

Fischer–Tropsch Synthesis over Modified Cobalt Catalysts

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Abstract: The catalysts of Co/Zr–SiO₂ were prepared by precipitation and the promoter of Pt was supported by impregnation. The reducibility of the cobalt oxide and the other physicochemical properties of the catalysts were characterized by TPR, TPD, BET and XPS. With the evaluation of the reduction temperature, the reduction degree increased but the surface area of the catalysts and the adsorption property for reactant CO distinctly decreased; The addition of Pt resulted in the improvement of the reducibility by decreasing the reduction temperature of cobalt oxide species. The FT-synthesis has been performed in a quartz fixed-bed reactor, and the experimental results showed that the best activity for promoted catalyst has been found at the reduction temperature of 400 °C, in spite of its uncompleted reduction.

Key words: FT synthesis; cobalt; reduction; XPS

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1 INTRODUCTION

Fischer–Tropsch (FT) synthesis is one of the most promising processes for producing liquid fuels from coal with metallic catalysts. Recently the rapid growth in the discovery of more natural gas reserves results in more interests to use natural gas as new energy carrier. Therefore several contributions are under development. One of them is that the natural gas via partial oxidation, followed by FT synthesis and hydrocracking, can be converted to transportation fuels^[1,2].

Cobalt catalysts receive great attention because of their high specific activity, long lifetime and especially low activity to water–gas–shift reaction. It has been reported that high dispersion and high degree of reduction are two crucial parameters to decide activity of catalyst^[3–5]. A wide array of studies has been made by using different supports and/or promoters as well as preparation methods (using different precursors and treatment conditions) to try to achieve more active catalysts. Only a few of reports can be found about the effects of reduction temperature on performance of the cobalt catalysts. Even among these, the results are not unanimous^[3]. As catalysts, in addition to cobalt, many catalysts recently reported contain a noble metal as promoter, however the function of this noble metal is

not clear.

In the present work, the Fischer–Tropsch catalysts containing three components of Co, Zr and Pt were studied. The effect of platinum modification on the behavior of these catalysts and the effects of reduction temperature on the activity and product selectivity were examined.

2 EXPERIMENTAL

2.1 Preparation of Catalysts

The catalyst Co/Zr–SiO₂ was prepared by precipitation from suspension of aerosol containing Co(NO₃)₂ and ZrOCl₂ with NH₃·H₂O at the temperature near the boiling point under strong stirring. The precipitate was washed and dried overnight at 110–120 °C in air. The precursor impregnated with H₂PtCl₆ by incipient wet method was dried once more at 110–120 °C. The compositions of the catalysts were analyzed with ICP–AES. The calcination was carried out under flowing argon at a heating rate of 5 °C/min to the final temperature of 400 °C, then held for several hours. After calcination, the catalysts were cooled down to ambient temperature. To perform the microreactor test, a quantity of catalyst was compressed into tablets, which were then broken and passed through sieves, in order to separate the particles with diameters in the range of

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0.18~0.25 mm.

2.2 Catalyst Characterization and FT Synthesis

The temperature-programmed reduction (TPR) was carried out under a mixture of 5% H₂ with N₂ at a flow rate of 40 mL/min with a heating rate of 5°C/min up to various final temperatures. The temperature-programmed desorption (TPD) was performed using a mixture of 5% CO with N₂ flowing at 30 mL/min, a thermal conductivity detector was used to determine the amount of consumptive or desorbed gas. The measurement for BET specific surface area was carried out with Quantachrome AUTOSORB-1. X-ray photoelectron spectroscopy (XPS) was conducted with Shimadzu ESCA Lab 220I-XL.

CO hydrogenation was performed in a quartz fixed-bed reactor. The catalyst bed was diluted with inert quartz. The flow rates of H₂ and CO were precisely controlled and measured. Constant pressure was kept with a pressure controller. A continuous stream of

products containing liquids, vapors and gases was withdrawn from the reactor at the reaction temperature and cooled, among which gas components were periodically analyzed by on-line gas chromatography using N₂ in the sample gas as the internal standard. The liquid fraction collected in a trap container was analyzed off-line by gas chromatography after the reaction.

3 RESULTS AND DISCUSSION

3.1 Properties of the Catalysts

The specific surface areas of the catalysts Co/Zr–SiO₂ and Co–0.15Pt/Zr–SiO₂ reduced at different temperatures are listed in Table 1. It is clear that the specific surface areas of both catalysts gradually decrease with the improvement of the reduction temperature, and the addition of the noble metal Pt has not the distinct influence on the area of the catalyst.

