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THERMOGRAVIMETRIC STUDY ON THE REDUCTION PROCESS OF UNSUPPORTED AND CARBON-SUPPORTED Fe, Mo AND Fe–Mo CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

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The catalytic performance of unsupported and carbon-supported Fe, Mo and Fe–Mo catalysts for Fischer-Tropsch synthesis is greatly influenced by the final reduction states of the catalysts. In this investigation, the reduction process of the catalysts by H_2 was studied by using TG-DTG. The reduction process depends not only on the reducibility of metals but also on the nature of the support. Methanation of the support occurred as soon as the supported metals were completely reduced for the carbon-supported catalysts. For these, the reduction temperature should by carefully selected so that the metal oxides are reduced as completely as possible, whilst the methanation of the support must be avoided to obtain optimum reduced catalysts.

Keywords: Fischer-Tropsch synthesis, TG-DTG

Introduction

The Fischer-Tropsch synthesis (F-T), i.e. the hydrogenation of carbon monoxide to hydrocarbons, is one of the most important means of conversion of coal to liquid fuels. Iron is widely used as the active component of the catalysts for F-T synthesis, and porous carbon-supported iron catalysts have been found to be very active and selective to high hydrocarbons (C_5^+ [1–3].

Molybdenum has also been found to be active for F-T synthesis, but very selective to lower hydrocarbons (C_2-C_5) [4–6]. It could be expected that Fe–Mo bimetallic catalysts would exhibit the catalytic behaviour of both iron and molybdenum, and thus that the selectivity of F-T synthesis may be improved with Fe-

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Mo bimetallic catalysts. It is apparent that the catalytic behaviour of Fe, Mo and Fe–Mo is greatly influenced by the final reduction species in the catalysts. Therefore, it is important to study the reduction process of the catalysts in order to obtain optimum reduction conditions for these. In this paper, the reduction process of unsupported and carbon-supported Fe, Mo and Fe–Mo catalysts as studied by TG-DTG is described.

Experimental

The unsupported Fe, Mo and Fe–Mo catalysts were prepared by decomposition of $Fe(NO_3)_3 \cdot 9H_2O$, $H_3PMo_{12}O_{40}$ and a mixture of $Fe(NO_3)_3 \cdot 9H_2O$ and $H_3PMo_{12}O_{40}$, respectively. The carbon-supported Fe, Mo and Fe–Mo catalysts were prepared by impregnating activated carbon (surface area: 1000 m^2/g) with the corresponding aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$, $H_3PMo_{12}O_{40}$ and a mixture of $Fe(NO_3)_3 \cdot 9H_2O$ and $H_3PMo_{12}O_{40}$, followed by drying in air at 120°C. TG-DTG determinations on the catalysts were performed in H_2 using a Shimadzu DT-20B thermal analyzer with range 10–20 mg, heating rate 10 $deg \cdot min^{-1}$, and chart speed 1.25 mm/min.

Results and discussions

Reduction behaviour of unsupported and carbon-supported iron catalysts

TG-DTG was first used to follow the reduction process of the iron catalysts. Figure 1 shows the TG-DTG curves of $Fe(NO_3)_3 \cdot 9H_2O$ reduced in H_2. Data from these curves are summarized in Table 1.

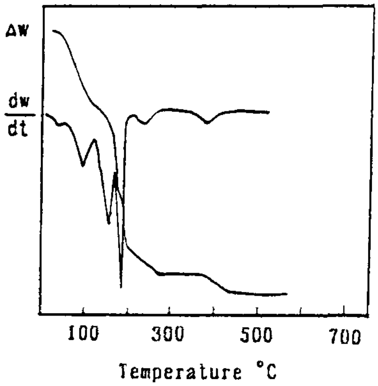

Fig. 1 TG-DTG curves of $Fe(NO_3)_3 \cdot 9H_2O$ reduced in H_2

Table 1 TG results for unsupported and carbon-supported Fe, Mo and Fe–Mo catalysts reduced in H_2

