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The Effect of Chlorine Addition on the Oxidative Dehydrogenation of Ethane at Millisecond Contact Times

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The effect of chlorine addition to the feed stream was studied for the oxidative dehydrogenation of ethane over Pt/α-Al_2O_3 monoliths at short contact times. The addition of 1 part Cl_2 per 100 parts O_2 (~0.25% of the feed) resulted in increased ethane conversion and increased ethylene selectivity, and consequently higher ethylene yields. However, higher levels of chlorine addition (up to 5 Cl_2 per 100 O_2), while resulting in even higher ethane conversion, resulted in reduced selectivity to ethylene and no improvement in ethylene yields. The catalysts demonstrated enhanced performance even after the chlorine was removed from the feed; this was attributed to modification of the catalyst surface. The addition of chlorine resulted in a doubling of Pt dispersion, which persisted even after chlorine was no longer present on the surface. It is hypothesized that this change in catalyst microstructure is responsible for the observed improvements caused by chlorine addition. © 2002 Elsevier Science (USA)

Key Words: **ethane; oxidative dehydrogenation; chlorine; platinum; millisecond-contact-time reactor.**

INTRODUCTION

Natural gas is an abundant fuel source and feedstock for the chemical industry. The challenge is to efficiently convert this abundant resource into value-added products. Ethylene production from ethane is one example of adding value to a natural gas component. Billions of pounds of ethylene are produced and consumed each year. The current industrial production method is steam cracking, which relies on high temperatures to dehydrogenate ethane.

Recent work has shown that ethylene can be produced at high yields from ethane over Pt monoliths at millisecond contact times (1–4). Ethylene selectivities of 60–70% are possible, with CO as the primary by-product. The current state of the art for these reactors is to add hydrogen to the feed over a bimetallic Pt/Sn monolith (5). Yields as high as 60% have been reported with this configuration. These reactors operate autothermally and nearly adiabatically, with the heat generated by oxidation allowing reaction to occur without external heating.

One of the fascinating aspects of these reactors is the balance between oxidation and ethylene production. Some oxidation of ethane is necessary to maintain autothermal operation at ~900°C. However, any ethane that is oxidized to CO or CO_2 results in lower ethylene selectivity. Finding a proper balance between ethane oxidation and ethane dehydrogenation is necessary to improve the ethylene yield in the millisecond-contact-time reactor.

Many previous investigators have reported that chlorine addition can lead to improved selectivity in oxidation reactions. For example, small amounts of dichloroethane are routinely added to improve ethylene oxide selectivity in ethylene epoxidation. Chlorine addition has also proven valuable in ethane oxidative dehydrogenation over metal oxides and methane oxidative coupling. In both of these processes, chlorine addition either to the catalyst itself or in the feed has increased reactant conversion and product selectivity by several percent (6–17).

Chlorine's effects on ethylene epoxidation have been primarily explained by its impact on oxygen. Grant and coworkers (6) proposed that the electron-withdrawing nature of adsorbed chlorine led to oxygen species more likely to make an electrophilic attack on the double bond of ethylene to form ethylene oxide than on the C–H bond, which they proposed led to CO_2 and water. Campbell and Paffett (7) found that adsorbed chlorine inhibited dissociative adsorption of oxygen on silver, leading to lower oxygen coverage and less CO_2 production. Similar effects have been noted for chlorine and oxygen coadsorption on platinum (18, 19).

These studies suggest that chlorine could have significant implications for the millisecond contact time reactor. Adding chlorine to the reactant feed could result in different oxygen coverages and a change in the balance between oxidation and dehydrogenation. For this reason, the effect of chlorine on the oxidative dehydrogenation of ethane in an autothermal, short-contact-time reactor has been investigated.

EXPERIMENTAL

Reactant gases consisting of ethane, oxygen, and nitrogen flowed from pressurized cylinders through stainless-steel

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tubing. Unit® model 7300 digital mass flow controllers regulated the flow of each component to within ±0.1% of each controller's maximum flow. Chlorine gas also flowed from a pressurized cylinder through stainless-steel tubing, but its flow was regulated by an Omega® (model FL-1802) rotameter. The reactant gases were premixed at room temperature prior to insertion into the reactor. The reactor was oriented vertically with gas flow downward.

The reactor setup was like that utilized by Hickman and Schmidt (20, 21), among others, in short-contact-time partial oxidation research. The reactor was a quartz tube with an internal diameter of 20 mm and a length of approximately 50 cm. The catalytic region was a fixed bed located near the midpoint of the reactor length. A commercially supplied reticulated foam monolith (92% Al_2O_3, 8% SiO_2) from Vesuvius Hi-Tech Ceramics® was employed as the catalyst support. It was supplied at 45 pores per linear inch (ppi) in cylindrical segments 17 mm in diameter and 10 mm in length. Three different monolith segments were located in the reactor—two uncoated (noncatalytic) monoliths, one on each side of a coated catalytic monolith, acted as radiation shields. These segments were stacked together and wrapped in an aluminosilicate mat (FiberFrax Paper 880F) to prevent reactants from bypassing the catalyst. An external insulating mat was also placed over the reaction zone once the reactor had been ignited to maintain near-adiabatic operation.

Catalytic monoliths were prepared using aqueous solutions of a hexachloroplatinic salt, $H_2PtCl_6 \cdot 6H_2O$ (Alfa Aesar 99.9+%), by the incipient wetness technique. Monoliths vary in weight, which suggests structural differences, and so monoliths of similar weight were selected for comparison tests. The concentration of solution used resulted in an approximate loading of 1.6–2.0 wt% platinum on each monolith. After being dried under atmospheric conditions, the monoliths were oxidized in air for 1 h at 100°C and then reduced in 10% H_2/N_2 for 4 h at 600°C.