Table 1 The BET results of the catalysts Co/Zr–SiO₂ and Co–0.15Pt/Zr–SiO₂ at different reduction temperatures

Reduction temperature (°C)	Catalyst	BET specific surface area (m ² /g)	Catalyst	BET specific surface area (m ² /g)
400		227		226
500	Co/Zr–SiO ₂	162	Co–0.15Pt/Zr–SiO ₂	160
600		134		132
700		96		97

The influence of the reduction gas on XPS spectra of Pt_{4f5/2} and Pt_{4f7/2} is shown in Fig.1(a). When the catalysts were treated under Ar at 250°C, the platinum existed only in oxidative state, the binding energy of the platinum oxide for Pt_{4f5/2} and Pt_{4f7/2} is 76.1 and 72.1 eV respectively. However, when the catalysts were reduced with 5% H₂ in Ar, these two peaks moved to the low energy direction with the binding energy about 75.0 and 71.5 eV, which corresponded to Pt_{4f5/2} and Pt_{4f7/2} of metallic Pt. With the help of XPS analysis software it is deduced that when the catalyst was reduced at 250°C

the oxidative platinum had been fully converted to the reductive metal platinum. Fig.1(b) presents the XPS spectra of Co_{2p1/2} and Co_{2p3/2} for the catalysts with different Pt contents after reduction at 400°C. It can be inferred that for unpromoted catalyst after reduction treatment the cobalt also existed only in oxidative state, for the catalyst supported with Pt two peaks of Co_{2p1/2} and Co_{2p3/2} shifted to the lower energy direction. Furthermore, the higher the Pt content in catalyst is, the greater the shift extent is. For example, the shift distance for Co_{2p1/2} was about 1.1 eV and 1.9 eV for the catalysts

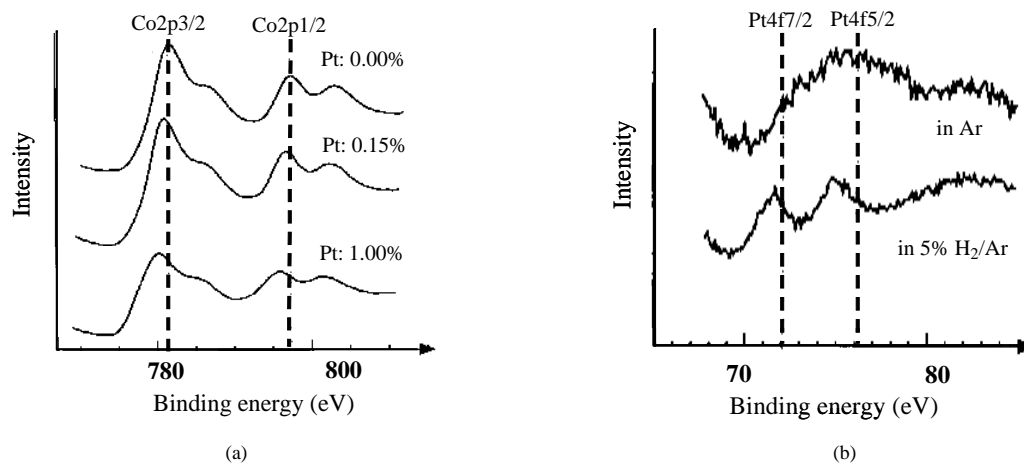


Fig.1 XPS spectra of the catalysts

with the Pt contents of 0.15% and 1.0% respectively. It can be demonstrated that with the increase of Pt loading in the catalyst the reducibility of cobalt oxide correspondingly becomes easier and the reduction degree of cobalt oxide becomes improved.

The TPR profiles of the catalyst Co/Zr-SiO₂ with different Pt contents are shown in Fig.2. For all catalysts, it was concluded that the TPR spectra contained a main peak at the higher temperature region among 400°C and 600°C, this peak could be assigned as the gradual reduction of CoO into metallic Co^[6-9]. The small peaks at the lower temperature region were frequently attributed to the reduction of Co₃O₄ to CoO^[6-9]. In TPR spectrum of unpromoted catalyst only one peak situated at about 600°C was observed, which means that in unpromoted catalyst cobalt is present only in CoO form. Moreover, compared with the promoted catalyst the temperature of reduction peak is the highest which indicates that the CoO in unpromoted catalyst was most difficult to reduce. This is also confirmed by XPS analysis as mentioned above. according to the peak area of TPR the reduction degree of CoO below 700°C was only 80%. The Pt-promoted catalysts presented two peaks and suggested co-existence of CoO and Co₃O₄ in the catalysts. Obviously, the calcination in an inert atmosphere of Ar did not prevent the formation of Co₃O₄ crystallites completely when the catalysts were promoted with Pt. The TPR profiles also show that the addition of platinum shifts the reduction temperature to lower region, moreover, the higher the Pt content in catalysts is, the lower the temperature of the reduction peak is. When the Pt content in the catalysts is 0.15% and 1.0%, the reduction peak with the minimum transformation of CoO to Co correspondingly situated at 520°C and 440°C.

