Adsorption of H_2 and CO on Iron-based Catalysts for Fischer-Tropsch Synthesis

Weixin Qian, Haitao Zhang, Hongfang Ma, Yongdi Liu, Weiyong Ying, Dingye Fang

Abstract—The adsorption properties of CO and H_2 on iron-based catalyst with addition of Zr and Ni were investigated using temperature programmed desorption process. It was found that on the carburized iron-based catalysts, molecular state and dissociative state CO existed together. The addition of Zr was preferential for the molecular state adsorption of CO on iron-based catalyst and the presence of Ni was beneficial to the dissociative adsorption of CO. On H2 reduced catalysts, hydrogen mainly adsorbs on the surface iron sites and surface oxide sites. On CO reduced catalysts, hydrogen probably existed as the most stable CH and OH species. The addition of Zr was not benefit to the dissociative adsorption of hydrogen on iron-based catalyst and the presence of Ni was preferential for the dissociative adsorption of hydrogen.

Keywords—adsorption, Fischer-Tropsch synthesis, iron-based catalysts

I. INTRODUCTION

AS a key step of liquid fuels synthesizing, Fischer-Tropsch synthesis (FTS) is recently receiving great attentions. In FTS, the syngas (CO and H_2) converted from natural gas, coal or biomasses reacts in presence of catalyst (commonly iron or cobalt) to form a mixture of alkanes, alkenes, alcohols and other oxygenates with a wide range of carbon number from 1 to more than 50 [1]-[4]. Fischer-Tropsch synthesis reaction is a typical CO hydrogenation on heterogeneous catalysts, which starts with the dissociation of CO and H_2 and follows with the hydrogenation and polymerization of surface carbon species.

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Iron-based catalysts have been used widely in Fischer-Tropsch synthesis, several scientific studies have been carried out using several experimental techniques like X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy, etc., in order to investigate the microstructures of iron-based catalysts and its active phase for Fischer-Tropsch synthesis, however, a controversy still exists on the composition of the catalytically active phase of iron for Fischer-Tropsch synthesis. In the Fischer-Tropsch synthesis process on iron-based catalysts, metallic iron, iron oxygenates and iron carbides coexist on the catalysts surface under the reaction conditions, the distribution of these phases changes obviously during the reaction. Early studies proposed that Fe_3O_4 is active for the CO hydrogenation[5]-[6]. However some researchers proposed that the active phase for Fischer-Tropsch synthesis is iron carbides and a small part of α-Fe[7]-[9].

Relative to the large amount of scientific studies devoted to the catalytic hydrogenation of CO and the active phase of iron for Fischer-Tropsch synthesis, the reports of the adsorption properties of CO and H_2 on iron-based catalysts is much fewer. Zhang[10] investigated the adsorption performance of CO and H_2 on Fe/SiO_2 and the effect of the presence of potassium, found that on H_2 reduced catalysts, hydrogen mainly adsorbs on the surface iron sites and surface oxide sites, on CO reduced catalysts, hydrogen probably existed as the most stable CH and OH species. Either on H_2 reduced catalysts or CO reduced catalysts, the addition of potassium eliminated the adsorption of hydrogen on iron-based catalysts. Bian[11] investigated the adsorption properties of precipitated Fe catalysts reduced by H_2, CO or Syngas by in situ diffuse reflectance FTIR using high-pressure Syngas as probe molecules. Syngas adsorption on the freshly reduced samples revealed the presence of fine metallic iron particles on H_2 reduced samples, and the existence of a mixture of fine metallic iron and iron carbide particles on syngas and CO reduced samples. The metallic iron and iron carbide particles can be converted to one another when treated by syngas or hydrogen under experimental conditions. On the other hand, the reduction conditions also have effects on the adsorption of CO and H_2.

In this work, three Fe/SiO_2 catalysts promoted with or without Zr and Ni were prepared by co-precipitation method and used to investigate the adsorption properties of carbon monoxide and hydrogen on iron-based catalysts reduced by hydrogen and 4.99%CO/95.01%He.

