Morphology control of Co_2C nanostructures via the reduction process for direct production of lower olefins from syngas

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ABSTRACT

Fischer-Tropsch to olefins (FTO) is recognized as a surface-catalyzed structure-sensitive reaction, and the catalytic performance is strongly influenced by the morphology and exposed facets of the active phase. Here we report the effect of the reduction process on the morphology of the active phase and the catalytic performance for FTO over the CoMn catalyst. For the catalysts reduced by 10% CO-300 °C, 10% H_2-300 °C and 10% H_2-250 °C, Co_2C nanoprisms were formed after reaching the steady state. However, for the catalysts reduced by CO-300 °C and 10% H_2-400 °C, Co_2C nanospheres were found instead. Both Co_2C nanoprisms and nanospheres were present for the spent sample reduced by 10% H_2-350 °C. Kinetic study found Co_2C nanospheres to possess higher activation energy, and are more sensitive to hydrogen than Co_2C nanoprisms. Density functional theory (DFT) calculations were also performed to clarify the structure-performance relationship of Co_2C nanostructures for syngas conversion.

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1. Introduction

Fischer-Tropsch synthesis (FTS) is a promising non-petroleum alternative route to obtain clean fuels and various chemicals from syngas derived from coal, natural gas and biomass [1–7]. Products produced from FTS include alkanes, olefins, alcohols and other oxygenates with different carbon numbers, and their selectivities typically follow the Anderson−Schulz−Flory (ASF) distribution. The selective formation of desired products remains a great challenge in the field of FTS. Recently, the direct production of lower olefins ($C_{2-4}^=$, usually referring to ethylene, propylene and butylene) from syngas has attracted increasing attention due to its simplified process with high carbon efficiency [8–14]. This is primarily driven by the fact that these lower olefins are extensively used by the chemical industry as building blocks to synthesize a wide range of products such as polymers, solvents, drugs, cosmetics and detergents. FT-based catalysts could be tuned to selectively produce lower olefins by adding appropriate electronic and structural promoters

[15–17]. Torres Galvis et al. developed a Na- and S-promoted iron catalyst using α-alumina or carbon nanofiber as weakly interacting supports, and found these catalysts to exhibit excellent performance for the selective formation of lower olefins (61C%) [18]. The Na promoter is beneficial for suppressing methane formation and increasing the chain growth probability, while the S promoter may contribute to the blocking of selected hydrogenation sites [11,18]. Very recently, Zhai et al. fabricated a Zn- and Na-promoted catalyst, where Zn serves as a structural promoter and Na makes the catalysts more active for CO activation by altering the electronic structure [19]. The modification of the electronic structure renders the catalyst unexpectedly selective toward olefins—especially the C_{5+} slate. However, the poor stability at the harsh reaction conditions and the high methane selectivity make the Fe-based FTO catalysts difficult for industrial application [19]. Thus, it is necessary to develop new FTO catalysts that possess simultaneously high selectivity for the production of lower olefins, low methane selectivity and high stability. Recently, we found Co_2C nanoprisms specifically exposing the (1 0 1) and (0 2 0) facets to exhibit high selectivity to lower olefins (∼60.8C%) and low selectivity to methane (∼5.0C%) under mild reaction conditions. The product distribution deviated greatly from the classical ASF distribution with the ratio of olefin to paraffin (O/P) for the C_{2-4} slate to be as high as 30 [20].

The FT reaction is a surface-catalyzed structure-sensitive reaction, and both the shape and the size of the catalysts are critical parameters affecting its performance. The catalytic performance of FT catalysts is strongly influenced by the nanoeffects such as the particle size and exposed facets of the active phase [21–23]. The nanoeffects of metallic Co and FeC_x catalysts have been widely investigated for syngas conversion [23]. Metallic Co can exist in two crystallographic phases, namely the hexagonal close-packed (HCP) phase and the face-centered cubic (FCC) phase. The HCP Co phase is more active than the FCC Co phase during the FT reaction [24–26]. The turn-over-frequency (TOF) for CO conversion and C_{5+} selectivity increase with the size of the Co particle up to 5.6–10.4 nm, and then remained almost unchanged [27]. However, methane selectivity presents the opposite trends [27–29]. For Fe-based catalysts, the iron carbide phase is the main active phase for the FT reaction. Generally, smaller iron carbide particles display higher TOFs for CO conversion but with high methane selectivity when the particle size is less than about 6 nm [12]. However, the olefin selectivity increases with the size of iron carbide up to a critical point of ∼6 nm and remains nearly constant for larger particles at medium pressure [12]. For Co_2C, strong facet effect in the FTO reaction was demonstrated in our previous study [20]. We found that the $Co_2C(1\,0\,1)$ surface benefited olefins formation, while the formation of methane was unfavorable on both $Co_2C(1\,0\,1)$ and $Co_2C(0\,2\,0)$. Obviously, the nanostructures of Co_2C play an important role in syngas conversion, and morphology control of Co_2C nanostructures is essential for the selective formation of lower olefins. However, little information is available for precise morphology control of the Co_2C nanostructures. In most of the previous reports, the morphology of the nanostructures was always controlled during the preparation of the precursors prior to their reductions [30–32]. In this study, we investigate the influence of the reduction process on the morphology of Co_2C from the CoMn catalyst and the catalytic performance for the FTO reaction. Several sets of reduction conditions with different temperatures and reducing gases were used. Kinetic study and DFT calculations were also conducted to further clarify the structure-performance relationship of Co_2C nanostructures for syngas conversion.