Lines downstream from the reactor were also stainless-steel tubing. The lines were heated and equipped with a pressure gauge and regulating valve. An in-line SRI® 8610C gas chromatograph equipped with an FID, methanizer, and TCD was used to analyze the product stream. An acid–gas adsorption bed containing Alcoa's chlorine adsorbent CL-750® was located prior to the GC to remove hydrochloric acid and chlorine. Reactor temperature was measured at the center of the downstream face of the catalytic monolith using a Pt/Pt13Rh (Type R) thermocouple tied from a 0.001-in. diameter wire. Measurements were taken with a voltmeter capable of measuring ±0.1 mV.

Reactant gases were flowed at 4 SLPM, or a GHSV of 118,000 h^{-1}, with chlorine gas added in addition. This corresponds to a contact time of ~7 ms at reaction temperature. Nitrogen was used as an internal standard, comprising 20% of the total flow. The reactor was operated at an absolute pressure of 1.2 atmospheres. Since chlorine was expected to compete with oxygen, fixed chlorine-to-oxygen ratios were maintained for all fuel-to-oxygen ratios. Chlorine flow rates were in the range of 1 to 5 parts chlorine per 100 parts oxygen, which corresponded to ~0.25–1.25% of the total feed. Mass balances for carbon and hydrogen closed to ±5%. The oxygen balance was forced closed to calculate the amount of water produced. Error bars were calculated from the standard deviation of 19 experimental trials on a catalyst at the same experimental condition.

Due to the hazardous nature of chlorine gas, the chlorine cylinder was kept in an operating fume hood. Gas lines for chlorine were checked for leaks using both standard leak-check surfactant solution and an ammonium hydroxide solution. A respirator was worn in and around the fume hood while chlorine flow was initiated until safe flow conditions were determined.

Surface studies of the catalysts were conducted using SEM, EDX, XPS, and H_2 chemisorption. For SEM, EDX, and H_2 chemisorption, four different states of the catalyst were examined. Platinum-coated monoliths were prepared as previously detailed, reduced, and then treated in one of four ways:

1. Left untreated following reduction.
2. Reacted at $C_2H_6/O_2 = 2$ with 20% N_2 at 4 SLPM for 4 h.
3. Reacted as in 2 but with Cl_2 continuously on flow at $Cl_2/O_2 = 1/100$.
4. Reacted as in 3 for 1 h and then chlorine free as in 2 for 3 h.

For XPS, in addition to the conditions above, the hexachloroplatinic salt and the deposited salt on the monolith prior to reduction were also examined.

Only the incident faces of the monoliths were examined with SEM and EDX. The scanning electron microscope used was a model S-3500N from Hitachi Science Systems, equipped with a model S-6542 absorbed electron detector. The X-ray detector was a Link Pentafet 7021 coupled with X-ray analysis software, Inca Energy, from Oxford Instruments Microanalysis Limited.

Both the incident faces and the exit faces were examined with XPS. All spectra were recorded on a SPECS Sage100 spectrometer operated in fixed analyzer transmission (FAT) mode using achromatic Mg $K\alpha$ (1253.6 eV) radiation at 240 W (12 kV and 20 mA) using a water-cooled X-ray gun cap. Survey spectra were collected with a pass energy of 30 eV; a pass energy of 15 eV was used for both core and valence band spectra. The C 1s, Pt 4d, and Cl 2p level spectra were recorded. The Pt 4f level spectrum could not be used for analysis because of the overlap with the alumina 2p level. Spectra were calibrated by taking the C 1s peak due to residual hydrocarbons as being at 284.6 eV.

An entire monolith was studied during hydrogen chemisorption tests. The hydrogen chemisorption procedure was adapted from a procedure proposed by Maffucci *et al.* (22) for the determination of Pd dispersion. A Micromeritics AutoChem 2910 was used for the chemisorption analyses; gas detection and measurement was done with TCD. The prepared and treated monoliths were first broken up (not pulverized) just enough for the pieces to fit into the U-tube of the Micromeritics unit. The catalyst was then treated with hydrogen at 400°C to ensure metal reduction, cooled to 125°C under argon, and then pulsed with oxygen to remove adsorbed hydrogen. Following the oxygen pulses, the catalyst sample was cooled under argon to 30°C and then pulsed with 10.3% H_2/Ar. Total adsorbed hydrogen was determined from the missing hydrogen peak area. A hydrogen stoichiometry factor of 1 was used to determine the platinum metal dispersion.

RESULTS

Effect of Chlorine at 1 Cl_2/100 O_2

One part chlorine per 100 parts oxygen was sufficient to cause a positive performance shift. Figure 1 shows the effect of chlorine addition on the conversion of ethane over a 1.6 wt% Pt/Al_2O_3 monolith. The addition of chlorine resulted in a 2.4% increase in conversion, from 75 to 77.4%, at a C_2H_6/O_2 ratio of 1.8, but only a 1.6% increase at a ratio of 2.0. The addition of chlorine also resulted in an increased selectivity to ethylene. As shown in Fig. 2, the selectivity increased by about 1% at each ethane/oxygen ratio tested below 2.0 but was unchanged at a C_2H_6/O_2 ratio of 2.2. Accordingly, the yield of ethylene increased 2.2%, from 45.9 to 48.1%, at an ethane/oxygen ratio of 1.8 and increased 1%, from 40.1 to 41.1%, at a ratio of 2.2.

