

SUPPRESSION OF COKE FORMATION IN THE STEAM CRACKING OF ALKANES: ETHANE AND PROPANE

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The effects of an H_2PtCl_6 additive on the rate of formation of coke deposits on quartz and Incoloy surfaces were investigated in the steam cracking of ethane and propane in a continuous flow thermogravimetric analyzer (TGA). The TGA operating conditions were: 1 atm pressure, 820-845°C temperature range, about 1.5 s reaction time, and a steam to hydrocarbon molar ratio of about 2. Specific coke formation rates consistently decreased in the presence of the additive, both for ethane and propane pyrolysis. For example, in ethane pyrolysis the specific coke formation rate on the quartz surface at 830°C decreased from 0.34 $\mu\text{g}/\text{cm}^2\text{-min}$ in the absence of the additive to 0.089 $\mu\text{g}/\text{cm}^2\text{-min}$ in the presence of additive, representing an improvement by a factor of about 4 in coking rates. On the Incoloy surface, coke formation decreased from 0.98 $\mu\text{g}/\text{cm}^2\text{-min}$ to 0.38 $\mu\text{g}/\text{cm}^2\text{-min}$. For the case of propane pyrolysis at 830°C, coke formation rate decreased from 0.51 $\mu\text{g}/\text{cm}^2\text{-min}$ to 0.33 $\mu\text{g}/\text{cm}^2\text{-min}$ on the quartz surface and from 1.9 $\mu\text{g}/\text{cm}^2\text{-min}$ to 1.0 $\mu\text{g}/\text{cm}^2\text{-min}$ on the Incoloy surface.

1. Introduction

Ethylene is one of the most important building blocks of synthetic, organic chemistry¹ and it is used in the manufacture of polyethylene and other products. Ethylene production rate has steadily increased over the years from 29 million lbs in 1985 to 46.7 million lbs in 1995. The ethylene production today is based predominately on the steam cracking or pyrolysis of alkanes, such as ethane, propane and butane, as well as heavier feedstocks such as naphtha and gas oil².

The steam cracking of a feedstock is accomplished in the coils of a pyrolysis furnace followed by quenching of the gas in a heat exchanger or the transfer line exchanger. Coke is an undesirable product of steam cracking. Due to its cumulative nature, coke deposits build up on reactor walls and influence reactor performance in a number of ways. First, due to coke deposition, the surface temperature of the coils increases, which adversely affects the service life of the coil and makes it impossible to obtain normal pyrolysis temperatures in the reactor. Secondly, pressure drops increase due to the reduction of the inner diameter of the coil upon coking.

Third, coking may lead to corrosion of the coil due to carbonization. As a consequence of these factors, decoking of the reactor coils has to be carried out periodically, resulting in a loss of production and in an increase in manufacturing costs. Typically in ethane cracking, commercial reactors must be decoked every 20-60 days³. Previous laboratory experiments were conducted to study coke formation during the cracking and steam cracking of ethane and propane. Sundaram *et al.*³ studied the thermal cracking of ethane in a nitrogen matrix within a temperature range of 750-870°C, in a mixed reactor. Major products reported were ethylene, methane, C₄H₆, and C₅+. The results indicated the gas phase decomposition to be the first order in ethane concentration with an apparent activation energy of 54.0 kcal/mol in agreement with previous studies in a tubular pilot reactor⁴. Similar results were reported more recently by Froment⁵ for the steam cracking of ethane. Coke was deposited on an Inconel 600 coupon suspended inside the reactor to the arm of an electrobalance. The rate of formation of coke was found to be time dependent, starting initially at a faster rate and reaching an asymptotic value later in the run. The initial fast coke formation rate was attributed to catalytic wall effects. Once the coke layer is deposited on the coupon, the rate reaches its asymptotic value corresponding to coke deposition on coke. The estimated activation energy for coke formation, based on a kinetic analysis of a reaction model, was in the range of 28.3-49.9 kcal/mole. Gas composition measurements also indicated the rapid formation rate of CO early in the experiments, which leveled off to an asymptotic value following the coverage of the metal surface by coke. Initial CO production was proposed to be due to metal catalyzed oxidation of hydrocarbon moieties on reactor walls, and subsequent CO formation was attributed to the steam gasification of carbon. These studies also indicated that higher steam dilutions decrease coke formation rates.

The decomposition of propane in a nitrogen matrix was studied by Sunderam and Froment⁶ in a mixed reactor in the temperature range of 720-870°C. Major products reported were ethylene, methane, and propene. The disappearance of propane was found to be the first order in propane concentration with an activation energy of 49.0 kcal/mol. This is in agreement with the results of Van Damme *et al.*⁷ and Froment⁵ in the steam cracking of propane. The activation energy for coke formation was estimated to be 75.0 kcal/mole, again based on the kinetic analysis of a reaction model. Coke formation on Fe-Cr-Ni alloys in the steam pyrolysis of propane was also studied by Trimm *et al.*⁸ using a microbalance reactor. These investigators reported an activation energy for coke formation of about 70 kcal/mole, consistent with the results of Sundaram and Froment⁶.

Crynes and Crynes⁹ also studied the formation of coke during the pyrolysis of light alkanes on Incoloy 800 coupons in a flow reactor. Temperature was maintained at 700°C by means of an electric furnace. They studied coking during the pyrolysis of methane, ethane, ethene, propane, propene, and isobutane. They found the following order for coking on the coupon: ethane<ethene< propene<propane<isobutane, with no coke deposition observed for methane under the experimental conditions. The effects of reactor surfaces on coke deposition rates during the pyrolysis of propane has been studied extensively by Renjun¹⁰ in an electrobalance reactor at 850°C. The order of increasing coke deposition rates was found to be nickel>stainless>quartz. High coking rates were also observed early on in the experiments, which later reached an asymptotic value upon surface coverage by coke.

