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Activation Temperature Study of Precipitated Fe/SiO₂ Catalyst for Fischer-Tropsch Synthesis

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The adsorption performance of H_2 and CO on a co-precipitated Fe/SiO_2 catalyst was studied by H_2-TPD, CO-TPD. XRD and Mössbauer spectrum to analyze the effect of activation temperature on the reaction performance and the composition of iron phases on catalyst surface. The results showed that hydrogen probably existed as the most stable CH and OH species on CO reduced catalysts, most of CO adsorbed as a dissociate state on CO reduced Fe/SiO_2 catalyst. On the reduced catalyst, the diffraction peaks intensity of iron carbides increased obviously while that of Fe_3O_4 diffraction peaks slightly reduced. On the used catalyst, the iron phases were mainly constituted by Fe_3O_4 and iron carbides. A higher activation temperature led to higher activity of catalyst, meanwhile, the weight fractions of CH_4 and C_{2-8} increased slightly while C_{9+} decreased with increasing activation temperatures.

Keywords: Fischer-Tropsch synthesis, Precipitated iron catalyst, Activation temperature, Reaction performance.

INTRODUCTION

Iron and cobalt are usually used as active metals of Fischer-Tropsch synthesis (FTS)[1,2]. The active phase of cobalt-based catalyst is Co while that of iron based catalyst is much more complicated[3,4]. Some researchers proposed that Fe_3O_4 was active for Fischer-Tropsch synthesis[5], others questioned it and suggested that the iron carbides (Fe_xC) were the active phases for Fischer-Tropsch synthesis while Fe_3O_4 was active for water-gas shift reaction[6,7].

The iron phase catalyst must be activated before it is used in Fischer-Tropsch reaction because the iron phase usually exists as Fe_2O_3 on the surface of calcined iron based catalyst which has no activation for Fischer-Tropsch reaction[8]. The constitution of iron phases on catalyst surface and the reaction performance (activity of catalyst and product distributions) are greatly affected by the activation temperature.

The effects of activation temperature on reaction performance of iron based catalyst are mainly caused by the following two factors. First, the constitution of iron phases is greatly affected by the activation temperature. Hao *et al.*[9] studied the influence of activation temperature (240-280 ºC) on the composition of iron phases by XRD and Mössbauer techniques and drew a conclusion that the iron phases on reduced catalyst gradually converted from the mixture of iron oxides and iron carbides to pure iron carbides when the activation temperature increased. And the second, during the activation process, the specific area of catalyst will decrease with increasing activation temperature because of the pore collapse on the catalyst surface and then the activity of catalyst decreases. Previous study indicated that the activity of catalyst decreased because of the decrease of the BET surface area with increasing reduction temperature. Duvenhage and Coville[10] investigated the BET surface of FeCo/TiO_2 catalyst reduced at different temperatures (250-400 ºC), the results indicated that the specific area of FeCo/TiO_2 catalyst decreased from 63 to 52 m^2/g when the activation temperature increased from 250 to 400 ºC and at the same time, the activity of catalyst also decreased while the reduction extent increased with increasing activation temperature. Based on these two factors, the reports of the effect of activation temperature on reaction performance gave some different results. The study of Hao *et al.*[6] indicated that the initial activity of catalyst reduced at a lower temperature (240 ºC) was much higher than that of catalyst reduced at 280 ºC. However the stability of catalyst would be improved by the increasing activation temperature. With the reaction progressed, the activity of catalyst reduced at different temperatures gradually approached each other. However, the activity of catalyst reduced at higher temperature was relatively lower when TOS < 500 h. Luo and Davis[11] gave an opposite result, they suggested that CO conversion increased with the increasing activation temperature from 230-270 ºC.

In this study, a Fe/SiO_2 catalyst was prepared by co-precipitation method. Temperature programmed desorption (TPD) technique including H_2-TPD and CO-TPD was adopted to study the adsorption of H_2 and CO on Fe/SiO_2 catalyst. The effect of activation temperature on the composition of iron phases was analyzed by comparing the XRD and Mössbauer results of reduced and used catalysts with different activation temperature and in syngas (H_2/CO = 0.69). The reaction performance of Fe/SiO_2 catalyst reduced at different temperatures was studied in a fixed bed reactor. The appropriate activation temperature of Fe/SiO_2 catalyst was determined in this study.

