

# Effect of Oxide Film of Heat Resistant Alloys on Coke Formation during Naphtha Pyrolysis

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The coking of cracking furnace tubes has been an important subject of ethylene plants. The coke formations rate on the heat resistant alloys of 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> covered with Al<sub>2</sub>O<sub>3</sub> oxide film and 25Cr-35Ni covered with Cr<sub>2</sub>O<sub>3</sub> oxide film during the thermal cracking of naphtha was quantitatively evaluated at temperatures ranging from 810 to 930°C. The experimental results showed that the coke formation rate on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> was lower than that on 25Cr-35Ni because of the difference of a catalytic activity to coke formation, especially in the case of a pre-carburized condition. Namely, the Al<sub>2</sub>O<sub>3</sub> formed on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> was stable even after carburization treatment and inert for catalytic coke formation, while coke formation on 25Cr-35Ni was under the control of catalytic coke formation, and carburization of 25Cr-35Ni accelerated catalytic coke formation. The stability of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in a hydrocarbon with steam environment was thermodynamically calculated in 0.1mol of steam, 0.2mol of ethylene and 0.1mol of methane at 1,100°C. The simulation result shows that Al<sub>2</sub>O<sub>3</sub> is exceedingly stable while Cr<sub>2</sub>O<sub>3</sub> could be decomposed partially into chromium carbide. Therefore, it is concluded that Al<sub>2</sub>O<sub>3</sub> on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> is more stable than Cr<sub>2</sub>O<sub>3</sub> on 25Cr-35Ni, and 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> is more resistant to coke formation and carburization than 25Cr-35Ni in a hydrocarbon with steam environment at high temperature.

**Keywords** : ethylene, naphtha pyrolysis, coking, coke, Al<sub>2</sub>O<sub>3</sub>

## 1. Introduction

In the high temperature process equipment of petrochemical industries such as the cracking furnaces of an ethylene plant, one of the serious problems is coke formation and carburization during operation on the inner surface of cracking furnace tubes. The coke on the inside of tubes is formed as a result of a decomposing reaction from naphtha diluted by steam to ethylene under high temperature. The coke formation inside tubes increases the pressure drops of furnace tubes and the tube metal temperature (TMT) due to decreasing heat transfer. For this reason, it is required for efficient ethylene production to minimize coke formation.

On the other hand, carburization also takes place on the inner surface of tubes and the degree of carburization controls tube life because the area carburized loses ductility and the strength of tubes become questionable.

It is well known that not only the types of feed, cracking temperatures and flow rates but also the types of furnace tube alloys influence coke formation. Coke formation on the inner surface of ethylene furnace tubes is classified as a pyrolytic reaction and a catalytic reaction.<sup>1)</sup> Iron,

nickel and cobalt are known as typical catalytic metals for coke formation.<sup>2)</sup> However, the main mechanism of coke formation in the thermal cracking of naphtha has not been clear. Therefore, the catalytic activity of the tube surface and the stability of the tube's oxide film are important factors for minimizing catalytic coke formation. They would be main properties for the coke formation resistance on tube surface.

In this study, coke formations on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni were examined quantitatively during the thermal cracking of naphtha diluted by steam to clear the influence of oxide types and carburization on coke formation. The result was discussed in relations between the analysis results of oxide formed on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni and a thermodynamic stability of oxide in the naphtha thermal cracking environment.

## 2. Experimental

Samples tested were pure Ni, pure Fe, 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub>, 25Cr-35Ni and SiO<sub>2</sub> (quartz). 25Cr-35Ni is commonly used for cracking furnace tubes in ethylene plants. Quartz was chosen as an inert material to a catalytic

**Table 1. Chemical composition of samples**

Samples	Cr	Ni	Fe	Al	Si	C	Mn	Ti	Y <sub>2</sub> O <sub>3</sub>
20Cr-4.5Al-0.5Y <sub>2</sub> O <sub>3</sub>	19.7	0.04	Bal	4.6	-	0.02	0.08	0.41	0.52
25Cr-35Ni	24.5	39.40	Bal	-	1.6	0.14	0.29	0.34	-
Fe	-	-	99.8	-	-	-	-	-	-
Ni	-	99.7	-	-	-	-	-	-	-

reaction. Chemical compositions of each sample except quartz are shown in Table 1.