In related studies, Jackson *et al.*^{11,12} studied coke formation on a series of FeNi-Cr alloys as well as other materials in the steam cracking of propylene and hydrogen using a microbalance reactor. The effects of alloy composition on coke formation and gasification rates were studied.

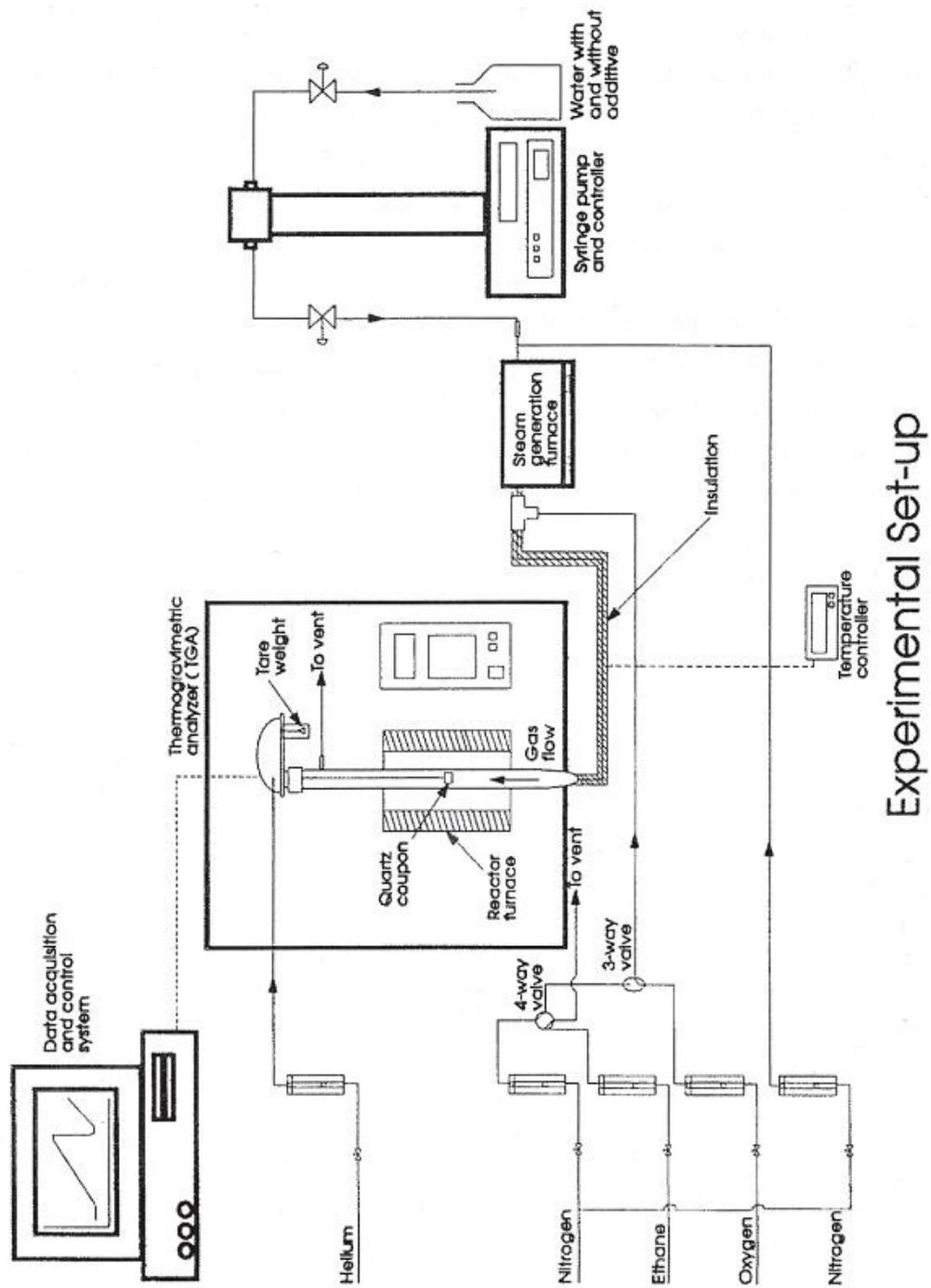
At present, three mechanisms have been proposed to account for coke formation in hydrocarbon pyrolysis in industrial and laboratory reactors: (1) Coke formation via surface-catalyzed reactions in which, for example, metal carbides have been proposed to be intermediates¹⁻¹³. The resulting coke is filamentous and contains 1-2 wt% metal; the metals are positioned primarily at the tips of the filaments. Filamentous coke has also been produced at low temperatures. This can be one of the coke formation mechanisms on metal reactors' surfaces. (2) Coke has also been proposed to form via polycyclic aromatic hydrocarbons (PAH) in the gas phase (e.g., Wang and Frenklach¹⁴, and Gargurevich¹⁵ studied chemical paths of coke in fuel-rich combustion), their nucleation and condensation into tar droplets followed by adsorption on surfaces where the tar proceeds to dehydrogenate into coke. This mechanism generally results in film or globular coke formation¹⁶. (3) Coke can also grow directly through the reactions of small gas phase species with sites on the coke surface. These species are likely to be acetylene or other olefins, butadiene, and free radicals such as methyl, ethyl, vinyl, phenyl or benzyl radicals. This mechanism should be favored by higher temperatures and with higher concentrations of acetylene in the gas phase (e.g., Marinov¹⁷ discussed surface growth mechanisms of soot particles in combustion).