EXPERIMENTAL

Catalyst preparation: The Fe/SiO_2 catalyst used in experiment was prepared by co-precipitation manner. $Fe(NO_3)_3\cdot 9H_2O$ was first dissolved in de-ionized water, mixed with silica solution and heated to 70 ºC. Ammonia water was used as precipitator. The pH value of co-precipitated slurry was controlled at 9. After the co-precipitation process, the slurry was left for 12 h and then filtered. The filter cake was washed by de-ionized water until the pH value of slurry reached about 7. The slurry was consequently dried under 110 ºC for 24 h and calcined at 450 ºC for 3 h; then the catalyst was grinded and sieved, the particles with diameter between 0.18 and 0.25 mm (60-80 mesh) was used in experiment.

Catalyst characterization: H_2-TPD and CO-TPD of Fe/SiO_2 catalyst were performed in an AutoChemaII 2920 chemisorption apparatus.

H_2-TPD process of H_2-reduced catalyst was as follows. The catalyst sample was first reduced under pure hydrogen gas flow (50 mL/min), the temperature was programmed from room temperature to 450 ºC with a rate 10 ºC/min, keep for 10 h and then cooled to 50 ºC. After that, the catalyst sample was purged with Ar (the flow rate 50 mL/min) until the baseline of H_2 signal leveled off, switched to H_2 and kept for 0.5 h. 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 ºC at a rate of 10 ºC/min in Ar and kept for 0.5 h.

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) (50 mL/min) with the temperature programmed from room temperature to 350 ºC at ramp 10 ºC/min and kept for 5 h, then cooled to 50 ºC. After that, the catalyst was purged in He for a while and in H_2 for 0.5 h, switched to He until the baseline of H_2 signal leveled off, finally the catalyst sample was heated to 800 ºC at ramp of 10 ºC/min in He and kept for 0.5 h (50 mL/min).

CO-TPD was used to investigate the CO adsorption and desorption behaviour on 4.99 % CO-95 % He (v/v)-reduced catalysts. The catalyst sample was reduced in 4.99 % CO-95 % He (V/V) (50 mL/min) with the temperature programmed from room temperature to 350 ºC at ramp 10 ºC/min and left for 5 h, then cooled to 50 ºC. After that, the catalyst was purged in He for a while and in CO for 0.5 h, switched to He until the baseline of CO signal leveled off, finally the catalyst sample was heated to 800 ºC at ramp of 10 ºC/min in He and kept for 0.5 h (50 mL/min).

X-ray diffraction of catalyst samples were carried out on a D/max-2550 X-ray diffractometer (Rigaku, Japan) equipped with a CuK_α radiation. The scanned range of diffraction angel is 10-80º with scanning rate 0.2 min^{-1}. Standard power XRD cards compiled by Joint Committee on Power Diffraction Standards (JCPDS) were used to identify the iron phase exsiting on the catalyst surface.

Mössbauer spectra of catalysts were recorded at room temperature using a Wissel constant acceleration Mössbauer spectrometer (Germany) with a 57Co(Pd) source. The spectra were collected over 512 channels in the mirror image format. Data analysis was performed using a nonlinear least square fitting routine that models the spectra as a combination of singlets, quadruple doublets and magnetic sextuplets based on a Lorentzian line shape profile. The components were identified based on their isomer shift (IS), quadruple splitting (QS) and magnetic hyperfine field (Hhf). Magnetic hyperfine fields were calibrated with the 330kOe field of α-Fe at ambient temperature.

Operating conditions, reactor system and product analysis: The FTS over an iron-based catalyst was carried out in a fixed-bed reactor under the reaction conditions: temperature 250 ºC, pressure 3.5 MPa, space velocity (Sv) 1000 h^{-1} and H_2/CO = 0.69. The activation conditions: temperature 250-350 ºC, pressure 0.1 MPa, Sv = 2000 h^{-1}, H_2/CO = 0.69. About 1.02 g catalyst with particle size of 60-80 mesh was loaded into the reactor.

