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Influence of Silicon and Silicon/Sulfur-Containing Additives on Coke Formation during Steam Cracking of Hydrocarbons

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The influence of the combination of two Si-containing additives, BTMS and TEOS, with DMDS on coke formation during steam cracking has been evaluated both on a laboratory scale and in a pilot plant unit. Under the optimal presulfidation conditions ($T = 1023\text{ K}$, $\text{H}_2\text{O} = 20\text{ g h}^{-1}$, DMDS in $\text{H}_2\text{O} = 750\text{ ppm wt}$, duration = 1 h), the combination of Si pretreatment + presulfidation + continuous addition of 2 ppm wt DMDS results in a decrease in the rate of coke formation up to 40% when hexane is cracked in the lab-scale unit. Under similar conditions in the pilot plant the coke formation is decreased by 70%, while the CO production decreases by more than 90%. Moreover, the suppressing effect on coke formation remains significant even after several coking/decoking cycles. Simulations of an industrial ethane cracker indicate that the application of Si- and S-containing compounds as additives for the suppression of coke formation can potentially double the run length of industrial steam crackers.

1. Introduction

Steam cracking of hydrocarbons is the major source of light olefins, diolefins, and aromatics. The typical capacity of an ethylene plant has reached 600 000 tons of ethylene/year. In steam cracking, two side reaction products, CO and coke formation on the inner surface of the cracking coils and the transfer line heat exchangers (TLE), detrimentally influence the process operation and profit margins. Using steam as a diluent results in the formation of CO, which is a poison for the metal catalysts used in the downstream hydrogenation units. To ensure on-spec ethylene production, fluctuations in the CO content of the effluent must be avoided. Accumulation of coke on the reactor wall reduces the open cross section of the tubes, resulting in an increase of the pressure drop over the reactor coil. Coke deposition also hampers the heat transfer from the furnace to the process stream. To maintain the product yields, the skin temperature of the cracking coils must be increased with increasing time on stream. When the allowable maximum pressure drop or the maximum skin temperature is reached, the furnace must be taken out of service to remove the coke via controlled burning off with an air–steam mixture. This lowers the production capacity.

In steam cracking, the reactor coils are usually constructed from heat-resistant alloys that contain Fe, Ni, and Cr as the major constituents. An inherent problem with these materials is their tendency to promote the production of CO and coke deposition.^{1–3} To control the production of CO, S-containing compounds, usually dimethyl disulfide (DMDS), are applied. For ethane cracking, a large dose of DMDS is used to presulfide the coil surface with steam as a carrier before the admission of ethane to the reactor coils. Then a small maintenance dose of DMDS is added continuously with the ethane feed during the cracking. For naphtha cracking, only a presulfidation is applied; the sulfur contained in the naphtha feed is relied upon to maintain a low and stable CO production. Control of CO and

coke is critical for the economy of the steam cracking process. Sulfur-containing compounds have been successfully used to control the CO production. For the suppression of coke, a lot of effort has been made in the past 30 years to find appropriate methods and additives.^{4–24} Investigations concerning the effect of S-containing compounds have been carried out in laboratory-scale reactors. The reported effect is contradictory.^{2,26–31} Besides S-containing compounds, other chemicals have been proposed as additives to suppress coke formation in steam cracking. These mainly include phosphorus-containing compounds,^{4–10} silicon-containing compounds,^{11–18} alkali and alkaline earth metal salt based additives,^{19,20} and tin- and antimony-based additives.^{21–24} By now none of these additives have been widely applied in steam cracking.

For the application of additives, three methods can be distinguished, i.e., pretreatment of the inner surface of the cracking coils, continuous addition of the additives during cracking, and the combination of pretreatment followed by continuous addition. The optimal application method for a specific additive depends mainly on the properties of the additives. Si-containing compounds have been reported to be able to suppress coke formation in steam cracking.^{10–17} These additives are commonly used to pretreat the inner surface of the cracking coils. This method offers the advantage that the pretreatment with silicon and silicon/sulfur-containing additives can be carried out at conditions similar to the decoking/cracking operations. In this study, the influence of two Si-containing compounds, bis-trimethylsilyl sulfide (BTMS) and tetraethyl orthosilicate (TEOS), applied by pretreatment of the Incoloy 800HT surface, on the coke formation during steam cracking of hexane is evaluated in a CSTR setup. Considering the fact that naphtha generally contains sulfur, the effect of Si pretreatment combined with DMDS is also investigated. Based on the experimental results in the CSTR, the effect of Si pretreatment and the combination of Si pretreatment with DMDS is evaluated in a pilot plant setup. Under the conditions used in the CSTR, cracking of hexane produces mainly light gaseous components similar to those of ethane cracking. Therefore, in the pilot plant ethane is used as the feed. Steam cracking of the hydrocarbons is carried out at conditions relevant to industrial ethylene furnaces.

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Table 1. Application Conditions of DMDS in CSTR Setup

	application method		
	presulfidation	presulfidation + continuous addition	
		presulfidation	continuous addition
$F_{\text{H}_2\text{O}}$ (g h ⁻¹)	20	20	
DMDS (ppm)	500–1000	750	2–80
F_{DMDS} (g h ⁻¹)	1.0×10^{-2} – 2.0×10^{-2}	1.5×10^{-2}	8.0×10^{-5} – 3.2×10^{-3}
temperature (K)	973–1123	1123	1148
duration (h)	0.5–3	1	

2. Experimental Section

2.1. CSTR Setup. The CSTR setup has been described previously by Reyniers and Froment² and Wang et al.³¹ The reactor is made of Incoloy 800HT with a volume of 5.23×10^{-6} m³. Distilled water and hexane are evaporated, mixed, and then preheated to about 843 K before entering the reactor. To determine the rate of coke formation, the electrobalance technique is used.^{2,32} A hollow cylinder made of Incoloy 800HT with a surface area of 7.5×10^{-4} m² is suspended at the arm of a Cahn 2000 electrobalance and positioned in the center of the reactor. The initial coking rate is calculated based on the amount of coke deposited between 15 and 30 min; the asymptotic coking rate is calculated based on the amount of coke deposited during the last 120 min. After cracking, the effluent is cooled, but not condensed, and led to a cyclone, in which tar and coke particles are separated from the gas. Next, nitrogen is added as internal standard for the gas chromatographic analysis. The conversion and product yields are calculated based on the absolute flow rate of the effluent components using eqs 1 and 2.

$$X = \frac{F_A^0 - F_A}{F_A^0} 100 \quad (1)$$

$$Y_i = \frac{F_i}{F_A^0} 100 \quad (2)$$

where F_A^0 is the mass flow rate of the reactant; F_A is the mass flow rate of the reactant in the effluent; X is the conversion of the reactant; F_i is the mass flow rate of product i ; Y_i is the yield of product i . The concentration of CO in the effluent is continuously measured with an infrared analyzer. For this purpose, the effluent is cooled with three water coolers and a methanol cooler at 263 K to remove the heavy components. Based on the volumetric flow rate of the effluent and the CO concentration, the yield of CO is calculated.

2.2. Experimental Procedures and Conditions in the CSTR Setup. 2.2.1. Preoxidation of the Incoloy 800HT Cylinders.

In industrial practice, a cracking run is usually started after decoking. This implies that the surface of the cracking coils is in an oxidized state. To be in line with industrial practice, the cleaned Incoloy 800HT cylinders as such or after being pretreated with Si (see 2.2.2) are oxidized in air (13 NL/h) for 14 h at 1023 K prior to cracking or to presulfidation followed by cracking. The preoxidized surface state is denoted as “O”.

2.2.2. Application of the Si Additives. In the CSTR setup, the Si-containing additives, BTMS (Fluka, $\geq 98\%$) and TEOS (Fluka, $\geq 98\%$), are applied by the dipping method. A cleaned and preweighted Incoloy 800HT cylinder is immersed in a pure Si-containing additive or in a mixture (BTMS:TEOS = 1:1 (wt)) of them for 1 min. Next the immersed cylinder is dried at ambient conditions for 20 min in the case of BTMS or for 40 min in the cases of TEOS and the mixture of BTMS/TEOS.

Table 2. Experimental Conditions in the Pilot Plant Setup

	TEOS pretreatment	presulfidation	cracking
temperature profile			
CIT cell 3 (K)	823	823	973
COT cell 3 (K)	873	873	1023
COT cell 4 (K)	1023	1023	1063
COT cell 5 (K)	1093	1093	1093
COT cell 6 (K)	1113	1113	1113
COT cell 7 (K)	1143	1143	1143
COP (MPa)	0.17	0.17	0.17
F_{steam} (g h ⁻¹)	4000	4000	1155
TEOS (g h ⁻¹)	10		
DMDS in steam (ppm)	0	750	
g of DMDS m ⁻² h ⁻¹ ^a		8.82	
duration (h)	1	1	6
F_{ethane} (g h ⁻¹)			3003
steam dilution (kg kg ⁻¹)			0.385

^a Surface area used to calculate g of DMDS m⁻² h⁻¹ is 0.34 m².

Then the immersion and drying steps are repeated once. The cylinder that bears the additive is dried in air at 573 K for 3 h. After cooling to room temperature, the cylinder is reweighed to determine the amount of the additive on it. The surface state after the Si pretreatment is denoted as “Si”. After mounting into the reactor, the Si-pretreated cylinder is oxidized at the preoxidation conditions (see 2.2.1) prior to a cracking run. This surface state is denoted as “Si + O”.

2.2.3. Application of DMDS. Presulfidation with DMDS (Aldrich, 99.0%) is carried out in steam. DMDS is dissolved in water and is fed to the evaporator using a syringe pump (ISCO 500D). The flow rate of water is 20 g h⁻¹. For the combination of preoxidation followed by presulfidation, the surface state is denoted as “O + S”. For the combination of Si pretreatment followed by preoxidation followed by presulfidation, the surface state is denoted as “Si + O + S”. After presulfidation, the temperature of the reactor is brought to the cracking temperature in a nitrogen stream in approximate 1 h. Then a cracking run is started. For continuous addition, DMDS is directly dissolved in the hexane feed. The detailed conditions for the application of DMDS in the CSTR setup are given in Table 1. The combination of preoxidation with continuous addition of DMDS is expressed by “O + CA Z”. The combination of Si pretreatment followed by preoxidation followed by presulfidation with continuous addition of DMDS is expressed by “Si + O + S + CA Z”. “Z” represents the concentration of continuously added DMDS in wt ppm based on the hexane feed.

2.2.4. Cracking of Hexane. In the CSTR setup, hexane is cracked at 1123 K and at 1148 K with a feeding rate of hexane of 40 g h⁻¹ and a steam dilution of 0.5 kg of steam/kg of hexane. All data reported in this study are reproduced in at least two repeat runs, and the values reported pertain to the mean values over the repeat runs. Mass balances closed within 3%.

