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Effective activation of montmorillonite and its application for Fischer-Tropsch synthesis over ruthenium promoted cobalt

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ABSTRACT

The natural Na-type montmorillonite (Na-MMT) suspended in the 20 wt.% HNO_3 aqueous solution at concentrations between 2-20 wt.% was activated at 70–104 °C for a period, respectively. The thus obtained materials were abbreviated as acid-MMT-m-t/T, where m, t and T are the concentration of Na-MMT suspension (wt.%), time (h), and temperature (°C) during the acid activation, respectively. The Co-Ru/acid-MMT (20 wt.% Co and 0.1 wt.% Ru) was prepared by the incipient impregnation method. The materials were characterized by XRD, FT-IR, XRF, N_2 adsorption-desorption at low temperature, H_2-TPR, H_2-TPD, oxygen titration, and NH_3-TPD techniques. In comparison to the results of the Na-MMT, the structural, textural, and acidic properties of the acid-MMTs were clearly changed, the extent of which is strongly dependent on the acid activation conditions. For the first time, the acid-MMT with desired properties were obtained using a high ratio of Na-MMT suspension, such as 10 wt.%, leading to a significantly improved process efficiency of the acid activation. The structural and compositional changes of acid-MMTs gave significant impacts on the reduction behavior of Co-Ru/acid-MMT catalysts. Moreover, the addition of Ru to Co/acid-MMTs decreased the peak temperatures of the two-step reduction of Co_3O_4 to Co via the CoO intermediate, leading to an increased extent of reduction of cobalt. The catalysts were comparatively investigated for Fischer-Tropsch (FT) synthesis in a fixed-bed reactor under the conditions of $H_2/CO = 2$, $W/F = 5.0\ g \cdot h \cdot mol^{-1}$, 235 °C, and 1.0 MPa. Results showed that the CO conversion was decreased in the order of Co-Ru/acid-MMT-2-12/104 > Co-Ru/acid-MMT-10-12/104 > Co-Ru/acid-MMT-20-12/104 ≫ Co-Ru/acid-MMT-2-12/70 > Co-Ru/acid-MMT-2-4/70 > Co/acid-MMT-2-4/70. Moreover, all of the Co-Ru/acid-MMT catalysts showed clearly higher selectivity of C_5-C_{12} hydrocarbons and lower selectivity of C_{21}^{+} hydrocarbons compared with Co/SiO_2 catalyst. The Co-Ru/acid-MMT-2-12/70 showed about 46% C_5-C_{12} selectivity at a reasonable CO conversion level.

1. Introduction

The Fischer-Tropsch (FT) synthesis is one of the most important processes to convert syngas ($H_2 + CO$) into hydrocarbons with significantly varied carbon numbers. Thus, FT synthesis has been receiving a considerable worldwide attention because of the increasing demand for clean fuels and efficient utilization of natural gas, coal, or biomass [1,2]. In the case of the FT catalysts, the supported cobalt shows the most superior and developing potentials due to its reasonable cost, high activity, high chain-growth probability, low water-gas shift activity, and high resistance to deactivation [3]. Therefore, it has been a hot topic to improve the catalytic activity of cobalt-based catalyst. It is well known that the activity of FT synthesis depends primarily on the number of active metallic cobalt sites, which is determined by the dispersion and reduction degree of cobalt. To facilitate the reduction of Co, the important strategy is to add a small amount of noble metal promoters such as Pt, Pd or Ru taking advantage of the hydrogen-spillover effect [4–8]. Moreover, the reduction degree and dispersion of cobalt over supported cobalt catalysts are significantly influenced by pore structures of the support. With increasing the average pore diameter of SiO_2 from 40 to 150 Å, the reduction degree of Co over Co/SiO_2 is found to be increased while the dispersion of Co is decreased [9]. The results of Khodakov et al. [10] indicate that cobalt particles in small mesoporous silica (20–25 Å) display a low reducibility, and the catalyst with a smaller pore size is less active than that with a larger one. In the case of γ-Al_2O_3 as a support, similar results are also reported [11].

