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THERMOGRAVIMETRIC STUDY OF THE CARBURIZATION AND COKING OF UNSUPPORTED AND CARBON-SUPPORTED Fe, Mo AND Fe–Mo CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

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Carburization and coke deposition of unsupported and carbon-supported Fe, Mo and Fe–Mo catalysts in syngas have been studied using thermogravimetry. Compositions of the carbides formed are evaluated on the basis of the amount of metals in the catalysts and amount of carbon deposited during carburization. It is shown that carburization temperature and the nature of the carbides formed (Fe_5C_2 and Fe_2C for iron and Mo_2C for molybdenum) depend on the metals but are influenced by the support and metal loading. Coke deposition on these catalysts takes place as soon as carburization is complete.

Keywords: carburization, Fischer-Tropsch synthesis, TG

Introduction

Formation of carbides and coking on active metals in catalysts for Fischer-Tropsch (F-T) synthesis ($CO+H_2$ for hydrocarbons) have long been problems [1–4]. It is known that metal carbides are the active species for F-T reaction and that coking is one of the main causes of deactivation of the catalysts. This paper deals with carburization and coking processes of unsupported and carbon-supported Fe, Mo and Fe–Mo catalysts in syngas studied by thermogravimetry.

Experimental

The catalysts studied were the same as those reported previously [5]. TG measurements of the catalysts were performed using a Shimadzu DT-20B thermal

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analyzer with range 2–20 mg, heating rate 10 deg·min^{-1}, and chart speed 1.25 mm/min. The catalysts were first reduced in H_2, also confirmed by TG-DTG [5], before the syngas ($H_2/CO = 2$) was introduced.

Results and discussion

Carburization and coking behaviour of unsupported and carbon-supported iron catalysts in syngas

Figure 1 shows the TG curve of the unsupported metallic iron when heated in syngas. The curve shows an increase in weight which can be divided into two stages. In the first stage (294°–445°C), the weight increase is relatively slow and can be attributed to carburization of iron. From the amount of iron in the sample (6.75 mg), derived from TG after complete reduction of the sample, and the amount of carbon deposited in the first stage (0.574 mg), the atomic ratio of iron to carbon was found to be 2.53. Thus the iron carbide formed during carburization should be Fe_5C_2, which is consistent with results from Mössbauer spectroscopy [6]. Above 445°C, the weight of the sample increases significantly as a consequence of coke deposition.

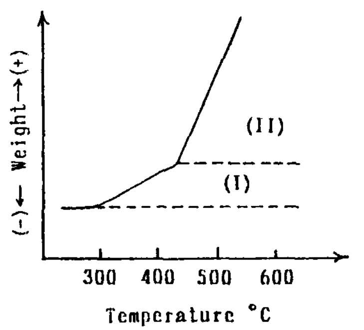

Fig. 1 TG curve of unsupported iron catalyst in syngas: (I) carburization; (II) coke deposition

Carbon-supported catalysts with different iron loadings exhibit similar carburization-coking behaviour. A typical TG curve is shown in Fig. 2 for the 20%Fe/C catalyst. This shows a weight loss at 180°–275°C, which may result from methanation of the carbon support [5]. The weight increases between 275° and 365°C and above 365°C can be attributed to carburization of iron and coke deposition on the catalyst, respectively. Compositions of the carbides formed during carburization can be calculated from TG results as summarized in Table 1. It is seen that different iron carbides are formed for the carbon-supported catalysts with different iron loadings. The carbide formed for the 8%Fe/C and

15%Fe/C catalysts is Fe_2C while that for the 20%Fe/C catalyst is Fe_5C_2; These Fe:C ratio are also in accord with those found by Mössbauer spectroscopy [6].