2.2.5. Decoking in the CSTR. The coke deposited on the surface of the CSTR and the cylinder is burnt off at 1073 K with a mixture of air (13 NL h⁻¹) and nitrogen (13 NL h⁻¹) for

Table 3. Decoking Conditions in the Pilot Plant Setup

	$F_{\text{H}_2\text{O}}$ (kg h ⁻¹)	F_{air} (NL h ⁻¹)	F_{N_2} (NL h ⁻¹)	$T_{\text{out,cell3}}$ (K)	$T_{\text{out,cell4}}$ (K)	$T_{\text{out,cell5}}$ (K)	$T_{\text{out,cell6}}$ (K)	$T_{\text{out,cell7}}$ (K)
pre-start	0	0	662	1023	1073	1073	1073	1073
start	1.008	662	0	1023	1073	1073	1073	1073
CO ₂ < 1 mol %	1.008	662	0	1023	1173	1173	1173	1173
CO ₂ < 0.1 mol %	0	662	0	1023	1173	1173	1173	1173

15 min to remove most of the coke. Then the nitrogen flow is stopped and only air (13 NL h⁻¹) is used for 15 min. Finally, the temperature is raised to 1173 K in 15 min and maintained at this temperature for 30 min. The completion of decoking is followed by the mass loss of the cylinders.

2.3. Pilot Plant Setup. The pilot plant unit has been described in previous papers.^{31,32} The furnace, built of silica/alumina brick (Li23), is fired by means of 90 premixed gas burners, arranged on the side walls in such a way as to provide a uniform distribution of heat. In this study, the cracking coil is made of Incoloy 800HT. It is 12.8 m long and has an internal diameter of 9 mm. These dimensions are chosen to achieve turbulent flow conditions in the coil with reasonable feed flow rates. Twenty thermocouples and five manometers are mounted along the coil to measure the temperature and pressure of the reacting gas. After cracking, a precisely known amount of nitrogen is injected into the effluent, serving as an internal standard for the gas chromatographic analysis. The product yields and conversion are calculated similarly as in the CSTR setup. After removal of the heavy components, the CO and CO₂ concentration in the effluent is measured continuously by means of infrared analyzers.

2.4. Experimental Procedures and Conditions in the Pilot Plant Setup. **2.4.1. Pretreatment with TEOS.** Before the pretreatment with TEOS, the surface of the cracking coil is in an oxidized state, which is realized by the decoking after the previous cracking run. The reactor is heated from the night regime at 773 K to the temperature profile as specified in Table 2 (TEOS) in the presence of 4 kg h⁻¹ steam in 2 h. To add TEOS uniformly and precisely, a 30 wt % TEOS solution in hexane is used. When the temperature profile for the pretreatment with TEOS is reached, the TEOS solution is introduced into the cracking coil at the inlet of cell 3 using an ISCO 500D syringe pump, where TEOS is mixed with high-temperature steam. The inlet temperature of cell 3 is kept at around 823 K to prevent blockage of the injection tube. During the pretreatment, the flow rate of steam is maintained at 4 kg h⁻¹. The detailed conditions for TEOS pretreatment in the pilot plant are given in Table 2.

2.4.2. Presulfidation. To add DMDS precisely and uniformly, a 20 wt % DMDS solution in hexane is used. The solution is introduced at the inlet of cell 1 using an ISCO 500D syringe pump. The detailed conditions for the presulfidation in the pilot plant are given in Table 2. For the presulfidation in the pilot plant setup, the concentration of DMDS in steam is maintained at 750 ppm for 1 h.

2.4.3. Cracking. In the radiant coil, cracking and coke deposition are considered to occur only in the cells where $T > 873$ K. For the temperature profiles used in this study, the reactor surface area available for coke deposition amounts to 0.34 m². Ethane with a purity of 99.5% (Air Liquide) is used as the hydrocarbon feed. After pretreatment, the cracking coil is heated under a steam flow of 4 kg h⁻¹ to the set temperature profile as specified in Table 2 (cracking). When the specified temperature profile is reached, the flow rate of steam is set to the desired value for cracking and ethane is introduced. Upon the introduction of ethane, the temperature in the cracking coil decreases by about 20 K due to the endothermic nature of the cracking

reactions. After about 20 min, the temperature of the cracking coil returns to the set value. Ethane is cracked at a COP of 0.17 MPa, a coil outlet temperature (COT) of 1142 K, and a steam dilution of 0.385 kg of steam/kg of ethane. The cracking conditions are maintained for 6 h.

2.4.4. Decoking. Decoking of the cracking coil is performed with a steam/air mixture at the conditions specified in Table 3. At the start of the procedure, the cracking coil is heated to 1073 K under a nitrogen flow, and then steam is introduced. After 3 min, the nitrogen flow is stopped, and air is admitted. Once most of the coke is removed, the temperature of the coil is increased to 1173 K. When practically all the coke is burnt off, the steam flow is stopped, and further decoking occurs in air only. The standard decoking time is 100 min. During decoking, the CO and CO₂ concentration in the effluent is determined by means of infrared analyzers. The volumetric flow rate of the effluent is measured using a metal tube flow meter. The concentration of CO and CO₂ and the flow rate of the effluent are automatically recorded every 10 s. These data are used to determine the total amount of coke deposited on the reactor surface. Note that the coke deposited on the reactor wall does not entirely consist of carbon.^{28,33–35} Typical carbon contents of the coke layer are 99 wt % or higher,^{28,33–35} although a value of 90% has been reported on Ni surfaces.³⁵

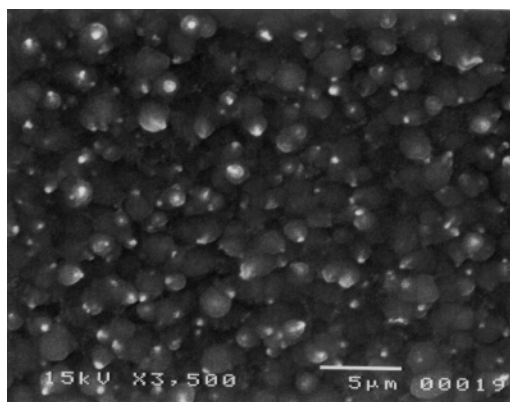
2.5. Scanning Electron Microscope and Energy Dispersive X-ray Analysis. The morphologies of the coke samples are studied using scanning electron microscopy (SEM). The surface composition of the alloy treated at various conditions and the metal content in the coke layer are determined using energy dispersive X-ray (EDX) analysis. EDX analysis is carried out with an accelerating voltage of 10 kV and an acquisition time of 15 min.³² The penetration depth of the electron beam is estimated using the empirical formula as proposed by Kanaya–Okayama.³⁶

$$h = \frac{0.0276 W_a E^{1.67}}{Z^{0.89} \rho} \quad (3)$$

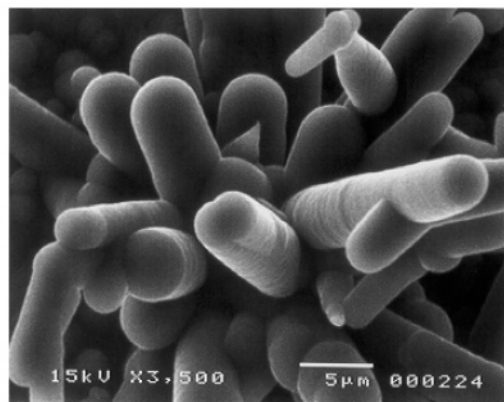
where h is the penetration depth (μm); W_a is the molar weight of the element (g mol^{-1}); Z is the atomic number; ρ is the density of the material (g cm^{-3}); E is the energy of the electron beam (kV). According to eq 3, the penetration depth differs for each element. The typical values for various elements at $E = 10$ kV are for C, $h = 1.7 \mu\text{m}$; for Cr, $h = 0.56 \mu\text{m}$; for Fe, $h = 0.50 \mu\text{m}$; and for Ni, $h = 0.44 \mu\text{m}$; resulting in a penetration depth of approximately $0.5 \mu\text{m}$ for the metals concerned in this work. The thickness of the coke layer is determined using eq 4:

$$L = \frac{M_C}{d S} 10^{-6} \quad (4)$$

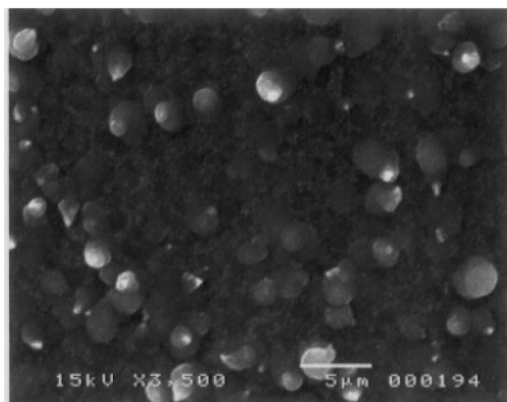
where L is the thickness of the coke layer (μm); M_C is the amount of coke deposited on the cylinders (g); d is the density of coke ($1.78 \times 10^6 \text{ g m}^{-3}$); S is the surface area of the cylinder ($7.565 \times 10^{-4} \text{ m}^2$). The density of the coke is taken from Bennett and Price.³⁷



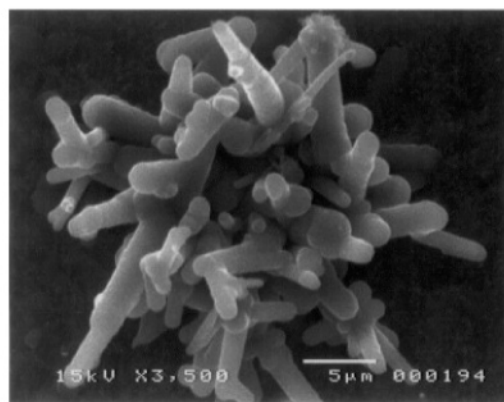
A: Globular coke formed on preoxidized Incoloy 800HT (magnification: 3500)



B: Filamentous coke formed on preoxidized Incoloy 800 HT (magnification: 3500)



C: Globular coke formed on TEOS pretreated Incoloy 800 HT (magnification: 3500)



D: Filamentous coke formed on TEOS Incoloy 800HT pretreated 800HT surface (magnification: 3500)

Figure 1. SEM photograph of coke deposited on Incoloy 800HT with and without Si pretreatment during steam cracking of hexane in CSTR. Cracking conditions: hexane = 40 g h⁻¹, steam dilution = 0.5 kg of steam/kg of hexane, and *T* = 1148 K.

