

Influence of coke thickness on the on-line SiO₂/S coating preparation and its thermal shock property

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Abstract. SiO₂/S coating was prepared on the surface of HP40 specimen with different thicknesses of coke. The influence of coke on the coating deposition and thermal shock property was studied. Scanning electron microscopy, X-ray diffractometry and X-ray energy dispersive spectroscopy were used for microstructure and microchemical analysis. The morphologies of cokes and SiO₂/S coatings were investigated. The results show that the oxide layer of HP40 specimen formed at 850°C for 2 hour is porous and mainly composed of (Cr, Fe)-spinel and a small amount of Fe₂O₃. The coking rate initially is high, then decreases with increasing cracking time, and finally reaches a stable value after 20 minutes. The diameter of coke changes from 1μm to 0.2μm, and then is about 0.5μm. The thickness of the coke layer changes from 0.56μm to 2.58μm. The thickness of coke layer has an important influence on the morphology and thermal shock property of the on-line SiO₂/S coating. With increasing the thickness of the coke layer, the coating becomes rough and incompact. When the thickness of the coke layer is 0.56μm, the coating can bear 13 thermal shock tests. And the coating is out of service when the coke layer is 2.58μm. It is suggested that a thorough decoking should be carried out to improve the adhesion between the on-line coating and the inner surface of the cracking tube.

Introduction

Steam cracking of hydrocarbon is the main process for light olefin production, such as ethylene, propylene, and butylenes. However, coke deposition on the inner surface of the cracking furnace tube is inevitable. Accumulation of coke hampers heat transfer and increases pressure drop over the furnace tube. Periodically, it is necessary to decoke the furnace tubes when the skin temperature of furnace tube reaches the maximum allowable value. Decoking will lower ethylene yield and deteriorate properties of furnace tube.

The formation of catalytic coke results from heterogeneous reactions catalysed by metal catalysts such as nickel, iron or their oxides. Catalytic coking is one of the main coking reasons for hydrocarbon thermal cracking, which presents a high coking rate at the beginning of ethylene production [1]. The process of catalytic effect continues until the metal particles are fully covered by coke. It is very concerned about new methods to alleviate catalytic coke. Some methods, such as some off-line coatings prepared on the inner surface of furnace [2], change of the materials of the reactor or adding the coking inhibitor [3, 4] have been applied to inhibit coking. The on-line coating is prepared at the preheating stage of cracking furnace after decoking. Compared with the off-line coating, it is much convenient for the on-line coating to operate. SiO₂/S coating has been prepared on the surface of HP40 alloy tube by the on-line technology to alleviate catalytic coke formation by Zhou [5]. And the coating has good anti-coking and thermal shock properties [5, 6]. However, the surface state of HP40 alloy specimen has significant influences on the coating deposition and the adhesion between coating and specimen [7, 8]. There is more or less some coke on the inner surface of cracking furnace

tube although we try our best to decoke. Therefore, it is necessary to study the influence of residual coke on the preparation and properties of the on-line coating.

In this paper, light naphtha was thermal cracked at 850°C for different cracking times, coke deposited on the surface of specimen was characterized and analyzed. Subsequently, SiO₂/S coatings were prepared on the coked specimens. And thermal shock test was performed by water quenching to investigate the influence of residual coke on the bonding between SiO₂/S coating and HP40 alloy specimen.

Experimental

Preparation of the SiO₂/S coating on the coked specimen. The coking tests were conducted in a quartz tubular reactor (380 mm length, 25mm I.D) that was vertically placed in a single-zone electrical furnace. The isothermal zone is 50mm in length within a temperature range ±1 °C in which the specimen was placed. The HP40 alloy specimens (40×10×4mm) used for coke deposition were wet ground on waterproof abrasive paper from 180 grits to 1200 grits. Then they were oxidized at 850°C for 2 hours in a muffle furnace, after which the specimens were ultrasonically cleaned in acetone and placed in the middle of the reactor. Deionized (DI) water and light naphtha were transported by metering pumps at the rate of 48g/h and 120g/h, respectively. And they were mixed and vaporized in an electronic furnace maintained at 400°C. The light naphtha mainly consists of paraffin and naphthene. The coking experiments were operated at 850°C for 2.5 min, 5 min, 10 min, 20 min, and 30 min. After coking, specimens were cooled down to room temperature under N₂. The specimens before and after coking experiment were weighed with a microbalance (0.1 mg accuracy). Then, SiO₂/S coating was prepared on the coked surface of the specimen. The preparation process has been described previously in reference [5].