Sample and weight / mg	Supposed process or reactions	Temp. range / °C	Theoretical weight loss / mg	Theoretical weight loss / %	Actual weight loss / mg	Actual weight loss / %
$Fe(NO_3)_3{\cdot}9H_2O$:						
19.65	Desorption of surface water	RT–57	–	–	0.50	–
19.15	$Fe(NO_3)_3{\cdot}9H_2O \rightarrow Fe(NO_3)_3+9H_2O$	57–165	7.68	40.1	8.10	42.3
11.47	$2Fe(NO_3)_3+3H_2 \rightarrow Fe_2O_3+6NO_2+3H_2O$	165–280	7.68	40.1	8.08	42.3
3.79	$Fe_2O_3+H_2 \rightarrow 2Fe+3H_2O$	360–520	1.13	6.0	1.16	6.1
20%Fe/C:						
20.10	Desorption of surface water	RT–155	–	–	4.36	–
15.74	$2Fe(NO_3)_3/C+3H_2 \rightarrow Fe_2O_3/C+6NO_2+3H_2O$	155–420	4.89	31.0	2.64	16.7
13.10	$Fe_2O_3/C+3H_2 \rightarrow 2Fe/C+3H_2O$	420–495	0.82	5.2	0.90	5.7
12.20	$Fe/C+2H_2 \rightarrow Fe+CH_4$	495–865	9.76	62.0	9.80	62.2
$H_3PMo_{12}O_{40}$:						
27.30	Desorption of surface water	40–140	–	–	4.52	–
22.78	$H_3PMo_{12}O_{40}+4H_2 \rightarrow 12MoO_3+4H_2O+PH_3$	325–475	1.22	5.3	1.14	5.0
21.56	$MoO_3+H_2 \rightarrow MoO_2+H_2O$	475–538	2.39	10.5	2.56	11.2
19.17	$MoO_3+H_2 \rightarrow Mo+2H_2O$	538–650	4.79	21.0	4.90	21.5
14%Mo/C:						
29.05	Desorption of surface water	40–140	–	–	1.75	–
27.30	$H_3PMo_{12}O_{40}/C+4H_2 \rightarrow 12MoO_3/C+4H_2O+PH_3$	350–460	0.27	1.0	0.35	1.3
26.95	$MoO_3/C+3H_2 \rightarrow Mo/C+3H_2O$	460–600	1.56	5.7	1.56	5.7
25.39	$Mo/C+2H_2 \rightarrow Mo+CH_4$	650–870	21.83	80.0	21.61	79.2
$Fe(NO_3)_3$–$H_3PMo_{12}O_{40}$:						
28.60	Desorption of surface water	25–195	–	–	5.60	–
9.00	$2Fe(NO_3)_3+3H_2 \rightarrow Fe_2O_3+6NO_2+3H_2O$	195–398	6.02	26.2	5.00	21.7
2.97	$Fe_2O_3+H_2 \rightarrow 2Fe+3H_2O$	398–530	0.89	3.8	0.90	3.9
14.00	$H_3PMo_{12}O_{40} \rightarrow 12MoO_3+H_3PO_4$					
13.25	$MoO_3+H_2 \rightarrow MoO_2+H_2O$	530–567	1.47	6.4	1.50	6.5
10.75	$H_3PO_4+4H_2 \rightarrow PH_3+4H_2O$					
11.78	$MoO_2+2H_2 \rightarrow Mo+2H_2$	567–800	3.69	16.0	3.70	16.1
4%Fe–10%Mo/C:						
23.40	Desorption of surface water	30–105	–	–	3.80	–
3.05	$2Fe(NO_3)_3/C+3H_2 \rightarrow Fe_2O_3/C+6NO_2+3H_2O$	105–398	2.19	9.3	1.30	5.5
2.80	$H_3PMo_{12}O_{40}/C \rightarrow 12MoO_3/C+H_3PO_4$					
1.00	$Fe_2O_3/C+3H_2 \rightarrow 2Fe/C+3H_2O$	398–555	1.18	5.0	1.20	5.1
2.65	$MoO_3/C+3H_2 \rightarrow Mo/C+3H_2O$					
17.54	$Fe\text{–}Mo/C+4H_2 \rightarrow Fe+Mo+CH_4$	555–850	17.54	74.9	17.06	72.9

It can be seen from Fig. 1 that there are five peaks on the DTG curve of $Fe(NO_3)_3{\cdot}9H_2O$, the precursor of the iron catalyst. According to the proposed reduction steps listed in Table 1, the theoretical weight losses of the different stages basically agree with experimental values. The actual weight loss at each stage is slightly greater than the theoretical value, due probably to the additional weight loss of the silica crucible by etching during reduction. Thus, the reduction process of $Fe(NO_3)_3{\cdot}9H_2O$ in H_2 as evaluated by TG-DTG suggests the following steps: 1, desorption of adsorbed water; 2, dehydration (57°–165°C); 3, decomposition of $Fe(NO_3)_3$ to Fe_2O_3 (165°–280°C); and 4, reduction of Fe_2O_3 to metallic iron.

