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

WEIXIN QIAN¹, HAITAO ZHANG¹, QIWEN SUN², YONGDI LIU³, WEIYONG YING^{1,*} and DINGYE FANG¹

¹School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P.R. China

²State Key Laboratory of Coal Liquefaction and Coal Chemical Technology, Shanghai 201203, P.R. China

³School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, P.R. China

*Corresponding author: Tel/Fax: +86 21 64252192; E-mail: wying@ecust.edu.cn; qwx0403@163.com

Received: 3 July 2013;

Accepted: 18 September 2013;

Published online: 30 January 2014;

AJC-14656

The adsorption performance of H₂ and CO on a co-precipitated Fe/SiO₂ catalyst was studied by H₂-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/SiO₂ catalyst. On the reduced catalyst, the diffraction peaks intensity of iron carbides increased obviously while that of Fe₃O₄ diffraction peaks slightly reduced. On the used catalyst, the iron phases were mainly constituted by Fe₃O₄ and iron carbides. A higher activation temperature led to higher activity of catalyst, meanwhile, the weight fractions of CH₄ and C₂₋₈ increased slightly while C₉₊ 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 Fe₃O₄ was active for Fischer-Tropsch synthesis⁵, others questioned it and suggested that the iron carbides (Fe₅C₇) were the active phases for Fischer-Tropsch synthesis while Fe₃O₄ 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 Fe₂O₃ on the surface of calcined iron based catalyst which has no activation for Fischer-Tropsch reaction⁸. 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 °C) 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 Coville¹⁰ investigated the BET surface of FeCo/TiO₂ catalyst reduced at different temperatures (250-400 °C), the results indicated that the specific area of FeCo/TiO₂ catalyst decreased from 63 to 52 m²/g when the activation temperature increased from 250 to 400 °C 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 °C) was much higher than that of catalyst reduced at 280 °C. 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 Davis¹¹ gave an opposite result, they suggested that CO conversion increased with the increasing activation temperature from 230-270 °C.

In this study, a Fe/SiO₂ catalyst was prepared by co-precipitation method. Temperature programmed desorption (TPD) technique including H₂-TPD and CO-TPD was adopted to study the adsorption of H₂ and CO on Fe/SiO₂ 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 (H₂/CO = 0.69). The reaction performance of Fe/SiO₂ catalyst reduced at different temperatures was studied in a fixed bed reactor. The appropriate activation temperature of Fe/SiO₂ catalyst was determined in this study.

EXPERIMENTAL

Catalyst preparation: The Fe/SiO₂ catalyst used in experiment was prepared by co-precipitation manner. Fe(NO₃)₃·9H₂O was first dissolved in de-ionized water, mixed with silica solution and heated to 70 °C. 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 °C for 24 h and calcined at 450 °C 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: H₂-TPD and CO-TPD of Fe/SiO₂ catalyst were performed in an AutoChemII 2920 chemisorption apparatus.

H₂-TPD process of H₂-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 °C with a rate 10 °C/min, keep for 10 h and then cooled to 50 °C. After that, the catalyst sample was purged with Ar (the flow rate 50 mL/min) until the baseline of H₂ signal leveled off, switched to H₂ and kept for 0.5 h. Then the catalyst sample was purged with Ar until the baseline of H₂ signal leveled off. Finally the catalyst sample was heated to 800 °C at a rate of 10 °C/min in Ar and kept for 0.5 h.

H₂-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 °C at ramp 10 °C/min and kept for 5 h, then cooled to 50 °C. After that, the catalyst was purged in He for a while and in H₂ for 0.5 h, switched to He until the baseline of H₂ signal leveled off, finally the catalyst sample was heated to 800 °C at ramp of 10 °C/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 °C at ramp 10 °C/min and left for 5 h, then cooled to 50 °C. 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 °C at ramp of 10 °C/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 10-80° 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 existing 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 °C, pressure 3.5 MPa, space velocity (Sv) 1000 h⁻¹ and H₂/CO = 0.69. The activation conditions: temperature 250-350 °C, pressure 0.1 MPa, Sv = 2000 h⁻¹, H₂/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 °C) and a cold-trap (0 °C) 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, H₂, N₂, CO₂ and CH₄ 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 H₂ as the carrier gas, respectively. C₁-C₆ hydrocarbons in tail gas were separated on a HP-AL/S capillary column and detected by a flame ionization detector (FID) with N₂ as the carrier gas. The components in tail gas were quantified by standard gas containing CO, H₂, N₂, CO₂, CH₄ and C₁-C₆ hydrocarbons, external standard method. The wax product from hot trap was first dissolved in CS₂ and analyzed on a HP-5 capillary column with temperature programmed in stages from 40-300 °C (8 °C/min), detected by FID (N₂ 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 N₂ as the carrier gas, the column temperature was programmed in stages from 40-240 °C (5 °C/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 N₂ as the carrier gas, the column temperature was programmed in stages from 40-150 °C (5 °C/min), qualified by external standard method.

