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KINETIC CHARACTERIZATION OF THE REDUCTION OF SILICA SUPPORTED COBALT CATALYSTS

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The reduction process of silica supported cobalt catalyst was studied by thermal analysis technique. The reduction of the catalyst proceeds in two steps:

$$Co_3O_4+H_2\rightarrow 3CoO+H_2O,\ 3CoO+3H_2\rightarrow 3Co+3H_2O$$

which was validated by the TPR and *in-situ* XRD experiments. The kinetic parameters of the reduction process were obtained with a comparative method. For the first step, the activation energy, E_a, and the pre-exponential factor, A, were found to be 104.35 kJ mol^{-1} and $1.18\cdot10^6$~$2.45\cdot10^9$ s^{-1} respectively. The kinetic model was random nucleation and growth and the most probable mechanism function was found to be $f(\alpha)=3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$ or in the integral form: $g(\alpha)=[-\ln(1-\alpha)]^{2/3}$. For the second step, the activation energy, E_a, and the pre-exponential factor, A, were found to be 118.20 kJ mol^{-1} and $1.75\cdot10^7$~$2.45\cdot10^9$ s^{-1} respectively. The kinetic model was a second order reaction and the probable mechanism function was $f(\alpha)=(1-\alpha)^2$ or in the integral form: $g(\alpha)=[1-\alpha]^{-1}-1$.

Keywords: *cobalt catalyst, Fischer-Tropsch synthesis, kinetic parameters, reduction, thermal analysis*

Introduction

Fischer-Tropsch synthesis (FTS) is a process for hydrocarbon production from synthesis gas. The synthetic fuel products via Fischer-Tropsch synthesis have some advantages like high cetane numbers, low sulfur and low aromatics contents. The fuel is suitable for diesel engines and environmental friendly [1, 2]. Cobalt catalyst is normally used for Fischer-Tropsch synthesis of long-chain paraffin because of its high activity, low water-gas shift activity and comparatively low cost [3]. Generally, the reducibility [4], dispersion [5] and interaction between cobalt and the support were studied with TPR, XRD, XPS and other characterization techniques [6, 7]. The thermal analysis technique was seldom used to study the reduction of cobalt catalyst for FTS, and the analysis of the kinetic model and the kinetic parameters for the catalyst reduction are rarely reported. Fouad [8] reported the study of the reduction of $WO_3\rightarrow WO_2\rightarrow W^0$ and Moura *et al.* [9] reported the kinetic characterization of the reduction of copper and nickel catalysts using thermal analysis technique. Kanerro [10] reported the kinetic parameters of alumina-supported vanadium oxide and Sarbak [11] reported thermal characterization of aluminum supported chromium and platinum-chromium catalysts using TPR data. Thermal analysis technique was limited to the surface characterization of solid state. However, it offers quantitative kinetic information, which is a distinct advantage; it is thus an important tool for the study of heterogeneous system [12].

Thermal analysis technique has been widely used in the study of kinetics of solid state reaction [13] for the determination of the activation energy, E_a, the mechanism function, $g(\alpha)$, and the pre-exponential factor, A [14]. Many kinetic methods including the integral method of Coats-Redfern [15], differential method of Achar [16], variable iso-conversional method [17], accommodated model of Gao [18] and the comparative method of Chen *et al.* [19] have been used. In general, the first step is to obtain the reliable activation energy by an Ozawa-iterative procedure or the KAS method [20–26]. The second step is to use the comparative method of Chen [19, 21] to determine the most probable mechanism function of the reaction and to calculate the pre-exponential factor A. In this paper, we report the thermal behavior of the reduction of the silica-supported cobalt catalysts used for Fischer-Tropsch synthesis and the determination of the kinetic parameters with the comparative method.

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Experimental

Catalyst preparation

The Co(7.6%)/SiO_2 catalyst prepared by incipient wetness impregnation was used for the study. Before the impregnation, the SiO_2 support (Qingdao Meigao Chemical Factory, China), with average pore size of 6.8 nm; pore volume of 0.78 $cm^3 g^{-1}$ and surface area of 457.3 $m^2 g^{-1}$, was calcined at 773 K for 6 h. Then the required amount of an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ (AR grade, Guoyao Chemical Co., Ltd.,China) was dissolved in an appropriate volume of deionized water and added to the calcined silica support. Subsequently, the catalyst was dried in air at 393 K for 12 h, and then calcined in air at 623 K for 5 h.