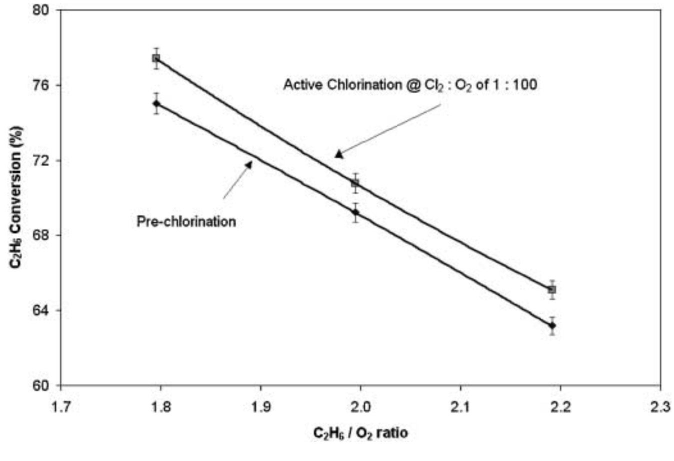

FIG. 1. Comparison of ethane conversion with and without chlorine addition as a function of C_2H_6 in O_2 with 20% N_2 over a 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

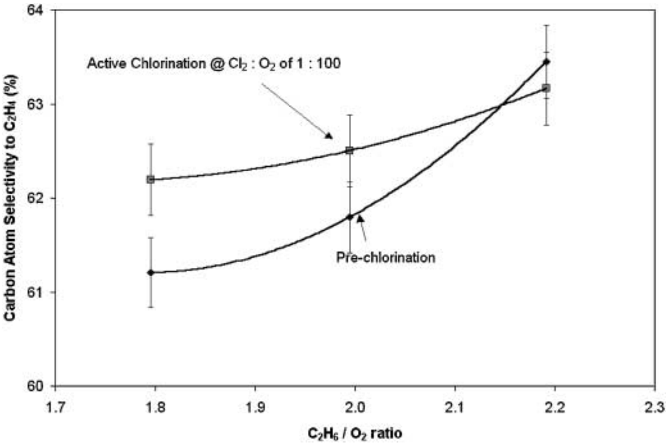

FIG. 2. Comparison of carbon selectivity to ethylene with and without chlorine addition as a function of C_2H_6 in O_2 with 20% N_2 over a 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

As for the carbon oxidation by-products, the introduction of chlorine at 1 part per 100 parts oxygen resulted in lower selectivity to carbon monoxide and higher selectivity to carbon dioxide. Figure 3 depicts the changes. Selectivity to carbon monoxide decreased by about 4% at all C_2H_6/O_2 ratios. Carbon dioxide selectivity increased by 1–2% for all ethane/oxygen ratios, with larger increases in selectivity for the more fuel-rich levels.

Figures 4 and 5 show the selectivity to minor components prior to chlorination and with chlorine on flow at 1 part per 100 parts oxygen. The presence of chlorine significantly increased methane production, as selectivity increased from 4.4 to 6.2%. Selectivity to acetylene and higher olefins (C_3+) increased with the introduction of chlorine. Acetylene selectivity increased by 0.1 to 0.3% and C_3+ olefin selectivity increased by 0.3 to 2.7%. Selectivity to higher

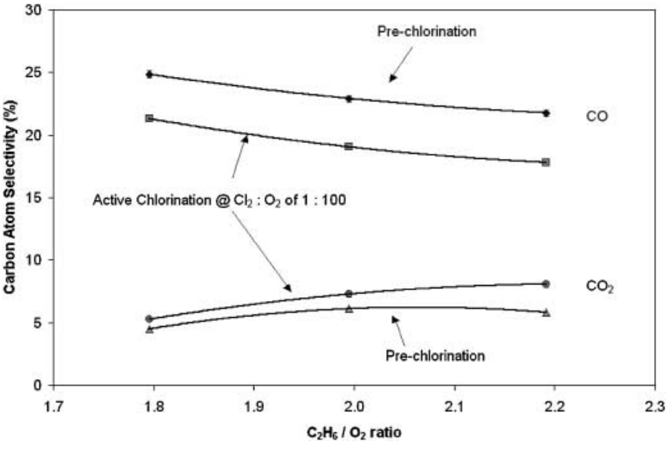

FIG. 3. Comparison of carbon selectivity to carbon monoxide and carbon dioxide with and without chlorine addition as a function of C_2H_6 in O_2 with 20% N_2 over a 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

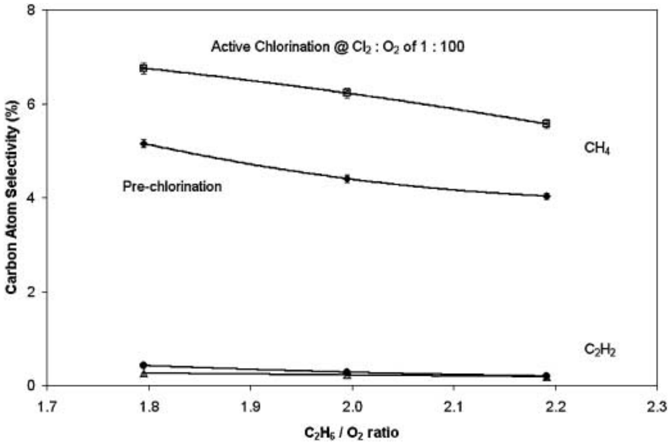

FIG. 4. Comparison of carbon selectivity to CH_4 and C_2H_2 with and without chlorine addition as a function of C_2H_6 in O_2 with 20% N_2 over a 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

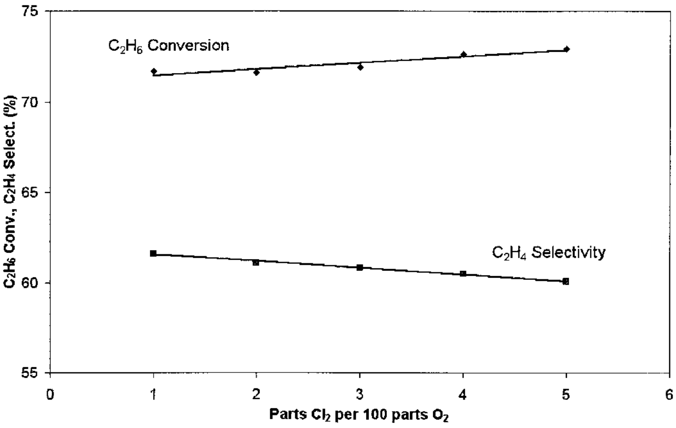

FIG. 6. Ethane conversion and carbon atom selectivity to C_2H_4 as a function of the level of chlorine addition at $C_2H_6/O_2 = 2$ with 20% N_2 over 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

(C_3+) alkanes remained unchanged at 2.3% following the introduction of chlorine.