Table 4. Surface Composition of Incoloy 800HT with and without Si Treatment As Determined Using EDX^a

	asypm R_C (mg m ⁻² s)	L (μm)	metal content (wt %)	composition (wt %)						
				Cr	Fe	Ni	Mn	Si	Ti	Al
Alloy										
fresh Incoloy 800HT				20.7	46.1	31.2	0.9	0.3	0.5	0.3
Si				21.3	45.7	27.9	1.0	3.4	0.5	0.3
O				71.5	2.2	0.9	21.2	0.1	4.1	0.1
Si + O				67.1	1.4	0.4	27.0	0.03	4.0	0.1
Si + O + S				70.9	5.5	2.0	17.1	0.3	4.0	0.1
Coke without Continuous Addition of DMDS ^b										
O	0.36	3.6	22.2	65.0	6.6	4.9	21.4	1.3	0.4	0.5
Si + O	0.24	3.0	24.7	70.0	7.4	1.3	19.7	0.8	0.4	0.3
Coke with Continuous Addition of 5 ppm DMDS ^b										
O	0.34	5.3	18.4	66.3	5.0	2.8	24.4	0.8	0.4	0.3
O + S	3.5	42.4	6.7	44.6	19.9	17.3	13.1	3.5	0.7	0.9
Si + O + S	0.35	4.4	26.1	68.0	3.4	1.8	25.7	0.5	0.4	0.2

^a Acceleration voltage = 10 kV; acquisition time = 15 min. The values presented in the table are the average values of 10 points over the surface.

^b Cracking conditions: *T* = 1148 K, hexane = 40 g h⁻¹, and δ = 0.5 kg of steam/kg of hexane.

3. Results and Discussion

3.1. Influence of Si Additives on Coke Formation. 3.1.1. Influence of Si Additives on Coke Formation in the CSTR.

In this study, the influence of the Si additives, BTMS, TEOS, and their mixture on the coke formation in steam cracking is first evaluated in the CSTR setup using hexane as feed. BTMS and TEOS are applied by pretreating the cleaned Incoloy 800HT cylinder (see 2.2.2). The amount of the Si-containing additives deposited on the cylinders ranges from 0.13 to 0.39 g m⁻². This corresponds to a thickness of a silica layer of 49–147 nm

assuming that the density of silica is 2.65 × 10³ kg m⁻³.³⁸ Cracking tests are carried out at 1123 and 1148 K with a feeding rate of hexane of 40 g h⁻¹ and a steam dilution of 0.5 kg of steam/kg of hexane. To determine the influence of the additives, blank runs in which the Incoloy 800HT surface is preoxidized only are first carried out.

As shown previously³² at the beginning of the cracking runs, the coking rate is high due to heterogeneous catalytic coke formation. With increasing time on stream, the coking rate decreases and reaches a stable value, the so-called asymptotic

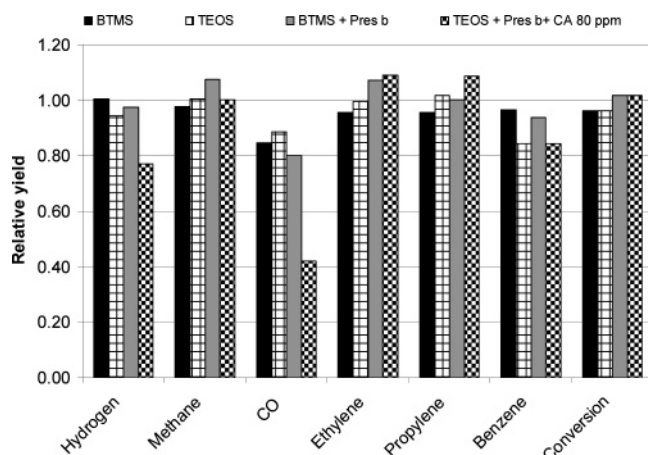


Figure 2. Influence of additives on yields and conversion during steam cracking of hexane in the CSTR setup. Yields and conversion relative to blank run values. Cracking conditions: hexane = 40 g h⁻¹, δ = 0.5 kg of steam/kg of hexane, and T = 1148 K. Presulfidation: T = 1123 K, H₂O = 20 g h⁻¹, DMDS in H₂O = 750 ppm, and duration = 1 h.

coking rate, corresponding to the heterogeneous noncatalytic coke formation stage. The amount of coke deposited on the cylinders and the coking rate increase with increasing cracking temperature.³² Heterogeneous catalytic coke formation is associated with the metal wall of the cracking coils. A significant characteristic of catalytic coke formation is filamentous coke, as shown in Figure 1. The filamentous coke (Figure 1B) formed at 1148 K has a diameter of 3–5 μ m and a length of 10–30 μ m and is scattered on the surface which has been in contact with the gas stream. Besides the coke filaments, coke globules with a diameter of 1–2 μ m are also formed (Figure 1A). Most of the surface in contact with the gas stream is covered by the globular coke. For the catalytic coke formation, the nature of the material on which coke is deposited is an important factor. Coke deposition on different materials has been found to proceed with different rates.^{39,40} Next to this, the composition of the metal surface is also important. The surface composition of a preoxidized Incoloy 800HT cylinder as determined by EDX is given in Table 4. Preoxidation results in a significant enrichment of Cr, Mn, and Ti and a significant depletion of Fe and Ni on the surface. As reported previously,³² the surface composition upon preoxidation indicates the formation of an oxide layer that contains mainly MnCr₂O₄ and Cr₂O₃, which is consistent with literature reports.^{41,42} Formation of such an oxide layer is desired for the protection of the alloy. With increasing time on stream, the metal surface is encapsulated by coke and the catalytic activity of the metal wall decreases. The main route for coke formation then shifts to the heterogeneous noncatalytic mechanism, where coke is formed via reactions of coke precursors in the gas phase with active sites located in the coke matrix.^{43–46} Heterogeneous noncatalytic coke formation is the most important coking mechanism since it operates practically over the entire cracking run. Coke formation via the homogeneous noncatalytic mechanism, so-called gas-phase coking,^{33–48} can be neglected when light feedstocks are cracked.

In Figure 2, the conversion and the yields of the main products are shown relative to the values observed during the blank run at 1148 K. Application of these additives causes a small but not unimportant change in the conversion of hexane and in the product distribution. The conversion at 1148 K changes from 38% in the blank run³² to 37% when BTMS is used, to 38% when TEOS is used, and to 39% when TEOS and BTMS are used. The changes for the methane yield, the ethylene yield, and the propylene yield compared to the value in the blank run

all are limited to at most 10% at 1148 K. The most important differences are observed for CO, as can be seen from Figure 2. CO is formed via the noncatalytic gasification of coke by steam and via metal-catalyzed removal of carbonaceous intermediates and/or coke by steam reforming.¹ As observed by Dhuyvetter,³¹ different pretreatment methods and/or continuous addition of DMDS can reduce the CO production by some 50%. The pretreatment with silicon additives also has a strong effect on the initial and asymptotic coking rate. As can be seen from Figure 3, pretreatment of the Incoloy 800HT cylinder with BTMS, TEOS, and their mixture results in a significant decrease of the amount of coke deposited on the cylinder and a decrease of the coking rate as compared to a blank run. On average, application of the Si additives results in a reduction of the initial coking rate by 48% and of the asymptotic coking rate by 31% at 1123 K. At 1148 K, the reduction in the initial and the asymptotic coking rates is practically the same, amounting to 24%. The data in Figure 3 indicate that there is no significant difference between BTMS and TEOS concerning the suppressing effect on the coke formation. This implies that BTMS and TEOS decrease the coke formation via the same mechanism and the sulfur contained in BTMS does not seem to play an important role. BTMS is a very unstable compound that readily decomposes, even at ambient conditions, releasing H₂S. After being dipped in BTMS, the cylinders are exposed to ambient for 20 min. Therefore, some of the sulfur in BTMS is probably already released at room temperature and adsorbed sulfur may exist on the surface of the Incoloy 800HT cylinder. Prior to their use in the cracking run, the Si-pretreated cylinders are preoxidized in air at 1023 K for 14 h. Under these conditions it can be assumed that sulfur is completely removed from the surface of the Incoloy 800HT cylinder and that the Si is converted to silicon oxide.

The data in Figure 3 also indicate that the amount of Si on the cylinder has a small influence on the observed reduction in coking rate. In general, higher amounts of additives used in the pretreatment lead to a smaller decrease of the coking rate. This seems to imply that the suppressing effect of TEOS and BTMS does not originate from the formation of a silica layer on the surface as in that case the degree of reduction would be expected at the very least to remain constant when more additives are used. To figure out the mechanism for the reduced coke formation upon the Si pretreatment, the surface composition of the Si-pretreated Incoloy 800HT cylinders has been determined using EDX and is given in Table 4. Compared to the preoxidized surface, Si pretreatment results in a reduction of Cr, Fe, and Ni and an increase of Mn in the oxide layer. It can be noticed that the content of Si is even lower compared to the oxidized surface without Si pretreatment. This also seems to imply that the suppressing effect of the Si pretreatment via the dipping method on the coke formation does not originate from the formation of a silica layer. The composition of the oxide layer formed upon oxidation of the Si-pretreated cylinder has been estimated using the thermodynamic calculation program, EKVICALC.⁴³ The calculation result indicates that the equilibrium molar composition of the oxide layer contains 65.7% MnCr₂O₄, 20.9% Cr₂O₃, 10.0% TiO₂ (rutile), 1.7% Fe₂O₃, 0.9% NiTiO₃, 0.6% SiO₂, and 0.3% Al₂TiO₅. Compared to preoxidation alone,³² the oxide layer with Si pretreatment contains more MnCr₂O₄, TiO₂ (rutile), and Al₂TiO₅, but less Cr₂O₃, NiTiO₃, and Fe₂O₃. The content of SiO₂ is practically the same.

