performed through the hydrothermal process with the same zeolite precursor solution and preparation procedure, as mentioned above, without adding Co/Al_2O_3 pellets. The crystallization temperature was 155 or 175 °C, and the crystallization time was 1, 2, or 3 days.

2.1.3. Preparation of hybrid catalyst

The mixture of Co/Al_2O_3 and H–β catalyst was prepared by mechanically mixing Co/Al_2O_3 FTS catalyst and H–β zeolite, synthesized with H–β zeolite precursor solution under the preparation condition that was the same as that used for the encapsulated catalysts. The weight of H–β zeolite was 23.1 wt%, a loading that was the same as that for the encapsulated catalyst. The obtained hybrid catalyst was denoted as H–β/Co/Al_2O_3-MX.

All the chemicals were supplied by Wako Pure Chemicals Ltd., unless indicated otherwise.

2.2. Catalysts characterization

The pore size distribution of the catalysts was obtained by N_2 physisorption using an automatic gas adsorption system (Quantachrome, Autosorb-1, Yuasa Co.) at −196 °C. The sample was outgassed at 200 °C overnight prior to N_2 physisorption.

Co dispersion of the Co/Al_2O_3 pellet catalysts prepared by the T3 pretreatment was determined by H_2 chemical adsorption with an apparatus that was the same as that used for the previous N_2 physisorption experiment. Prior to the measurement, the samples were degassed at 300 °C and at 3.0 Pa for 1 h, reduced in flowing H_2 at 400 °C for 10 h, and evacuated at 350 °C for 1 h to desorb any H_2, followed by cooling to 100 °C. The H_2 chemisorbed uptakes were measured with the double-isotherms method at 100 °C by assuming that one cobalt atom was covered by one hydrogen atom [32,33], and the dispersion percentage $D\%$ was calculated with the following equation:

$$D\% = \frac{1.179X}{Wf} \tag{1}$$

where X is the total H_2 uptake in micromoles per gram catalyst, W is the weight percentage of cobalt, and f is the fraction of cobalt reduced to the metal determined from O_2 titration.

The O_2 titration experiment was carried out at 400 °C to determine the reduction degree of the pre-reduced catalysts with the assumption that the metallic cobalt atoms oxidized totally to