Only peaks associated with nonchlorinated species were observed. This suggests that chlorinated by-products were formed only in amounts below the FID detection limits (~10 ppm), if at all. Condensate collected from the reactor outlet had a low pH, likely from the presence of HCl. From this it can be concluded that chlorine is converted almost completely to HCl and not to chlorinated hydrocarbons.

Effect of Higher Chlorine Levels

Increased levels of chlorine resulted in further changes in outlet composition. Figure 6 shows the effect of increased chlorine levels up to 5 parts per 100 parts oxygen on ethane conversion and ethylene selectivity at a C_2H_6/O_2 ratio of 2.0. As depicted, ethane conversion increased with increased chlorine levels, from about 71% at 1 part chlorine to 73% at 5 parts chlorine. However, selectivity to ethylene declined from about 62 to 60% over the range of increasing chlorine levels, and thus, the yield of ethylene remained essentially unchanged at about 44%.

With higher levels of chlorine, the selectivity to carbon monoxide increased by about 3%, from about 19 to 22%, while the selectivity to carbon dioxide fell by about 1%, from about 7 to 6%, as shown in Fig. 7. Figure 8 shows the selectivity to minor hydrocarbon products. Selectivity to acetylene and C_3+ olefins remained constant over the range of 1 to 5 parts chlorine per 100 parts oxygen. Methane selectivity increased by 1%, from about 6 to 7%, while selectivity to C_3+ alkanes decreased by 1%, from about 2 to 1%.

Investigations of the effect of elevated chlorine levels inherently led to observations on the sustainability of the autothermal operation of the reactor. The trials showed

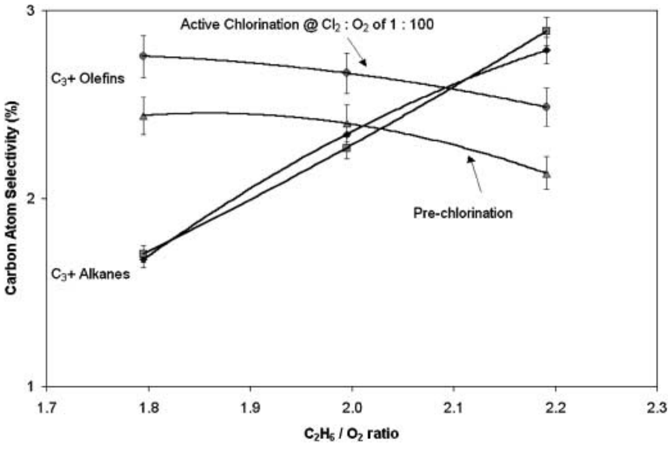

FIG. 5. Comparison of carbon selectivity to C_3+ alkanes and C_3+ olefins with and without chlorine addition as a function of C_2H_6 in O_2 with 20% N_2 over a 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

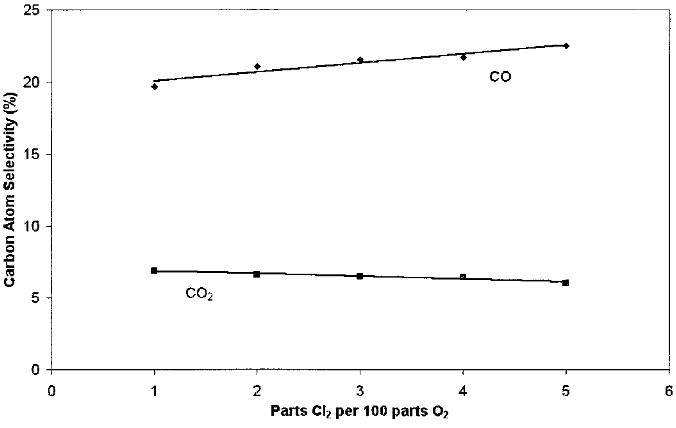

FIG. 7. Carbon selectivity to CO and CO_2 as a function of the level of chlorine addition at $C_2H_6/O_2 = 2$ with 20% N_2 over 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

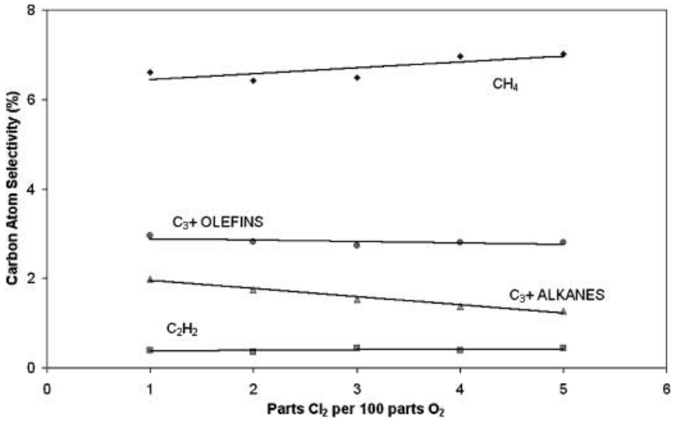

FIG. 8. Carbon selectivity to CH_4, C_2H_2, C_3+ alkanes, and C_3+ olefins as a function of the level of chlorine addition at $C_2H_6/O_2 = 2$ with 20% N_2 over 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith.

continued reactor operation at all chlorine levels tested up to 5 parts per 100 parts oxygen. Levels exceeding 5 parts chlorine per 100 parts oxygen were not investigated, but reactor extinction was seen with chlorine levels in excess of 15 parts per 100 parts oxygen. This does not imply sustainability of autothermal operation at all levels below 15 parts chlorine per 100 parts oxygen.