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II. Experimental

A. Catalysts Preparation

The catalysts with different content of ZrO_2 and Ni used in experiment were prepared by co-precipitation manner. The experiment flow chart of catalyst preparation was shown in Fig.1. The preparation process was described as follows. Certain amount of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (or $Zr(NO_3)_4 \cdot 5H_2O$) was first dissolved in 500ml deionized water, after that, adding a certain amount of silica solution, mix well, then the solution was added into flask 1 (the left one in Fig.1) which was heated by electric heating tape (70℃); 90ml ammonia water was diluted to 500 ml by adding deionized water, then added into flask 1 (the right one in Fig.1) and heated to 70℃; the nitrate solution and ammonia water was co-precipitated in a beaker placed in a 70℃ thermostatic water-bath, the PH value co-precipitated slurry was controlled at about 9.0; after the co-precipitation process, let the slurry rest for 12h, then the slurry was filtered and the filter cake was washed by deionized water until the PH value of slurry reached about 7.0; the slurry was consequently dried under 110℃ for 24h and calcined at 450℃ for 3h; then the catalysts were

grinded and sieved, the particles with diameter between 0.18mm and 0.25mm (60~80 mesh) was used in experiment.The catalysts with different kinds of promoters (ZrO_2 and Ni) are listed in table I.
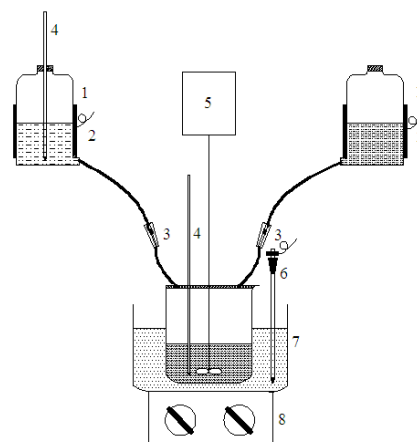

Fig. 1 Experiment flow chart of catalyst preparation 1- flask; 2- electric heating tape; 3- flatjaw pinchcock; 4- thermometer; 5- agitator; 6- contact thermometer; 7- thermostatic water-bath; 8- magnetic stirrer

TABLE I
CATALYSTS PREPARED IN EXPERIMENT

Serial number / Component	C-1	C-2	C-3
	Content ratio (weight)		
Fe	100	100	100
ZrO_2	0	15	0
Ni	0	0	0.9
SiO_2	20	20	20

B. Characterization of catalysts

The Temperature programmed desorption process was used to investigate the adsorption property of H_2 and CO on catalyst surface (H_2-TPD and CO-TPD respectively).

H_2-TPD was used to measure the hydrogen adsorption and desorption on H_2-reduced and CO-reduced catalysts, the loading weight was 0.20g. The H_2-TPD process of H_2-reduced catalyst was as follows. The catalyst sample was first reduced under pure hydrogen gas flow (50ml/min), the temperature was programmed from room temperature to 450℃ with rate 10℃/min, keep for 10h and then cooled to 50℃; after that, the catalyst sample was purged with Ar (the flow rate 50ml/min) until the baseline of H_2 signal leveled off, switched to H_2 and kept for 30min, then the catalyst sample was purged with Ar until the baseline of H_2 signal leveled off. Finally the catalyst sample was heated to 800℃ at a rate of 10℃/min in Ar and kept for 30min. The H_2-TPD process of 4.99%CO-95%He (V/V)-reduced catalyst was as follows. The catalyst sample was reduced under 4.99%CO-95%He (V/V) (50ml/min) with the temperature programmed from room temperature to 350℃ at

ramp 10 ℃/min and kept for 5h, then cooled to 50℃; after that, the catalyst was purged in He for a while and in H_2 for 30min, switched to He until the baseline of H_2 signal leveled off, finally the catalyst sample was heated to 800℃at ramp of 10℃/min in He and kept for 30 min (50ml/min).