Samples were cut in 15 mm (L) x 8 mm (W) x 2 mm (T) sizes as the exposure area to test environments. These were polished using up to #800 emery paper, rinsed with ethanol.

### 2.1 Pre-oxidation and pre-carburization treatment of samples

The inner surface of ethylene furnace tubes is exposed to an oxidation environment during the decoking operation, which is required to burn the coke with a mixture of steam and air during the shut-down of a plant, and the carburization environment during ethylene production, alternatively. Pre-oxidation was conducted to simulate the surface condition of a new furnace tube and pre-oxidation of 25Cr-35Ni was simulated in the initial decoking operation. Pre-carburization was conducted to simulate the surface condition of cracking furnace tubes after several years' operation.

Pre-oxidation conditions of the samples are summarized in Table 2. Pre-oxidation condition of 25Cr-35Ni was simulated in the initial decoking operation, as was pre-

**Table 2. Oxidation conditions**

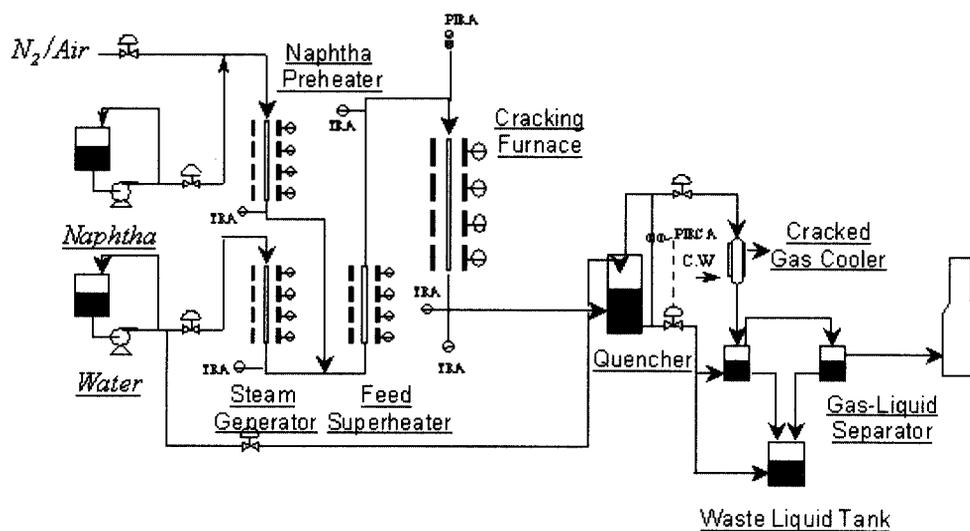
20Cr-4.5Al-0.5Y <sub>2</sub> O <sub>3</sub>	1300 × 0.5hr
25Cr-35Ni	980 × 1hr
Ni	1000 × 0.5hr
Fe	600 × 10min

**Table 3. Test conditions**

Fluid Temp.	810-930
Flow Rate	1.3 Nm <sup>3</sup> /hr
Ratio of Naphtha/Steam	2/1
Duration	20min.-4hrs

oxidation condition of 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> the same as the final heat treatment. Pre-carburization treatment was performed at 1100°C for 45hrs. in a box stuffed with a carburization agent to accelerate carburization of the samples, which were the pre-oxidized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni. Following carburization, these samples were oxidized again at 900°C for 2hrs. to remove the excess carbon and simulate decoking.

Fig. 1 shows the simplified process flow diagram of the experimental equipment. The coke formation test was carried out in an environment which simulated the ethylene plant condition. Test conditions are shown in Table 3. A sub-900°C 4-hr. test was carried out, and, in addition, an above 900°C 20-min. test was carried out to evaluate accurately the coke formation rate, because the rate is extremely high and coke may easily shed due to the vertical position of samples. Further, the 20-min. test was expected