Postchlorination Performance

Following active, on-stream chlorination, the performance of the reactor failed to return to levels observed prior to chlorine exposure. After halting chlorine flow, the reactor operated at an intermediate state between initial performance prior to any chlorine exposure and active chlorination. Table 1 shows performance data for a C_2H_6/O_2 ratio of 2.0 for each of the three states: prior to chlorination, active chlorination, and postchlorination with no chlorine flowing into the reactor. Similar performance shifts were noted for C_2H_6/O_2 of 1.8 and 2.2, with postchlorination results above prechlorination but below active chlorination performance. The postchlorination performance levels were more similar to those under active chlorination than to those prechlorination.

Temperature

Temperature comparisons between chlorine-free and chlorinated operations were made once reaction sustainability was determined. The observed temperatures of 850 to 950°C from the chlorine-free trials agreed well with the temperatures reported by Huff and Schmidt (1) and Bodke *et al.* (4, 5) for the partial oxidation of ethane. Temperature measurements at the outlet face of the catalyst showed no measurable difference between the three operational states (in regard to catalyst chlorination—pre, active, or post).

Over the range of chlorine levels, from chlorine free, to 1 part chlorine per 100 parts oxygen, to 5 parts chlorine per 100 parts oxygen, there was no measurable change in the steady-state temperature for all ethane-to-oxygen ratios investigated. Thus, the addition of low levels of chlorine to the reactant gases had no lasting effect on the outlet temperature of the reactor. However, upon the initial addition of chlorine or subsequent increases in chlorine flow, a temporary (<1 min) reduction in outlet temperature was observed. This could have been from chlorine interactions with the thermocouple.

Catalyst Stability and Longevity

The performance of the catalyst was stable both under conditions of active chlorination and postchlorination for at least 16 h. Over 16 h with chlorine on flow no decrease in conversion was observed. Instead, a small but steady increase (<1%) in conversion was observed, while selectivity to ethylene remained essentially constant. The enhanced performance of catalysts that had been exposed to chlorine was maintained over 16 h of observation with no sign of a decline from the postchlorination levels. The changes in catalyst performance between chlorination states occurred rapidly. Samples were analyzed approximately every 30 min, and the transition to a new steady-state performance occurred within two sampling cycles.

Resumption of chlorine flow resulted in a return to the same active chlorination state, while cessation of chlorine flow resulted in the same postchlorination state. Cycling

TABLE 1

Product Selectivity for Each Stage of Catalyst Chlorination[a]

	Prechlorination	Active chlorination	Postchlorination
C_2H_6 conversion (%)	69.2	70.8	70.2
C_2H_4 selectivity (%)	61.8	62.4	62.4
Carbon selectivity to minor products (%)			
CO	22.9	19.0	19.7
CO_2	6.1	7.3	6.9
$CO + CO_2$	29.0	26.3	27.5
CH_4	4.4	6.2	5.7
C_2H_2	0.2	0.3	0.3
C_3+ alkanes	2.3	2.3	2.4
C_3H_8	1.0	1.1	1.1
C_4H_{10}	1.3	1.2	1.3
C_3+ olefins	2.4	2.7	2.6
C_3H_6	1.6	1.8	1.8
C_4H_8	0.8	0.9	0.8
Hydrogen select. (%)			
H_2	11.5	11.4	10.6
H_2O	18.7	18.8	19.5

[a] Typical results over a 1.6 wt% Pt/α-Al_2O_3 45 ppi foam monolith with $C_2H_6/O_2 = 2.0$, nitrogen = 20%, flow = 4 SLPM. Active $Cl_2 = 1$ Cl_2 per 100 O_2.

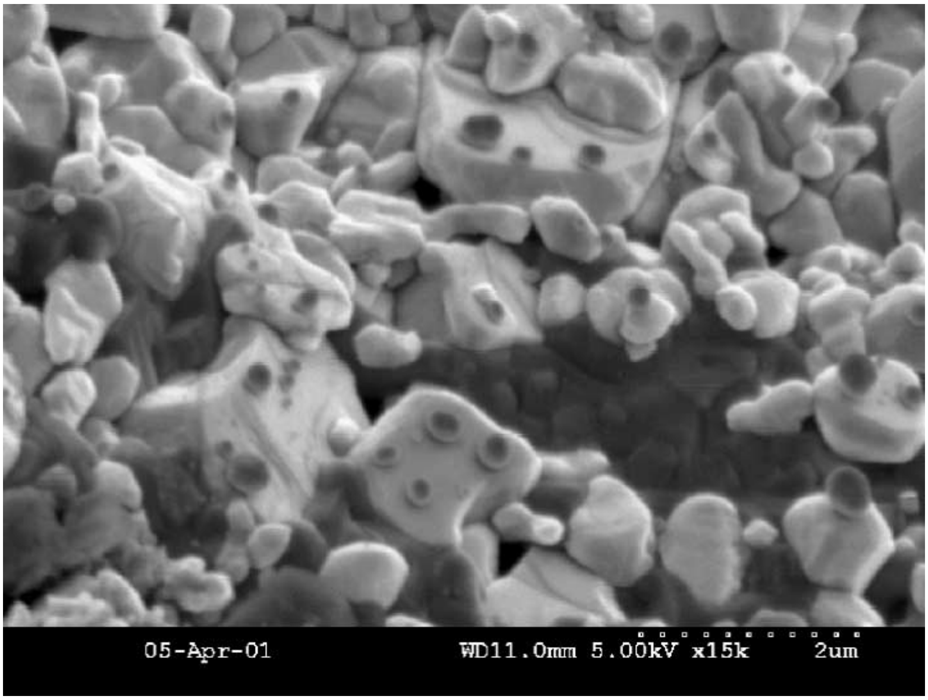

FIG. 9. Image of incident face of Pt/α-Al_2O_3 monolith following treatment 3—continuously chlorinated oxidative dehydrogenation of ethane.