Thermal shock test. Thermal shock test was performed by water quenching. The specimen was pushed into the muffle furnace. After being held for 10 min at 900°C, the specimen was quenched into the water [9]. The temperature of the water was at about 20°C during thermal shock test. More than 10% of the spalled region of the surface of SiO₂/S coating was adopted as criteria for the failure of the coating [10].

Characterization. The morphologies of the oxide layer, coke and the SiO₂/S coating were studied by the Scanning Electron Microscopy (SEM). The structure of the oxide layer was analyzed by X-Ray Diffraction (XRD). The components of the oxide layer and coke were examined by the X-ray energy dispersive spectroscopy (EDS).

Results and Discussion

Coke formation. An oxide layer formed on the surface of the HP40 alloy specimen after the oxidation. The characterization of the oxide layer is shown in Fig.1. It can be seen that the oxide layer is porous and rough. The oxide layer has mainly Cr, O, Fe, Mn, Si, Ni and C elements. And it is mainly composed of (Cr, Fe)-spinel and a small amount of Fe₂O₃. In a carburizing atmosphere, (Cr, Fe)-spinel and iron oxide can be reduced to fine metallic particles which can act as catalysts for the formation of filamentous coke [11, 12].

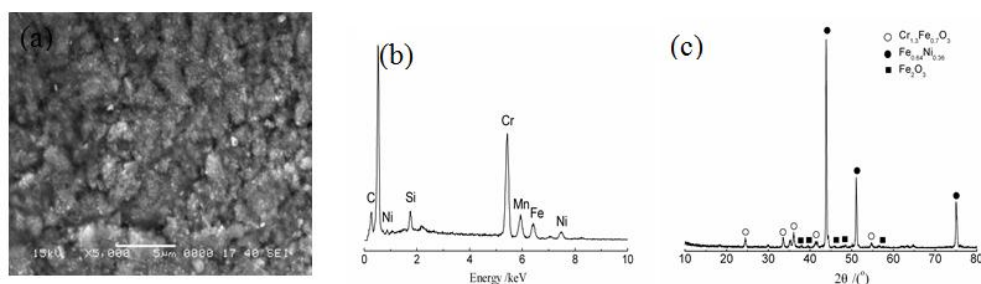


Fig.1.

Characterization of oxide layer formed on the surface of HP40 alloy specimen after oxidation at 850°C for 2 hours. (a) SEM; (b) EDS; (c) XRD.

The influence of the cracking time on the coking rate is shown in Fig. 2. The coking rate is initially $0.08 \text{ mg.cm}^{-2}.\text{min}^{-1}$, and then drops with increasing cracking time. The coking rate reaches a constant value of $0.01 \text{ mg.cm}^{-2}.\text{min}^{-1}$ after 20 minutes. In the initial stage of thermal cracking, the coking mechanism is mainly catalytic coking and filamentous coke is the typical morphology of the catalytic coke. The active metal particle is at the top of filamentous coke. The catalytic activity decreases when the metal surface is covered with coke, and the coke formation rate decreases rapidly. Meanwhile, the coke mechanism changes from catalytic coking to pyrolytic coking which has a steady-state coking rate [12, 13]. Coke will grow by the reactions of gas-phase species with active sites on the coke surface. Acetylene or other olefins, butadiene and free radicals such as methyl, ethyl, vinyl, phenyl, or benzyl radicals are likely to be the coking precursors [13]. At the same time, some compounds of higher molecular mass, such as aromatics and multi-ring aromatics in the gas phase, also form coke through dehydrogenation/nucleation [13]. Therefore, pyrolytic coking has an important effect on coke formation at the later stage of light naphtha steam cracking.