**Fig. 1. Process flow diagram of the coke formation test equipment**

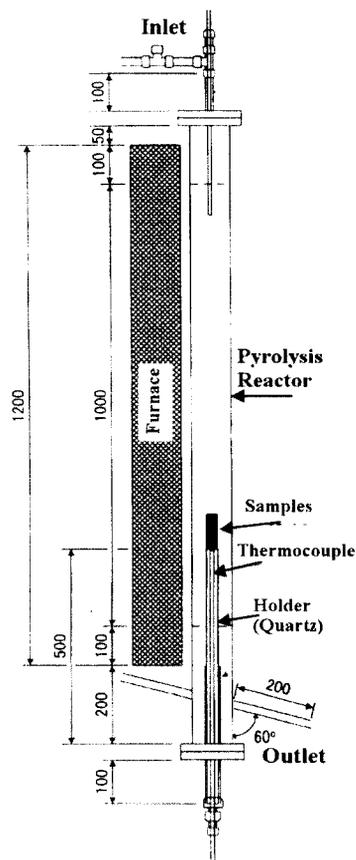


Fig. 2. Coking Reactor

to show the initial coke formation by catalytic reaction between the surface of  $20\text{Cr-4.5Al-0.5Y}_2\text{O}_3$  and  $25\text{Cr-35Ni}$  and hydrocarbon.

Detail of the coking reactor is shown in Fig. 2. Two samples were held simultaneously at the center of the coking reactor with a sample holder made of quartz.

The coke formation rate was evaluated by measuring the weight change of samples before and after the coke formation test. Microstructure cross sections near the surface of  $20\text{Cr-4.5Al-0.5Y}_2\text{O}_3$  and  $25\text{Cr-35Ni}$  were investigated metallurgically.

### 3. Results and discussion

#### 3.1 Difference of catalytic activity of Ni and Fe

It is well known that Ni and Fe have a catalytic activity on coke formation and that the morphology of catalytic coke is mainly filamentous coke.<sup>3)</sup> But there are no reports of the catalytic activity being investigated quantitatively during a thermal cracking of naphtha diluted by steam. Therefore, the catalytic coke formation activities of Ni and Fe were evaluated in a naphtha cracking condition.

Fig. 3 shows the comparison of appearances of pre-



Fig. 3. Ni and Fe after Coke formation

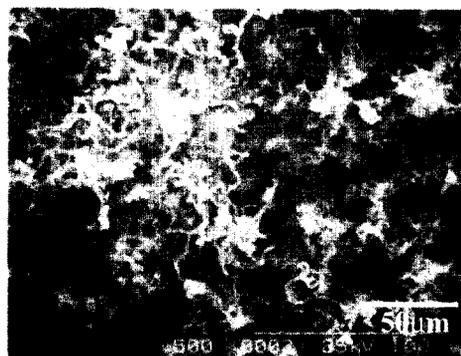


Fig. 4. Coke formed on Ni sample (SEM Image)

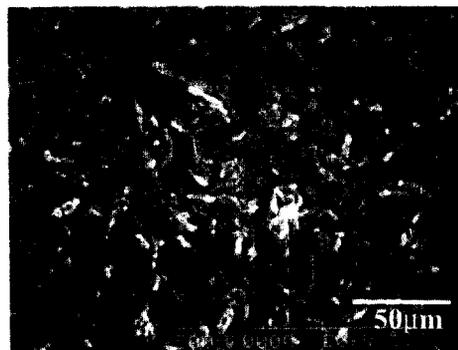


Fig. 5. Coke formed on surface of Fe sample (SEM Image)

oxidized Ni and Fe after the coking test at  $815\text{ }^\circ\text{C}$  for 2hrs. The coke formed on Ni was significant and catalytic filamentous coke was observed on Ni as shown in Fig. 4. On the other hand, very little coke formed on Fe, and was not filamentous (Fig. 5).

Table 4 shows the total amount of coke formed on Ni and Fe. The amount of coke formed on Ni was almost 40 times greater than that on Fe. It is clear that the catalytic activity of Ni for coke formation under the naphtha cracking condition was much higher than that of Fe.

**Table 4. Coke deposition on Ni and Fe**

	Test temperature	Test time(h)	Coke deposition(mg/h)
Ni	815	2	842
Fe	815	2	23

### 3.2 Influence of oxide film formed on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni on coke formation

Fig. 7 shows the result of the coke formation test on pre-oxidized and pre-carburized 25Cr-35Ni and quartz from 810 to 900°C. Coke formed on quartz is regarded as coke by a pyrolytic reaction because quartz is an inert material to coke formation. Since the amount of coke formed on pre-oxidized 25Cr-35Ni and quartz was similar between 810 and 900°C, pre-oxidized 25Cr-35Ni, which forms Cr<sub>2</sub>O<sub>3</sub>, was inert to catalytic coke formation. On the other hand, the influence of carburization on coke formation was remarkable over 850°C and coke formation on pre-carburized 25Cr-35Ni was 4 times greater at 900°C compared with pre-oxidized 25Cr-35Ni. This result suggests that the Cr<sub>2</sub>O<sub>3</sub> on pre-carburized 25Cr-35Ni had not covered perfectly and that the catalytic coke formation effect appeared by the progress of carburization.