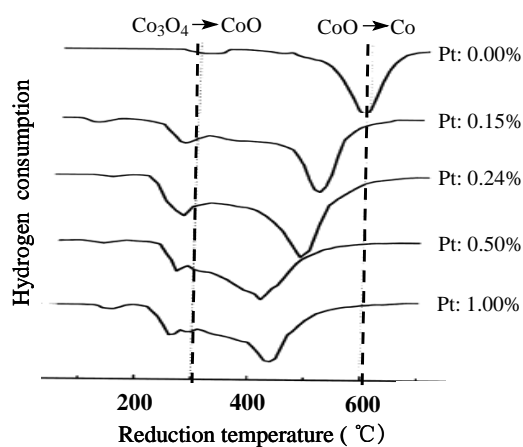


Fig.2 TPR of Co/Zr-SiO₂ promoted with different Pt contents

CO is one of the two reactants involved in the FT synthesis, for this reason, the manner of the CO adsorption in catalyst may have a great impact on the reaction.

The CO TPD diagrams of the catalyst Co-0.15Pt/Zr-SiO₂ reduced respectively at temperature of 400°C and 700°C are presented in Figs.3 and 4.

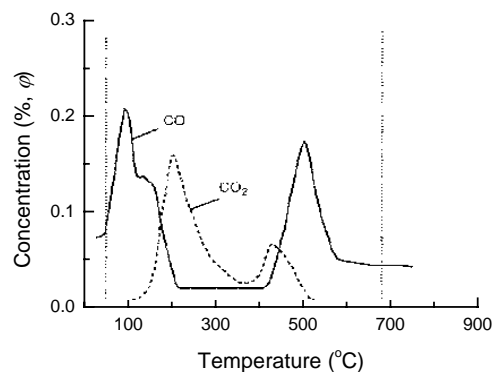


Fig.3 TPD of promoted catalysts Co-0.15Pt/Zr-SiO₂ reduced at 400°C

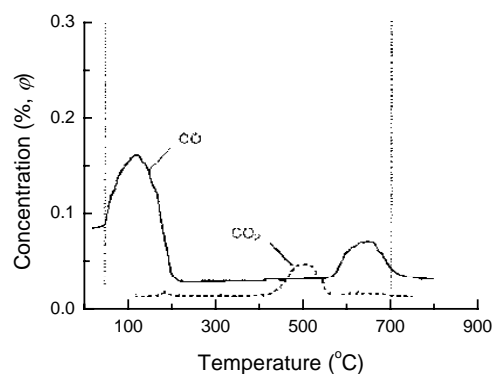


Fig.4 TPD of promoted catalysts Co-0.15Pt/Zr-SiO₂ reduced at 700°C

It is showed that there are two CO desorbed peaks in both diagrams, the first peak around 100°C was the result of the physical adsorption of CO, the second one at high temperature corresponded to the chemisorption of CO. The comparison of CO desorbed diagrams shows that the desorbed temperature of the chemisorption CO in the catalyst reduced at 700°C is about 100°C higher than that at 400°C, but the amount of adsorbed CO in the catalyst reduced at 700°C is much smaller than that in the case of reduced at 400°C. It is concluded that the interaction between reactant CO and catalyst is stronger and the dispersion of the active component cobalt is lower when the catalyst is reduced at higher temperature. This conclusion can be also confirmed by the BET results mentioned above. Despite

of the CO peaks there are also CO₂ peaks in both diagrams, the catalyst reduced at 400°C presents two peaks situated at ca. 200°C and 440°C, whereas the catalyst reduced at 700°C only one CO₂ peak at the temperature around 500°C. The presence of CO₂ peak at ca 200°C indicates that the unreduced cobalt oxide (CoO) during the reduction at 400°C could be further reduced with stronger reduction reagent CO as the following reaction shows:



This reaction occurred at 190°C, near the temperature of FT synthesis, it can be concluded that when the reduction temperature is lower, the unreduced cobalt oxide in catalyst can be in-situ reduced with reactant CO. At the same time, the CO₂ peak at lower temperature has not been found with the catalyst reduced at 700°C, owing to the completed reduction of cobalt, as shown in Fig.2.

Figure 5 presents the CO TPD diagram of the unpromoted catalyst Co/Zr–SiO₂ reduced at 400°C. There is only a CO peak at low temperature, it would be logical to suggest that the unpromoted catalyst does not chemisorb any CO and the unreduced cobalt oxide does not convert the reactant CO to CO₂.