The influence of Si on the composition and structure of the oxide layer formed during the oxidation of alloys has been noted for a long time. Fe–Ni–Cr alloys are frequently used at high

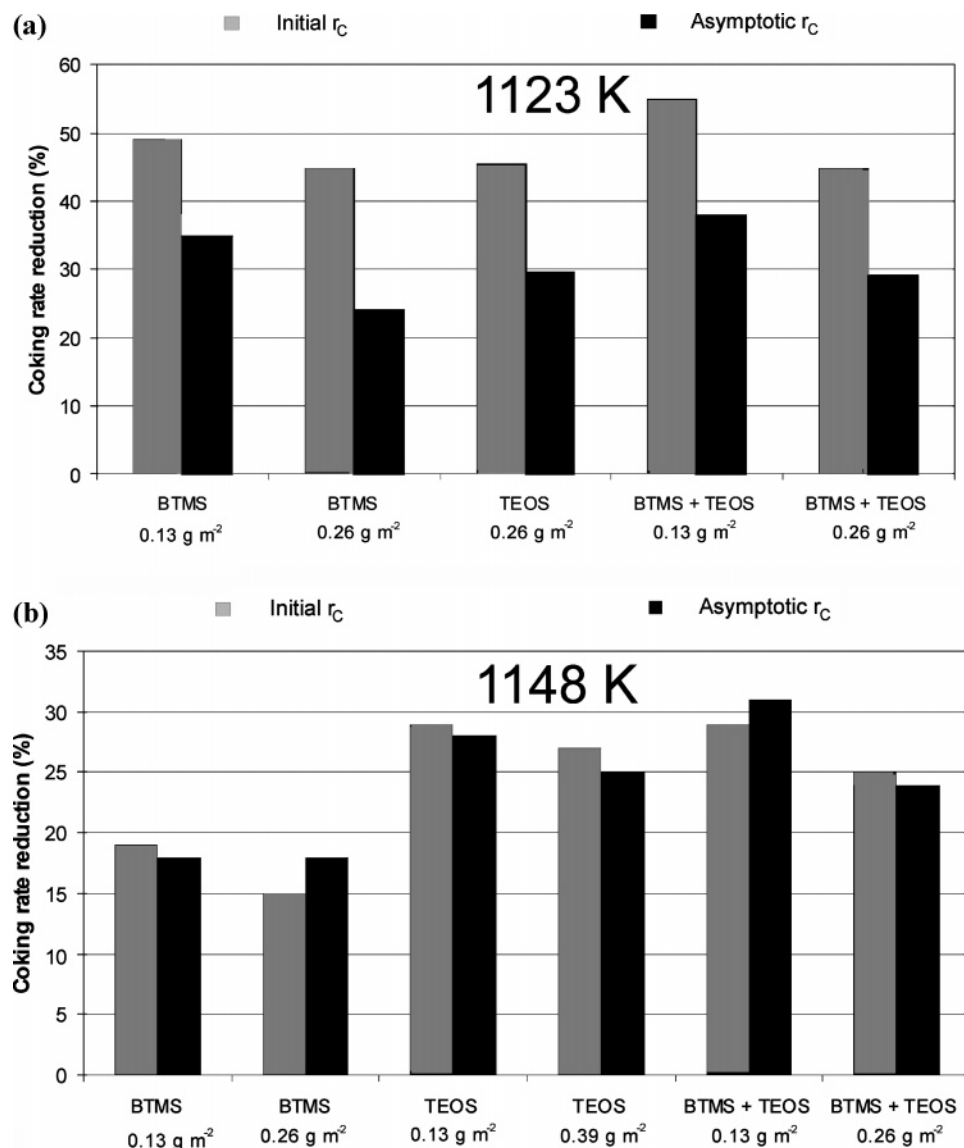


Figure 3. Influence of additives on the initial and asymptotic coking rate during steam cracking of hexane in the CSTR setup. Cracking conditions: hexane = 40 g h⁻¹, and δ = 0.5 kg of steam/kg of hexane. Presulfidation: T = 1123 K, H₂O = 20 g h⁻¹, DMDS in H₂O = 750 ppm, and duration = 1 h.

temperatures and in corrosive atmospheres. Anticorrosion of these alloys relies on the formation of a protective Cr₂O₃ layer. Generally, at least 20 wt % Cr is required to ensure the formation of a Cr₂O₃ layer during oxidation.^{48,49} Before being exposed to the process stream, preoxidation of an alloy is carried out to form a protective oxide layer on the alloy surface. The composition and the structure of the oxide layer depend mainly on the bulk composition, on the type and amount of the minor alloy elements, and on the oxidation conditions.⁵⁰ For heat-resistant alloys containing Fe, Cr, and Ni, formation of a Cr₂O₃ layer during preoxidation is preferred due to its good stability.⁴⁹ Si is believed to facilitate the formation of a Cr₂O₃ layer and to improve the resistance to oxidation.^{51–53} Based on studies concerning the oxidation of Fe–24% Cr–24% Ni alloy, Baxter et al.⁵¹ proposed that the effect of SiO₂ on the formation of a Cr₂O₃ layer is to provide additional sites for the lateral growth of the Cr₂O₃ layer and to promote a rapid growth of a continuous Cr₂O₃ layer. Huntz et al.⁵² investigated the effect of Si on the oxidation of a 9% Cr steel. Without addition of Si, an oxide layer consisting of mainly iron oxides is formed upon oxidation at 873 and 1273 K in 0.1 MPa of O₂. In contrast, addition of 2–4% Si, results in the formation of a Cr₂O₃ film of iron oxides. The effect of Si is attributed to the segregation of Si at the outer

surface and to the formation of a thin SiO₂ film in the early stage of the oxidation. In the further stage of the oxidation, the SiO₂ film only allows the formation of a layer containing Cr and Mn oxides as the oxygen activity, thermodynamically imposed by the silica, is too small for developing iron oxide. Addition of Si to the alloy surface by some surface modification techniques such as by ion implantation has also been found to have a beneficial effect on the formation of the Cr₂O₃ layer during oxidation of alloys.⁵³ The effect of Si is likely to form SiO₂ in the initial oxidation stage. The SiO₂ particles at the surface then act as nucleation sites for the formation of Cr₂O₃ layer. For Fe–Ni–Cr alloys containing a minimal amount of Mn and Si, the oxide layer formed during oxidation generally has a layered structure with MnCr₂O₄ on top of Cr₂O₃.^{54,55} Si is found in the form of SiO₂, which can be a continuous or discontinuous layer beneath Cr₂O₃.⁵⁰ Although the structure of the oxide layer is not analyzed in detail this study, based on the composition of the oxide layer as determined using EDX, it is believed that the Si applied by the pretreatment method has been covered by an oxide layer consisting of mainly MnCr₂O₄ and Cr₂O₃ during the preoxidation procedure. Accordingly, the suppressing effect of the oxidized Si-pretreated Incoloy 800HT on the coke formation in the steam cracking

of hexane can then be attributed to the modification of the composition and the structure of the oxide layer and to a decreased diffusion of metals into the coke layer during cracking.

The metal content and the metal composition of the coke layer in contact with the gas phase are also determined with EDX and are shown in Table 4. In the coke layer deposited on the preoxidized Incoloy 800HT surface, the main metal constituents are Cr, Mn, Fe, and Ni. These metals are also the main constituents in the coke layer deposited on the oxidized Si-pretreated Incoloy 800HT surface. Previously³² an inverse correlation between the metal content and the thickness of the coke layer has been found for the coke formed in the blank runs. According to this correlation, the metal content in a coke layer having a thickness of 3 μm can be estimated to be 29.0 wt %. The experimentally determined metal content in the coke layer formed with TEOS pretreatment amounts to 24.7 wt %. This may imply that TEOS pretreatment somewhat suppresses the diffusion of metals into the coke layer. In addition, TEOS pretreatment also results in a change of the metal distribution in the coke layer. The most pronounced change is found for Ni, which is one of the most active elements for the catalytic coke formation. Upon the TEOS pretreatment, the content of Ni in the coke layer decreases by 73%.

Baker et al.⁵⁶ investigated the influence of Si on the growth of filamentous coke on a Fe–Ni surface during the decomposition of acetylene using controlled atmosphere electron microscopy. They found that the growth rate and the length of filamentous coke are significantly reduced on a Si-pretreated Fe–Ni alloy. The suppressing effect of Si on the growth of coke filaments was attributed to the reduced diffusion of coke through the metal particles, the rate-limiting step for the coke formation. The morphology of coke deposited at 1148 K on the Incoloy 800HT cylinder with and without the TEOS pretreatment has been examined using SEM. Representative microphotographs are shown in Figure 1. Upon the pretreatment with TEOS, the coke still consists mainly of globular coke (Figure 1C) with a diameter of 1–3 μm and needle-shaped coke filaments (Figure 1D) with a diameter of 1–2 μm and a typical length of 5–15 μm . Compared to the coke deposited on the preoxidized Incoloy 800HT surface, TEOS pretreatment does not cause a significant change in the diameter of the globular coke but causes a decrease in its population. Moreover, the diameter and the length of the needle shaped filamentous coke are decreased. These findings are consistent with the observations of Baker et al.⁵⁶ Moreover, the more pronounced reduction of the initial coking rate compared to the reduction of the asymptotic coking rate also shows that the Si pretreatment has a more pronounced effect on the catalytic coke formation. Upon the pretreatment with the Si additives, the initial coking rate decreases by 48% at 1123 K; see Figure 3. At 1148 K it decreases by 24%, which is 50% less than that at 1123 K. At 1123 K, Si pretreatment decreases the asymptotic coking rate by 31%. At 1148 K it decreases by 24%, which is 23% less than that at 1123 K. These observations also imply that Si pretreatment has a stronger effect on the catalytic coke formation than on the heterogeneous coke formation, in agreement with the influence of Si on the composition and the structure of the surface layer mentioned above.

3.1.2. Influence of TEOS on the Steam Cracking of Ethane in a Pilot Plant. The influence of one of the Si-containing additives, TEOS, on the coke formation and CO production in steam cracking of ethane has been evaluated in a pilot plant setup. Since BTMS and TEOS do not show a significant

difference in the suppressing effect on coke formation in steam cracking of hexane, in the pilot test TEOS is used due to its much lower price and ease of handling compared to BTMS. In an industrial ethylene furnace, a temperature profile exists along the cracking coils. To simulate this situation, during pretreatment with TEOS, a temperature profile is set along the cracking coil in the pilot plant setup (Table 2, TEOS pretreatment). In the pilot plant, TEOS is applied by pretreatment of the oxidized Incoloy 800HT surface obtained by decoking of a previous coking run. Hence, in the pilot plant the sequence consists in 1, decoking; and 2, TEOS treatment. This is different from the sequence in the CSTR, where it is 1, TEOS; and 2, oxidation. The different sequence used in the pilot plant is of course due to that the fact that it is impossible to use a new reactor coil in each run. The results with the application of TEOS, together with those of a blank run, are summarized in Table 5.

In the blank run, the conversion of ethane amounts to 70%; the yield of ethylene and CO is 52 and 1.7 wt %, respectively. The total amount of coke deposited on the inner surface of the cracking coil during 6 h cracking is 1.56 g. Upon the pretreatment with TEOS, no significant change in the conversion of ethane and in the product selectivities are observed. The yield of CO decreases to 0.2 wt %, which is 88% lower compared to the values observed in the blank run. The amount of coke deposited during 6 h amounts to 0.63 g, which is 60% lower compared to that of the blank. The CO content in the effluent as a function of time on stream is shown in Figure 4. Upon the TEOS pretreatment, the CO spike appearing at the beginning of the blank run is completely eliminated. The CO concentration in the effluent remains almost constant over the entire run.