The outlet of the reactor was connected with a hot-trap (180 ºC) and a cold-trap (0 ºC) for the separation of components with high and low boiling point, respectively. The tail gas was vented through a soap-foam flow-meter or analyzed by a gas chromatograph (Agilent 7890A).

CO, H_2, N_2, CO_2 and CH_4 in tail gas were separated on a 5A molecular sieve packed columns and Propack Q packed columns, then detected by two thermal conductivity detectors (TCDs) with pure He and H_2 as the carrier gas, respectively. C_1-C_6 hydrocarbons in tail gas were separated on a HP-AL/S capillary column and detected by a flame ionization detector (FID) with N_2 as the carrier gas. The components in tail gas were quantified by standard gas containing CO, H_2, N_2, CO_2 CH_4 and C_1-C_6 hydrocarbons, external standard method. The wax product from hot trap was first dissolved in CS_2 and analyzed on a HP-5 capillary column with temperature programmed in stages from 40-300 ºC (8 ºC/min), detected by FID (N_2 carrier gas). The oil products were separated on a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm), detected by FID with N_2 as the carrier gas, the column temperature was programmed in stages from 40-240 ºC (5 ºC/min). The wax and oil products were qualified by the proportion of area percentage. The products in water were separated on a DB-WAX capillary column, detected by FID with N_2 as the carrier gas, the column temperature was programmed in stages from 40-150 ºC (5 ºC/min), qualified by external standard method.

RESULTS AND DISCUSSION

Adsorption and desorption of CO and H_2 on Fe/SiO_2 catalyst: CO-TPD, H_2-TPD results of Fe/SiO_2 catalyst activated in 4.99 % CO/95.01 % He, pure H_2 and 4.99 % CO/95.01 % He are shown in Figs. 1-3, respectively.

It can be seen from Fig. 1 that there are three desorption peaks on the CO-TPD curves of Fe/SiO_2 catalyst reduced in 4.99 % CO/95.01 % He, the desorption peaks at 100, 300 and