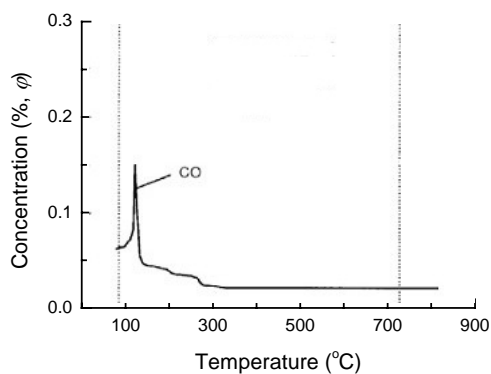


Fig.5 TPD of unpromoted catalysts Co/Zr–SiO₂ reduced at 400°C

3.2 FT Synthesis in Microreactor

The reaction results of both catalysts with dependence of the reduction temperature are shown in Table 2. As suggested in Fig.2, when the catalyst of

Co/Zr–SiO₂ was reduced at 400°C, cobalt was present only in oxidative form, the lack of metallic cobalt in catalyst means that no chemisorption of CO takes place on surface of the catalyst, as shown in Fig.5, naturally no FT synthesis could proceed and the conversion of the CO [abbreviated $c(\text{CO})$] is certainly very low. For other reduction temperatures, the Pt-promoted catalyst is about 3 times more active than unpromoted one at the identical reduction temperature. The difference of the selectivity for products CH₄ and C₂–C₄ between both catalysts is very small, the selectivity for CH₄ [$S(\text{CH}_4)$] is about 10~14.5%, for C₂–C₄ [$S(\text{C}_2\text{--C}_4)$] about 23%~27%, implying that the addition of Pt in the catalyst Co/Zr–SiO₂ has no pronounced effect on the improvement of the selectivity of products.

With the increase of reduction temperature the CO conversion in unpromoted catalyst was not influenced significantly (exception of reduction temperature of 400°C). As showed in Table1, owing to the thermal sintering the specific surface area of both catalysts decreased with the increase of the reduction temperature, it suggests that the FT synthesis on unpromoted catalyst is a structure-insensitive reaction. Table 2 also shows that the CO conversion at the Pt-promoted catalyst drops down markedly with the increase of the reduction temperature, implying a structure-sensitive reaction of the FT synthesis on Pt-promoted catalyst. This result could be interpreted in the following two aspects. Firstly, the specific surface area of the metallic cobalt in Pt-promoted catalyst decreased with the enhancement of the reduction temperature although the reduction degree increased. That is to say, for the Pt-promoted catalyst the decrease of surface area of the cobalt with the increase of reduction temperature could not be compensated by the more complete reduction or increased reduction degree of cobalt. Secondly, the lower the reduction temperature is, the higher the content of the unreduced cobalt oxide in catalyst is, which could be reduced by reactant CO according to the equation (1), therefore the best activity of the Pt-promoted catalyst, which was reduced at temperature of 400°C, could be also explained.

Table 2 Results of FT synthesis on catalysts Co/Zr–SiO₂ (Co/Zr) and Co–0.15Pt/Zr–SiO₂ (CoPt/Zr) at different reduction temperatures

RT (°C)	Catalyst	$c(\text{CO})$ (%)	$S(\text{CH}_4)$ (%)	$S(\text{C}_2\text{--C}_4)$ (%)	Catalyst	$c(\text{CO})$ (%)	$S(\text{CH}_4)$ (%)	$S(\text{C}_2\text{--C}_4)$ (%)
400	Co/Zr	<1	-	-	CoPt/ Zr	55	9.9	27.4
550		12	10.7	24.2		37	11.6	26.6
600		13.5	11.2	23.8		32	11.7	26.2
700		10	11.8	23.0		30	13.5	25.1

Note: Reaction conditions: $T=190^\circ\text{C}$, $P=0.5\text{ MPa}$, $\text{H}_2/\text{CO}=2:1$, $\text{GSHV}=300\text{ h}^{-1}$, $m_{\text{cat}}=2\text{ g}$. RT denotes reduction temperature of the catalyst.

4 CONCLUSIONS

The Co/Zr-SiO₂ catalysts were prepared by precipitation method and the CO conversion rate was low in it. Addition of a trace amount of noble metal Pt to the catalysts drastically improved the activity, the conversion of CO for promoted catalyst was about three times superior to that for unpromoted catalyst, but no effect on selectivity of the products. The promoter Pt played a role in reducing the cobalt oxide of the catalyst to metallic state at lower temperature, the higher the content of Pt in catalyst, the lower the temperature of the reduction peak in TPR diagram.

The best results of CO conversion were obtained with the promoted catalyst reduced at 400°C, in spite of its uncompleted reduction. The TPD experiments showed that the unreduced cobalt oxide in promoted catalyst could be in-situ reduced with reactant CO and the higher specific surface area of the metallic cobalt reduced at lower temperature was obtained.

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