After the run with TEOS pretreatment, four cracking runs, the so-called memory test runs (Si-M-I to Si-M-IV), are carried out in order to evaluate the durability of the effect of TEOS on the coke formation and CO production. In these memory test runs, no significant variation in the conversion of ethane and the main product yield are noticed, as illustrated by the data in Table 5 (Si-M-I). The amount of coke and the CO yield as a function of the number of the memory test run are given in Figure 5. After four coking/decoking cycles, the amount of coke and the yield of CO does not completely return to the value of the blank run. The decrease in the coke formation still amounts to 20%. The decrease in the yield of CO still amounts to 40%.

Unlike in the CSTR, application of TEOS in the pilot reactor results in a significant reduction not only in the coke formation but also in the CO production. The amount of TEOS used during the pretreatment in the pilot plant is 10 g, which can produce 2.89 g of SiO_2 . Assuming that all the SiO_2 is uniformly deposited on the inner surface of the cracking coil of the pilot plant setup, the thickness of the SiO_2 layer is 3.2 μm . Therefore, it is likely that in the pilot plant pretreatment of the cracking coil with TEOS would form a thin layer of SiO_2 on its inner surface. The formation of a SiO_2 layer on the metal surface upon the pretreatment with Si-containing additives has been demonstrated by Brown et al.^{11,12} and Woerde et al.¹⁷ It is thought that this layer of SiO_2 acts as a physical barrier to prevent direct contact between the process gas stream and the alloy that shows a high catalytic activity for the formation of coke and CO production.

In the memory test runs, the SiO_2 layer still shows a suppressing effect on coke formation and CO production. However, the effect on the CO production decreases with increasing number of coking/decoking cycles. One of the important reasons is likely the spalling off of the SiO_2 layer, which is caused by the thermal shock in the coking/decoking operation.

Table 5. Conversion, Main Product Yields, and Coke Formation of Ethane Steam Cracking in the Pilot Plant Setup

run name	blank	TEOS	Si-M-I	Si/S-I	Si/S-M-I	Si/S-II
TEOS (g h ⁻¹)	0	10	0	10	0	10
presulfidation ^a	no	yes	no	yes	no	no
continuous addition of DMDS (ppm)	0	0	0	2	0	2
ethane (g h ⁻¹)	3003	3003	3003	3003	3003	3003
steam dilution (kg kg ⁻¹)	0.387	0.383	0.384	0.383	0.385	0.383
COT (K)	1142	1142	1142	1142	1142	1142
COP (MPa)	0.17	0.17	0.17	0.16	0.16	0.16
conversion (%)	69.8	70.2	69.4	69.7	68.2	70.0
residence time (s)	0.28	0.29	0.29	0.29	0.29	0.29
duration of cracking (h)	6	6	6	6	6	6
product yield (wt %)						
H ₂	5.1	5.0	4.9	4.9	5.0	4.9
CO	1.7	0.2	0.5	0.1	0.3	0.1
methane	3.7	3.8	3.7	3.7	3.5	3.8
acetylene	0.5	0.6	0.6	0.6	0.6	0.6
ethylene	52.0	53.2	52.6	52.8	53.0	52.6
propane	0.1	0.1	0.1	0.1	0.1	0.1
propylene	1.1	1.1	1.1	1.1	1.1	1.1
<i>n</i> -butane	0.2	0.2	0.2	0.2	0.2	0.2
1,3-butadiene	2.0	2.1	2.1	2.0	2.1	2.1
benzene	0.4	0.6	0.5	0.5	0.5	0.5
toluene	0.1	0.1	0.1	0.1	0.1	0.1
burnt coke (g)	1.31	0.34	0.91	0.34	0.85	0.38
coke in filter (g)	0.25	0.29	0.19	0.15	0.15	0.27
total amount of coke (g)	1.56	0.63	1.10	0.49	1.00	0.65
reduction of coke (%)		60	29	69	36	58
reduction of CO yield (%)		86	71	94	81	92

^a Presulfidation conditions: steam = 4 kg h⁻¹, DMDS in steam = 750 ppm, and duration = 1 h.

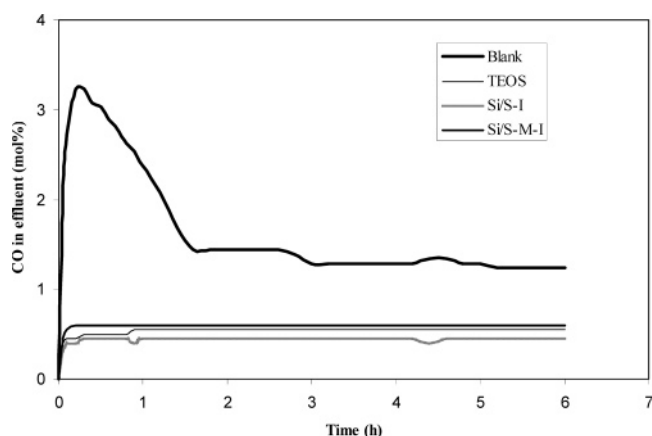


Figure 4. CO content in effluent as a function of time on stream during ethane cracking in the pilot setup. Cracking conditions: ethane = 3003 g h⁻¹, steam dilution = 0.385 kg steam/kg ethane, COT = 1142 K, COP = 0.17 MPa.

3.2. Influence of Si/DMDS on the Coke Formation of Steam Cracking. **3.2.1. Influence of Si/DMDS on the Coke Formation of Hexane Cracking in the CSTR.** To evaluate the effect of the combination of Si + DMDS on the coke formation in steam cracking of hexane in the CSTR setup, an Incoloy 800HT cylinder is first pretreated with one of the Si additives by the dipping method (see 2.2.2). Then it is mounted into the reactor and oxidized at the preoxidation conditions (see 2.2.1). Finally it is presulfidized with DMDS in the presence of steam (see 2.2.3). After presulfidation, a cracking run with or without continuous addition of DMDS is carried out.

3.2.1.1. Influence of Si Pretreatment + Presulfidation in the CSTR. To determine the optimal presulfidation conditions under which the least amount of coke is formed, the influence of the concentration of DMDS in steam, the temperature, and the duration used for the presulfidation on the coke formation during steam cracking of hexane has been investigated. In these experiments, BTMS is used to pretreat the Incoloy surface.

BTMS pretreatment followed by presulfidation does not have a significant influence on the conversion of hexane, and the main product yields are only marginally influenced as shown in Figure 2. Compared to the blank runs and the Si-pretreatment run, the CO concentration in the effluent does not show a significant difference from that of the Si-pretreatment run.

The influence of the presulfidation conditions on the coke deposition on the BTMS-pretreated Incoloy 800HT surface is presented in Table 6. In this table the effect of the BTMS pretreatment + presulfidation on the coke formation is expressed in terms of the relative coking rate, which is the ratio of the coking rate observed for BTMS pretreatment + presulfidation to that of a blank. Presulfidation of the BTMS-pretreated Incoloy 800HT surface at $T = 1073$ K for 1 h with a concentration of DMDS ranging from 500 to 1000 ppm in steam results in an increase in both the initial and the asymptotic coking rates. At $T = 1073$ K, a minimum coking rate is found at 750 ppm DMDS. When presulfidation is carried out with 750 ppm DMDS for 1 h, at 973 and 1023 K, the initial coking rate decreases by 40% while the asymptotic coking rate decreases by about 70%. When presulfidation is carried out with 750 ppm DMDS at 1073 and 1123 K, the initial coking rate increases by 10–20% and the asymptotic coking rate increases by 15–20%. When presulfidation is carried out at 1023 K with 750 ppm DMDS for a duration of 1–3 h, the initial coking rate decreases by 11–39% and the asymptotic coking rates decreases by 6–33%. With regard to minimal coke formation, the optimal presulfidation conditions for the combination of BTMS pretreatment followed by presulfidation are H₂O = 20 g h⁻¹, $T = 1023$ K, DMDS in H₂O = 750 ppm, and duration = 1 h. Under these conditions, the initial coking rate is reduced by 39% and the asymptotic coking rate is reduced by 33% compared to that of a blank.

The composition of the TEOS-pretreated + preoxidized + presulfidized Incoloy 800HT surface as determined using EDX is presented in Table 4 (Si + O + S). It can be seen that presulfidation of TEOS-pretreated followed by preoxidation of

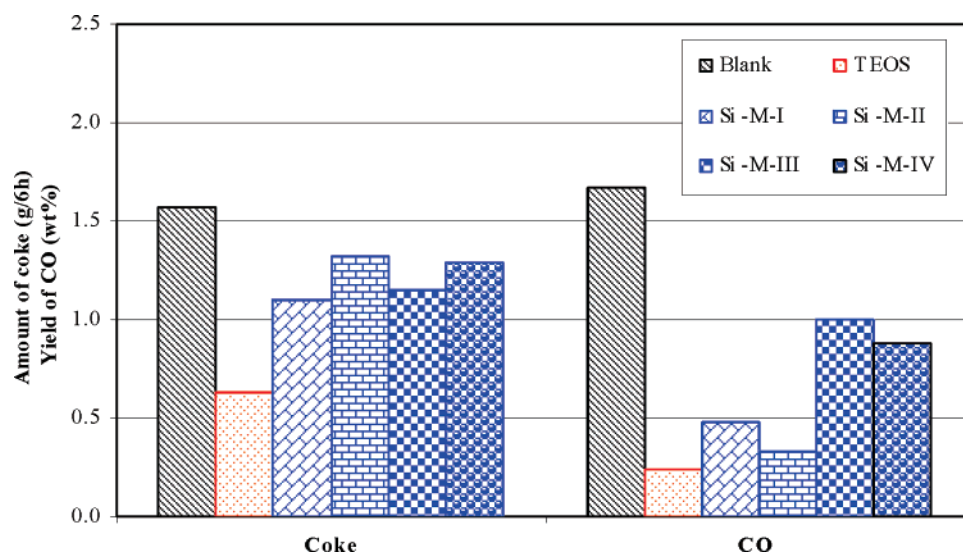


Figure 5. Amount of coke deposited on the surface and CO yield as a function of number of the memory test run during the steam cracking of ethane in the pilot plant setup. Cracking conditions: ethane = 3003 g h⁻¹, steam dilution = 0.385 kg of steam/kg of ethane, COT = 1142 K, COP = 0.17 MPa, and duration = 6 h.