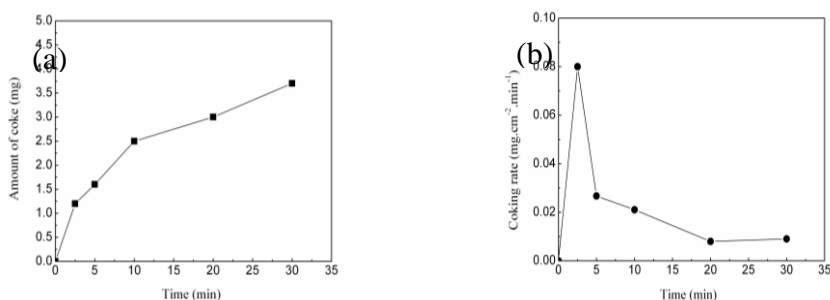


Fig.2. Effect of coking test time on coke formation on the oxidized surface of HP40 alloy specimens. (a) Amount of coke with time; (b) Coking rate with time.

The morphologies of cokes for different cracking times are shown in Fig.3. At 2.5 min, coke begins to nucleate on the surface of specimen. And the diameter of coke nucleation is about $1 \mu\text{m}$. The surface is fully covered by coke nucleation at 5 minutes. The diameter of coke nucleation is still about $1 \mu\text{m}$. The worm-like coke can be clearly seen at 10 minutes. And the diameter of coke is about $0.5 \mu\text{m}$. The worm-like coke grows and becomes long filamentous coke at 20 minutes. However, the diameter of filamentous coke is only about $0.2 \mu\text{m}$. In addition, the long filamentous coke has serious deformation and interweaves with each other. It is well known that active metal particles initiate catalytic reaction and produce filamentous coke. And the size of metal particle decreases during catalytic coking. The loss parts of metal particle are encapsulated in the filamentous coke, which makes the diameter of filamentous coke thinner [14]. The diameter of filamentous coke is about $0.5 \mu\text{m}$ at 30 minutes. Filamentous coke obviously grows in diameter. The reason may be that catalytic coke plays a role in pyrolytic coke formation. At the later stage of catalytic coking, the mechanism of coke formation changes from catalytic coking to pyrolytic coking. Filamentous coke acts as a filter to catch the pyrolytic coke in the gas phase and provides additional surfaces promoting pyrolytic coke formation through gas-solid reaction [13]. Consequently, filamentous coke begins to grow in radius. Furthermore, the particles of pyrolytic cokes also pile up among the pores of filamentous cokes.

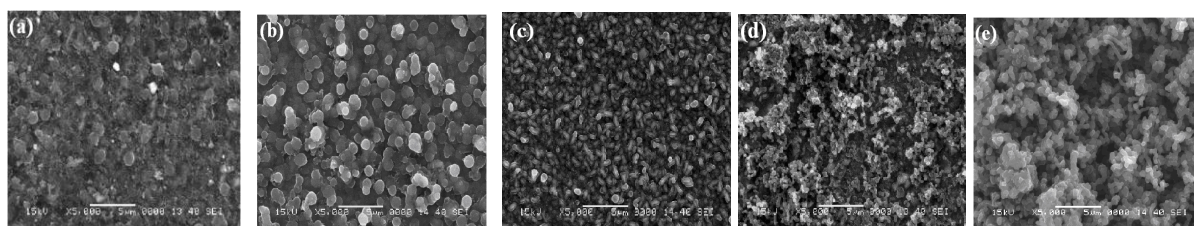


Fig.3 Morphologies of coke formation on the oxidized surface of HP40 alloy specimens for different cracking time. (a) 2.5min; (b) 5min;(c) 10min; (d) 20min; (e) 30min.

The thickness of the coke formed on the surface of specimen may be calculated using equation (1):

$$L = M_c \times d^{-1} \times S^{-1}. \quad (1)$$

Where L is the thickness of the coke layer (μm), M_c is the amount of coke deposited on the specimen (g), d is the density of coke ($1.78 \times 10^6 \text{ g/m}^3$). The density of the coke is taken from reference [12], which was obtained from the measurement of coke produced during an industrial naphtha cracking. S is the surface area of the specimen ($12 \times 10^{-4} \text{ m}^2$). According to our calculation, the thickness of coke on the specimen are about $0.56 \mu\text{m}$, $0.75 \mu\text{m}$, $1.17 \mu\text{m}$, $1.40 \mu\text{m}$ and $2.58 \mu\text{m}$ when the cracking time are 2.5min, 5min, 10min, 20min and 30 min, respectively.