The development of coke inhibitors have paralleled the various coke formation mechanisms described. The techniques commonly used today to reduce coke formation include the pretreatment of feedstocks, changing the materials of construction of the reactor, altering the surface chemistry of the reactor, or the addition of coke inhibitors to the feedstock^{10,18}. The development and use of additives appears to be the most effective and practical method. Coke inhibitors reported in the literature include salts of alkali metals or alkali-earth metals at parts per million (ppm) quantities, which are believed to promote coke gasification by steam. In addition, the use of organic polysiloxane compounds in ppm quantities have been shown to reduce the adhesion of coke to the coil walls. Sulfur compounds have also been used widely to suppress coke formation, especially early on in the pyrolysis process, by passivating metal surfaces^{8,10}. Compounds containing tin, antimony, copper, phosphorous and chromium were also reported to have a beneficial effect in suppressing coke formation¹⁰.

In this communication, we report on the effects of about 1 ppm H₂PtCl₆ additive in water on coke formation in the steam pyrolysis of ethane and propane. This was accomplished by comparing the amounts and rates of coke production on quartz and Incoloy surfaces both in the absence and presence of the additive.

2. Experimental Section

The experimental apparatus used to study the formation of coke during the steam cracking of ethane and propane is illustrated in Figure 1. The apparatus is a modified version of the setup used previously in the pyrolysis and oxidative pyrolysis of methane and methyl chloride¹⁹. The main component of the experimental system is a Cahn 131 thermogravimetric analyzer (TGA, Madison, WI) that has a detection sensitivity of 1 μg . The system has an electronic microbalance which continuously measures and records the mass loss or gain of a substrate material, or coupon, which is suspended from the balance by means of a 0.0127 cm diameter platinum hang-down wire. The furnace temperature profile and coupon mass data are acquired and stored by the data acquisition and control system. The data acquisition hardware consists of an IBM compatible PC and software provided by Cahn Systems. The software allows for the operation of the furnace for any temperature time history. Two coupons were used in the experiments; quartz (SiO_2) and Incoloy (Fe 46.6%, Ni 30.3%, Cr 20.5%, Mn 0.46%, Ti 0.57%, Cu 0.054%, Al 0.42%, C 0.065%, Si 0.60%, S 0.001%). The coupon dimensions were about 2 cm wide x 2 cm long x 0.1 cm thick. The coupons were centrally located inside a 3.5 cm internal diameter x 32.5 cm long quartz reactor that was vertically placed inside a single zone electrical furnace. The heating elements inside the furnace span a distance of about 15 cm, thereby



Experimental Set-up

Figure 1 Sketch of the experimental facility.

allowing the establishment of a near isothermal central zone of about 2 cm in length, where the coupon was placed¹⁹. Deionized (DI) water or water containing 1 ppm H₂PtCl₆ additive (ATG, Monrovia, CA) was pumped using a high precision metering syringe pump (ISCO-2600 with a Series D Controller, Lincoln, NE), and was vaporized in an electric furnace maintained at 400°C. Nitrogen gas was introduced into the liquid at the upstream of the steam furnace as a gas carrier. The reactant gases consisting of ethane or propane, and some additional nitrogen carrier gas were then mixed with the steam and transported to the reactor through electrically heated lines. All gas flows were regulated by high accuracy rotameters (Matheson, Cucamonga, CA) that were calibrated before the experiments. The weighing components of the TGA were protected from the reaction products by passing helium purge gas through the chamber. The gases used were obtained from Matheson (Cucamonga, CA), unless otherwise indicated, and had the following stated purities: He: 99.99 %, C₂H₆: 99.9%, C₃H₈: 99.99%, N₂: 99.999%, and O₂: 99.9% (Liquid Air Co.).

All the experiments were conducted at an atm pressure of 1 for a 1 hour total reaction time. Before each run, the reactor was purged with N₂ for about 10 min and then decoked using 15% O₂ (balance N₂) mixture to ensure that the reactor walls and the coupon were coke free. This was accomplished by visually observing the appearance of the coupon through an observation hole in the furnace and by monitoring the weight of the coupon during the decoking process. If the appearance of the coupon was transparent and nonluminous (for the quartz coupon only), and its weight did not decrease with time, the coupon was assumed to be coke free. It should be noted that some coke remains on the hangdown wire even after the decoking process. This systematically increases the apparent weight of the coupon as measured by the TGA during one of the experiments. The reactor was again purged with N₂ for about 10 min, after which the hydrocarbon reactants and steam were introduced. The primary reason, for the nitrogen purge before and after the decoking experiments, was to minimize the accumulation of potentially explosive mixtures in the reactor. Each run was repeated at least five times to ensure reproducibility and to assess the range of experimental errors associated with the experiments.