Fig. 8 shows the result of the coke formation test on pre-oxidized and pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> with quartz from 810 to 900°C for 4hrs. It is evident that pre-oxidized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> is completely stable and inert compared with pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and quartz to coke formation between 810 and 900°C. The weights of coke on pre-oxidized and pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and quartz were very small.

Fig. 9 shows the result of pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni and quartz for 20 minutes up to 930°C. There was the large peak of coke formation on pre-carburized 25Cr-35Ni around 870-880°C while the coke formed on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and quartz increased slightly with temperature. This result means that pre-carburized 25Cr-35Ni has remarkable catalytic activity between 850 and 930°C. It was estimated that almost 70% of the coke on pre-carburized 25Cr-35Ni was caused by catalytic coke formation at around 875°C in this short-term naphtha cracking test condition.

### 3.3 Microstructure and EPMA of pretreated 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni samples

Fig. 10 shows the cross-section microstructure of pre-carburized and pre-oxidized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni before the coke formation test. The microstructure of 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> did not change by pre-carburization treatment at all, whereas the surface of

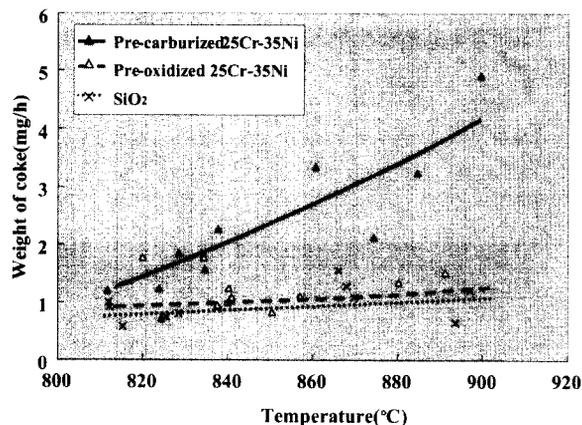


Fig. 7. Coke formed on pre-oxidized and pre-carburized 25Cr-35Ni with quartz.

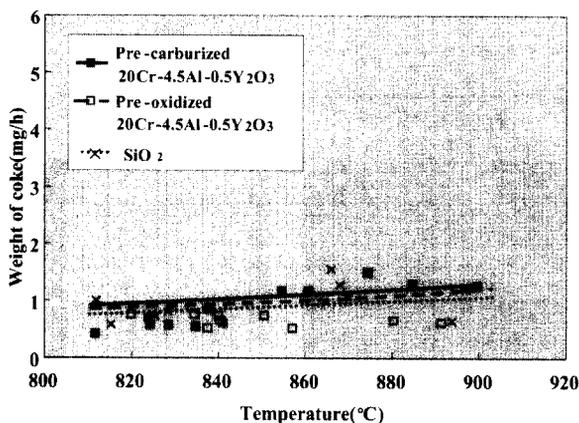


Fig. 8. Coke formed on pre-oxidized and pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> with quartz.

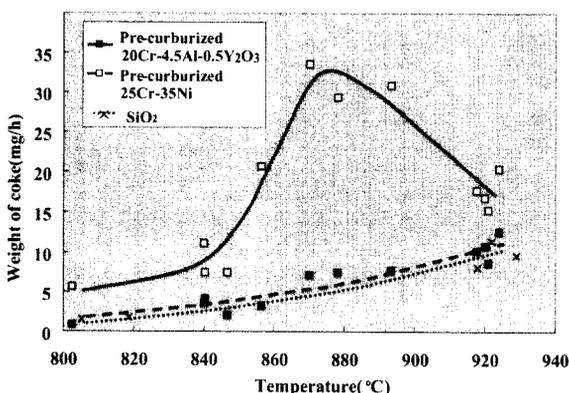


Fig. 9. Coke formed on pre-oxidized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni with quartz.

pre-carburized 25Cr-35Ni became rough by carburization. This result of pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> was coincident with a previous report which showed its excellent carburization resistance.<sup>4),5)</sup>