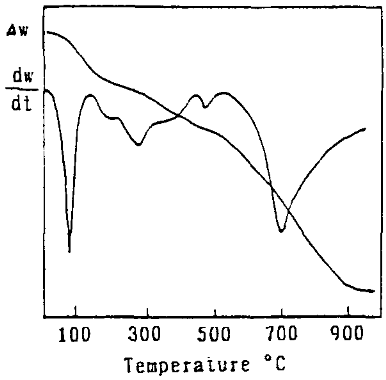

Fig. 2 TG-DTG curves of the 20%Fe/C catalyst reduced in H_2

Figure 2 shows TG-DTG curves of the carbon-supported iron catalyst (20%Fe/C) reduced in H_2. These curves are notably different from those for unsupported $Fe(NO_3)_3{\cdot}9H_2O$. Four DTG peaks can be seen. Results from these TG-DTG curves are listed in Table 1. The first weight loss corresponds to desorption of free water in the catalyst. The second step (155°–420°C) can be attributed to decomposition of the precursor $Fe(NO_3)_3$. The actual weight loss is smaller than the theoretical value, indicating that the precursor $Fe(NO_3)_3$ has been partially decomposed during preparation of the catalyst. The third step (420°–495°C) corresponds to reduction of Fe_2O_3 to metallic iron. At the final step (>495°C), the weight loss is 9.8 mg, which is almost equivalent to the amount of support in the catalyst (9.78 mg). We therefore attribute this weight loss to hydrogenation of the carbon support to methane.

Reduction behaviour of unsupported and carbon-supported molybdenum catalysts

Figure 3 shows the TG-DTG curves of the reduction of $H_3PMo_{12}O_{40}$, the precursor of the molybdenum catalysts. Four main peaks can be observed on the

DTG curve. According to the reactions summarized in Table 1, weight losses of the four reaction stages are in good agreement with calculated values. Hence, reduction of $H_3PMo_{12}O_{40}$ in H_2 as evaluated by TG-DTG should include desorption of surface-adsorbed water, decomposition of $H_3PMO_{12}O_{40}$ to MoO_3 (325°–475°C), reduction of MoO_3 to MoO_2 (475°–538°C), and finally reduction of MoO_2 to metallic molybdenum (538°–650°C).

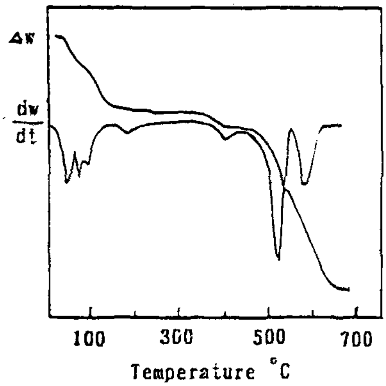

Fig. 3 TG-DTG curves of $H_3PMo_{12}O_{40}$ reduced in H_2

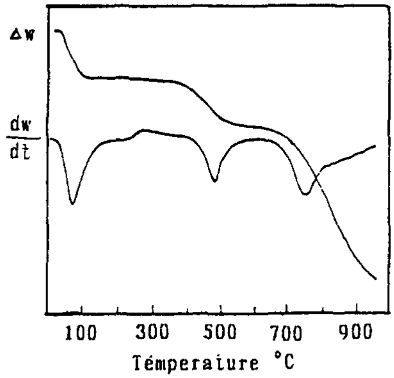

Fig. 4 TG-DTG curves of 14%Mo/C catalyst reduced in H_2

TG-DTG curves of the 14%Mo/C catalyst are shown in Fig. 4. Three peaks and an apparent small peak (350°–460°C) can be seen on the DTG curve, which is thus different from that of the unsupported catalyst. The first weight loss below 140°C corresponds to desorption of free water, while subsequent weight losses agree well with the reactions listed in Table 1. Thus, the weight losses at 350°–460°C and 460°–600°C resulted from decomposition of $H_3PMo_{12}O_{40}$ to form

MoO_3 and reduction of MoO_3 to metallic Mo, respectively. Above 600°C, the large weight loss can be attributed to hydrogenation of the carbon support to methane. The measured weight loss is 21.61 mg, which is consistent with the amount of carbon support in this sample (21.89 mg). It should be noted that the temperature of methanation of the carbon support of the 14%Mo/C catalyst is 100°C higher than that of the 20%Fe/C catalyst, indicating that the 14%Mo/C catalyst is more stable in H_2 than the 20%Fe/C catalyst.