RESULTS AND DISCUSSION

Adsorption and desorption of CO and H₂ on Fe/SiO₂ catalyst: CO-TPD, H₂-TPD results of Fe/SiO₂ catalyst activated in 4.99 % CO/95.01 % He, pure H₂ 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/SiO₂ catalyst reduced in 4.99 % CO/95.01 % He, the desorption peaks at 100, 300 and

Fig. 1. CO-TPD of Fe/SiO₂ catalyst activated in 4.99 % CO/95.01 % He Fig. 2. H₂-TPD of Fe/SiO₂ catalyst activated in pure H₂ Fig. 3. H₂-TPD results of Fe/SiO₂ catalyst reduced in 4.99 % CO/95.01 % He

630 °C, 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 °C and a dissociative state at 527 °C. 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/SiO₂ and FeK/SiO₂ 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 °C and the CO desorption peaks on FeK/SiO₂ catalyst show a multi-peak overlapped curve with maximum peak position at 548 °C, this kind of CO desorption peak is close to the CO desorption peak caused by a dissociative state CO adsorption on catalyst

surface¹⁴. A majority of iron phases on iron-based catalyst surface reduced by CO or syngas exists as χ -Fe₅C₂ and ϵ '-Fe_{2.2}C, only a small part exists as oxidation state (Fe₃O₄). Generally, the CO adsorbed on χ -Fe₅C₂ 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 -Fe₅C₂ or ϵ '-Fe_{2.2}C. Thus it can be seen that a small part of CO adsorbs on the surface of Fe/SiO₂ catalyst as a molecular state and a large part adsorbs on χ -Fe₅C₂ and ϵ '-Fe_{2.2}C as a dissociative state.

Fig. 2 shows the H₂-TPD results of Fe/SiO₂ catalyst reduced in H₂. It can be seen from Fig. 2 that there are three peaks located at 150, 505 and 680 °C on the H₂-TPD curves of Fe/SiO₂ which could be attributed to the desorption of H species that adsorbs on metallic Fe surface (150 °C) and the cleavage of OH species on the difficultly reduced oxide surface on catalysts (505 and 680 °C)¹⁵.

Fig. 3 gives the H₂-TPD results of Fe/SiO₂ catalyst reduced in 4.99 % CO/95.01 % He. It can be seen from Fig. 3 that the H₂-TPD curves of Fe/SiO₂ catalyst reduced in 4.99 % CO/95.01 % He shows an intense peak at 645 °C and a somewhat less defined shoulder at 580 °C. Generally, iron carbides is considered as the active phase on iron-based catalyst surface, however, there is few papers dealing with the H₂ adsorption on iron carbides surface (or on iron-based catalysts reduced in CO or syngas). Most of H₂ adsorption studies were carried out on the iron surface. The H₂-TPD results on iron surface shows that the H₂ desorption temperature on iron surface is less than 250 °C, this desorption peak can be attributed to the weak chemical bond between Fe and H. Nevertheless the temperature of H₂ desorption peaks on Fe/SiO₂ catalyst in this study is higher than 500 °C, there is an intense chemical bond between the adsorbed H and the catalysts surface. The work of Bruker and Rhodin¹⁶ showed that the adsorbed H₂ 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/SiO₂ catalyst reduced in 4.99 % CO/95.01 % He, Fe exists as χ -Fe₅C₂, ϵ '-Fe_{2.2}C and Fe₃O₄, hydrogen exists as a stable state (CH and OH) on χ -Fe₅C₂, ϵ '-Fe_{2.2}C and Fe₃O₄, therefore, the desorption peaks on H₂-TPD curves of Fe/SiO₂ 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/SiO₂ catalyst: X-ray diffraction of reduced and used (for 24 h) Fe/SiO₂ catalysts at different activation temperatures (250, 275, 300 and 350 °C) are shown in Figs. 4 and 5, respectively.