2. Experimental section

2.1. Catalyst preparation

The CoMn catalysts ($Co_xMn_{3-x}O_4$) were prepared by co-precipitation. $Co(NO_3)_2 \cdot 6H_2O$, Na_2CO_3 and 50 wt% $Mn(NO_3)_2$ aqueous with analytical grade purchased from Sinopharm Chemical Reagent Co., Ltd. were used without further purification. 2 M metal solution (Co/Mn (mol(mol) = 2/1) and 2 M Na_2CO_3 solution were added simultaneously into a beaker containing 100 ml deionized water under strong stirring. The pH of the solution was fixed at 8.0 ± 0.1, and the temperature was kept at 30 ± 1 °C during the co-precipitation. The as-prepared mixture was aged at 30 °C for 2 h, then washed for several times until the pH reached ca. 7.0. After drying at 120 °C for 10 h, the sample calcined at 330 °C for 3 h at atmospheric pressure and static air.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray powder diffractometer using Cu Kα radiation with the wavelength of 1.54056 Å at 40 kV and 40 mA with a scanning angle (2θ) ranging from 30 to 80°. The different phases were identified by comparing the observed patterns with JCPDS standard files. The content of the different phases was calculated by means of Rietveld refinement using the GSAS-II program [33]. Structural

data for the Co_2C, MnO and $Co_xMn_{1-x}O$ phases were taken from the Inorganic Crystal Structure Database (ICSD, accession numbers 16895, 643195 and 9865, respectively). Lattice parameters of Co_2C and MnO were predetermined in a separate refinement for the spent sample after 50 h of time on-stream and kept fixed during the refinements. For all specimens, the scale factors, profile shape and broadening parameters, asymmetry and corrections for the preferred orientation were refined during the quantitative analysis. Besides, the parameters of Co_2C were calculated by the MDI Jade software. According to half-width of the diffraction peak in the XRD, the crystallite sizes and edge length of the Co_2C particles were deduced from the Scherrer equation.

Temperature-programmed reduction (TPR) experiments were performed using a Micromeritics Autochem-II 2920 instrument equipped with a thermal conductivity detector (TCD) and an MKS Cirrus 2 mass spectrometer. The catalysts were pretreated under a helium flow at 200 °C for 2 h. Once the TCD signal is stable, the gas stream was switched to 5% (v/v) H_2/Ar, and the temperature was then increased from 50 to 800 °C at a rate of 10 °C/min.

For transmission electron microscopy (TEM) measurements, the samples were analyzed on a JEOL-JEM 2011 electron microscope with 200 kV accelerating voltage. The samples were prepared by dispersing the catalyst powder in ethanol followed by ultrasonication. One droplet of the suspension was dropped onto carbon-coated copper grids for measurement.

2.3. Catalytic testing and kinetic measurement

Catalytic performance was tested in a stainless steel (9 mm) fixed-bed reactor under the following conditions: H_2/CO (V/V) of 2, weight hourly space velocity (WHSV) of 2000 ml·g_{cat}^{-1}·h^{-1}, 250 °C, 1 bar. Generally, 1.5 g catalyst of 40–60 mesh mixed with 3 g silica sand of 40–60 mesh was loaded into a stainless steel reactor. Prior to the reaction, the catalyst was reduced in-situ under CO-300 °C, 10% CO-300 °C, 10% H_2-300 °C, 10% H_2-250 °C, 10% H_2-350 °C and 10% H_2-400 °C (CO: pure CO; 10% CO: 10% CO with 90% N_2; 10% H_2: 10% H_2 with 90% N_2), and the reduction process lasted for 5 h, with WHSV of 8000 ml·g_{cat}^{-1}·h^{-1}. Then, the reactor was cooled to the desired temperature under the reduction atmosphere, and the flowing gas was switched to syngas ($H_2/CO/N_2$ = 64.7/32.3/3, $H_2/CO/N_2$ = 48.5/48.5/3 or $H_2/CO/N_2$ = 32.3/64.7/3). 3v % of nitrogen was introduced into the feed gas as an internal standard. For the freshly reduced catalysts, when the reactor was cooled to room temperature, a flow of 1% (v/v) O_2/N_2 mixture was introduced to passivate the catalyst for 1 h, then the catalyst was removed from the reactor and kept in a sealed glass bottle for structural characterization. Besides, the spent catalyst was obtained after reaction for 50 h as the catalytic performance was stable at the desired reaction conditions and a flow of He (50 ml/min) was introduced to cool it down to the room temperature after the FTO reaction. In addition, the reactor effluent was analyzed online by an Agilent 7890A gas chromatograph equipped with two columns and two detectors after passing through a hot trap (100 °C) and a cold trap (ice-water bath). N_2, H_2, CO, CH_4, and CO_2 were analyzed using a packed column (J&W Q&5A), and a thermal conductivity detector (TCD) using He as the carrier gas. Hydrocarbons from C_1 up to C_7 analyzed using a capillary column (Agilent 19095P-K25) and a flame ionization detector (FID). The reaction temperature was varied to measure the activation energy according to the Arrhenius equation: $k = Ae^{-Ea/RT}$, and the partial pressures of H_2 and CO were varied to measure the reaction orders of H_2 and CO according to the reaction rate equation: $r = k[CO]^\alpha[H_2]^\beta$. The CO conversion level for the study of kinetic results was less than 5% in order to avoid the influence of diffusion.