Thermogravimetry (TG)

Thermal gravimetric analysis (TG) was performed on a Perkin-Elmer TGS-2 thermobalance with various heating rates. The catalyst (6.00~8.00 mg) was first heated under a nitrogen flow at a rate of 60 mL min^{-1} from 303 to 423 K and held at 423 K for 30 min, cooled down to room temperature, and heated again from 303 to 1073 K under a hydrogen flow at a rate of 60 mL min^{-1}. The temperature was raised linearly with heating rates of 5, 10, 15, 20, 25 K min^{-1}. The mass loss was automatically recorded using a computer.

Temperature programmed reduction (TPR)

The H_2-TPR measurements were performed with a Zeton Altamira AMI-200 catalyst characterization instrument. The sample (0.15 g) was placed in a quartz tubular reactor. Prior to the TPR measurement, the catalyst was flushed with high purity argon at 423 K for 1 h, then cooled down to 323 K. High purity hydrogen was switched on and the flow rate through the reactor was controlled at 60 mL min^{-1}. The temperature was raised at a rate of 10 K min^{-1} from 323 to 1073 K. The H_2 consumption (thermal conductivity detector, TCD, signals) was recorded automatically.

X-ray powder diffraction (XRD)

The phase change of the catalyst with reduction temperature was detected in situ by a Bruker-D8 X-ray diffractometer with Cu-K_α radiation under hydrogen atmosphere. The scan range was 20–80° with 0.015° steps. The catalyst was first heated under N_2 atmosphere from 303 to 423 K and held at 423 K for 30 min and then cooled down to room temperature, then heated again from 303 to 1073 K at a heating rate of 10 K min^{-1} under H_2 atmosphere. The sample was scanned at the temperatures of 383, 533, 603, 703, 823 and 873 K.

Results and discussion

The analysis of reduction of Co_3O_4 in the Co_3O_4/SiO_2 catalyst

Four peaks at the temperature ranges of 300–391, 463–543, 543–704 and 704–840 K are observed in the DTG curve (Fig. 1) demonstrating that the reaction preceded in four steps. From the TPR curve (Fig. 2), three hydrogen consumption peaks marked peaks I, II and III are observed. This indicates that hydrogen consumption consisted of three steps.

Two reference experiments, one for TG of the catalyst under nitrogen atmosphere, the other for TG of the support under hydrogen atmosphere, were done. The results are shown in Figs 3 and 4. No phase change and reduction of the catalyst under nitrogen and of the silica support under hydrogen are observed except the dehydration process occurring at the temperature range of 303–391 K. From the DTG and TPR curves in Figs 1 and 2, it is observed that peaks II, III and IV in the DTG curve corresponds to peaks I, II and III of the TPR curve, indicating that the oxygen mass loss process in the thermal gravimetric experi-

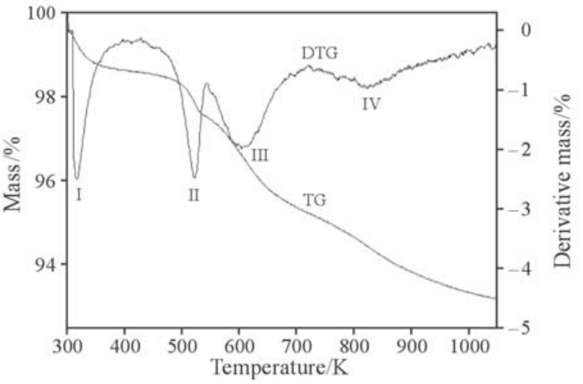

Fig. 1 TG-DTG curves of Co_3O_4/SiO_2 catalyst under hydrogen; heating rate 10 K min^{-1}