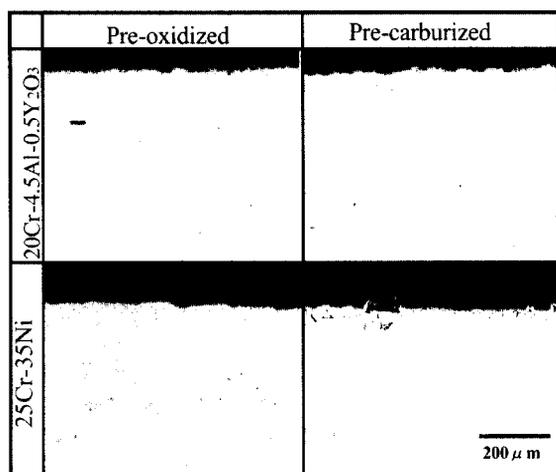


Fig. 10. Optical micrograph of microstructure of pre-carburized / oxidized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni before coke formation test.

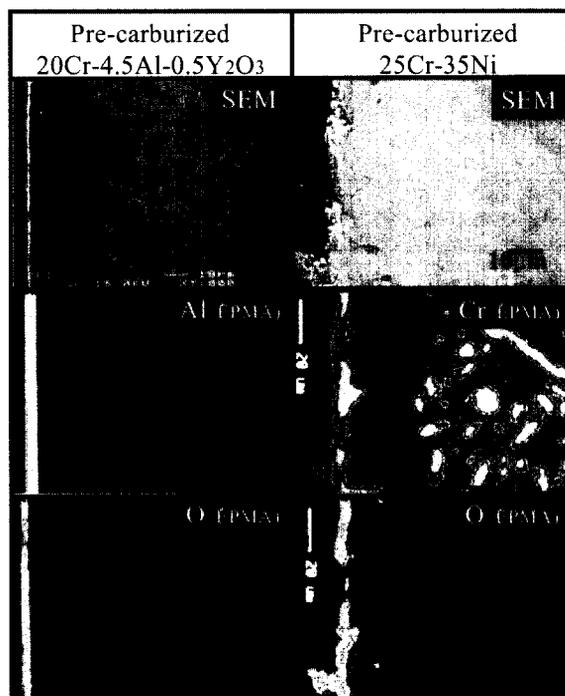


Fig. 11. SEM Image and EPMA of pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub>

Fig. 11 shows the EPMA result on cross sections of pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> and 25Cr-35Ni. Continuous Al<sub>2</sub>O<sub>3</sub> was found on the surface of 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> even after the pre-carburization treatment. On the other hand, the concentrations of Cr and O on the surface of pre-carburized 25Cr-35Ni were partially very low and parts of the Cr<sub>2</sub>O<sub>3</sub> film had not completely covered the 25Cr-35Ni by pre-carburization treatment. In addition, the

depletion of Cr was recognized along the surface of the pre-carburized 25Cr-35Ni. From this result, the carburization of 25Cr-35Ni makes it difficult to reproduce stable Cr<sub>2</sub>O<sub>3</sub> due to depletion of the Cr concentration. Consequently, Ni and Fe appeared on the surface of pre-carburized 25Cr-35Ni; Ni and Fe rich surfaces cause catalytic coke formation.

### 3.4 Stability of aluminum oxide and chromium oxide

The stability of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in a hydrocarbon + steam environment was evaluated by a thermodynamic equilibrium calculation to explain the results that the coke formation rate on pre-carburized 25Cr-35Ni is higher than that on the oxidized sample, whereas pre-carburized 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> had no significant change.

The simulation environments were selected to simulate the coking and decoking operations in ethylene plants. 0.1mol of steam, 0.2mol of ethylene and 0.1mol of methane at 1100°C, which are the product components obtained by actual plants, were used to simulate a coking environment. 0.1mol of steam at 950°C was used to simulate a decoking environment. Fe, Cr, Al and Ni were selected as metal elements. Carbides and oxides of Fe, Cr, Ni and Al were selected for this calculation. And, equilibrium compositions of the selected compounds were calculated using the Gibbs Free Energy Minimization Method.