Influence of coke on the SiO_2/S coating deposition. SiO_2/S coating was prepared on the coked surface of HP40 alloy specimen. The morphology of SiO_2/S coating is shown in Fig.4. It can be seen that the size of SiO_2/S coating particle is about $0.6 \mu\text{m}$ when the thickness of coke layer is $0.56 \mu\text{m}$, and the coating is smooth and compact. No cokes are observed on the surface of coating. When the thickness of coke layer is $0.75 \mu\text{m}$, the size of the coating particle is about $1 \mu\text{m}$. The coating particles are surrounded by coke and the combination among the coating particles is loose with a spatial interval of $0.5 \mu\text{m}$. When the thickness of coke layer is $1.17 \mu\text{m}$, the surface morphology of coating has a significant change. The size of the coating particle is about $3\text{--}4 \mu\text{m}$. But the shape of the particle is irregular. The coating has many defects and voids. The combination among the particles is looser. When the thickness of coke layer is $1.40 \mu\text{m}$, the coating has a weak adhesion to specimen. Some coating particles spall. The size of the coating particle is not homogenous. When the surface is fully covered by filamentous coke, the coating particle is first deposited in the interspaces of the interwoven filaments and on the surface of filamentous coke [15,16]. And with the proceeding of coating deposition, the coke layer is gradually covered by the coating. When the thickness of coke layer is $2.58 \mu\text{m}$, there are not any coating particles on the surface of specimen, which implies that the coating absolutely spalls.

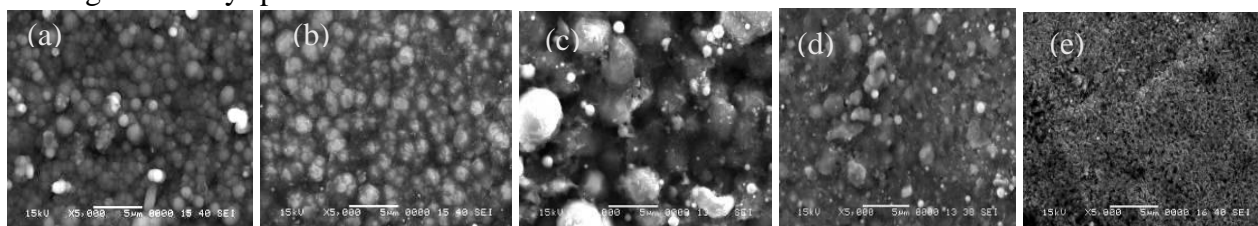


Fig.4. Morphologies of SiO_2/S coatings on the coked surface of HP40 alloy specimens with different thickness of coke layer. (a) $0.56 \mu\text{m}$ (2.5min); (b) $0.75 \mu\text{m}$ (5min); (c) $1.17 \mu\text{m}$ (10min); (d) $1.40 \mu\text{m}$ (20min); (e) $2.58 \mu\text{m}$ (30min).

Influence of coke on the thermal shock property of the SiO_2/S coating. The quenching test is commonly used to determine thermal shock resistance of coatings [17,18]. During thermal shock tests, the coating would suffer damage or complete fracture. Thermal expansion differences between coating and the metal matrix can lead to stresses at the interface. And a large difference may result in debonding of the coating at the interface. The number of thermal shock cycles until failure is given in Table 1. The coating has no spalling until 13 cycles when the thickness of the coke layer is $0.56 \mu\text{m}$ (2.5min). But it could only bear 3 cycles when the thickness of coke layer is $1.40 \mu\text{m}$ (20min). And the coating has absolutely spalled before thermal shock test when the thickness of coke layer is $2.58 \mu\text{m}$ (30min). Therefore, it is not necessary to test its thermal shock property. The number of thermal shock cycles is 16 for the coating deposited on the preoxidized specimen [9], which shows more resistance toward the spalling.

Table1. Thermal shock results of SiO₂/S coatings on the coked surface of HP40 alloy specimens with different thickness of coke layer.