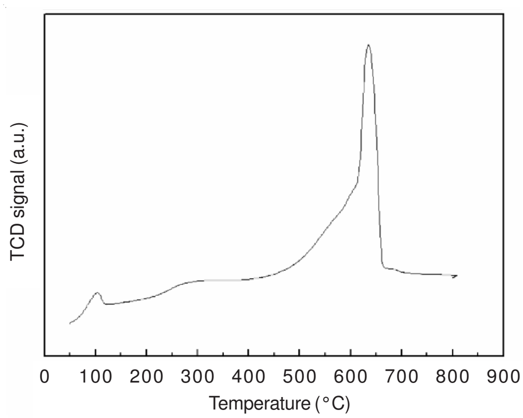

Fig. 1. CO-TPD of Fe/SiO_2 catalyst activated in 4.99 % CO/95.01 % He

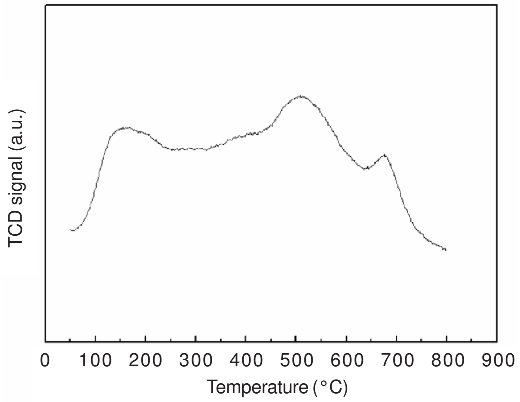

Fig. 2. H_2-TPD of Fe/SiO_2 catalyst activated in pure H_2

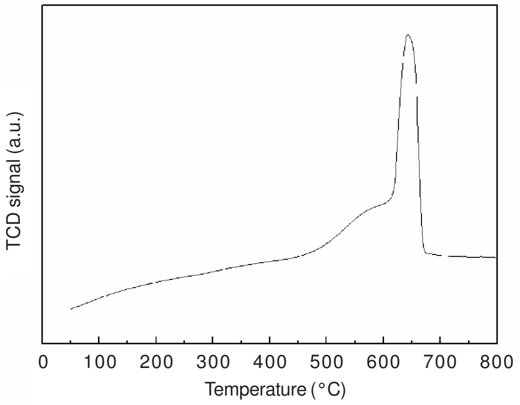

Fig. 3. H_2-TPD results of Fe/SiO_2 catalyst reduced in 4.99 % CO/95.01 % He

630 ºC, respectively. As reported in literatures[12,13], the CO adsorption on a clean Fe surface resulted in four desorption peaks, which were designated as three molecular states at -23, 67 and 157 ºC and a dissociative state at 527 ºC. However, the CO desorption peaks on iron-based catalysts activated by CO or syngas is much more complicated. The results of CO-TPD process of Fe/SiO_2 and FeK/SiO_2 catalysts reduced by 5 % CO/95 % He show that the CO desorption peaks on catalysts surface all located in the temperature range of 300-600 ºC and the CO desorption peaks on FeK/SiO_2 catalyst show a multi-peak overlapped curve with maximum peak position at 548 ºC, this kind of CO desorption peak is close to the CO desorption peak caused by a dissociative state CO adsorption on catalyst surface[14]. A majority of iron phases on iron-based catalyst surface reduced by CO or syngas exists as χ-Fe_5C_2 and ε'-$Fe_{2.2}C$, only a small part exists as oxidation state (Fe_3O_4). Generally, the CO adsorbed on χ-Fe_5C_2 and ε'-$Fe_{2.2}C$ is hard to break away from the catalyst surface because of the existence of a strong chemical bond between CO and χ-Fe_5C_2 or ε'-$Fe_{2.2}C$. Thus it can be seen that a small part of CO adsorbs on the surface of Fe/SiO_2 catalyst as a molecular state and a large part adsorbs on χ-Fe_5C_2 and ε'-$Fe_{2.2}C$ as a dissociate state.

Fig. 2 shows the H_2-TPD results of Fe/SiO_2 catalyst reduced in H_2. It can be seen from Fig. 2 that there are three peaks located at 150, 505 and 680 ºC on the H_2-TPD curves of Fe/SiO_2 which could be attributed to the desorption of H species that adsorbs on metallic Fe surface (150 ºC) and the cleavage of OH species on the difficultly reduced oxide surface on catalysts (505 and 680 ºC)[15].

Fig. 3 gives the H_2-TPD results of Fe/SiO_2 catalyst reduced in 4.99 % CO/95.01 % He. It can be seen from Fig. 3 that the H_2-TPD curves of Fe/SiO_2 catalyst reduced in 4.99 % CO/95.01 % He shows an intense peak at 645 ºC and a somewhat less defined shoulder at 580 ºC. Generally, iron carbides is considered as the active phase on iron-based catalyst surface, however, there is 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 shows that the H_2 desorption temperature on iron surface is less than 250 ºC, this desorption peak can be attributed to the weak chemical bond between Fe and H. Nevertheless the temperature of H_2 desorption peaks on Fe/SiO_2 catalyst in this study is higher than 500 ºC, there is an intense chemical bond between the adsorbed H and the catalysts surface. The work of Bruker and Rhodin[16] 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 surface of Fe/SiO_2 catalyst reduced in 4.99 % CO/95.01 % He, Fe exists as χ-Fe_5C_2, ε'-$Fe_{2.2}C$ and Fe_3O_4, hydrogen exists 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 catalyst reduced in 4.99 % CO/95.01 % He can be attributed to the dissociation of CH and OH.

Composition of iron phases on Fe/SiO_2 catalyst: X-ray diffraction of reduced and used (for 24 h) Fe/SiO_2 catalysts at diffe-rent activation temperatures (250, 275, 300 and 350 ºC) are shown in Figs. 4 and 5, respectively.