CO-TPD was used to investigate the CO adsorption and desorption behavior on 4.99%CO-95%He (V/V)-reduced catalysts. The catalyst sample was reduced in 4.99%CO-95%He (V/V) (50ml/min) with the temperature programmed from room temperature to 350℃ at ramp 10 ℃/min and kept for 5h, then cooled to 50℃; after that, the catalyst was purged in He for a while and in CO for 30 min, switched to He until the baseline of CO signal leveled off, finally the catalyst sample was heated to 800 ℃ at ramp of 10 ℃/min in He and kept for 30 min (50ml/min).

III. Results

A. CO-TPD

The comparison of CO-TPD results of Fe/SiO_2 and

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FeZr/SiO$_2$, Fe/SiO$_2$ and FeNi/SiO$_2$ reduced in 4.99%CO/95.01%He were shown in Fig.2 and Fig.3. It can be seen from Fig.2 and Fig.3 that there were three desorption peaks on the CO-TPD curves of Fe/SiO$_2$ and FeZr/SiO$_2$, Fe/SiO$_2$ and FeNi/SiO$_2$ reduced in 4.99%CO/95.01%He, the desorption peaks at about 100℃, 250~350℃ and 550~650℃ respectively. As reported in literatures, the CO adsorption on a clean Fe(1 0 0) surface resulted in four desorption peaks, which were designated as three molecular states at -23℃, 67℃, 157℃ and a dissociative state at 527℃[12]-[13].
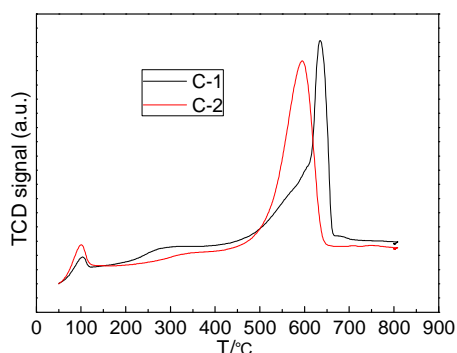

Fig. 2 CO-TPD profiles on Fe/SiO$_2$ and FeZr/SiO$_2$ catalysts reduced in 4.99%CO/95.01%He
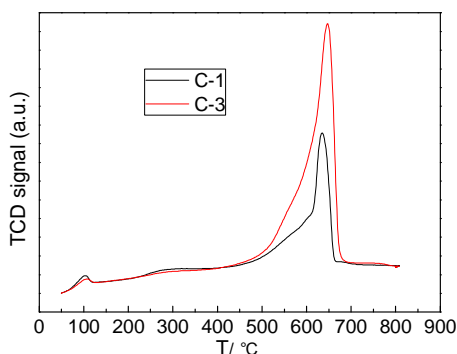

Fig. 3 CO-TPD profiles on Fe/SiO$_2$ and FeNi/SiO$_2$ catalysts reduced in 4.99%CO/95.01%He

However, the CO desorption peaks on iron-based catalysts activated by CO or syngas was much complicated, the results of CO-TPD process of Fe/SiO$_2$ and FeK/SiO$_2$ catalysts reduced by 5%CO/95%He showed that the CO desorption peaks on catalysts surface all located in the temperature range of 300~600℃ and the CO desorption peaks on FeK/SiO$_2$ catalyst showed a multi-peak overlapped curve with maximum peak position at about 548℃, this kind of CO desorption peak was close to the CO desorption peak caused by a dissociative state CO adsorption on catalyst surface[10]. As reported in literatures, a majority of Fe on iron-based catalyst surface reduced by CO or syngas existed as χ-Fe$_5$C$_2$ and ε'-Fe$_{2.2}$C, only a small part existed as oxidation state (Fe$_3$O$_4$). Generally, the CO adsorbed on χ-Fe$_5$C$_2$ and ε'-Fe$_{2.2}$C was very hard to break away from the catalyst surface because of the existence of a strong chemical bond between CO and χ-Fe$_5$C$_2$ or ε'-Fe$_{2.2}$C.