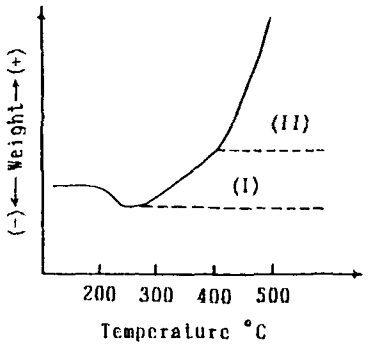

Fig. 2 TG curve of 20%Fe/C catalyst in syngas: (I) carburization; (II) coke deposition

Carburization and coking behaviour of unsupported and carbon-supported molybdenum catalysts in syngas

Figure 3 shows the TG curve of unsupported metallic molybdenum in syngas. In common with the TG curve of unsupported iron, this curve also shows an increase in weight, and in two distinct stages. The weight increase during the first stage between 301° and 550°C can be assigned to carburization of molybdenum. From the amount of molybdenum in the sample (15.76 mg) obtained from TG after complete reduction of this sample, and the amount of carbon deposited in the first stage (1.012 mg), the atomic ratio of molybdenum to carbon was found to be 1.95, suggesting that the carbide formed is Mo_2C. Above 550°C, the abrupt weight increase is due to coke deposition.

Table 1 TG results of carburization of carbon-supported iron catalysts

Catalyst	Sample	Iron	Carburization		Carbides
	Wt. / mg		Temp. / °C	Carbon deposited / mg	formed
8%Fe/C	29.45	1.66	290–375	0.17	Fe_2C
15%Fe/C	26.80	2.95	270–370	0.29	Fe_2C
20%Fe/C	32.95	4.57	277–365	0.40	Fe_5C_2

Figure 4 shows the TG curve of the 14%Mo/C catalyst. Surprisingly, it shows a loss in weight. Three stages can be identified. In the first stage below 120°C, the weight loss may be caused by gasification of the carbon support. In the following stage, the rate of weight loss gradually decreases and the weight of the sample is constant between 220° and 323°C. This indicates that carbon deposition resulting from the dissociative adsorption of CO occurs during this stage, and that gasification of the carbon support and carbon deposition counterbalance each other. From the amount of Mo in the sample (4.298 mg) and the amount of carbon (0.54 mg) deposited during this stage (220°–323°C), the Mo/C atomic ratio was found to be equal to 1, indicating that the carbide formed in the 14%Mo/C catalyst might be MoC. Above 323°C, the weight loss may be the result of further gasification of the carbon support.

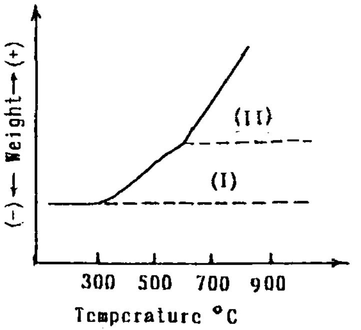

Fig. 3 TG curve of unsupported molybdenum catalyst in syngas: (I) carburization; (II) coke deposition

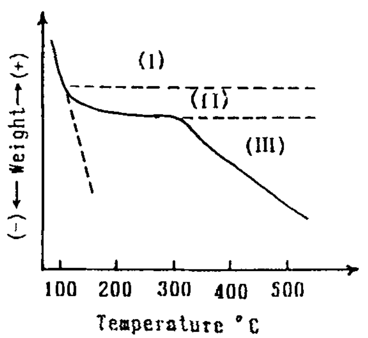

Fig. 4 TG curve of 14%Mo/C catalyst in syngas: (I) and (III) gasification of the carbon support; (II) coke deposition

Carburization and coking behaviour of unsupported and carbon-supported iron–molybdenum catalysts in syngas

Figure 5 shows the TG curve of the unsupported Fe–Mo catalyst (weight ratio: Fe/Mo = 0.4) in syngas. In common with those of unsupported iron and molybdenum, this curve shows two stages of weight increase. The first stage between

452° and 595°C corresponds to the carburization of iron and molybdenum. The total weight of metals in this sample was found to be 13.77 mg by TG after the sample had been completely reduced, and hence the weights of Fe and Mo in the sample were 3.946 mg and 9.824 mg respectively. According to the amounts of metals and the amount of carbon deposited (0.99 mg) at this stage, the carbides formed in this sample were found to be Fe_5C_2 and Mo_2C. Above 595°C, the abrupt weight increase is due to coke deposition.