The XRD patterns are plotted for 2θ values ranging from 30-70º since the most intensive peak of Fe_2O_3, Fe_3O_4 and iron carbides fall within this range. It can be seen from Fig. 4 that the composition of iron phases on the surface of reduced catalyst is obviously affected by the activation temperature. X-ray diffraction results indicate that the iron phases of reduced catalyst are mainly mixture of Fe_3O_4 and iron carbides. With the increasing activation temperature, the diffraction peaks intensity of iron carbides increase obviously and instead, the intensity of Fe_3O_4 diffraction peaks slightly reduce. The study of Hao *et al.*[9] gave the same results. They found that the mixture of Fe_3O_4 and iron carbides on catalyst surface was gradually replaced by iron carbides when the activation temperature increased, which was preference for the improvement of activity of catalyst.

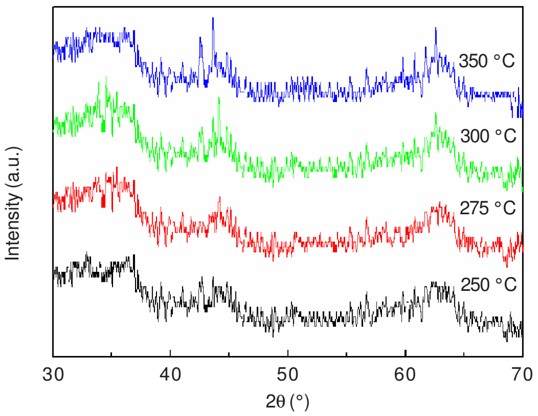

Fig. 4. XRD results of reduced Fe/SiO_2 catalysts at different activation temperatures

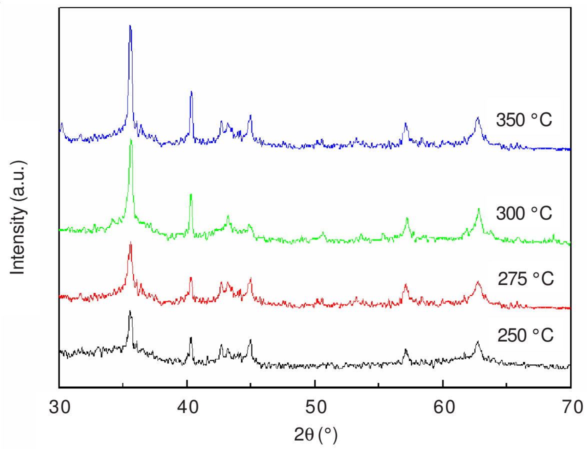

Fig. 5. XRD results of used Fe/SiO_2 catalysts (24 h) at different activation temperatures

Fig. 5 shows the XRD patterns of used Fe/SiO_2 catalysts (for 24 h) activated at different temperatures. The XRD results indicate that the iron phases on the surface of used catalysts are mainly constituted by Fe_3O_4 and iron carbides, the intensity of diffraction peaks increases with increasing activation temperature. For the existence of H_2O and CO_2 during the Fischer-Tropsch reaction, the iron carbides would gradually be oxidized. Most of the diffraction peaks of XRD patterns are the overlapping peaks which contain Fe_3O_4 and iron carbides, taking the increasing CO conversion and selectivity of CO_2 in account, the increase of diffraction peaks intensity could be attributed to the increase of Fe_3O_4 and iron carbides.

Table-1 gives the results of Mössbauer spectrum of Fe/SiO_2 catalyst reduced at 250, 275 and 300 ºC. The iron phases of used catalysts (for 60 h) reduced at different temperatures contains Fe^{3+}(spm), Fe^{2+}(spm), Fe_3O_4, χ-Fe_5C_2 and ε'-$Fe_{2.2}C$ on the surface. The catalyst reduced at 250 ºC comprises 13.2 Fe^{3+} (spm), 26.8 % Fe^{2+}(spm), 6.4 % Fe_3O_4, 22.1 % χ-Fe_5C_2 and 31.5 % ε'-$Fe_{2.2}C$. The amount of Fe^{3+}(spm), Fe_3O_4 and ε'-$Fe_{2.2}C$ increase when the activation temperature is increased while the amount of Fe^{2+}(spm) and χ-Fe_5C_2 shows an opposite tendency. The reasonable explanation is that χ-Fe_5C_2 is transformed to ε'-$Fe_{2.2}C$ and at the same time Fe^{2+}(spm) is oxidized to Fe^{3+} (spm) because of the existence of H_2O and CO_2. With the increase of activation temperature, the total amount of iron carbides increases slightly while that of Fe_3O_4 increases apparently. Consequently, the increase of intensity of overlapping peaks in Fig. 6 could be most attributed to the increase of Fe_3O_4. In order to avoid forming large amount of CO_2, the activation temperature should not be too high.