Table 6. Influence of Presulfidation Conditions on the Coke Deposition on the Oxidized BTMS-Pretreated Incoloy 800HT Surface^a

<i>T</i> (K)	presulfidation		relative coking rate to blank	
	DMDS (ppm)	<i>t</i> (h)	initial	asymptotic
1073	500	1	1.32	1.52
1073	750	1	1.18	1.21
1073	1000	1	1.39	1.58
973	750	1	0.61	0.70
1023	750	1	0.61	0.67
1123	750	1	1.11	1.15
1023	750	2	0.68	0.78
1023	750	3	0.89	0.94

^a Cracking conditions: *T* = 1148 K, hexane = 40 g h⁻¹, and steam dilution = 0.5 kg kg⁻¹.

Incoloy 800HT at the optimal conditions results in an enrichment of Cr, Fe, Ni, and Si and a depletion of Mn in the surface layer compared to the Si + O pretreatment. The change in the surface composition caused by presulfidation of a preoxidized Incoloy 800HT surface, i.e., without TEOS pretreatment, has been determined previously.³² Presulfidation of a preoxidized Incoloy 800HT surface at 973 K with 500 ppm DMDS for 0.5 h results in a significant depletion of Mn and a significant enrichment of Fe and Ni compared to preoxidation alone. It can thus be stated that the effect of presulfidation on the “Si + O” surface is the same as on the “O” surface. These results are in agreement with the influence of sulfidation on the composition of the oxide layer that is performed during oxidation of alloys (Fe–25 wt % Cr–20 wt % Ni) as reported by Baxter et al.⁵⁷

In a previous paper,³² the possibility of the formation of metal sulfides from the preoxidized Incoloy 800HT surface has been discussed based on phase diagrams and thermodynamic calculations using EKVICALC.⁴³ Presulfidation of the preoxidized Incoloy 800HT surface at 973–1123 K with 500–1000 ppm DMDS for 0.5–2 h does not lead to the formation of stable metal sulfides; only adsorbed sulfur is present on the surface. The suppressing effect of presulfidation on the coke formation in steam cracking of hexane was attributed to the chemisorbed sulfur, which weakens/blocks the adsorption of hydrocarbon molecules and suppresses the diffusion of metals into the coke layer. In this study, the same method as in the previous paper³² has been used to evaluate the possible presulfidation products from the Si-pretreated followed by preoxidized Incoloy 800HT surface. As for the preoxidized Incoloy 800HT surface, presulfidation of the Si-pretreated followed by preoxidized Incoloy

800HT surface does not lead to the formation of stable metal sulfides; only adsorbed sulfur is present on the surface. In this case, too, the reduced coke formation upon presulfidation can thus be attributed to the presence of adsorbed sulfur at the surface.

3.2.1.2. Influence of Si Pretreatment + Presulfidation + Continuous Addition of DMDS in the CSTR. To evaluate the effect of Si pretreatment + presulfidation + continuous addition of DMDS, a series of tests have been carried out with continuous addition of DMDS (2–80 ppm) in the hexane feed. For the Si pretreatment, TEOS is used. Presulfidation is performed at the optimal conditions as discussed in the previous section, i.e., *T* = 1023 K, H₂O = 20 g h⁻¹, DMDS in H₂O = 750 ppm, and duration = 1 h. Figure 2 shows that application of these additives does not have a significant influence on the conversion of hexane. Compared to the blank run, a slight decrease of the hydrogen yield and a slight increase of the ethylene yield and propylene yield can be noticed. The CO concentration is significantly lower than that observed in the blank run, in the Si-pretreatment run, and in the Si-pretreatment + presulfidation run. Figure 2 clearly indicates that the significantly reduced CO production upon the application of Si pretreatment + presulfidation + continuous addition of 80 ppm DMDS in the CSTR is due to the continuously added DMDS. The reduced production of H₂ and CO and the increased production of ethylene and propylene are in agreement with the effect of continuously added DMDS reported previously,³² indicating that DMDS suppresses steam reforming reactions that lead to the formation of H₂ and CO from hydrocarbons.

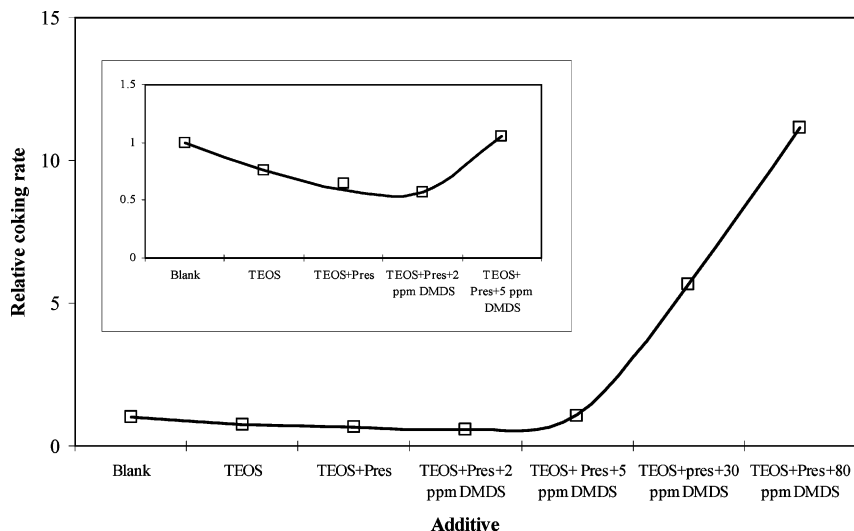


Figure 6. Influence of TEOS and TEOS/DMDS on coke formation during steam cracking of hexane in the CSTR. Presulfidation (optimal conditions): $\text{H}_2\text{O} = 20 \text{ g h}^{-1}$, DMDS in $\text{H}_2\text{O} = 750 \text{ ppm wt}$, $T = 1023 \text{ K}$, and $t = 1 \text{ h}$. Cracking conditions: hexane = 40 g h^{-1} , steam dilution = $0.5 \text{ kg of steam/kg of hexane}$, and $T = 1148 \text{ K}$.

The effect of continuously added DMDS on the asymptotic coking rate on the TEOS-pretreated and presulfided Incoloy 800HT surface during steam cracking of hexane is presented in Figure 6. As can be seen from this figure, continuous addition of 2 ppm DMDS results in a further decrease of 7% of the asymptotic coking on the TEOS-pretreated and presulfided Incoloy 800HT surface. Compared to the blank run, TEOS pretreatment + presulfidation + continuous addition of 2 ppm DMDS results in a decrease of the asymptotic coking rate by 40%. TEOS pretreatment + presulfidation + continuous addition of 5 ppm DMDS gives practically the same coking rate as the blank. When the continuously added DMDS is higher than 5 ppm, the coking rate is higher than that of the blank and increases with increasing amount of continuously added DMDS. The asymptotic coking rate with TEOS pretreatment + presulfidation + continuous addition of 80 ppm DMDS is 11 times higher than that of the blank. From the study on the effect of DMDS on the coke formation during steam cracking of hexane in the CSTR, it can be stated that *the optimal conditions* concerning the coke formation for the combination of Si additives with DMDS are Si pretreatment + presulfidation + continuous addition of 2 ppm DMDS.

The results presented above indicate that the influence of DMDS on the coke formation in the combination of Si and DMDS depends on the application method as well as on the amount of DMDS used. Presulfidation of the Si-pretreated Incoloy 800HT surface (TEOS + PreS) under optimal conditions results in a decrease of 33% of the asymptotic coking rate compared to that on the Si-pretreated Incoloy 800HT surface (TEOS). Continuous addition of 2 ppm wt DMDS further decreases the asymptotic coking rate on the Si-pretreated + presulfided Incoloy 800HT surface by 7%. Continuous addition of higher amounts of DMDS increases the coking rate on the Si-pretreated + presulfided Incoloy 800HT surface. The promotional effect of the continuously added DMDS is in agreement with the observations on presulfided Incoloy 800HT in the absence of Si pretreatment.³²

It is interesting to know if the suppressing effect of Si pretreatment of the Incoloy 800HT on coke formation can still be maintained in the presence of DMDS in the feedstock. This can be determined by comparing the coking rate observed for Si pretreatment + presulfidation + continuous addition of

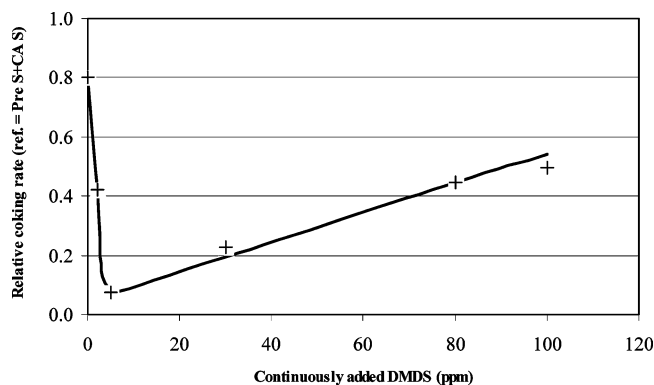
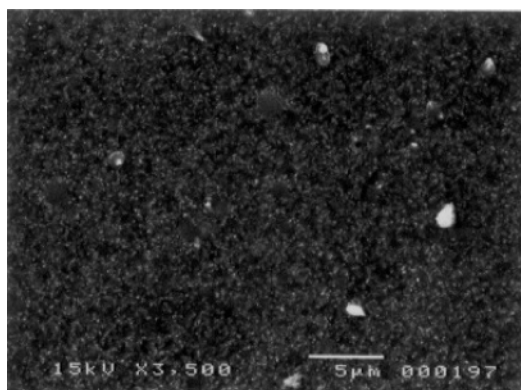


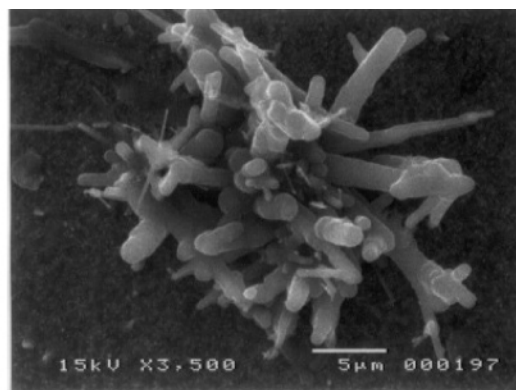
Figure 7. Effect of Si pretreatment on coke deposition in the presence of DMDS during steam cracking of hexane. Presulfidation: optimal conditions, DMDS in $\text{H}_2\text{O} = 750 \text{ ppm wt}$, $\text{H}_2\text{O} = 20 \text{ g h}^{-1}$, $T = 1023 \text{ K}$, and $t = 1 \text{ h}$. Cracking conditions: hexane = 40 g h^{-1} , steam dilution = $0.5 \text{ kg of steam/kg of hexane}$, and $T = 1148 \text{ K}$.