3. Results and Discussion

There are several issues regarding the experimental conditions used and the analysis of experimental data that must be discussed first. Since the TGA had a sensitivity limit on a microgram level, it was necessary to determine the optimum gas flow rates that did not result in excessive fluid dynamic noise, yet allow the acquisition of reliable coking data over the range of concentrations and temperatures to be used during the experiments. Following the initial scoping studies, a total gas flow rate of about 2.5 cm³/s, measured in STP, was determined to be suitable. Higher flow rates led to the establishment of undesirable flow patterns in the reactor that cause lateral movement of the hangdown wire and result in its contact with the baffle inside the reactor. Note that at 2.5 cm³/s, the flow regime in the reactor would be laminar and corresponds to a nominal residence time of 15 s and about 1.5 s to cross the quartz coupon. This residence time was determined by taking into account the volume occupied by the baffle²⁰.

Overall reactant conversions, measured separately by gas chromatography at the exit of the reactor, were generally in the range 2-5%. However, because the quartz coupon occupied a small fraction of the reactor volume, it should be subjected to a nearly constant gas composition along the flow direction due to the differential conversion of the reactants within the 1.5 s reaction time. Consequently, one would expect uniform coke layer formation along the coupon if

diffusion limitations were also absent. If diffusion limitations were present, the variation of the boundary layer thickness along the coupon would lead to non-uniform coke deposition. Coke formation appeared to be uniform along the coupon, as determined by SEM in previous studies¹⁹, indicative of the absence of transport limitations under the experimental conditions investigated.

The following pre-reaction flow rates and temperature ranges were used: (1). Ethane Experiments: C₂H₆ 0.714 cc/s, H₂O 1.45 cc/s, N₂ 1.22 cc/s, temperature range 830-845°C; (2). Propane experiments: C₃H₈ 0.75 cc/s, H₂O 1.48 cc/s, N₂ 1.24 cc/s, temperature range 820-830°C. Coke formation rates were determined at these fixed gas compositions but over a range of temperatures both in the absence and presence of the additive. The temperature ranges studied varied for different mixtures because of differences in the onset of decomposition of C₂H₆ and C₃H₈. Consequently, all the experiments conducted did not correspond to identical residence times because of differences in gas velocities caused by different temperatures. In addition, changes in the number of moles caused by the reaction process would also alter residence times. These issues, however, should have a relatively small effect on the results presented here. For example, differences in reactor temperatures should introduce a variation in residence times no larger than about 2.3% between the lowest and highest temperature experiments, i.e., $100 \times (840-820)/(820+273) = 2.3\%$. This uncertainty is well below the measurement errors with these types of experiments. Similarly, percent change in the total number of moles across the coupon would be extremely small due to small conversions involved and the presence of steam and nitrogen dilution.

Figure 2 is representative of the raw data obtained by the TGA using the quartz coupon for the steam pyrolysis of ethane. The results obtained using the propane feedstock and the Incoloy coupon were similar, thus will not be presented. The reproducibility of the experiments was excellent, well within 10% from one set to another, provided the first coking cycle is excluded. A close inspection of the individual experiments show that coking rates, i.e. the slope of the weight vs time lines, were generally initially higher, but level off to an approximately constant value. The latter rate, corrected for the baseline shift due to the loss or gain of coke on the hang-down wire after the decoking process, has been designated as the coke formation rate, R_{TGA} , in $\mu\text{g}/\text{min}$ units. High initial coking rates were consistent with the results of other investigators^{6, 7, 19, 21}. There can be several reasons for the high initial coking rates observed. First, the bare, carbon free, coupon surface may indeed have a higher propensity for coke formation than a coked surface. Second, the surface temperature of the bare coupon may be higher than the coked surface due to its lower emissivity and radiation effects. While a worthwhile endeavor, the study of the early coke formation rates was not the focus of this investigation.

An important issue that must also be addressed is the physical meaning of the weight change measured by the TGA. As evident from the experimental system previously described, the TGA simply measures the weight change experienced by the coupon. The weight change can be affected directly by molecular events, e.g. chemical reactions that result in the growth and/or destruction of molecular entities on the surface, or by macroscopic events, such as soot (tar particle collisions with the coupon). Clearly, TGA measurements cannot distinguish between these two type of mechanisms. Consequently, these lumped sets of events, as detected by TGA has been referred to as the coke formation process.

The specific coke formation rate (r_c , $\mu\text{g}/\text{cm}^2\text{-min}$) was then determined from the equation:

$$r_c = R_{\text{TGA}}/A, \quad (1)$$

where A is the surface area of the coupon. The specific coke formation rate can also be represented by the following phenomenological expression:

$$r_c = k_0 \exp(-E/RT)f(C) \mu\text{g}/\text{cm}^2 - \text{min}, \quad (2)$$

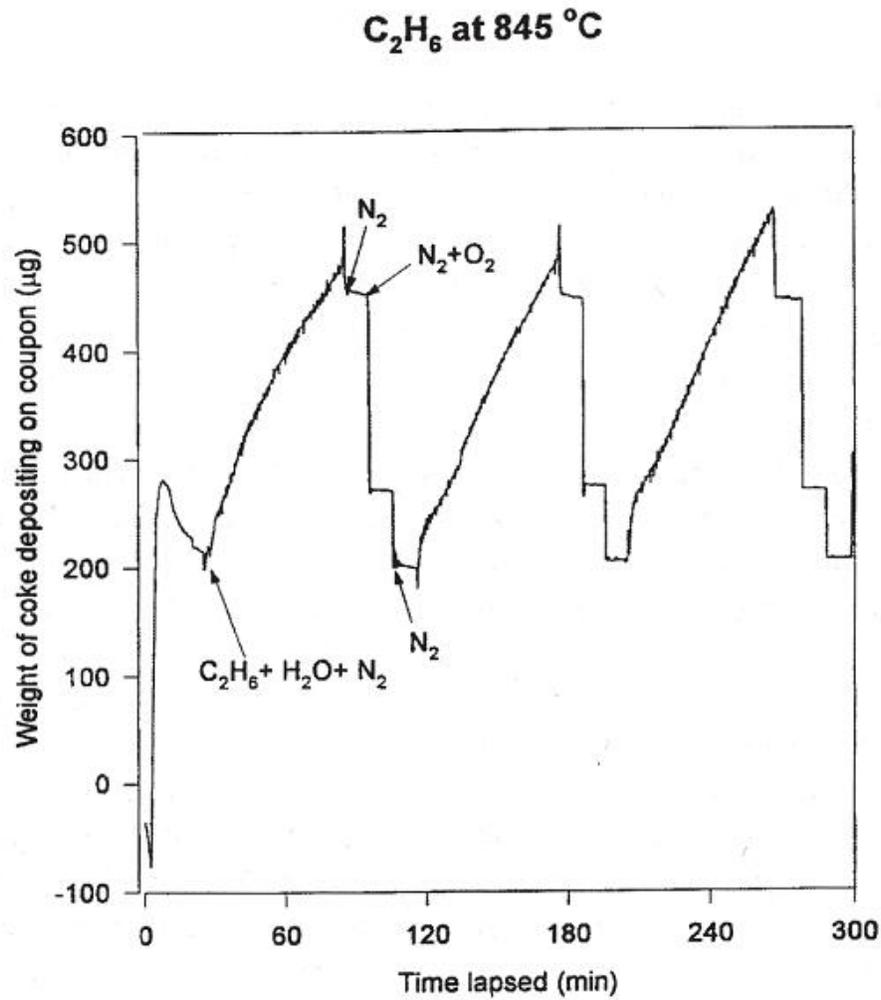


Figure 2 Representative raw data for ethane steam pyrolysis.

where k_0 is the specific rate constant for coke formation, E is the apparent activation energy, and $f(C)$ is a functional dependency of coke formation on the composition of the gas phase. This type of a rate expression has often been used to model coke formation kinetics (e.g., Froment⁵, Sundaram and Froment⁶, Tran and Senkan¹⁹, Renjun²¹). As evident from the above expression, under differential conversions that should be observed along the coupons, $f(C)$ would be nearly constant. The determination of $f(C)$ was not the objective of this experiment.

In Figure 3, the weight of coke deposited on the quartz coupon are presented as a function of on-stream time for the steam pyrolysis of ethane at 830 and 845°C, to illustrate the effects of the additive. The specific coke formation rates, determined from the slopes of these lines by the least squares fit method and the surface area of the coupons, are presented in Table I. The amount of coke deposited on the coupon steadily increased with increasing time and reaction temperature; these results are totally consistent with previous studies^{5, 19, 21}. What is important, however, is the significant and consistent reduction in coke deposition in the presence of the additive in the feedstream. For example, at 830°C, coke formation rate decreased from a high value of 0.34 $\mu\text{g}/\text{cm}^2\text{-min}$ in the absence of the additive to a low value of 0.089 $\mu\text{g}/\text{cm}^2\text{-min}$, representing a 3.8 factor decrease in coke formation in the presence of the additive. Similarly, at 845°C, the coke formation rate decreased from 0.49 to 0.23 $\mu\text{g}/\text{cm}^2\text{-min}$, corresponding to a 2.2 factor improvement.

Significantly more coke formation was observed in the pyrolysis of C_3H_8 than C_2H_6 at the same reaction temperature (Table 1). The result is consistent with previous studies⁹ and with the lower C-C bond dissociation energy of C_3H_8 ²². As evident from the results in Table I, the additive also significantly decreased the rate of coke deposition on the quartz coupon in propane pyrolysis. It is interesting to note that the effectiveness of the additive in suppressing coke formation decreased with increasing temperature. The result is consistent with a mechanism of coke suppression by the additive through the modification of surface reactions. Increasing temperatures increase the relative importance of gas-phase-induced coke formation. One would not expect to see a significant change in the coke suppression behavior of the additive if the mechanism of action was through the modification of gas phase reactions.