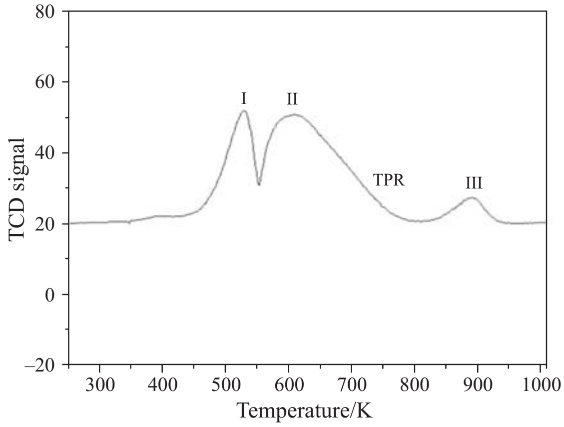

Fig. 2 the TPR curve of Co_3O_4/SiO_2 catalyst under hydrogen; heating rate 10 K min^{-1}

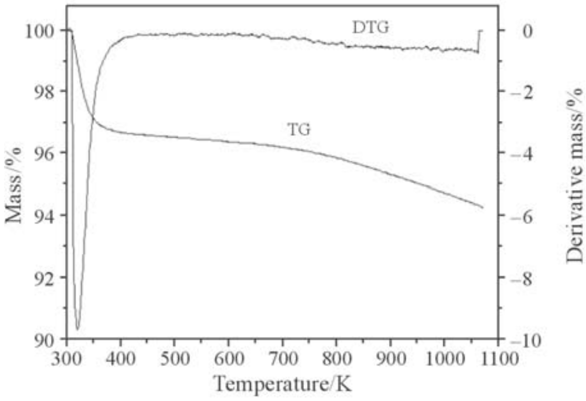

Fig. 3 TG-DTG curves of sample under nitrogen

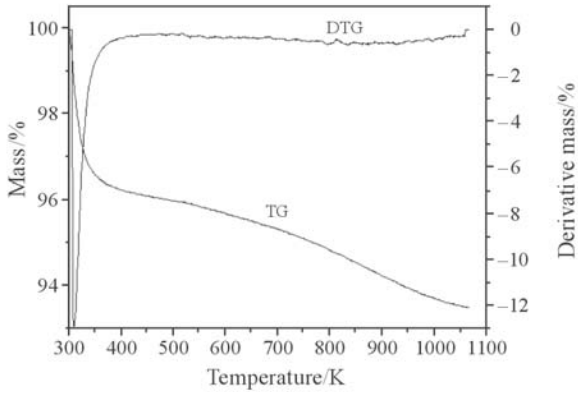

Fig. 4 TG-DTG curves of support under hydrogen

ment corresponds to the hydrogen consumption process in the TPR experiments.

Thus, steps II, III and IV are due to the reduction of the Co_3O_4/SiO_2 catalyst. Quantitatively, the mass losses at steps II and III are 0.887 and 2.093% respectively, while the mass loss at step III is approximately three times that at steps II. From the TPR profiles, the area of peak II is also about three times the area of peak I. Thus, the reduction of Co_3O_4/SiO_2 proceeds as follow:

1st step: $Co_3O_4+H_2\rightarrow 3CoO+H_2O$

2nd step: $3CoO+3H_2\rightarrow 3Co+3H_2O$

This is consistent with previous studies [4, 6, 29]. Steps IV at 703–840 K could be the reduction of the interaction between cobalt and silica support [7, 29].

From the XRD patterns (Fig. 5), under hydrogen atmosphere only Co_3O_4 phase can be found after heating at 383 K. Increasing the temperature from 383 to 533 K, Co_3O_4 crystallites disappeared and CoO crystals were formed. Increasing the temperature from 533 to 703 K the CoO is no longer detectable, being replaced by Co° crystallites indicating that the reduction of Co_3O_4 has been completed at temperature below 703 K, it is consistent with the TG and the TPR experiments. We did not found the interaction phase by XRD, probably due to the small crystal size.

