Properties of active sites on CoPt/TiO_2 Fischer-Tropsch synthesis catalysts affected by plasma treatment

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Abstract: The effects of traditional calcination and plasma treatment on the catalytic structure and properties of active sites on CoPt/TiO_2 catalysts were investigated by a series of characterizations. Plasma treatment seems to have remarkable effects on not only the number but also the properties of active sites for Fischer-Tropsch synthesis (FTS). The catalysts with short plasma treating duration (< 3h) possessed higher concentration of active sites with weak adsorption of reactants, were more active in Fischer-Tropsch reaction.

Keywords: Fischer-Tropsch synthesis, Glow discharge plasma, Cobalt catalysts.

1. Introduction

Development of alternative approaches such as syn-fuel process (including Fischer-Tropsch synthesis (FTS)) is extremely important for long-term strategic consideration to solve the energy problem. Supported cobalt catalysts are one type of widely used materials for low temperature FTS, to obtain long linear chain ultraclean hydrocarbons.[1-2] Before catalytic tests, thermal calcination and reduction are usually required to activate the catalysts. Since the traditional calcination process is rather energy consuming, development of efficient precursor decomposition techniques is with high potential. Compared with other chemical techniques, plasma discharges offer an unique advantage because non-equilibrium reactions can be performed at low temperature, and requires much less amount of compressed gases and energy consumption.[3]

Further investigation and analysis of plasma effects is helpful for better understanding the nature of plasma treatment on cobalt surface structure and on properties of FTS active sites in cobalt-based catalysts. In present work, traditional thermal calcination and glow discharge plasma treatment with various durations were applied to decompose the catalyst precursors, and CoPt/TiO2 catalyst system were used as research target. The selection of titania as support was under the consideration of its well-known high SMSI (Strong Metal Support Interaction) effect, which could maintain the cobalt structure stable under subsequent reduction and reaction conditions; meanwhile, platinum was chosen as a reductive promoter, to eliminate the reducibility effect on the concentration of active sites.

2. Experimental

The CoPt/TiO_2 catalysts were prepared by incipient wetness co-precipitation method, using Degussa P25 TiO_2 as supports, $Co(NO_3)_2\bullet 6H_2O$ and $Pt(NO_2)_2(NH_3)_2$ as precursors. The cobalt and platinum loadings are 12 wt.% and 0.5 wt.%, respectively. The impregnated catalyst was dried in an oven at 110 °C for 12h. After that, the sample was divided into two parts, one part was calcined at 210 °C in muffle furnace in air for 5h, and denoted as CoPt/TiO_2-C; the other part was treated by glow discharge plasma, and named as CoPt/TiO_2-PN, where N indicated the plasma treating duration, with unit of hour.

Characterizations such us N_2 adsorption-desorption, XRD, XPS, FT-IR, Raman, STEM, H_2-TPD and O_2- titration were applied to investigate the properties and structure of the catalysts.

3. Results and discussion

Based on N_2 adsorption-desorption results, pore structure of the catalysts was not apparently affected by plasma treatment. XRD and STEM results (Figure 1) clearly illustrated that plasma treatment could significantly improve the dispersion of cobalt species, especially in 4h plasma treated CoPt/TiO_2-P4 catalyst, cobalt particles with size less than 1 nm were homogeneously dispersed on the support. Raman and FT-IR results confirmed that the chemical state of plasma treated catalysts were similar, all in the form of Co_3O_4, while in calcine sample, due to the low calcination temperature (210 ^oC), residual nitrate species was detected, suggesting that plasma is an effective technique to decompose the catalyst precursors. XPS spectra verified the significant enhancement of surface cobalt dispersion by plasma, and the plasma treated samples possessed much more amount of adsorbed oxygen species than the calcined counterpart.

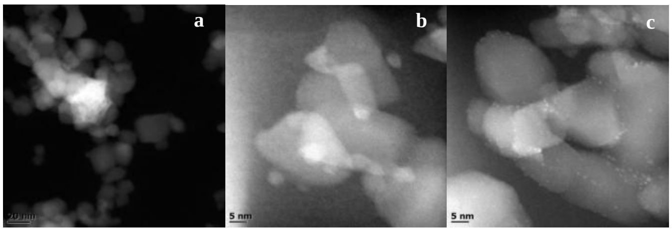

Figure 1. STEM images of the catalysts, a：CoPt/TiO_2-C；b：CoPt/TiO_2-P1；c：CoPt/TiO_2-P4.

TPR, TPD and O_2 titration results showed that both the calcined and plasma treated catalysts presented similar reducibility (51-54 %) after reducing in hydrogen at 330 ^oC for 10 h. Since H_2 is one of the major reactant for FTS, its desorption amount on the catalyst is in proportion to the number of active sites. Carefully analysis of H_2-TPD spectra of the catalysts (Figure 2) illustrated that the calcined CoPt/TiO_2-C catalyst possessed much less active sites. As to the three catalysts with plasma treatment (CoPt/TiO_2-P1, CoPt/TiO_2-P3 and CoPt/TiO_2-P4), their total desorption amount of hydrogen was almost the same, however, very different desorption process was observed. With increasing plasma treating duration, the surface area of low temperature desorption peak diminished rapidly, the desorption peaks shifted to higher temperatures, especially for CoPt/TiO_2-P4 catalyst, most of the adsorbed hydrogen could not be desorbed below 210 ^oC.

Figure 3 shows catalysts with short plasma treating duration (< 2h) had a significant improvement in catalytic activity, the cobalt-time yield was 2.4 times higher than that on the calcined one; further increase of plasma treating duration led to a decrease in FTS activity, especially in CoPt/TiO_2-P4 catalyst, when the treating duration reached 4 h, the catalyst activity sharply decreased, the CO conversion was only below 4%, which may due to the occupation of most of the active sites by strongly bonded hydrogen, and thus preventing the adsorption of CO during the reaction.

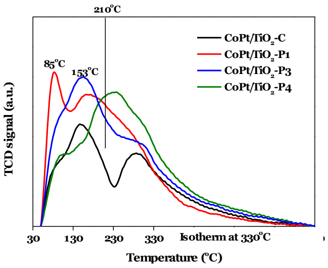

Figure 2. H_2-TPD spectra of calcined and plasma treated CoPt/TiO_2 catalysts

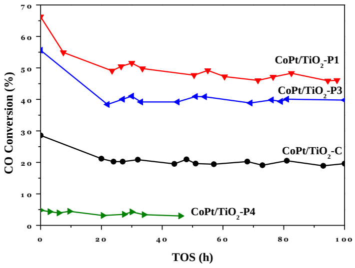

Figure 3. CO conversion as a function of time on stream (TOS) on CoPt/TiO_2 catalysts
(P=1.0 MPa, T=210 ^oC, H_2/CO= 2, GHSV= 4 SL h^{-1} g^{-1})

4. Conclusions

Glow discharge plasma is an effective way to completely decompose CoPt/TiO_2 catalyst precursors. The plasma treated catalysts with various treating durations possessed similar amount of active sites, however, significant change in FTS activities were observed. Combined with characterizations results, the FTS activities were determined by not only the number but also the properties of active sites, only weak and medium strength bonded sites were active in Fischer-Tropsch synthesis. Most of the sites in CoPt/TiO_2-P4 catalyst are strongly bonded with hydrogen, which cannot be desorbed below 210 ^oC and occupied the sites for further CO activation; therefore, very low FTS activity was presented in this catalyst.

References

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