Fischer-Tropsch synthesis over cobalt/montmorillonite promoted with different interlayer cations
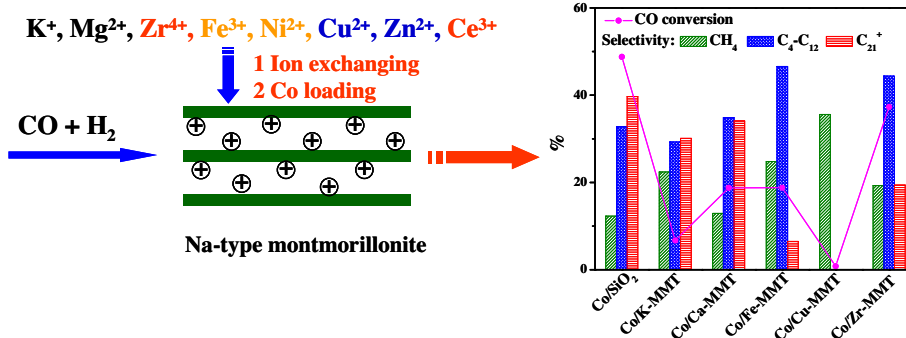
Qing-Qing Hao, Guang-Wei Wang, Yong-Hua Zhao, Zhao-Tie Liu, Zhong-Wen Liu *

Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, MOE, Xi'an 710062, China
School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China

HIGHLIGHTS

► K^+, Mg^{2+}, Zr^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ce^{3+} was ion-exchanged with Na-MMT, respectively.
► Effect of interlayer cations on Co/MMT for FT synthesis was investigated.
► Reduction behavior of Co/MMT significantly affected by interlayer cations.
► High selectivity to liquid FT hydrocarbon and low selectivity to wax over Co/MMT.
► Co/Zr-MMT is an important FT catalyst for selectively synthesizing liquid fuels.

GRAPHICAL ABSTRACT

ABSTRACT

The effect of the montmorillonite (MMT) interlayer cations on the performance of Co/MMT catalysts for Fischer-Tropsch (FT) synthesis was comparatively investigated in this work. By ion-exchanging the natural Na-type MMT (Na-MMT) with K^+, Mg^{2+}, Zr^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ce^{3+}, respectively, MMTs with different interlayer cations were obtained after calcination at 500 °C for 4 h. The natural Na-MMT, Ca-MMT, and the ion-exchanged MMTs were loaded with 20 wt.% Co by the incipient impregnation method. The materials were characterized by XRD, SEM/EDS, N_2 adsorption–desorption at low temperature, H_2-TPR, and NH_3-TPD techniques. Results indicate that the textural properties of the MMTs were strongly dependent on the interlayer cations. Moreover, an enhanced acidity, which slightly depends on the interlayer cation, was observed for the ion-exchanged MMTs. Remarkably, the reduction behavior of the Co-supported samples was strongly dependent on the MMT interlayer cations. In a fixed-bed reactor, the Co/MMT catalysts were evaluated for FT synthesis under the conditions of 1.0 MPa, 235 °C, H_2/CO = 2, and W/F = 5.02 g h mol^{-1}. Results indicate that the CO conversion was decreased in the order of Co/Zr-MMT > Co/Ce-MMT > Co/Ca-MMT ≈ Co/Fe-MMT > Co/Ni-MMT ≈ Co/Mg-MMT ≈ Co/K-MMT > Co/Na-MMT > Co/Cu-MMT ≈ Co/Zn-MMT. Moreover, the product selectivity over Co/Zr-MMT, Co/Ce-MMT, Co/Mg-MMT, Co/Fe-MMT, and Co/Ni-MMT, i.e., 40–50 wt.% of C_4–C_{12} hydrocarbons and 7–20 wt.% of C_{21}^+ hydrocarbons, was significantly different from that over Co/SiO$_2$. The reaction results were well explained based on the characterization results of the samples. The reduction behavior of Co/MMT catalysts was revealed to be responsible for the significantly varied CO conversions while the acidity of the MMTs played the crucial role in determining the product distribution. Considering the simple ion-exchange method, high activity, and high selectivity to C_4–C_{12} hydrocarbons, Co/Zr-MMT can be an important FT catalyst for selectively synthesizing liquid fuels.