TABLE-1
IRON PHASE IDENTIFIED BY MÖSSBAUER SPECTRA IN USED Fe/SiO_2 CATALYST (FOR 60 h) REDUCED AT DIFFERENT ACTIVATION TEMPERATURES

Activation temp. (ºC)	Area (%)				
	Fe^{3+}	Fe^{2+}	Fe_3O_4	χ-Fe_5C_2	ε'-$Fe_{2.2}C$
250	13.2	26.8	6.4	22.1	31.5
275	14.2	19.3	11.2	18.4	36.9
300	15.3	10.2	17.5	16.3	39.7

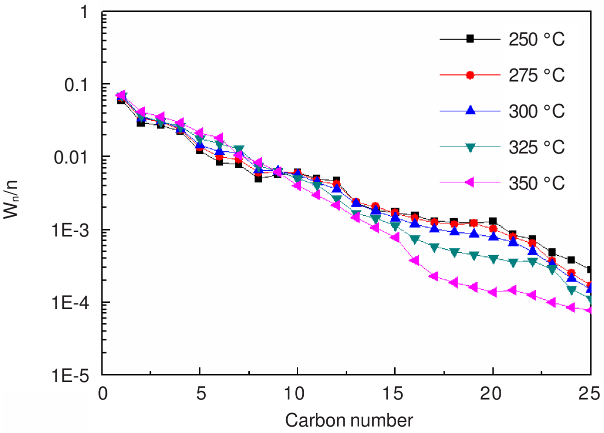

Fig. 6. Effect of activation temperature on product distributions of Fischer-Tropsch synthesis over Fe/SiO_2 catalyst

Product distributions: The CO conversion and selectivity of CO_2 over Fe/SiO_2 catalysts activated at different temperatures (250, 275, 300, 325 and 350 ºC) are listed in Table-2. Fig. 6 describes the production distributions of Fischer-Tropsch synthesis over Fe/SiO_2 catalysts activated at different temperatures, the reaction conditions are as follows: 250 ºC, 3.5 MPa, 25 mL/min, H_2/CO = 0.69.

TABLE-2
CONVERSION OF CO AND SELECTIVITY OF CO_2 OVER Fe/SiO_2 CATALYSTS ACTIVATED AT DIFFERENT TEMPERATURES

Activation temperature (ºC)	x_{CO} (%)	S_{CO_2} (%)
250	5.69	19.43
275	8.81	22.13
300	21.37	23.36
325	26.81	25.22
350	31.41	27.26

The catalysts are activated in syngas (H_2/CO = 0.69) at different temperatures. Table-2 shows that CO conversion increases from 5.69 to 31.41 % when activation temperature increases from 250 to 350 ºC, the activity of catalyst apparently increases. It was reported that the iron mainly existed as Fe_2O_3 on the fresh Fe/SiO_2 catalyst surface. When the catalyst was reduced in syn-gas, the iron phase first converted into Fe_3O_4 and then gradually be reduced to Fe and iron carbides which was identified as the active phase of Fischer-Tropsch synthesis. It can be seen from Table-2 and Fig. 5 that the increasing activation temperature is good for the formation of iron carbides and further improve the activity of Fe/SiO_2 catalyst. Some literatures reported the effect of activation temperature on activity of iron-based catalyst reduced in H_2. It was reported that the catalyst activity decreased with the increasing temperature and the reason for this phenomenon was attributed to the increasing amount of H_2O and the following sintering of catalyst which reduced the activity of catalyst. Consequently, a lower activation temperature leads to higher catalyst activity for H_2-reduced catalyst. However, the results of this study show an opposite tendency, it is found that a higher activation temperature leads to higher activity of catalyst. Hao *et al.*[9] studied the influence of activation temperature (240-280 ºC) on the composition of iron phases by XRD and Mössbauer techniques and drew a conclusion that the iron phases on reduced catalyst gradually converted from the mixture of iron oxides and iron carbides to pure iron carbides when the activation temperature increased.