chlorine flow on and off did not lead to further catalyst modification or reactor enhancement. This suggests that changes to the catalyst/reactor are rapid and long lasting, at least on the order of tens of hours.

Reproducibility of Results

The performance enhancement upon the introduction of chlorine was not the same for each catalyst; catalysts that exhibited higher initial conversion and selectivity were improved less than those that exhibited poor initial performance. However, exposure to chlorine did not result in similar final states of performance among the catalysts. Although the performance gap was not as wide as prior to chlorination, catalysts with poor initial performance continued to underperform even after chlorine exposure.

Surface Studies

Examination of the incident faces of the monoliths by SEM revealed little visible difference between the monoliths subjected to the three reaction conditions (treatments 2, 3, and 4). Histograms of particle size prepared from the SEM pictures of the reacted monoliths did not show any differences in the size distribution of larger, visible metal particles. The only observation of note was an apparent darkening of the metal particles on the continuously chlorinated samples (treatment 3), as seen in Fig. 9. The catalyst surface following chlorine addition and then chlorine-free flow showed little darkening, appearing very similar to the image of the catalyst never exposed to chlorine (Fig. 10). The unreacted catalysts (not shown) had not been exposed to the severe conditions of reaction and thus had smaller metal particles, as would be expected prior to sintering.

EDX analyses detected residual chlorine only on the catalysts following continuous chlorination. XPS analyses confirmed the EDX results, with chlorine detected only on the catalysts that had been continuously chlorinated. It is possible that chlorine was present on the catalysts subjected to treatment 4 at levels below the detection limits of EDX and XPS. XPS results also showed that the continuously chlorinated monolith had a significant surface coverage of carbon, especially on the incident face of the catalyst.

Table 2 shows the Pt dispersions measured for each treatment of the Pt/α-Al_2O_3 monoliths. One repeat monolith

TABLE 2

Platinum Metal Dispersions and Average Particle Diameters[a]

Catalyst treatment	Dispersion (%)	Avg. particle diameter (nm)
1. Fresh	9.0	12
2. Reacted	0.9	125
3. Chlorinated	1.8	64
4. Chlorine, stripped	2.0	57

[a] For 2.1 wt% Pt/α-Al_2O_3 catalysts following four different treatments.

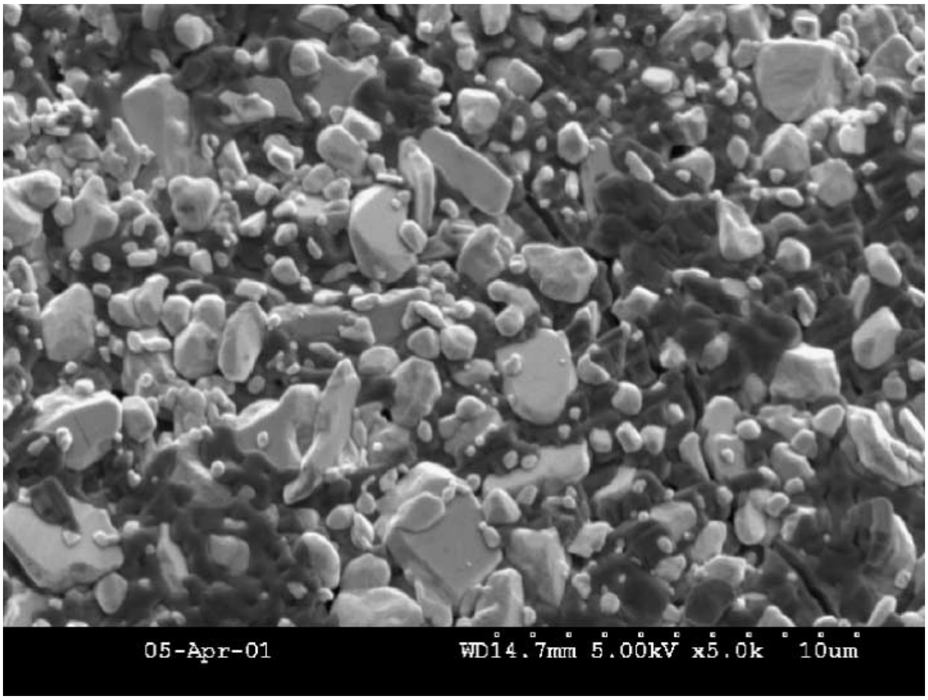

FIG. 10. Image of incident face of Pt/α-Al_2O_3 monolith following treatment 2—unchlorinated oxidative dehydrogenation of ethane.

for the reacted treatment (treatment 2) was made and the results agreed within 10% of that listed in the table. Repeated measurements of each sample yielded results within 0.1% of one another, except for treatment 1, which varied by ~1%.

DISCUSSION

The results indicate that chlorine addition at levels even less than 0.25% of the total feed resulted in improved ethane conversion and ethylene selectivity, especially at conditions where the feed is less fuel rich. The rate of dehydrogenation increased for all hydrocarbons, as C_2, C_3, and C_4 olefin selectivities all increased during chlorine addition. However, increasing the chlorine level in the feed further led to a decrease in ethylene selectivity, even as ethane conversion increased.