* Corresponding author at: School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China. Tel.: +86 29 8153 0801; fax: +86 29 8153 0727.
E-mail address: zwliu@snnu.edu.cn (Z.-W. Liu).

1. Introduction

Fischer-Tropsch (FT) synthesis is an effective technology to indirectly upgrade the abundant coal, natural gas, and renewable biomass resources into high-value added fine chemicals and super clean fuels [1,2]. Recently, because of the increased concern on the energy supply security and the implementation of more stringent environmental legislations on liquid fuels, FT synthesis has received considerable worldwide attention in both industrial and academic domains [1–4]. Indeed, the cobalt-based catalyst has been widely investigated for FT synthesis due to its high activity, high resistance to deactivation, low water–gas shift activity, and reasonable reservoir of cobalt. In order to achieve high surface active sites (Co^0), supported catalysts are commonly used by dispersing cobalt precursors on high-surface-area oxides with either irregular pores, such as SiO_2 and Al_2O_3 [4], or ordered mesopores, e.g., MCM-48 [5], MCM-41 [6], and SBA-15 [7,8]. Moreover, the pursuit of new support materials to improve FT performance has never been stopped, and PILCs [9], ITQ-2 [10], SiC [11], and even oxidized diamond [12] are investigated as support materials for FT catalysts. More importantly, due to a significant influence of promoter on the dispersion, particle size, and reducibility of cobalt species, wide ranges of promoters, such as Ru, Zr, La, Re, Pt, and Pd, have been explored to increase the cobalt-time-yield of FT synthesis [2].

However, some elements have poisoning effects on FT activity over Co-supported catalysts, such as sulfur, nitrogen, alkali, and alkaline earth metals [13]. Recently, the effect of impurities in biomass-derived syngas on FT synthesis over Co-based catalysts has been increasingly concerned [14]. To investigate the possible effects of impure elements, e.g., Na, Mg, Mn, and Fe, on the performance of Co-based catalysts for FT synthesis, the corresponding nitrates are added during the preparation of the catalyst. Results indicate that these promoters not only change the FT activity but also alter the product distribution to some extents [14]. However, the effect of some elements is still controversial [15–20], which may be due to the variances in the adding method, the quantity, and the distribution of the promoters on the catalyst.

Clay is recognized as an important material of the 21st century because of its abundance, cheapness, environmental compatibility, and more importantly, the versatile and facile tailoring in porosity, acidity, hydrophilicity, and so on [21,22]. Thus, in recent years, the clay science and its application have received increasingly wide attention in the areas of physics, chemistry, environmental, and materials science [23]. Montmorillonite (MMT), a 2:1 layered dioctahedral aluminosilicate of smectite-type clay, is one of the most investigated clay minerals. The primary structure of MMT is composed of two tetrahedral sheets with Si in the cationic sites sandwiching an octahedral Al sheet. The partial substitution of Al^{3+} for the tetrahedral Si^{4+} and Mg^{2+} for the octahedral Al^{3+} makes the MMT layers negatively charged, and the alkali metal ions, commonly sodium ion, as charge-balance cations located in the clay interlayer, are exchangeable. Thus, MMT can be modified via bonding of molecules covalently to the atom in the MMT layer or replacing the interlayer exchangeable cations in the gallery region with different cations [24,25]. Moreover, being a simple, economic, and efficient method, ion-exchanging of clays with suitable cations leads to significant changes in surface area, porosity, and acidity besides the functions of the cations [26]. Since these changes are closely pertinent to catalysis, in recent years, ion-exchanged clays have been extensively investigated as catalysts or support materials in organic syntheses [25,27–31].