Montmorillonite (MMT) is a kind of natural minerals with the crystal structure of 2:1 layered silicates. The alkali metal ions, commonly sodium ion, as charge-balance cations located in the clay interlayer, are exchangeable [12]. Considering the composition and layered structure of MMT, mesopores can be created via several methods such as acid or alkaline activation, ion exchange, and pillaring [3,12–16]. These adjustable properties make MMT an important material for catalysts or catalytic supports. Among the available modification methods, the acid activation has been proved one of the most simple and efficient routes

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to adjust the porosity and acidity of MMT [13,17–19]. Results from Temuujin et al. [17] indicate that porous silica with a card-house mesoporous structure (6-10 nm) is formed by treating the clay with hydrochloric acid. Recently, we investigated the activation of Na-MMT with HNO_3 (acid-MMT) under varied conditions, and the acidic and textural properties of the acid-MMT are significantly dependent on the activation conditions [13], i.e., 1) the MMT activated by 20 wt.% HNO_3 under mild conditions (80 °C and 12 h) shows a narrowed pore size distribution centered at about 3.7 nm and the maximum amount of acidic sites; 2) the MMT activated by 20 wt.% HNO_3 under severe conditions (100 °C and 24 h) has a very broad pore size distribution centered at about 15.6 nm and a significantly low acidity. Meanwhile, it is proved that cobalt-supported acid-MMT is beneficial for selectively controlling the FT product distribution [13]. However, the acid activation is limited at a low concentration of the Na-MMT suspension (2 wt.%). As a result, the efficiency of the acid activation is low. To the best of our knowledge, a low concentration of clay suspension, 2 wt.% in general, is commonly used during the process of the acid activation, and the effect of the clay-suspension concentration on the structural, textural, and acidic properties of the acid activated clay is not reported in the open literature. In the case of the catalytic applications such as FT synthesis, the textural, structural, and acidic properties of the acid activated clay play an important role in determining the activity and product selectivity of the catalyst.

Based on these understandings, this work aims at studying the effect of concentration of Na-MMT suspension on the structural, textural, and acidic properties of the acid-MMT. Thus, Na-MMT suspension with significantly varied concentrations from 2 to 20 wt.% was treated with a 20 wt.% HNO_3 aqueous solution under the mild (70 °C) and the severe (104 °C) conditions, respectively. The incipiently impregnated Co on the acid-MMT was evaluated for FT synthesis. The impact of the structural, textural, and acidic properties of the acid-MMT as well as the addition of a small amount of Ru promoter on the FT performance of Co/acid-MMT catalysts was comparatively investigated. Delightfully, the catalyst based on the 20 wt.% Na-MMT suspension activated at 104 °C for 12 h exhibited a high selectivity of C_5-C_{12} hydrocarbons and a low selectivity of long-chain FT hydrocarbons (C_{21}^{+}) at a reasonable CO conversion.

2. Experimental

2.1. Catalyst preparation

The purified Na-MMT (Zhejiang Sanding Group Co., Ltd.) was directly used without a further purification. The Na-MMT at concentrations from 2 to 20 wt.% was suspended in the distilled water, and was activated with 20 wt.% of HNO_3 aqueous solution at 70–104 °C for 4–12 h, respectively. After this, the suspension was centrifuged, washed, dried, and calcined at 550 °C for 4 h. The obtained materials were abbreviated as acid-MMT-m-t/T, where m, t and T are the concentration of Na-MMT suspension (wt.%), time (h), and temperature (°C) during the acid activation, respectively.

The 20 wt.% Co and 0.1 wt.% Ru loaded catalysts were prepared by the incipient impregnation method using cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.0%) and ruthenium trichloride ($RuCl_3 \cdot 3H_2O$, 99.0%) as a precursor of Co and Ru, respectively. After impregnation, the samples were dried at 120 °C for 12 h, and then calcined at 200 °C for 2 h with a heating rate of $2\ °C \cdot min^{-1}$. To give an insight on the promotional effect of Ru, 20 wt.% Co was loaded on acid-MMT-2-4/70 as a control catalyst by using the same procedure and parameters.

2.2. Characterization techniques

N_2 adsorption-desorption isotherms were measured with BelSorp-Max (Bel Japan Inc.) at −196 °C. The samples (ca. 150 mg) were previously outgassed at 350 °C for 5 h. The surface area was estimated by the BET method, and the pore size distribution was calculated based on the Barret-Joyner-Hallender (BJH) method by using the data of adsorption branches.