Coke formation during the steam pyrolysis of ethane

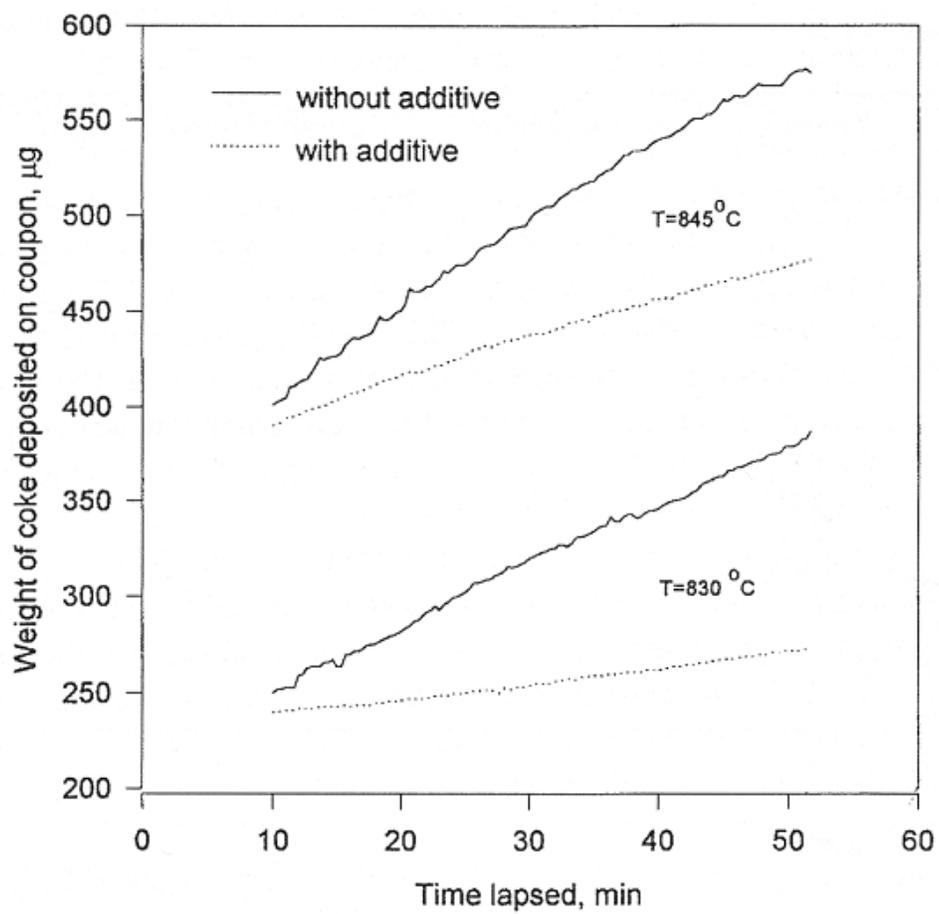


Figure 3 Effects of the additive on coke formation in the steam pyrolysis of ethane at 830° and 845°C.

Table I Specific Coke Formation Rate (r_c , $\mu\text{g}/\text{cm}^2\text{-min}$)

Quartz Surface				
Reactant	Temperature	$r_{c,n}$ (no additive)	$r_{c,a}$ (with additive)	$r_{c,n}/r_{c,a}$
Ethane	830°C	0.34	0.089	3.8
	840°C	-	0.16	-
	845°C	0.49	0.23	2.2
	E(kcal/mole)	59.	150.	
Propane	820°C	0.44	0.19	2.3
	825°C	-	0.27	-
	830°C	0.51	0.33	1.6
	E(kcal/mole)			
Incoloy Surface				
Ethane	830°C	0.98	0.38	2.6
	835°C	1.3	0.56	2.3
	840°C	1.6	0.88	1.9
	E (kcal/mole)	130.	200.	
Propane	830°C	1.5	0.58	2.5
	830°C	1.7	0.78	2.2
	830°C	1.9	1.03	1.9
	D (kcal/mole)	64.	140.	

Coke formation rates were also significantly higher on Incoloy surfaces than on quartz (Table 1). Results are consistent with previous studies¹⁰. In fact, for ethane pyrolysis, the experiments at 845°C had to be abandoned because of excessive coke formation. The coking rates on Incoloy surfaces also followed a pattern similar to the quartz surface. That is, the rate of coke formation was higher in propane pyrolysis compared to ethane. The additive consistently suppressed coke formation under all the conditions investigated, and the effectiveness of the additive diminished

at higher temperatures.

The Arrhenius plots (Figure 4), for the specific coke formation rate (r_c) in the steam pyrolysis of C_2H_6 are presented in accordance with equation (2). For the quartz surface, the slope of these lines which correspond to apparent activation energies, were 59.0 and 150 kcal/mole, without and with the additive, respectively. Activation energies were 130 and 200 kcal/mole, respectively, for the Incoloy surfaces. The change in apparent activation energies suggests that the additive must have altered the rate limiting steps leading to the deposition and/or gasification of coke.

The activation energies determined were significantly high, which is indicative of the absence of transport limitations. If coke formation rates were limited by transport phenomena, the measurements would be less sensitive to temperature and the apparent activation energies would have been in the range 1-5 kcal/mole. An upper limit to coke formation rates was also determined using the wall collision frequency at the process conditions. The wall collision frequency based (diffusion limited) coke deposition rate was calculated using the following relationship²³:

$$r_w = 1/4 C_{C_2H_6} (8RTM_{C_2H_6}/\pi)^{1/2} \text{ gm/cm}^2 - \text{min}, \quad (3)$$

where $C_{C_2H_6}$ is the molar concentration of ethane, R the gas constant, T temperature, and $M_{C_2H_6}$ the molecular weight of ethane. These calculations indicated that coke formation rates measured by TGA (r_c) were several orders of magnitude below the maximum limit set by the collision theory (r_w).

The apparent activation energy of 59.0 kcal/mole for coke formation on quartz surfaces is consistent with the results of Sundaram *et al*³. It is also considerably lower than the C-C bond dissociation energy of C_2H_6 (90 kcal/mole) and this is suggestive of the importance of free radical reactions leading to coke or coke