Fig. 6 gives the production distributions of Fischer-Tropsch synthesis over Fe/SiO_2 catalysts activated at different temperatures. It is found that the profiles of product distributions show a decreasing tendency with the increasing carbon number. It deceases along a straight line when $n < 15$ while deviates from the line when $n > 15$. When the activation temperature increases from 250 to 350 ºC, the weight fractions of CH_4 and hydrocarbons with low carbon number (C_2-C_8) increase slightly while hydrocarbons with high carbon number (C_{9+}) decrease with increasing activation temperatures. When the activation temperature is higher than 300 ºC, the weight fraction of C_{9+} shows a more obvious decreasing tendency than that under lower activation temperatures.

On the basis of above analysis, for the sake of higher Fischer-Tropsch synthesis activity, selectivity of hydrocarbons with high carbon number and lower selectivity of CO_2, 300 ºC could be chosen as the appropriate activation temperature of Fe/SiO_2 catalyst.

Activity and stability: Fig. 7 shows the variation of CO conversion with TOS over Fe/SiO_2 catalyst reduced at 300 ºC, 0.1 MPa in syngas ($H_2/CO = 0.69$) with flow rate 54.4 mL/min, the reaction condition: $H_2/CO = 0.69$, 250 ºC, 3.51 MPa, 25 mL/min. It is found from Fig. 7 that the CO conversion increases rapidly with TOS from 0 to 6 h, then decreases apparently until it is close to 21 % at about TOS = 24 h, the stable CO conversion is 21 %. When 24 h < TOS < 300 h, CO conversion fluctuates nearby 21 %, which indicates that the activity of Fe/SiO_2 catalyst is stable during Fischer-Tropsch reaction when 24 h < TOS < 300 h.

Conclusion

The Fischer-Tropsch synthesis over a precipitated Fe/SiO_2 catalyst reduced at different temperatures was studied in a fixed-bed reactor. The effect of activation temperature on the constitution of iron phases on catalyst surface and the reaction performance (activity of catalyst and product distribution) was investigated.

The constitution of iron phases on catalyst surface was influenced apparently by activation temperature. X-ray diffraction of reduced and used catalysts indicated that the amount of iron carbides determined the reactivity of catalysts. Results of Mössbauer spectrum indicated that the amount of Fe^{3+}(spm), Fe_3O_4 and ε'-$Fe_{2.2}C$ increased with the increasing activation temperature while the amount of Fe^{2+}(spm) and χ-Fe_5C_2 showed an opposite tendency.

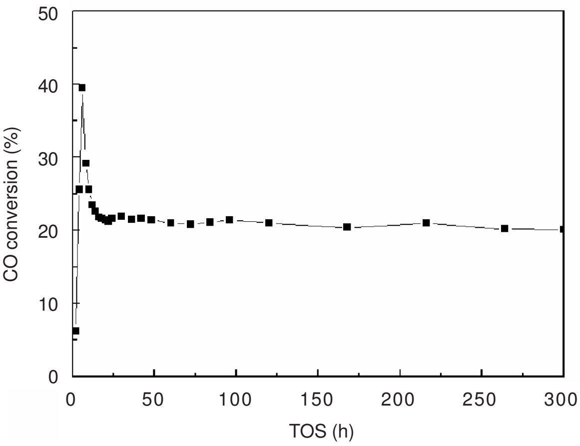

Fig. 7. Variation of CO conversion with TOS

The profiles of product distributions over Fe/SiO_2 catalysts reduced at different temperatures demonstrated that a higher activation temperature was not good for the formation of high carbon number hydrocarbons but good for the formation of CO_2, thus the activation temperature should not be too high.

For the sake of higher Fischer-Tropsch synthesis activity, selectivity of hydrocarbons with high carbon number and lower selectivity of CO_2, 300 ºC was used as the appropriate activation temperature for the precipitated Fe/SiO_2 catalyst.

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