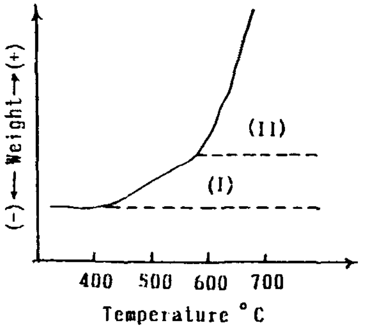

Fig. 5 TG curve of unsupported Fe–Mo catalyst in syngas: (I) carburization; (II) coke deposition

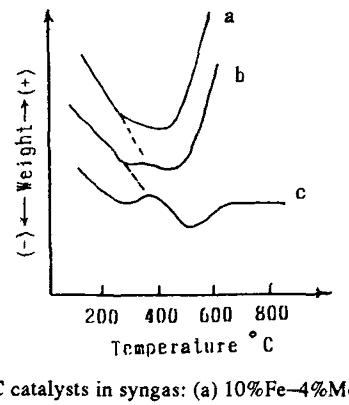

Fig. 6 TG curves of Fe–Mo/C catalysts in syngas: (a) 10%Fe–4%Mo/C, (b) 7%Fe–7%Mo/C, and (c) 4%Fe–10%Mo/C

TG curves of the carbon-supported Fe–Mo catalysts with different Fe/Mo ratios are shown in Fig. 6. The TG curves of 10%Fe–4%Mo/C and 7%Fe–7%Mo/C are similar and can be divided into three stages; the TG curve for 4%Fe–10%Mo/C is different and rather difficult to analyse. In common with that of the 14%Mo/C catalyst under the same conditions, weight losses of the 10%Fe–4%Mo/C and 7%Fe–7%Mo/C catalysts during the first stage may result from gasification of the carbon support. During the next stage in the 257°–496°C

Table 2 TG results of carburization of carbon-supported iron–molybdenum catalysts

Catalyst	Sample	Total*	Fe	Mo	Carburization		Carbides formed
	Weight / mg				Temp. / °C	Carbon deposited mg	
10%Fe–4%Mo/C	40.10	27.78	2.778	1.111	257–450	0.340	Fe_2C–Mo_2C
7%Fe–7%Mo/C	39.48	27.36	1.915	1.915	270–496	0.316	Fe_2C–Mo_2C
4%Fe–10%Mo/C	34.65	27.85	1.114	2.785	-	-	-

*'Total weight' signifies weights of Fe, Mo and the carbon support in the catalysts, which are obtained after the catalysts are completely reduced.

region, the weight of each of the two catalysts is almost constant because rates of carbon deposition and gasification of the carbon support roughly balance. From this, the weight of carbon deposited and therefore the carbides formed at this stage can be obtained. Table 2 gives the results of carburization of the carbon-supported Fe–Mo catalysts. The carbides formed are Fe_2C and Mo_2C for both of the 10%Fe–4%Mo/C and 7%Fe–7%Mo/C catalysts. During the third stage, the large weight increases of these two catalysts in syngas definitely result from coke deposition.

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Zusammenfassung — Mittels Thermogravimetrie wurden Aufkohlungen und Koksablagerungen an Fe-, Mo- und Fe/Mo-Katalysatoren mit und ohne Trägermaterial in Synthesegas untersucht. Die Zusammensetzung der gebildeten Carbide wurde anhand der Metallmenge im Katalysator und des bei der Aufkohlung abgelagerten Kohlenstoffes geschätzt. Es wurde gezeigt, daß die Aufkohlungstemperatur und die Art der gebildeten Carbide (Fe_5C_2 und Fe_2C für Eisen und Mo_2C für Molybdän) vom Metall abhängen, jedoch durch das Trägermaterial und die Metalldosierung beeinflußt werden. Koks wird an diesen Katalysatoren abgelagert, sobald die Aufkohlung beendet ist.