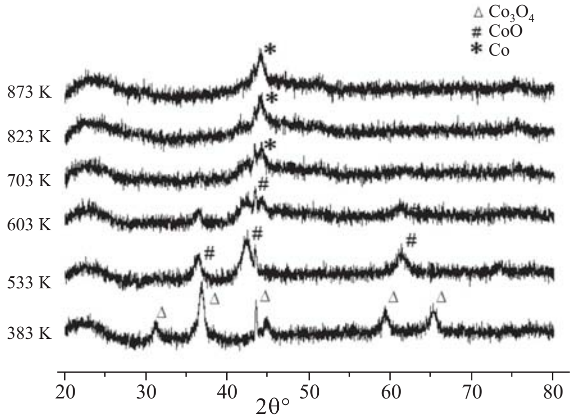

Fig. 5 XRD patterns of the catalyst

Calculation of activation energy (E_a)

The TG-DTG curves at different heating rates show that the reduction temperature increased with increasing heating rate (Figs 6 and 7). The smaller the heating rates, and the lower the reduction temperature, it's clear that the lower heating rate was useful for the occurrence of reduction processes. According to the basic thermal theory for the KAS method and Ozawa method, the parameters α, T, $d\alpha/dT$ were used to calculate the activation energy.

The average E_a values calculated using the iterative procedure for the first and the second reduction steps are 104.35 and 118.20 kJ mol^{-1} respectively.

Variations of activation energy, E_a, with reduction reaction fraction, α, by the KAS method for the two reduction steps are shown in Figs 8 and 9. It can be seen that the activation energy of both the reduction processes changed little with α. The reduction proceed under rather moderate conditions.

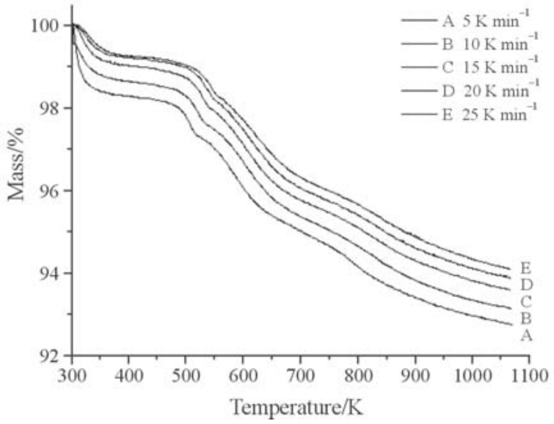

Fig. 6 TG curve of catalyst under hydrogen at different heating rates

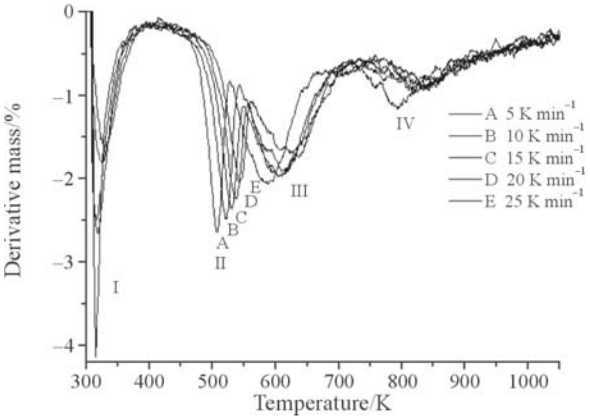

Fig. 7 The DTG curve of catalyst under hydrogen at different heating rates

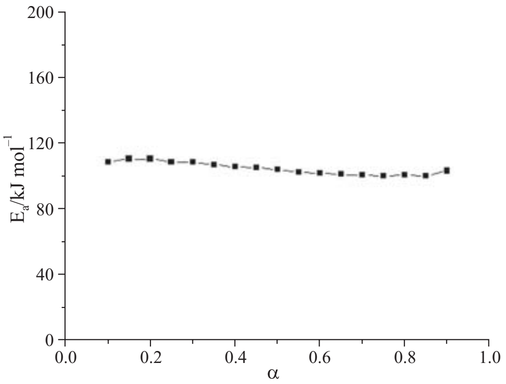

Fig. 8 The change in activation energy, E_a, with α for the first reduction step

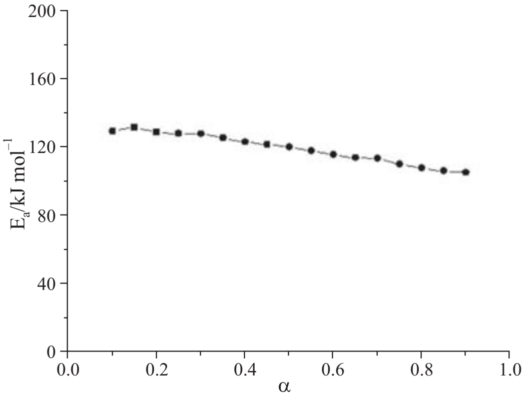

Fig. 9 The change in activation energy, E_a, with α for the second reduction step