X-ray diffraction (XRD) patterns were obtained at room temperature on a Bruker D8 Advance X-ray diffractometer using monochromatised Cu/Kα radiation (40 kV, 40 mA). The samples were scanned with a step size of 0.02° and a counting time of 0.2 s per step. The average crystallite size of Co_3O_4 was estimated by using the (440) diffraction at 2θ of about 65.2° and the Scherrer's equation. The crystal size of the metallic cobalt in the reduced catalysts was calculated according to the equation of $d\ (Co^0) = 0.75\ d\ (Co_3O_4)$.

Fourier transform infrared spectroscopic (FT-IR) analysis was conducted on a Bruker Tensor 27 spectrometer. FT-IR spectra in the transmittance mode were recorded in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} using the KBr pressed disk technique.

The hydrogen temperature-programmed reduction (H_2-TPR) was carried out on a Micromeritics Autochem 2920 apparatus. After charging each catalyst of about 50 mg, the system was purged at room temperature in an argon flow for 30 min. Then, it was switched to 10 vol.% H_2 in Ar with a flow rate of 30 $cm^3 \cdot min^{-1}$, and H_2-TPR was started at a heating rate of $10\ °C \cdot min^{-1}$ until 900 °C. The water generated during the reduction was retained by a downstream 2-propanol/liquid N_2 trap. The hydrogen consumption was recorded with the thermal conductivity detector (TCD) previously calibrated using the reduction of CuO as a reference.

To estimate the metallic Co dispersion, the temperature-programmed desorption of hydrogen (H_2-TPD) was performed on a Micromeritics Autochem 2920 apparatus. Firstly, the catalyst (ca. 100 mg) was reduced at 400 °C for 4 h in a high-purity hydrogen at a flow rate of 30 $cm^3 \cdot min^{-1}$. Then, it was cooled to 70 °C. After this, an Ar flow of 30 $cm^3 \cdot min^{-1}$ was switched, and was hold for 1 h to remove any physically adsorbed hydrogen. Finally, H_2-TPD was started by increasing the temperature at a ramp of $10\ °C \cdot min^{-1}$ until 400 °C. The desorbed hydrogen was monitored by a TCD detector. The integrated area of the TPD profile below 400 °C was used to determine the volume of the chemisorbed H_2. To calculate the dispersion and surface average crystallite size of cobalt, a spherical geometry and H to Co molar ratio of 1 were assumed, and the contribution from the very small amount of ruthenium over all of the catalysts was neglected. With the formula given in the reference [20], the dispersion of cobalt (D%) was determined, i.e., D% = number of Co^0 atom on surface/number of Co atoms in sample × 100. The surface average crystallite size ($d(Co^0)$) was calculated from the equation of $d(Co^0) = 96 \cdot D^{-1}$ [20,21]. After the H_2-TPD process, a series of pulses of 3 vol. % O_2 in Ar were injected to reoxidize the reduced catalyst at 400 °C. By assuming that all of the metallic Co was converted to Co_3O_4 during the oxygen pulses, the reduction degree of the catalyst was estimated based on the oxygen consumed without considering the oxidation of Ru to RuO_2.

The temperature-programmed desorption of NH_3 (NH_3-TPD) were performed on a Micromeritics Autochem 2920 instrument. After pretreating the sample (ca. 50 mg) in an Ar flow at 550 °C for 1 h, it was cooled to 120 °C. Subsequently, the sample was exposed to a flow of 10 vol % NH_3 in He for 0.5 h. Then, the system was purged for 2 h in a flow of He at the same temperature. Finally, NH_3-TPD was performed by raising the temperature to 550 °C at a heating rate of $10\ °C\ min^{-1}$ under a He flow of 30 $mL \cdot min^{-1}$.

X-ray fluorescence (XRF) spectra were recorded on a Shimadzu XRF-1800 X-ray fluorescence spectrometer.

2.3. FT reaction

The catalytic reaction was tested in a fixed-bed reactor. Before FT reaction, the catalyst (0.5 g, 40–60 mesh) diluted with 0.5 g quartz sands was in situ reduced at 400 °C and atmospheric pressure for 4 h in a flow of pure H_2 (50 $cm^3 \cdot min^{-1}$). After reduction, the temperature was decreased to 190 °C. The syngas ($H_2/CO = 2$, 4% Ar as an internal standard)