DMDS (Si + PreS + CA S) to that observed for presulfidation + continuous addition of DMDS (PreS + DMDS) which has been reported in the previous paper.³² Taking the coking rate observed on presulfidation followed by continuous addition of DMDS (PreS + CA S) as a reference, the relative coking rate as a function of the amount of continuously added DMDS is shown in Figure 7. The suppressing effect of Si pretreatment on coke formation with the application of DMDS is clearly demonstrated. When no DMDS is added continuously with the feed, it can be seen that silylation of the surface with TEOS prior to the presulfidation treatment results in a decrease of the coking rate of approximately 20% compared to presulfidation only. The magnitude of the effect of silylation depends on the amount of continuously added DMDS. The most pronounced reduction is observed when 5 ppm wt DMDS is added continuously with the feed, where silylation of the surface with TEOS prior to the presulfidation treatment results in reduction of the coking rate of approximately 90% compared to the presulfidation treatment only.

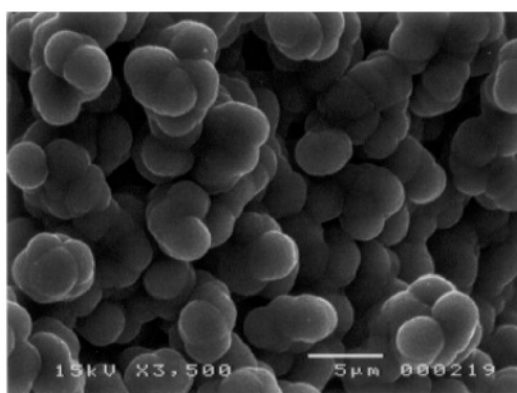
The morphology of the coke deposited at 1148 K on the Incoloy 800HT cylinder with application of TEOS pretreatment + presulfidation + continuous addition of DMDS has been examined using SEM. Representative microphotographs are shown in Figure 8. Figure 8A,B shows the images of the coke formed with the application of Si pretreatment + DMDS at the



A: Globular coke formed with TEOS-pretreatment + presulfidation + continuous addition of 2 ppm DMDS (magnification 3500)



B: Filamentous coke formed with TEOS + pretreatment + continuous addition of 2 ppm DMDS (magnification 3500)



C: Porous coke formed with TEOS pretreatment + presulfidation + continuous addition of 30 ppm DMDS (magnification 3500)

Figure 8. SEM photograph of coke formed with application of TEOS treatment + presulfidation + continuous addition of DMDS during steam cracking of hexane in the CSTR. Cracking conditions: hexane = 40 g h⁻¹, steam dilution = 0.5 kg of steam/kg of hexane, and $T = 1148$ K.

optimal conditions, i.e., Si pretreatment + presulfidation + continuous addition of 2 ppm DMDS. Two kinds of coke can be distinguished: globular coke and needle-shaped filamentous coke. This is the same as observed for the coke formed in the blank run as shown in Figure 1. However, the diameter of the globular coke particles is much smaller. Moreover, the population of the globular coke particles is much less compared to that of the blank. The needle-like coke filaments typically have a diameter of 1–2 μm and a length of 5–15 μm , which is also significantly smaller than that observed for the filamentous coke in the blank run. The changes in the coke morphology are consistent with the reduced coke formation under the optimal application conditions of the Si pretreatment + DMDS. With continuous addition of a higher amount of DMDS (>5 ppm), only a porous type of coke is observed on the sulfided Si-pretreated surface. Figure 8C shows an image of the coke surface with the application of Si pretreatment + presulfidation + continuous addition of 30 ppm DMDS, which is very similar to the coke deposited on the preoxidized and presulfided Incoloy 800HT with continuous addition of a higher amount of DMDS.³² The mechanism explaining the increase in coking rate with continuous addition of the higher amount of DMDS has been discussed in a previous paper.^{2,32} It mainly originates from the interference of HS radical, derived from the decomposition of

DMDS, with the heterogeneous noncatalytic radical reactions responsible for the growth of the coke layer in the asymptotic stage.

The results presented above indicate that continuously adding DMDS results in pronounced changes in the coke deposition on the Incoloy 800HT surface pretreated at different conditions. In an attempt to figure out a possible reason, the metal content in the coke layers deposited on Incoloy 800HT surfaces, which are pretreated at different conditions, i.e., preoxidation (O), preoxidation + presulfidation (O + S), and Si pretreatment + preoxidation + presulfidation (Si + O + S), with continuous addition of 5 ppm DMDS has been determined with EDX and is presented in Table 4. It can be seen that the content of Fe and Ni in the coke deposited on the preoxidized + presulfidized surface is the highest; on these surfaces the higher coking rates are observed. On the Si-pretreated + preoxidized + presulfided surface, the content of Fe and Ni is the lowest; on these surfaces the lower coking rates are observed. Therefore, it seems reasonable to assume that, in the presence of sulfur-containing species in the feed, the rate of coke formation is correlated to the amount of Fe and Ni in the coke layers. The suppressing effect of Si pretreatment on coke formation can then, at least partially, be attributed to the suppression of the diffusion of Fe and Ni into the coke layer.

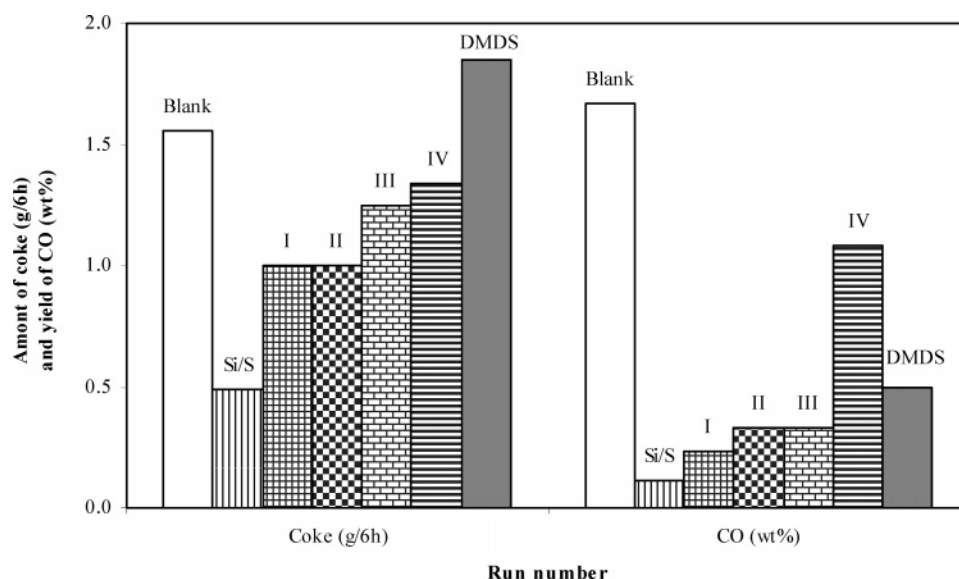


Figure 9. Amount of coke and yield of CO as a function of memory test run number after application of TEOS pretreatment + presulfidation + continuous addition of 2 ppm DMDS in the pilot plant. Cracking conditions: COT = 1443 K, COP = 1.7 bar, and steam dilution = 0.385 kg kg⁻¹. DMDS: pretreatment with 750 ppm DMDS + 2 ppm CA of DMDS (Wang et al.³²).

3.2.2. Influence of Si/S-Containing Additives on the Steam Cracking of Ethane in the Pilot Plant. The influence of one of the Si additives, TEOS, in combination with DMDS on the steam cracking of ethane has been evaluated in the pilot plant. In these tests, the oxidized Incoloy 800HT surface obtained by decoking of a previous run is silylated using TEOS. Thus in the pilot the sequence is 1, decoking; 2, TEOS treatment; and 3, sulfidation. In the CSTR it is 1, TEOS; 2, oxidation; and 3, sulfidation. DMDS is applied at the optimal conditions as determined in the CSTR setup, i.e., presulfidation with 750 ppm DMDS in steam for 1 h followed by continuous addition of 2 ppm DMDS. To be in line with the industrial practice, a temperature profile is set along the cracking coil during TEOS pretreatment and presulfidation. The detailed conditions for the TEOS pretreatment, presulfidation, and cracking in the pilot plant are given in Table 2.

The conversion of ethane, the main product yields, and the amount of coke deposited on the inner surface upon the application of TEOS and DMDS are given in Table 5 (Si/S-I). Application of the Si/S additives at the above-mentioned conditions does not have a significant influence on the conversion of ethane and the main product yields. The amount of coke deposited on the inner surface during 6 h decreases by 69% compared to the blank run. The yield of CO decreases by 94%. If no presulfidation is used, more coke is deposited on the reactor wall (Si/S-II). The amount of coke deposited on the inner surface during 6 h of cracking decreases with 58% compared with the blank run. The CO concentration in the effluent as a function of time on stream is shown in Figure 4. Upon the application of TEOS pretreatment + presulfidation + continuous addition of 2 ppm wt DMDS (Si/S-I), the CO spike appearing at the beginning of the blank run completely disappears. The CO concentration in the effluent remains almost constant over the entire cracking run.

After the application of TEOS pretreatment + presulfidation + continuous addition of 2 ppm wt DMDS, four memory test runs are carried to evaluate the durability of the effect of the additives. The conversion of ethane and the main product yields are given in Table 5 (Si/S-M-I). No significant change in the conversion of ethane and the main product yields is noticed compared to the blank. Figure 4 shows that, similar to the additive run Si/S-I, no CO spike appears at the beginning of the run and that

Table 7. Characteristics of the Ethane Furnace and Operating Conditions

Furnace	
length (m)	9.304
height (m)	13.450
depth (m)	2.100
thickness of refractory material (m)	0.230
thickness of insulation material (m)	0.050
number of burners	128
Operating Conditions	
total hydrocarbon flow rate (ton h ⁻¹)	14
inlet temperature (K)	873
process gas outlet pressure (MPa)	0.18
steam dilution (kg of steam/kg of ethane)	0.35
Cracking Coil	
number of reactors	4
type	swaged coils
passes	8
total length	100.960
internal diameter (m)	
passes 1–6	0.124
passes 7 and 8	0.136
external diameter (m)	
passes 1–6	0.140
passes 7 and 8	0.152
tube wall thickness (m)	0.008

the CO production remains low and stable over the entire cracking run. This behavior of CO production is maintained for three memory test runs, though the yield of CO increases slightly with increasing run number. The amount of coke deposited on the cracking coil during 6 h cracking of ethane and the yield of CO as a function of the number of the memory test run are shown in Figure 9. The amount of coke deposited and the CO yield increase with increasing number of the memory test run. After four coking/decoking cycles, the amount of coke is still 14% lower than the value observed for the blank, while the CO yield is still 35% lower.