Estimation of the mechanism of the reduction reaction

The values of α, T and $d\alpha/dT$ obtained from the TG curves, were inserted into the 31 types of the mechanism functions [21], the E_a, A and the linear correlation coefficients (R) were calculated by the linear least squares method. Furthermore, when the 'real' kinetic model is obtained, the activation energies obtained from KAS equation or iterative procedure will conform to Achar equation [27] and Coats-Redfern equation [28] with better correlation coefficients. The results from the different heating rates display the same trend (Table 1).

Comparing the results of the 31 types of mechanism function, the function No. 8, $f(\alpha)=3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, is the most probable mechanism function of the first reduction process of

Table 1 E_a, A and R obtained by Achar method and Coats-Redfern method from different heating rates

Reduction steps	β/ K min^{-1}	Function No.	Coats-Redfern method			Achar method		
			E_a/kJ mol^{-1}	ln$A$/s^{-1}	R	E_a/kJ mol^{-1}	ln$A$/s^{-1}	R
II	5	8	107.94	20.08	0.9989	114.13	21.62	0.9978
	10	8	85.55	14.69	0.9949	104.39	19.23	0.9926
	15	8	85.18	14.67	0.9957	103.68	19.06	0.9913
	20	8	82.09	13.98	0.9934	104.62	19.28	0.9819
	25	8	94.48	16.83	0.9986	103.81	19.03	0.9758
III	5	22	123.62	19.63	0.9988	127.00	20.45	0.9878
	10	22	116.93	17.99	0.9986	120.06	18.73	0.9886
	15	22	111.57	17.08	0.9982	108.83	16.68	0.9899
	20	22	115.52	17.99	0.9978	116.37	18.30	0.9838
	25	22	113.75	17.52	0.9978	114.32	17.76	0.9821

Table 2 The most probable mechanism function of different reduction process

Reduction steps	Function No.	Sign	Mechanism	$f(\alpha)$	$g(\alpha)$
II	8	A1.5	Avrami-Erofee	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
III	22	F2	Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$

Co_3O_4/SiO_2 catalysts, its kinetic model was random nucleation and growth model. The function No. 22, $f(\alpha)=(1-\alpha)^2$, is the most probable mechanism function for the second reduction process, its kinetic model was a second order chemical reaction.

The most probable mechanism function of reduction process of Co_3O_4 in Co_3O_4/SiO_2 are shown in Table 2.

Conclusions

The reduction behavior and the reduction kinetic parameters of the Co_3O_4 in Co_3O_4/SiO_2 catalyst for Fischer-Tropsch synthesis were determined using the thermal analysis technique and the thermal analysis kinetic method. The conclusions are summarized as follows:

The reduction process proceeds in two steps:

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$$

$$3CoO + 3H_2 \rightarrow 3Co + 3H_2O$$

The reduction process proposed is consistent with previous study, demonstrating that the thermal analysis technique could be reliably used to study the reduction of heterogeneous system.

- The kinetic parameters and the kinetic model of the reduction process were obtained. The kinetic model of the first reduction process is random nucleation and growth. The activation energy, E_a, and the pre-exponential factor, A, was determined to be 104.35 kJ mol^{-1} and $1.18 \cdot 10^6 \sim 2.45 \cdot 10^9$ s^{-1} respectively. The most probable mechanism function in the differential form is $f(\alpha)=3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$ or in integral form, $g(\alpha)=[-\ln(1-\alpha)]^{2/3}$. The kinetic model for the second reduction process is a second order reaction. The activation energy is 118.20 kJ mol^{-1}, and the pre-exponential factor is $1.75 \cdot 10^7 \sim 2.45 \cdot 10^9$ s^{-1}. The most probable mechanism function in differential form is $f(\alpha)=(1-\alpha)^2$ or in integral form $g(\alpha)=[1-\alpha]^{-1}-1$.

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