The XRD patterns are plotted for 2 θ values ranging from 30-70° since the most intensive peak of Fe₂O₃, Fe₃O₄ 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 Fe₃O₄ and iron carbides. With the increasing activation temperature, the diffraction peaks intensity of iron carbides increase obviously and instead, the intensity of Fe₃O₄ diffraction peaks slightly reduce. The study of Hao *et al.*⁹ gave the same results. They found that the mixture of Fe₃O₄ 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/SiO₂ catalysts at different activation temperatures

Fig. 5. XRD results of used Fe/SiO₂ catalysts (24 h) at different activation temperatures

Fig. 5 shows the XRD patterns of used Fe/SiO₂ 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 Fe₃O₄ and iron carbides, the intensity of diffraction peaks increases with increasing activation temperature. For the existence of H₂O and CO₂ 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 Fe₃O₄ and iron carbides, taking the increasing CO conversion and selectivity of CO₂ in account, the increase of diffraction peaks intensity could be attributed to the increase of Fe₃O₄ and iron carbides.

Table-1 gives the results of Mössbauer spectrum of Fe/SiO₂ catalyst reduced at 250, 275 and 300 °C. The iron phases of used catalysts (for 60 h) reduced at different temperatures contains Fe³⁺(spm), Fe²⁺(spm), Fe₃O₄, χ -Fe₅C₂ and ϵ' -Fe_{2.2}C on the surface. The catalyst reduced at 250 °C comprises 13.2 % Fe³⁺(spm), 26.8 % Fe²⁺(spm), 6.4 % Fe₃O₄, 22.1 % χ -Fe₅C₂ and 31.5 % ϵ' -Fe_{2.2}C. The amount of Fe³⁺(spm), Fe₃O₄ and ϵ' -Fe_{2.2}C increase when the activation temperature is increased while the amount of Fe²⁺(spm) and χ -Fe₅C₂ shows an opposite tendency. The reasonable explanation is that χ -Fe₅C₂ is transformed to ϵ' -Fe_{2.2}C and at the same time Fe²⁺(spm) is oxidized to Fe³⁺(spm) because of the existence of H₂O and CO₂. With the increase of activation temperature, the total amount of iron carbides increases slightly while that of Fe₃O₄ increases apparently.

TABLE-1
IRON PHASE IDENTIFIED BY MÖSSBAUER SPECTRA
IN USED Fe/SiO₂ CATALYST (FOR 60 h) REDUCED
AT DIFFERENT ACTIVATION TEMPERATURES

Activation temp. (°C)	Area (%)				
	Fe ³⁺	Fe ²⁺	Fe ₃ O ₄	χ -Fe ₅ C 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

Consequently, the increase of intensity of overlapping peaks in Fig. 6 could be most attributed to the increase of Fe₃O₄. In order to avoid forming large amount of CO₂, the activation temperature should not be too high.

Fig. 6. Effect of activation temperature on product distributions of Fischer-Tropsch synthesis over Fe/SiO₂ catalyst

Product distributions: The CO conversion and selectivity of CO₂ over Fe/SiO₂ catalysts activated at different temperatures (250, 275, 300, 325 and 350 °C) are listed in Table-2. Fig. 6 describes the production distributions of Fischer-Tropsch synthesis over Fe/SiO₂ catalysts activated at different temperatures, the reaction conditions are as follows: 250 °C, 3.5 MPa, 25 mL/min, H₂/CO = 0.69.