Thus it can be seen that a small part of CO adsorbed on the surface of Fe/SiO$_2$、FeZr/SiO$_2$ and FeNi/SiO$_2$ as a molecular state and a large part adsorbed on χ-Fe$_5$C$_2$ and ε'-Fe$_{2.2}$C as a dissociate state. It can also be seen from Fig.2 that the intensity of CO desorption peak at about 100℃ increased with addition of ZrO$_2$, on the contrary, the intensity of Co desorption peaks about 300℃ and 550~650℃ slightly decreased, the desorption temperature of the CO desorption peak between 550~650℃ reduced with addition of ZrO$_2$. It is indicated that the addition of ZrO$_2$ was preferential for the molecular state adsorption of CO on iron-based catalyst. It is shown from Fig.3 that the intensity of CO desorption peak between 500~700℃ caused by the dissociate state CO desorption increased obviously with addition of Ni which indicated that the addition of Ni is beneficial to the dissociative adsorption of CO on iron-based catalyst surface.
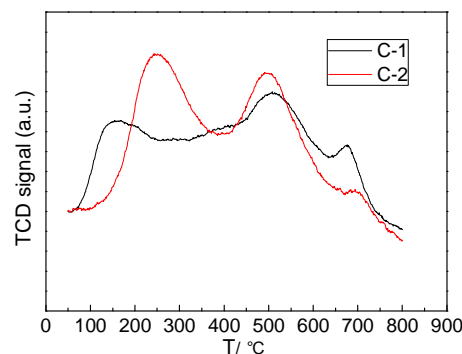
B. H$_2$-TPD

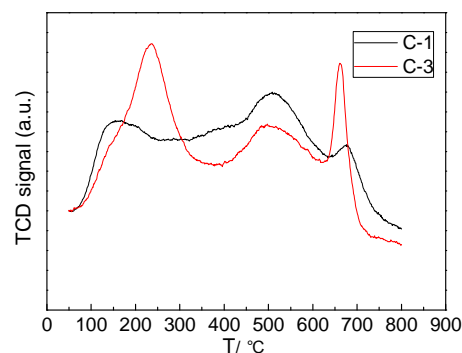Fig.4 H$_2$-TPD profiles on Fe/SiO$_2$ and FeZr/SiO$_2$ catalysts reduced in H$_2$

Fig. 5 H$_2$-TPD profiles on Fe/SiO$_2$ and FeNi/SiO$_2$ catalysts reduced in H$_2$

Fig. 4 and Fig.5 showed the H$_2$-TPD results of Fe/SiO$_2$ and FeZr/SiO$_2$、Fe/SiO$_2$ and FeNi/SiO$_2$ reduced in H$_2$. It can be seen from Fig.4 that the H$_2$-TPD curves of Fe/SiO$_2$ showed three peaks located at 100℃, 500℃ and 700℃ which could be attributed to the desorption of H species that adsorbed on metallic Fe surface (100℃) and the cleavage of OH species on

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the difficultly reduced oxide surface on catalysts (500℃ and 700℃)[14]. In the presence of Zr, the intensity of first two peaks increased markedly and the third one decreased. In Fig.5, in the presence of Ni, the intensity of the first and the third peaks increased obviously and the second peak reduced.
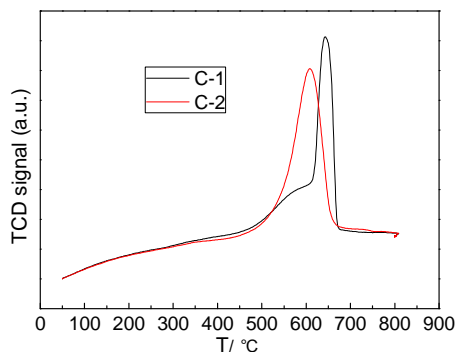

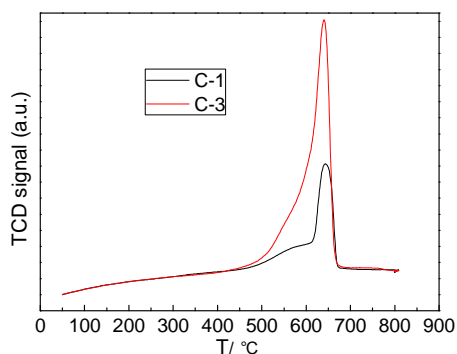Fig. 6 H_2-TPD profiles on Fe/SiO_2 and $FeZr/SiO_2$ catalysts reduced in 4.99%CO/95.01%He