The pilot plant runs with Si-containing compounds can also be compared with the current industrial practice, i.e., presulfiding + continuous addition of DMDS.¹ Figure 9 also contains the results reported by Wang et al.³² (DMDS) for presulfidation with DMDS and continuous addition of 2 ppm DMDS. The presulfidation conditions and cracking conditions in Wang et al.³² are identical to those used in this study. Pretreatment with

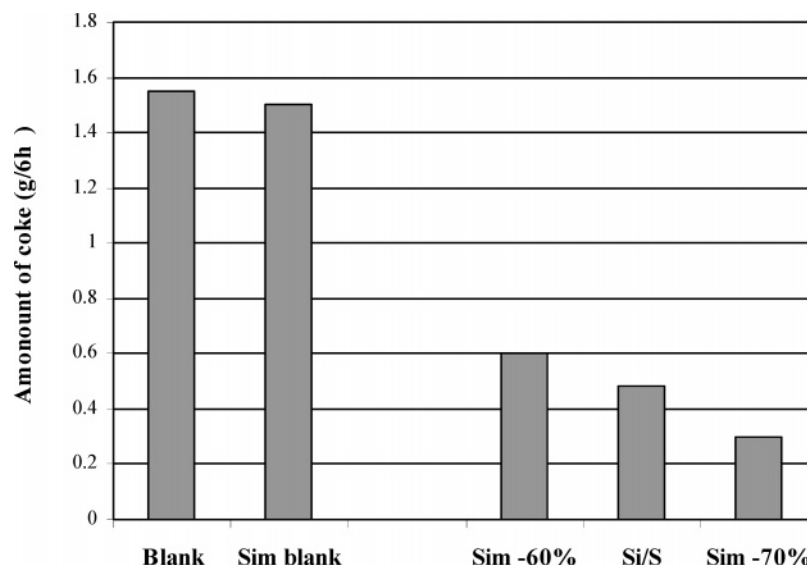


Figure 10. Comparison between simulated and experimentally obtained amounts of coke obtained in the pilot plant with ethane cracking before and after the application of TEOS pretreatment + presulfidation + continuous addition of 2 ppm DMDS in the pilot plant.

DMDS only resulted in higher CO yields compared to the values observed when only TEOS is used for pretreatment. Compared to the blank runs, a decrease of 65% is observed with DMDS pretreatment while the decrease amounts to 90% with TEOS pretreatment. For coke formation it has been shown previously^{2,31,32} that the combination of pretreatment with DMDS and continuous addition of DMDS does not lead to a decrease of the amount of coke formed in the reactor. Figure 9 shows that presulfiding + continuous addition of 2 ppm DMDS (DMDS) leads to an increase of the amount of coke formed of 25%. Continuous addition of higher amounts of DMDS results in a drastic increase of the amount of coke.³² This shows that the combination of Si-containing additives and continuous addition of DMDS is beneficial compared to the currently used industrial practice for suppressing coke.

3.2.3. Simulation of the Run Length of an Industrial Ethane Cracker with the Application of the Si/S Additives. To evaluate the effect of the Si/S additives on the coke formation in an industrial ethane cracker, simulation of the coke formation and run length has been performed using the simulation packages available at the Laboratorium voor Petrochemische Techniek, Universiteit Gent.^{60,61} The characteristics of the furnace and the detailed operation conditions of the cracking coils are given in Table 7. The furnace is a rectangular firebox. Its walls are made of refractory material. The heat required for the thermal cracking of ethane is provided by 128 radiation burners which are located in the side walls of the furnace on both sides of the coils. The burners are arranged in eight rows, and each row has eight burners. In the center of the furnace, four coils are suspended side by side. Each coil makes eight passes through the furnace. The internal diameter of the coils in the first six passes is 0.14 m; in the last two passes it is 0.152 m. The cracking coils are made of Incoloy 800H (31 Ni/21 Cr). The total flow rate of ethane is 14 tons h⁻¹. The inlet temperature of the process gas is 873 K. The outlet pressure is 0.18 MPa. During cracking a steam dilution of 0.35 kg of steam/kg of ethane is applied. The semiempirical coking model of Plehiers⁵⁸ is used for simulating the coking rate. The coking rate is then calculated via the following equation:

$$R_C = A_{C_2H_4} \exp\left(-\frac{E_{a,C_2H_4}}{RT}\right) + A_{C_3H_6} \exp\left(-\frac{E_{a,C_3H_6}}{RT}\right) \quad (5)$$

The coking model of Plehiers,⁵⁸ coupled to a one-dimensional reactor model, has been used to predict the run length of several industrial-cracking units,^{59–61} showing a good agreement between industrial and simulated results. Also, for the amount of coke obtained in the pilot plant a good agreement is obtained between simulated and experimental data. As shown in Figure 10, 1.57 g of coke is formed during 6 h of ethane cracking in the pilot plant reactor under the conditions specified in Table 2. Simulation of ethane cracking in the pilot plant under these fixed conditions during 6 h results in 1.51 g of coke, as shown in Figure 10. Assuming that the effect of the Si/S additives is temperature independent, the influence of the use of the additives on the amount of coke deposited can be simulated by multiplying the preexponential factors in eq 5 with a reduction coefficient. Figure 10 shows the simulated amount of coke assuming a uniform reduction of the coking rate of 60% and 70%. The simulation results indicate that a uniform reduction of the coking rate by approximately 65% corresponds to the amount of coke observed in the pilot setup upon Si/S pretreatment followed by a continuous addition of 2 ppm of DMDS with the ethane feed. These results can be extrapolated to estimate the maximal achievable run length in an industrial ethane furnace pretreated and operated under the same conditions. The run length as a function of the uniform reduction of the coking rate is given in Figure 11. A given reduction in the coking rate results in a more than proportional increase of the run length. For instance, a reduction in the coking rate of 50% increases the run length from 45 to 98 days; the increase in run length amounts to 115%. Application of the Si/S-containing additives at the optimal conditions in the pilot plant setup decreases the coke formation by approximately 65%. Assuming that the same reduction of the coking rate can be obtained in an industrial ethane cracker, its run length can reach 150 days, i.e., an increase of 233%. Note that these simulation results are obtained if the decrease in coking rate is assumed to be temperature independent.

4. Conclusions

The influence of the combination of two Si-containing additives, BTMS and TEOS, with DMDS on the steam cracking of hexane has been evaluated in a CSTR setup. Application of the Si additives does not cause a significant change in the

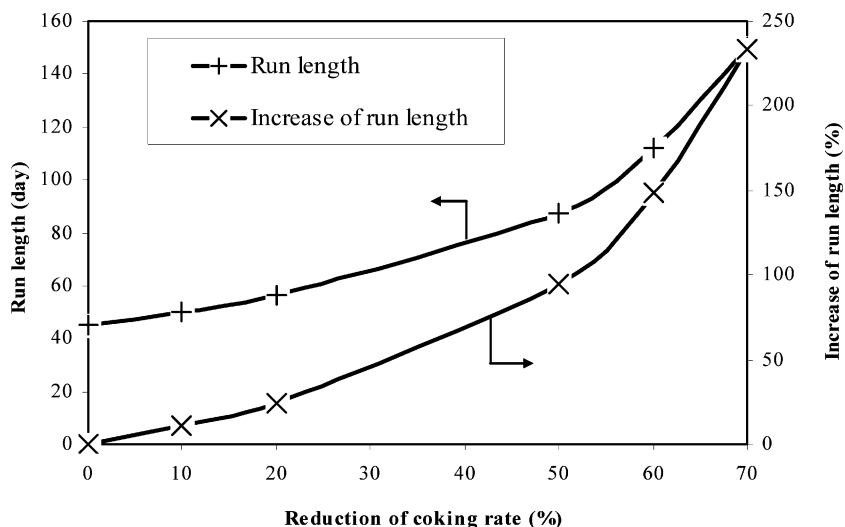


Figure 11. Simulated run length of an industrial ethane furnace as a function of the uniform reduction of coke formation. Cracking conditions: COP = 0.18 MPa, steam dilution = 0.35 kg of steam/kg of ethane, and COT = 1103 K.

conversion of hexane and the product selectivities. For the combination of Si pretreatment with presulfidation, the coke formation during the steam cracking of hexane is found to be affected by the amount of DMDS, the temperature, and the duration of the presulfidation. Optimal conditions for presulfidation are $T = 1023$ K, $\text{H}_2\text{O} = 20$ g h⁻¹, DMDS in $\text{H}_2\text{O} = 750$ ppm wt, and duration = 1 h. Under these optimal presulfidation conditions, coke deposition is minimal and the combination of Si pretreatment + presulfidation results in a decrease in the rate of coke formation of 32%. The influence of continuously added DMDS on the coke deposition on the Si-pretreated + presulfided Incoloy 800HT surface depends on the amount of DMDS used. Continuous addition of 2 ppm wt DMDS further decreases the rate of coke formation to 40%, while adding higher amounts of DMDS results in a significant increase in the coke formation but in a decrease in the CO production. A comparison of the coking rate between Si pretreatment + presulfidation + continuous addition of DMDS and presulfidation + continuous addition of DMDS indicates that Si pretreatment is also effective in reducing coke formation in the presence of sulfur. The suppressing effect of the Si pretreatment via the dipping method on the coke formation seems not to originate from the formation of a silica layer, but is related to a change in the composition of the surface oxide layer of the cylinder.

To confirm the suppressing effect observed in the CSTR setup, the influence of the combination of Si/S-containing additives on the steam cracking of ethane is evaluated in the pilot plant. Application of the Si/S-containing additives does not cause a significant change in the conversion of ethane and the product selectivities. Si pretreatment + presulfidation + continuous addition of 2 ppm wt DMDS reduces the coke formation by approximately 70% and the CO production by more than 90%. The Si/S-containing additives show a memory effect. After four coking/decoking cycles, the suppressing effect on coke formation still amounts to 14% while on CO production it still amounts to 35%. The suppressing effect of the Si pretreatment in the pilot plant is most likely caused by the deposition of a thin layer of SiO_2 on the inner surface of the reactor acting as a physical barrier and preventing direct contact between the process gas stream and the alloy.

Simulation of the run length for an industrial ethane cracker indicates that the run length can at least be doubled if the reduction of the coking rate reaches 65%, as is observed in the pilot plant tests. The use of a combination of Si- and S-

containing compounds offers a promising method to effectively reduce coke formation and CO production in steam cracking of hydrocarbons.

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