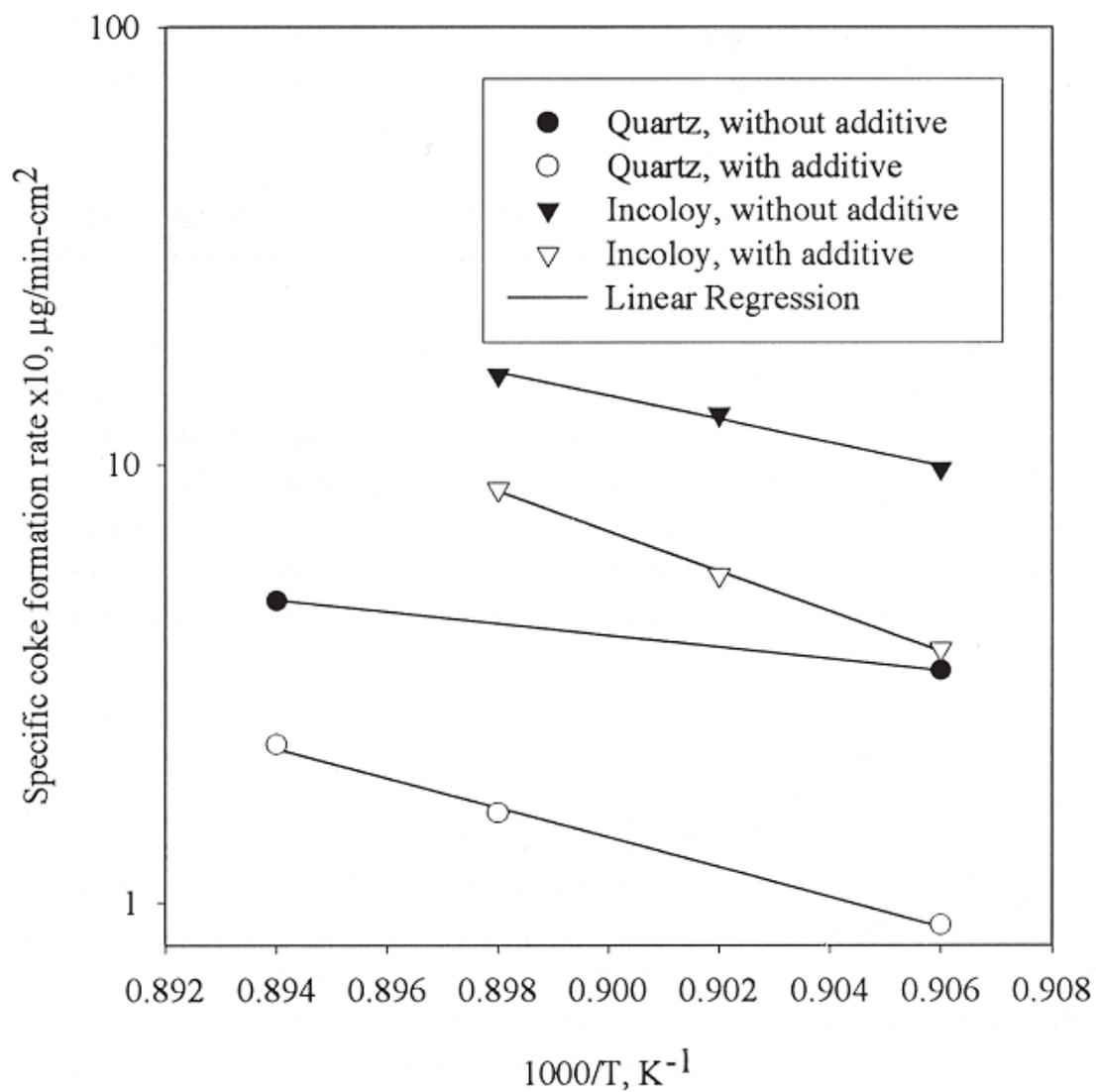


Figure 4 Arrhenius plots for the rate of formation of coke in the steam pyrolysis of ethane on quartz and incoloy surfaces.

precursors in the gas phase. On the other hand, the activation energy of 149 kcal/mole is substantially higher than the C-C bond dissociation energy, and indicates autocatalysis as the mechanism for coke deposition¹⁸. Under autocatalytic conditions, the coke formation measured by the TGA would be the result of a complex sequence of chemical and physical events influenced by surfaces and cannot simply be related to the unimolecular decomposition rate of C₂H₆ in the gas phase. The high activation energies of 130 and 200 kcal/mole observed on Incoloy surfaces suggest the autocatalytic deposition of coke both in the absence and presence of the additive. Again, the observed differences in activation energies indicate changes in the rate determining steps, in the presence of the additive.

Arrhenius plots for the specific coke formation rates in the steam pyrolysis of C₃H₈ are presented in Figure 5. For the quartz surface, the apparent activation energies were 35 and 130 kcal/mole, in the absence and presence of the additive, respectively. Although these values are somewhat lower than those observed for ethane, they are still high and thus support that reaction kinetics, not transport limitations control coke formation rates in the experiments. The activation energy of 35 kcal/mole determined in our studies is in reasonable agreement with the 4055 kcal/mole range estimated by Renjun *et al.*²¹ based on the analysis of experimental data of propane pyrolysis in a nitrogen matrix. The activation energies for coke formation on Incoloy surfaces were 64 and 138 kcal/mole in the absence and presence of the additive, respectively. The former activation energy is consistent with the 71 kcal/mole value reported by Trimm *et al.*⁸ over a different Fe-Cr-Ni alloy.

Based on bond dissociation energy considerations, i.e., gas phase reactions, propane is expected to undergo pyrolysis at lower temperatures, and should produce more coke and coke precursors than ethane at a given temperature. In addition, metal surfaces are known to catalyze hydrocarbon reactions, thus can promote surface coke formation¹⁰. The experimental results are consistent with these issues. The formation of gas phase coke or coke precursors involve the decomposition of the reactant followed by the polymerization of the decomposition products. Further molecular weight growth processes then lead to the formation of polycyclic aromatic hydrocarbons (PAH), tar, soot^{14,17} and ultimately coke.