Reduction behaviour of unsupported and carbon-supported iron–molybdenum catalysts

Figure 5 shows TG-DTG curves of the mixture of $Fe(NO_3)_3$ and $H_3PMo_{12}O_{40}$, the precursor of the Fe–Mo catalysts, reduced in H_2. The DTG curve shows several peaks, corresponding to weight losses during different reduction stages. Analysis of the TG-DTG results shown in Table 1 reveals that, besides desorption of adsorbed water at 25°–195°C, the mixture of $Fe(NO_3)_3$ and $H_3PMo_{12}O_{40}$ when treated in H_2 undergoes mainly decomposition of $Fe(NO_3)_3$ (195°–398°C) and reduction of Fe_2O_3 to metallic Fe (398°–530°C), followed by decomposition of $H_3PMo_{12}O_{40}$, reduction of MoO_3 to MoO_2 (530°–567°C), and, finally reduction of MoO_2 to metallic Mo (567°–800°C).

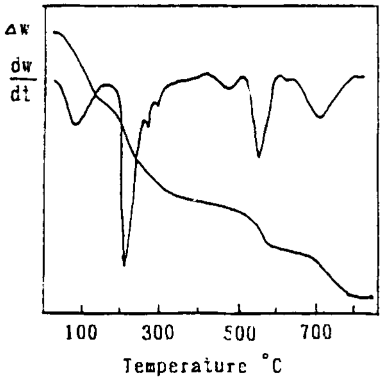

Fig. 5 TG-DTG curves of $Fe(NO_3)_3$–$H_3PMo_{12}O_{40}$ reduced in H_2

TG-DTG curves of the carbon-supported 4%Fe–10%Mo/C catalyst shown in Fig. 6 differ from those of the unsupported catalyst. Four separate peaks can be seen on the DTG curve, and corresponding processes and reactions are listed in Table 1. The first DTG peak at 30°–105°C can be assigned to desorption of free water from the sample. The second small DTG peak at 105°–398°C may be due to decomposition of $Fe(NO_3)_3$ and $H_3PMo_{12}O_{40}$. The actual weight loss (5.5%) is smaller than calculated (9.3%), probably due to partial decomposition of

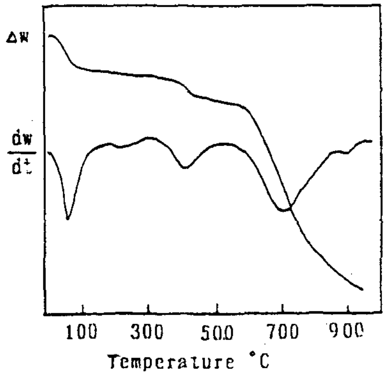

Fig. 6 TG-DTG curves of the 4%Fe–10%Mo/C catalyst reduced in H_2

$Fe(NO_3)_3$ during preparation of the catalyst. The third stage at 398°–555°C apparently corresponds to reduction of $Fe(NO_3)_3$ and $H_3PMo_{12}O_{40}$ to metallic Fe and Mo, because the weight loss is in good agreement with the theoretical value as shown in Table 1. The final weight loss above 555°C results from methanation of the carbon support.

Conclusions

TG-DTG shows that the catalyst precursors $Fe(NO_3)_3{\cdot}9H_2O$ and $H_3PMo_{12}O_{40}$ undergo decomposition and progressive reduction to metals by heat treatment in H_2; an additional methanation process takes place for the carbon-supported catalysts after iron and molybdenum are completely reduced.

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Zusammenfassung — Die katalytische Darstellung von Fe-, Mo- und Fe/Mo-Katalysatoren mit und ohne Kohlenstoff-Trägermaterial für die Fischer-Tropsch-Synthese wird in großem Maße durch die abschließende Reduktionsphase beeinflußt. Vorliegend wird die Reduktion des

Katalysators mit H_2 mittels TG/DTG untersucht. Der Reduktionsprozeß hängt nicht nur von der Reduzierbarkeit der Metalle, sondern auch von der Art des Trägermateriales ab. Bei Katalysatoren auf Kohle-Trägermaterial erfolgt sofort eine Methanierung des Trägermateriales, sobald das darauf befindliche Metall vollständig reduziert wurde. Deshalb muß die Reduktionstemperatur sorgfältig gewählt werden, damit die Metalloxide so weitgehend wie möglich reduziert werden, eine Methanierung des Trägermateriales jedoch vermieden wird, um optimale reduzierte Katalysatoren zu erhalten.