Table 5 shows the calculation results of various oxides and carbides assumed in these environments. Under steam at 950°C on 25Cr-35Ni, Cr<sub>2</sub>O<sub>3</sub> has the highest content, in other words, it is the most stable. Therefore, Cr<sub>2</sub>O<sub>3</sub> is preferably formed on 25Cr-35Ni in steam at a high temperature as in a decoking environment. Under hydrocarbon

Table 5. Equilibrium components of aluminum and chromium oxide/carbide in hydrocarbon+steam environment

Oxide/ Carbide	25Cr-35Ni		20Cr-4.5Al-0.5Y <sub>2</sub> O <sub>3</sub>	
	Steam only 950(mol)	Hydrocarbon +steam 1100(mol)	Steam only 950(mol)	Hydrocarbon +steam 1100(mol)
FeO	5.8.E-05	1.5.E-04	7.4.E-05	5.6.E-05
Fe <sub>3</sub> O <sub>4</sub>	9.7.E-17	6.7.E-15	1.3.E-16	1.6.E-16
Fe <sub>2</sub> O <sub>3</sub>	4.7.E-14	1.4.E-12	4.8.E-14	7.0.E-14
Cr <sub>2</sub> O <sub>3</sub>	3.0.E-02	2.5.E-04	8.3.E-03	4.2.E-06
Al <sub>2</sub> O <sub>3</sub>	–	–	2.5.E-02	2.5.E-02
Al <sub>4</sub> C <sub>3</sub>	–	–	–	5.5.E-31
NiO	1.1.E-06	5.7.E-06	–	–
Cr <sub>2</sub> C	–	7.9.E-03	–	–
Cr <sub>3</sub> C <sub>2</sub>	–	6.8.E-02	–	5.4.E-02
Cr <sub>4</sub> C	–	–	–	6.5.E-03

in the environment of naphtha pyrolysis

and steam at 1100°C, the contents of chromium carbide such as  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_2\text{C}$  are much higher than that of  $\text{Cr}_2\text{O}_3$ . This result suggests that  $\text{Cr}_2\text{O}_3$  on 25Cr-35Ni is decomposed partially into chromium carbide in the environment of naphtha pyrolysis.

On the other hand, the content of  $\text{Al}_2\text{O}_3$  is the highest in both environments, steam at 950°C and hydrocarbon + steam at 1100°C. It means that  $\text{Al}_2\text{O}_3$  is more stable than  $\text{Cr}_2\text{O}_3$  in the naphtha cracking environment, because it is much more difficult to form aluminum carbide than chromium carbide.

Changing into chromium carbide from chromium oxide on 25Cr-35Ni causes some part of the  $\text{Cr}_2\text{O}_3$  film on the surface of 25Cr-35Ni to fail to cover completely the 25Cr-35Ni. This imperfection in chromium oxide allows dissolution and the diffusion of atomic carbons inside alloys to form  $\text{Cr}_2\text{C}_3$ . As a result of the deficiency of chromium, Ni will be disposed to a hydrocarbon environment and finally accelerate coke formation. For 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub>, it is concluded that coke formations do not occur because stable  $\text{Al}_2\text{O}_3$  covers the surface of 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> completely.

#### 4. Conclusions

1) Ni has a higher catalytic activity of coke formation compared with Fe in a naphtha and steam environment of 810 to 900°C.

2)  $\text{Al}_2\text{O}_3$  on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> prevents catalytic coke formation.

3) The quantity of catalytic coke formed on 25Cr-35Ni

increased due to carburization of the 25Cr-35Ni surface because of the instability of chromium oxide in a naphtha cracking environment.

4) Even after carburization treatment, the  $\text{Al}_2\text{O}_3$  formed on 20Cr-4.5Al-0.5Y<sub>2</sub>O<sub>3</sub> is stable and remained an inert surface for catalytic coke formation.

5) It is simulated in thermodynamic equilibrium that chromium oxide could change into chromium carbide, whereas aluminum oxide is stable in 0.1mol of steam, 0.2mol of ethylene and 0.1mol of methane at 1100°C.

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#### References

1. L. F. Albright and J. C. Marek, *Ind. Eng. Chem. Res.*, **27**, 755 (1988).
2. P. L. Walker Jr. and J. M. Thomas, *Carbon*, **8**, 103 (1970).
3. E. L. Evans and J. M. Thomas, *Carbon*, **11**, 441, (1973)
4. K. Hosoya, K. Sato, and K. Yamamoto, AIChE2000 12th Annual Ethylene Producers Conference, Paper No.86e Proc. Atlanta, GA (2000).
5. B. A. Baker, G. D. Smith, and C. S. Tassen, CORROSION96 Paper No.138, NACE International(1996).