Fig. 7 H_2-TPD profiles on Fe/SiO_2 and $FeNi/SiO_2$ catalysts reduced in 4.99%CO/95.01%He

Fig. 6 and 7 gave the H_2-TPD results of Fe/SiO_2 and $FeZr/SiO_2$、Fe/SiO_2 and $FeNi/SiO_2$ reduced in 4.99%CO/95.01%He. It can be seen from Fig.4 and Fig.5 that the H_2-TPD curves of $FeZr/SiO_2$ and $FeNi/SiO_2$ reduced in 4.99%CO/95.01%He showed an intense peak between 500~700℃ (about 580℃ for $FeZr/SiO_2$ and 600 ℃ for $FeNi/SiO_2$), and for Fe/SiO_2, there was an sharp peak at about 650℃ and a somewhat less defined shoulder between 500~600℃. Generally, iron carbides was considered as the active phase on iron-based catalyst surface, however, there was few papers dealing with the H_2 adsorption on iron carbides surface (or on iron-based catalysts reduced in CO or syngas). Most of H_2 adsorption studies were carried out on the iron surface.

The H_2-TPD results on iron surface showed that the H_2 desorption temperature on iron surface was less than 250℃, this desorption peak can be attributed to the weak chemical bond between Fe and H. Nevertheless the H_2 desorption peak on Fe/SiO_2、$FeZr/SiO_2$和$FeNi/SiO_2$ catalysts in this work were larger than 500℃, there was a intense chemical bond between

the adsorbed H and the catalysts surface. The work of Bruker[15] showed that the adsorbed H_2 on carbonated iron-based catalysts led to the formation of CH which was the most stable surface species on carbonated Fe. On the Fe/SiO_2、$FeZr/SiO_2$ and $FeNi/SiO_2$ catalysts surface reduced in 4.99%CO/95.01%He, Fe existed as χ-Fe_5C_2、ε'-$Fe_{2.2}C$ and Fe_3O_4, hydrogen existed as a stable state (CH and OH) on χ-Fe_5C_2、ε'-$Fe_{2.2}C$ and Fe_3O_4, therefore, the desorption peaks on H_2-TPD curves of Fe/SiO_2、$FeZr/SiO_2$ and $FeNi/SiO_2$ catalysts reduced in 4.99%CO/95.01%He could be attributed to the dissociation of CH and OH. Fig.6 showed that the intensity of H_2 desorption peak and the desorption temperature reduced with addition of ZrO_2 which indicated that the addition of ZrO_2 was not benefit to the dissociative adsorption of H_2 on iron-based catalyst. It can be seen from Fig.7 that the intensity of desorption peak increased obviously, however, the desorption temperature was almost the same. It is indicated that the addition of Ni was preferential for the dissociative adsorption of hydrogen on catalyst surface but almost had no effect on the desorption temperature.

IV. CONCLUSION

Three Fe/SiO_2 catalysts promoted with or without Zr and Ni were prepared by co-precipitation method and used to investigate the adsorption properties of CO and H_2 on iron-based catalysts.

Temperature programmed desorption technique was used in experiment. The CO-TPD results of three catalysts showed that on carburized iron-based catalysts, a small part of CO adsorbed on the surface of Fe/SiO_2、$FeZr/SiO_2$ and $FeNi/SiO_2$ as a molecular state and a large part adsorbed on χ-Fe_5C_2 and ε'-$Fe_{2.2}C$ as a dissociate state, the addition of Zr was preferential for the molecular state adsorption of CO on iron-based catalyst and the presence of Ni was beneficial to the dissociative adsorption of CO. The results of H_2-TPD on H_2 reduced catalysts and carburized catalysts investigated that on H_2 reduced catalysts, hydrogen mainly adsorbs on the surface iron sites and surface oxide sites, on CO reduced catalysts, hydrogen probably existed as the most stable CH and OH species.

The study on adsorption properties of CO and H_2 on iron-based catalysts has directive significance on the understanding of reaction mechanism and the derivation of reaction kinetics model of Fischer-Tropsch synthesis.

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