It is interesting that the effect of chlorine continued even after chlorine was removed from the feed. This strongly suggests that the main effect of chlorine was to modify the surface in some way that favored dehydrogenation and suppressed oxidation, although the presence of chlorine in the feed provides some additional enhancement. The literature suggests a number of ways the chlorine could be affecting short-contact-time oxidative dehydrogenation, including chemical and physical modification as well as increased gas-phase chemistry. The surface studies and longevity tests serve as a starting point for deciding which mechanism is most important.

Surface Effects of Chlorine

Platinum chlorides. Reaction between platinum and chlorine readily form platinum chlorides. It is possible that the formation of platinum chloride species occurrs as chlorine is added to the reactor and that the chlorides result in advantageous activity for oxidative dehydrogenation of ethane. However, platinum chlorides are generally unstable, and in the reducing conditions of these experiments, it would be expected that the chlorides would be depleted over time. A change in performance over the 16 h over which the longevity tests were run might be expected.

In fact it was shown by XPS and EDX results that significant chlorine is present on the surface of catalysts exposed to chlorine-containing feed. However, this chlorine is stripped from the surface over time when chlorine is removed from the feed. This is not surprising, since the reactor operates under reducing conditions, runs at high temperatures, and contains significant amount of steam formed during reaction. The stripping of chlorine from catalysts with steam, especially during salt decomposition, is a well-known phenomenon.

The fact that little change in catalytic results was noted in 16 h, while surface levels of chlorine decreased in only hours, argues against platinum chlorides being primarily responsible for the observed changes. So, too, did experiments comparing catalytic performance of fresh catalysts prepared from a platinum–chloride salt with and without a high-temperature reduction treatment. Instead of reductive decomposition, the 10% H_2/N_2 gas mix was replaced with air during the 4 h at 600°C. Without the reductive treatment, there would be residual chlorine from the platinum salt on the monolith, so this served as another means for testing the role of surface chlorine. It was found that the nonreduced catalyst gave a worse performance than the reduced catalyst, again suggesting that surface chloride may not be the major reason that ethane oxidative dehydrogenation improved with addition of chlorine to the feed.

Catalyst acidification. It would be expected that extensive chlorination of a catalyst would increase catalyst acidity. Increased acidity would lead to increased formation of cracking products. This is in agreement with what was seen experimentally: addition of chlorine led to increased methane production and carbon formation. Acidification of the catalyst definitely plays a role while chlorine is the feed, as evidenced by the formation of coke. Acidification could play a role after chlorine is removed from the feed, though the question of the lifetime of chlorine on the surface relative to the time over which chlorine's effects persist comes into play. Improved conversion and selectivity were maintained for 16 h, while XPS and EDX results showed a dramatic loss of chlorine in only 3 h. Stripping of chlorine over time would decrease acidity, and catalytic results should change as well, but this was not the case. Acidity effects cannot be completely ruled out, however, since only minute quantities of chlorine may be sufficient to effect considerable changes.

Redispersion. Numerous studies have shown Pt group metals to migrate across catalyst surfaces at high temperature, resulting in loss of metal dispersion. The rate of migration depends on the support characteristics and the specific conditions to which the catalyst is exposed. Torniainen and co-workers have shown that the structure of noble metal catalysts changes over time in the short-contact-time reactors (23). Small metal particles agglomerate at reaction conditions, resulting in larger globules of metal and less catalytic surface area. However, no efforts have gone into measuring metal dispersion and it is generally thought that the metal microstructure is unimportant, since sintering appears to be inevitable.

Oxy-chlorination is a well-known and commonly used technique for the regeneration or reactivation of Pt catalysts by redistribution of the catalytic metal on the support (24–28). During the process, oxygen and chlorine (often HCl) are passed across heated catalysts, resulting in the formation of mobile metal–oxychlorides (MOCl), which migrate across the support and disperse the catalytic metal (24, 28). The presence of chlorine is also known to delay migration or sintering, especially on alumina, because of greater metal–support interactions that occur with acidic alumina (24–30).

It is generally considered that particle size does not influence the rate of dehydrogenation of alkanes, but Nakamura *et al.* (31) have shown that it can affect the selectivity to products. However, the total reactive surface area could influence the rate of reaction. Thus, on catalysts with equal metal loadings, a higher dispersion would indicate more surface area available for reaction and consequently might lead to higher conversion. Since chlorine is known to redisperse sintered catalysts and since it affected the metal dispersions on the catalysts in this work, the possibility of metal dispersion effects causing the change in reactor performance is obvious.

Experimentally, significant changes in platinum dispersion resulted from different reaction conditions. The fresh catalyst lost 90% of its dispersion upon being run for 4 h. However, addition of chlorine to the feed doubled the platinum dispersion. This higher dispersion was maintained for at least 3 h after chlorine had been removed from the feed, as the measured dispersion was approximately the same. Note that the apparent slightly higher dispersion (2.0 vs 1.8%) for the catalyst stripped of chlorine may have been due to underestimation of the dispersion of the catalyst following chlorination because hydrogen chemisorption may have been inhibited by adsorbed chlorine or deposited carbon.

What is unclear is where the increase in dispersion occurs. It might occur only at the front face, where an oxidative environment exists, or possibly throughout the length of the monolith. If the redispersion occurs only at or near the incident face, then the doubling of metal dispersion when measured for the entire catalyst masks the much greater dispersion that would exist at the face of the monolith.