Alternately, coke formation can also proceed through surface reactions; however, our present day understanding of the fundamental elementary processes leading to coke formation on surfaces is still quite primitive and inadequate to make definitive statements. Nevertheless, the results presented here and elsewhere clearly support the important role surface chemistry and physics play in promoting coke formation, as evidenced, for example, by higher coking rates observed on Incoloy surfaces compared to quartz. It is likely that both the gas phase and surface induced reactions contribute to coke formation in our experiments.

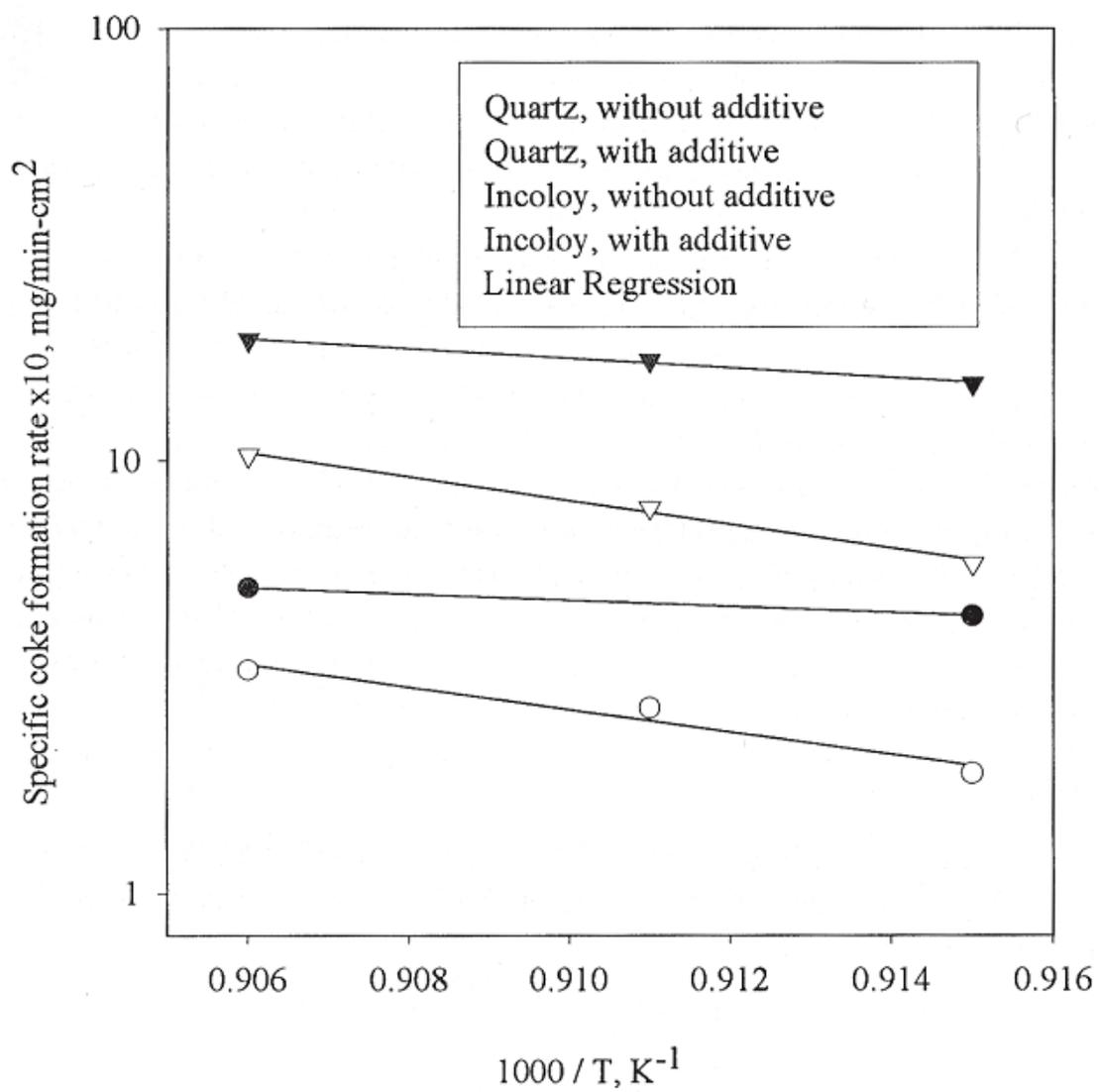


Figure 5 Arrhenius plots for the rate of formation of coke in the steam pyrolysis of propane on quartz and incoloy surfaces.

As previously discussed, coke formation rates decreased in the presence of the additive, although the apparent activation energies increased. These results coupled with reduced effectiveness of the additive with increasing temperature suggest that the primary impact of the additive must be on the surface coke formation processes. The additive may preferentially adsorb on the surfaces and retard the adsorption of coke precursors, tar droplets or soot particles. In addition, the additive may chemically interfere with the surface reaction processes thus preventing the buildup of coke. Third, the additive may promote the surface gasification of coke and/or precursors.

Further research is warranted to better understand the mechanism by which the additive suppresses coke deposition and/or alters the reaction pathways leading to coke formation in the steam pyrolysis of alkanes. This will be necessary to establish optimal reactor design and operating conditions that will result in maximum ethylene production rates while minimizing the rates of formation of coke in production facilities.

4. Acknowledgements

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