Specimens	1	2	3	4	5	6	7	8	9	10	11	12
0.56μm(2.5min)	a	a	a	a	a	a	a	a	a	a	a	a
0.75μm(5min)	a	a	a	a	a	a	a	a	a	b	c	
1.17μm(10min)	a	a	a	a	a	b	b	c				
1.40μm(20min)	a	a	b	c								
2.58μm(30min)	Spalling											

a—good, b—begin spalling, c—failure.

The morphologies of SiO₂/S coatings on the coked surface of HP40 alloy specimens after thermal shock tests are shown in Fig.5. The coatings are more susceptible to cracking and delamination with increasing the thickness of the coke layer. And the spalling mainly occurs in the central areas of the surfaces of specimens, which indicates a poor adhesion between the surface and the coatings. However, the spalling starts from the edges of the specimen for the coating deposited on the preoxidized specimen [6]. It is because that the discontinuity of SiO₂/S coating at the edges leads to the stress concentration during the thermal cracking tests.

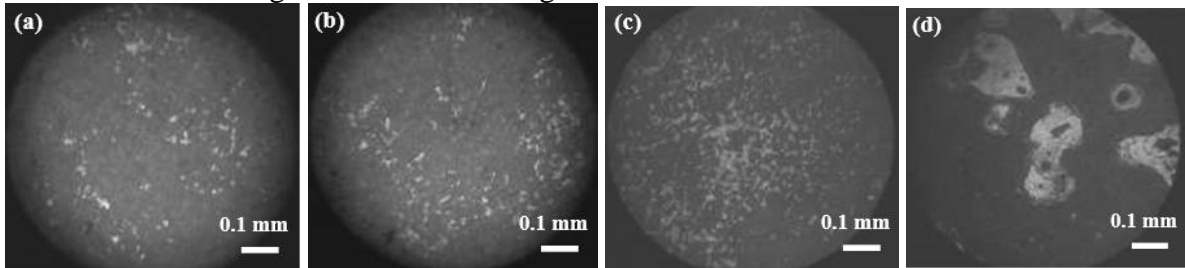


Fig.5 Morphologies of SiO₂/S coatings on the coked surface of HP40 alloy specimens with different thickness of coke layer after thermal shock tests. (a) 0.56μm (2.5min); (b) 0.75μm (5min); (c) 1.17μm (10min); (d) 1.40μm (20min).

According to above analysis, the residual coke on the surface of specimen has an important influence on thermal shock property of coating and limits the application of the coating. The reason may be that the coke layer has a weak adhesion to the surface of the oxidized HP40 alloy with increasing the thickness of the coke layer. Therefore, thermal shock cycles of the coating notably reduce with increasing the thickness of the coke layer. It is suggested that the decoking should be thoroughly carried out to improve the combination between the on-line coating and the cracking tube.

Conclusion

The on-line SiO₂/S coating was prepared on the coked surface of HP40 specimen. The influences of coke on the coating deposition and thermal shock property were studied. The following conclusions can be reached.

(1) The oxide layer of HP40 specimen formed at 850°C for 2 hour is porous, rough, and mainly composed of (Cr, Fe)-spinel and a small amount of Fe₂O₃.

(2) The coking rate initially is 0.08 mg.cm⁻².min⁻¹, and then decreases with increasing cracking time. The coking rate reaches a constant value of 0.01 mg.cm⁻².min⁻¹ after 20 minutes. The diameter of coke changes from 1μm to 0.2μm, and then is about 0.5μm. The filamentous coke begins to grow in radius at the later stage of catalyzed coking. The change of coking rate with coking time indicates that the coking mechanism has changed from catalytic coking to the pyrolytic coking.

(3) When the thickness of the coke layer is 0.56μm (2.5min), the coating can sustain 13 thermal shock cycles. With increasing the thickness of the coke layer, the coating becomes rough and incompact. And the spalling mainly occurs in the central areas of the surfaces of specimens. When the thickness of the coke layer is 2.58μm, the coating has absolutely spalled before thermal shock test. Therefore, it is suggested that the coke should be thoroughly removed from the inner surface of cracking furnace tube.

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