TABLE-2
CONVERSION OF CO AND SELECTIVITY OF CO₂
OVER Fe/SiO₂ CATALYSTS ACTIVATED AT
DIFFERENT TEMPERATURES

Activation temperature (°C)	x _{CO} (%)	S _{CO₂} (%)
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 (H₂/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 °C, the activity of catalyst apparently increases. It was reported that the iron mainly existed as Fe₂O₃ on the fresh Fe/SiO₂ catalyst surface. When the catalyst was reduced in syn-gas, the iron phase first converted into Fe₃O₄ 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/SiO₂ catalyst. Some literatures reported the effect of activation temperature on activity of iron-based catalyst reduced in H₂. 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 H₂O and the following sintering of catalyst which reduced the activity of catalyst. Consequently, a lower activation temperature leads to higher catalyst activity for H₂-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 °C) 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/SiO₂ catalysts activated at different temperatures. It is found that the profiles of product distributions show a decreasing tendency with the increasing carbon number. It decreases along a straight line when $n < 15$ while deviates from the line when $n > 15$. When the activation temperature increases from 250 to 350 °C, the weight fractions of CH₄ and hydrocarbons with low carbon number (C₂–C₈) increase slightly while hydrocarbons with high carbon number (C₉₊) decrease with increasing activation temperatures. When the activation temperature is higher than 300 °C, the weight fraction of C₉₊ 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 CO₂, 300 °C could be chosen as the appropriate activation temperature of Fe/SiO₂ catalyst.

Activity and stability: Fig. 7 shows the variation of CO conversion with TOS over Fe/SiO₂ catalyst reduced at 300 °C, 0.1 MPa in syngas (H₂/CO = 0.69) with flow rate 54.4 mL/min, the reaction condition: H₂/CO = 0.69, 250 °C, 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/SiO₂ catalyst is stable during Fischer-Tropsch reaction when 24 h < TOS < 300 h.

Conclusion

The Fischer-Tropsch synthesis over a precipitated Fe/SiO₂ 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 Fe³⁺(spm),

Fig. 7. Variation of CO conversion with TOS

Fe₃O₄ and ε'-Fe₂C increased with the increasing activation temperature while the amount of Fe²⁺(spm) and χ-Fe₅C₂ showed an opposite tendency.

The profiles of product distributions over Fe/SiO₂ 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 CO₂, 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 CO₂, 300 °C was used as the appropriate activation temperature for the precipitated Fe/SiO₂ catalyst.

ACKNOWLEDGEMENTS

The financial support from the Major State Basic Research Development Program of China (973 plan) (Project No. 2010CB736203), the National High Technology Research and Development Plan of China (863 plan) (Project No. 2011AA05A20401) and the Fundamental Research Funds for the Central Universities (Project No. 222201314052) are gratefully acknowledged.

REFERENCES

1. M.E. Dry, *Catal. Today*, **71**, 227 (2002).
2. Y.N. Wang, Y.Y. Xu, Y.W. Li, Y.-L. Zhao and B.-J. Zhang, *Chem. Eng. Sci.*, **58**, 867 (2003).
3. W. Zhou, J.G. Chen, K.G. Fang and Y.-H. Sun, *Fuel Process. Technol.*, **87**, 609 (2006).
4. W. Chu, P.A. Chernavskii, L. Gengembre, G. Pankina, P. Fongarland and A. Khodakov, *J. Catal.*, **252**, 215 (2007).
5. J.P. Reymond, P. Meriadeau and S.J. Teichner, *J. Catal.*, **75**, 39 (1982).
6. Q.L. Hao, L. Bai, H.W. Xiang and Y. Li, *J. Nat. Gas Chem.*, **18**, 429 (2009).
7. R.J. O'Brien, L.G. Xu, R.L. Spicer and B.H. Davis, *Energy Fuels*, **10**, 921 (1996).
8. D.B. Bukur, K. Okabe, M.P. Rosynek, C.P. Li, D.J. Wang, K.R.P.M. Rao and G.P. Huffman, *J. Catal.*, **155**, 353 (1995).
9. Q.L. Hao, F.X. Liu, H. Wang, J. Chang, C.-H. Zhang, L. Bai, H.-W. Xiang, Y.-W. Li, F. Yi and B.-F. Xu, *J. Mol. Catal.*, **261**, 104 (2007).
10. D.J. Duvenhage and N.J. Coville, *Appl. Catal.*, **233**, 63 (2002).
11. M.S. Luo and B.H. Davis, *Fuel Process. Technol.*, **83**, 49 (2003).
12. J. Benziger and R.J. Madix, *Surf. Sci.*, **94**, 119 (1980).
13. D.W. Moon, D.J. Dwyer and S.L. Bernasek, *Surf. Sci.*, **163**, 215 (1985).
14. C.H. Zhang, G.Y. Zhao, K.K. Liu, Y. Yang, H. Xiang and Y. Li, *J. Mol. Catal.*, **328**, 35 (2010).
15. F. Bozso, G. Ertl and M. Weiss, *Appl. Surf. Sci.*, **1**, 103 (1977).
16. C. Brucker and T. Rhodin, *J. Catal.*, **47**, 214 (1977).