These results suggest that chlorine causes platinum redispersion, and this effect lasts even after chlorine has been removed from the feed. It is possible that platinum redispersion leads to a platinum microstructure (i.e., more-disperse, smaller platinum particles) that favors dehydrogenation over oxidation. Essentially, this is an argument for structure sensitivity, whereby smaller platinum particles catalyze different reaction pathways than do larger particles. Structure sensitivity is a well-known phenomenon for supported metal catalysts, although there are numerous contradictions in the literature about whether specific reactions are structure sensitive. Alkane hydrogenolysis is a well-known structure-sensitive reaction (32–34). Schmidt and Krause (35) reported that ethane hydrogenolysis to methane occurs ∼10 times faster on smaller platinum particles resulting from oxidation than on sintered, reduced platinum particles. This is consistent with the trend observed in this work: the smaller particles present following chlorine produce higher methane selectivities. The literature is less clear on whether alkane oxidation is structure sensitive. Briot *et al.* (36) reported that larger Pt particles had significantly higher turnover ratios in methane oxidation.

Garetto and Apestequia (37) also found higher methane oxidation rates over larger particles and found an even larger effect for a larger hydrocarbon, cyclopentane. Burch and Loader, however, reported no structure sensitivity in methane catalytic combustion (38). It is hypothesized in this work that the different catalyst microstructure affects the oxidation pathways so that less ethane is oxidized to CO, resulting in higher ethylene yields.

Effects on coke formation. The XPS results showed a significant level of carbon on the continuously chlorinated catalysts, much greater than that on any of the other reacted catalysts. This presence of carbon may explain the darkening of the metal particles observed with SEM. The higher levels of carbon on the continuously chlorinated monoliths resulted in a visibly noticeable darkening at the catalyst entrance. However, the deposited carbon did not attain coverage levels at which deactivation occurred. As shown by SEM and XPS analyses, upon cessation of chlorine flow, the solid carbon was reacted off of the catalyst surface. This strongly suggests a direct relationship between chlorine and coke formation.

Huff and Schmidt (1) examined the equilibrium formation of coke (C_s) in the oxidative dehydrogenation of ethane. They found that equilibrium conditions predicted significant formation of coke but little C_2H_4. However, no coke deposition was observed on either Pt or Rh while C_2H_4 and syngas were the primary products, respectively. Palladium, on the other hand, coked rapidly with subsequent deactivation.

An interesting aspect of the coke formation occurring with chlorine addition is that the coke deposition is heaviest at the entrance of the monolith, where oxidation reactions occur. Such a phenomenon might suggest a propagating carbon front resulting in gradual deactivation, but as discussed earlier, deactivation does not occur, even over several days of operation. The coke deposition, while heavier with chlorine than without, seems to reach an equilibrium level such that deactivation does not occur.

XPS revealed higher levels of solid carbon on the catalyst surface at the monolith exit, as well as the entrance. This indicates that increased carbon deposition occurred throughout the catalyst, which is common with increased catalyst acidity. The formation of solid carbon when chlorine is being added to the feed could also simply be a result of a change in the Pt–H interaction. Chlorine, when adsorbed on Pt, causes a reduction in the hydrogen-sticking coefficient, which translates to a lower density of hydrogen on the catalyst surface. Coke formation would be favored at reaction conditions when less hydrogen is present on the catalyst.

Role of gas-phase chemistry. While chlorine's primary effect seems to be on surface chemistry, it is possible that chlorine enters into gas-phase chemistry. Gas-phase reactions have been shown to result in significant production of ethylene, even without chlorine present (39). When chlorine is present, it could dissociate into radicals and act to activate ethane by extracting a hydrogen atom:

$$Cl^{\bullet} + C_2H_6 \rightarrow HCl + C_2H_5{\cdot}.$$

It is possible that chlorine has some effect on gas-phase reactions in this work. It was noted that conversion and selectivity were higher when chlorine was being flowed than after it had been removed. This could suggest an effect on gas-phase chemistry, though effects on surface chemistry, for example by affecting oxygen chemisorption, hydrogen spillover, or surface acidity, could possibly explain this trend.

The results when higher amounts of chlorine were added to the feed could further indicate how chlorine affects gas-phase chemistry. In those experiments, ethane conversion increased as chlorine levels increased, while selectivity to ethylene dropped. This is the trend that would be expected as the amount of oxidant increased. Indeed, gas-phase simulations using a detailed hydrocarbon oxidation model (40) predict the same trend as the C_2H_6/O_2 ratio was decreased. However, it took more oxygen to effect the same changes that were produced by a few parts per thousand of chlorine. This speaks to the high reactivity of chlorine.

CONCLUSIONS

The addition of 1 part Cl_2 per 100 parts O_2 (~0.25% of total flow) to the oxidative dehydrogenation of ethane improved both C_2H_4 selectivity and C_2H_6 conversion. Addition of Cl_2 at higher levels resulted in further increase in conversion, but lower C_2H_4 selectivity, and accordingly flat to lower yields.

Improved results were maintained even after chlorine was removed from the feed, suggesting that chlorine caused a modification of the catalyst that lasted at least 16 h. This may have been due to redispersion of the platinum catalyst caused by chlorine. Surface chemical effects of chlorine do not appear to explain the experimental results, since XPS and EDX noted significant loss of chlorine from the surface in only hours while catalytic results remained essentially constant. Surface chemical effects cannot be completely ruled out, however, since minute quantities of chlorine may be all that is needed to effect the observed changes.

Deposition of carbon on the catalyst surface was noted with chlorine addition. However, this carbon deposition did not result in deactivation, as stable operation was maintained for 16 h. The solid carbon was reacted off the surface once chlorine had been removed from the feed.

Following chlorination of catalysts, a slight change in conversion and product selectivity was observed as chlorine was added to and removed from the feed stream. This indicated that chlorine played a role in the chemistry, but it is unclear whether it directly participates in homogeneous chemistry via radical chain reactions.

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