Effect of cobalt loading on reducibility, dispersion and crystallite size of Co/Al₂O₃ Fischer-Tropsch catalyst

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Abstract: Co/Al₂O₃ Fischer-Tropsch synthesis catalysts with different cobalt loadings were prepared using incipient wetness impregnation method. The effects of cobalt loading on the properties of catalysts were studied by means of X-ray diffraction (XRD), temperature programmed reduction (TPR), hydrogen temperature programmed desorption (H₂-TPD) and O₂ titration. Co-support compound formation can be detected in catalyst system by XRD. For the Co/Al₂O₃ catalysts with low cobalt loading, CoAl₂O₄ phase appears visibly. Two different reduction regions can be presented for Co/Al₂O₃ catalysts, which belong to Co₃O₄ crystals (reduction at 320 °C) and cobalt oxide-alumina interaction species (reduction at above 400 °C). Increasing Co loading results in the increase of Co₃O₄ crystallite size. The reduced Co/Al₂O₃ catalysts have two adsorption sites, and cobalt loading greatly influences the adsorption behavior. With the increase of cobalt loading, the amount of low temperature adsorption is increased, the amount of high temperature adsorption is decreased, and the percentage reduction and cobalt crystallite size are increased.

Key words: Fischer-Tropsch synthesis; cobalt/alumina catalyst; temperature programmed reduction; hydrogen temperature programmed desorption

1 INTRODUCTION

Cobalt-based catalysts are highly attractive due to their high selectivity for heavy hydrocarbons and low CO₃ selectivity in Fischer-Tropsch synthesis (FTS). Various studies have been performed on the influence of the support material, such as silica, titania, alumina. Conventionally, SiO₂ is usually used for the support of cobalt-based catalysts, and Al₂O₃-supported cobalt catalyst is also employed in oil refinery.

Alumina support is in favor of dispersing metal Co on cobalt alumina catalysts, which is attributed to the formation of spinel with Co₃O₄. This catalyst has a limited reducibility due to a strong interaction between the support and cobalt oxides. Various methods were reported to improve the reducibility of Co/Al₂O₃ catalysts. For instance, the reducibility of Co/Al₂O₃ catalysts can be improved, to a certain extent, by promotion with noble metal promoters such as Pt, Re or Zr. Such modifiers also affect the activity and the selectivity of catalysts. The calcined Co/Al₂O₃ catalysts have a complicated composition on the surface of the support, which have been found to be a mixture of Co₃O₄, cobalt-aluminate species and other species. The reduction of unsupported cobalt oxide (Co₃O₄) proceeds in a two-stage process, which is ascribed to the successive reductions of Co₃O₄ to CoO, and CoO to Co. Khasisin et al. considered that Co₃O₄ spinel phase is reduced to Co at 280 °C in a single step or to CoO and Co in two steps at 250 °C and 350 °C, respectively. Normally, the temperature programmed reduction (TPR) peak shape of Co₃O₄ spinel phase depends on the mode of preparation and pretreatment. For bulk Co₃O₄, the two reduction steps are not always observed as separate peaks. Arnoldy et al. obtained TPR spectrum of calcined 9.1% Co/Al₂O₃ (mass fraction) catalyst and found different reduction regions which were attributed to four Co phases (I, II, III and IV). (I) is bulk Co₃O₄ (reduction at 250 - 370 °C); (II) is Co²⁺ dispersed surface species (reduction at 470 °C); (III) is Co³⁺ dispersed surface species (reduction at 600 °C); and (IV) is either surface Co³⁺ ions with more Al³⁺ ions in their surrounding than in phase III (reduction at 880 °C) or subsurface Co³⁺ ions, occurring in

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diluted $\text{Co}^{2+}$-$\text{Al}^{3+}$ spinel or in $\text{CoAl}_2\text{O}_4$.

Temperature programmed reduction is a sensitive technique to obtain the “structural information” for supported cobalt catalysts,[12] which can be used to obtain the interaction of two components and to confirm the extent of reduction. Temperature programmed desorption (TPD) can be used to characterize the active sites on the surface of the catalysts. O$_2$ titration experiment reveals the reducibility of catalysts, and the actual dispersion and cluster size of reduced cobalt metal.

Many methods, such as impregnation, precipitation etc have been used to prepare FTS catalysts[13,14]. In this paper, a series of Co/Al$_2$O$_3$ catalysts with different cobalt loadings were prepared by incipient wetness impregnation (IWI) method. Some characterization techniques, such as X-ray diffraction (XRD), TPR, H$_2$-TPD, O$_2$ titration were used to study the catalysts.