In a previous work [32], we found that Co/Na-MMT is an inefficient catalyst for FT synthesis, which is explained as the poisoning effect of sodium cations in the MMT interlayer. In contrast, after simple exchanging Na-MMT with NH_4^+ (transformed into protons

after calcination), Co^{2+}, and Al^{3+}, a high FT activity is obtained over the Co/ion-exchanged MMT catalysts. More importantly, clear promotional effects of the interlayer Co^{2+} and Al^{3+} on both the activity and product distribution of FT synthesis are observed [32]. From the ion-exchange principle and the MMT structure, the exchanged cations are mainly restricted in the MMT interlayer. To this point, MMT is a desirable model support for investigating the promotional effects of different elements, which may give insights on the controversial effects of some promoters on supported Co catalysts for FT synthesis.

Based on these understandings, this work aims at probing the promotional effect of cations restricted in the MMT interlayer on the FT performance over Co/MMT catalysts. Thus, a natural Na-MMT was ion-exchanged with the selected cation of K^+, Mg^{2+}, Zr^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ce^{3+}, respectively, and the MMTs impregnated with cobalt species were comparatively studied for FT synthesis. For a comparison purpose, the natural Na-MMT and Ca-MMT were also studied. Remarkably, effects of the interlayer cations were clearly revealed from the significantly varied CO conversions over Co/MMT catalysts. Moreover, FT product distribution was strongly dependent on the specific cation in the MMT interlayer. These prominent results were well correlated with the acidic and textural properties of the MMTs, and the reduction behavior of the catalysts, which are characterized by H_2-TPR, NH_3-TPD, XRD, and N_2 adsorption at low temperature.

2. Experimental

2.1. Catalyst preparation

Purified Na-MMT (Zhejiang Sanding Group Co., Ltd.) as a starting material was ion exchanged with selected cations for the preparation of MMT having different interlayer cations. The cations for ion exchanging were K^+, Mg^{2+}, Zr^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ce^{3+}, respectively. All the ion-exchange experiments were carried out at 80 °C for 4 h by stirring the suspension of Na-MMT (3.0 g) in nitrate aqueous solutions (0.25 mol L^{-1}, 150 mL, and $ZrO(NO_3)_2$ aqueous solution for Zr^{4+}). After this, the suspension was centrifuged, and the resulting clay was thoroughly washed with distilled water. Then, the samples were dried at 60 °C, and calcined at 500 °C for 4 h. The thus obtained MMTs with the interlayer cations of K^+, Mg^{2+}, Zr^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ce^{3+} were abbreviated as K-MMT, Mg-MMT, Zr-MMT, Fe-MMT, Ni-MMT, Cu-MMT, Zn-MMT, and Ce-MMT, respectively. In the case of MMT with the interlayer Ca^{2+} (Ca-MMT), a purified natural Ca-MMT provided by Zhejiang Sanding Group Co., Ltd. was directly used.

The catalysts were prepared by the incipient impregnation method, and the metallic cobalt loading was kept at 20 wt.% for all the catalysts. Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.0%,) was used as the precursor for the metallic cobalt. The catalysts were dried at 120 °C for 12 h, and calcined in air at 200 °C for 2 h by increasing the temperature at a heating rate of 2 °C·min^{-1}.

2.2. Characterization techniques

N_2 adsorption–desorption isotherms were measured with a BelSorp-Max (Bel Japan Inc.) at −196 °C. Prior to analysis, the sample (150 mg) was degassed at 350 °C for 5 h. The surface area was determined by the BET method.

XRD patterns were obtained at room temperature in a Rigaku D/Max-3c X-Ray diffractometer using monochromatised Cu Kα radiation (40 kV, 40 mA). The samples were scanned using a step size of 4° (2θ) per minute. The crystal size of the Co_3O_4 in the (400) and (440) diffractions was estimated based on the Scherrer formula. To minimize the error in estimating the crystal size of the