2 EXPERIMENTAL

2.1 Catalyst preparation

γ-Al$_2$O$_3$ pellets ($d = 3 - 5$ mm, BET surface area $150$ m$^2$/g, pore volume $0.42$ mL/g), made in Jiangyan Chemical Factory, China, were calcined at $350$ °C for 5 h in air. Co-based catalysts (5%, 7%, 10%, 15%, 20%, 25% as metal Co, mass fraction) were prepared by incipient wetness impregnation technique. Co(NO$_3$)$_2$•6H$_2$O (AR) was dissolved in an appropriate volume of deionized water and then added to ground alumina support (0.107-0.250 mm). Subsequently, the catalysts were aged for 12 h in air at room temperature, followed by drying and calcination. The samples were dried in air stream at atmospheric pressure at $120$ °C for 12 h, and then calcined in air at $350$ °C for 5 h.

2.2 Characterization techniques

In order to study the structural properties of Al$_2$O$_3$ supported Co catalysts, TPR, TPD and O$_2$ titration experiments were performed with AMI-200 device (Zeton Altamira), which incorporates a thermal conductivity detector (TCD). For TPR experiment, the effluent gas was sent through a cooling trap (below $-50$ °C) to condense and collect the water generated by the reduction process.

2.2.1 X-ray diffraction

X-ray diffraction measurements were carried out on the catalysts in a SHIMADZU-6000 spectrometer using the CuKα radiation. The spectra were scanned at a rate of 4°/min, and 2θ angle ranged from 10° to 80° was examined. Cobalt phases were detected by comparing the diffraction patterns with those in the standard powder XRD file compiled by the joint committee on powder diffraction standards (JCPDS) published by the International Center for Diffraction Data. Co$_3$O$_4$ crystallite sizes were calculated using the Scherrer equation as follows:

$$d = \frac{0.89 \lambda}{B \cos \theta} \times \frac{180°}{\pi}$$

where $d$ is the mean crystallite diameter, $\lambda$ is X-ray wave length (15.405 6 nm), and $B$ is the full width half maximum (FWHM) of Co$_3$O$_4$ diffraction peak.

2.2.2 Temperature programmed reduction

The experiment of temperature programmed reduction was carried out by adding 0.15 g catalyst into a tubular reactor with a high-purity mixture of 10%H$_2$ in argon. The reactor is made of quartz and includes a small thermowell for continuous temperature measurement. The reactor was heated with a furnace designed and built to stabilize the temperature gradient and minimize the temperature error. Prior to the hydrogen temperature programmed reduction measurement, the calcined Co/Al$_2$O$_3$ catalysts were flushed with high-purity argon at $150$ °C for 1 h to drive away the water or impurities, and then cooled down to 50 °C. The flow rate of gas through the reactor was kept at 30 mL/min and the temperature was raised at a rate of 10 °C/min from 50 °C to 800 °C. Subsequently, the sample was kept at 800 °C for 30 min. The signal of H$_2$ consumption was recorded automatically by TCD.

2.2.3 Temperature programmed desorption and O$_2$ titration

0.22 g catalyst was activated at 350 °C for 12 h using a flow of high purity hydrogen and then cooled to 100 °C in hydrogen stream. The sample was held in flowing argon at 100 °C for 1 h to avoid physisorption of weakly bonded species prior to increasing the temperature slowly to 350 °C. At this temperature, the catalyst was held in flowing argon to desorb the remaining chemisorbed hydrogen so that the TCD signal returned to the baseline and began to register the signal. TPD profile was integrated and the mole number of desorbed hydrogen determined by comparing to the areas of mean calibration of hydrogen pulses. Prior to experiments, the sample loop was calibrated with pulses of nitrogen in helium flow and compared with calibration line produced from gas tight syringe injections (100 µL) of nitrogen in the helium flow.

After hydrogen TPD being finished, the sample was reoxidized at 350 °C by injecting pulses of pure oxygen in helium referenced to helium gas. After oxidation of cobalt metal particle, the mole number of oxygen consumed was determined, and percentage reduction was calculated, assuming that Co was reoxidized to Co$_3$O$_4$.

The uncorrected dispersion (cluster size) are based on the assumption of complete reduction, and the corrected dispersion should be calibrated