Conversion of ethane to ethylene and synthesis gas with cerium oxide. Promoting effect of Pt, Rh and Ru

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The reaction between ethane and cerium oxide with and without noble metal promoters has been studied at temperatures up to 700 °C in a pulse apparatus. The cerium oxide was supported on γ-Al_2O_3 and promoted by reimpregnation with Pt, Rh or Ru. The promoters drastically enhanced the conversion of ethane, but the yield of ethylene was highest with unpromoted cerium oxide and at high temperatures. The product yield depended strongly on the degree of reduction of the material samples. Carbon dioxide was formed in reaction with the fresh unpromoted cerium oxide. The yield of ethylene increased as the degree of reduction of the cerium oxide increased at 700 °C. No water was formed simultaneously with the production of ethylene. This shows that the dehydrogenation that took place was non-oxidative. Ethane in reaction with the fresh promoted cerium oxide material samples yielded mostly carbon dioxide and water. The product yields changed towards carbon monoxide and hydrogen together with methane and coke as the promoted materials were being reduced. Some ethylene was formed also with the platinum-promoted material sample with a high degree of reduction.

KEY WORDS: ethane; dehydrogenation; oxidation; ethylene; synthesis gas; cerium oxide; platinum; rhodium; ruthenium

1. Introduction

Petroleum refineries produce large quantities of light paraffins unsuitable for application in traditional transportation fuels. Large quantities of C_2–C_4 paraffins are usually condensed out of wet natural gas before the dry natural gas is piped to its final market. Light paraffins can be converted to olefins, which then are the basic feedstock for production of polymers. Dehydrogenation of paraffins to olefins and hydrogen is endothermic and requires energy input at high temperatures.

Is has been proposed that paraffin dehydrogenation alternatively can be done exothermally by adding oxygen to the feed [1]. This provides heat internally in the reactor by the formation of water instead of hydrogen and the overall process becomes exothermal. Catalytic oxidative dehydrogenation with many different catalytic systems has been extensively studied [2]. There are several proposed mechanisms in the literature and they strongly depend on the catalyst and the conditions applied.

It has been shown that if the reaction is carried out at very high temperatures, the role of the catalyst is mainly to ignite and facilitate combustion reactions that provide necessary heat for thermal dehydrogenation to take place homogeneously [3–6]. At low temperatures (<500 °C) the oxidative dehydrogenation has been shown to take place catalytically and it appears that the VMgO system is one of the most promising [1,2]. However, this catalyst indeed has severe selectivity problems and the olefin yield is limited due to unwanted combustion reactions between the hydrocarbon feed and oxygen. Cyclic operation of the paraffin and oxygen feed over the VMgO catalyst has been proposed in order to improve the selectivity and yield of such processes [7,8]. This means that the olefin yield can improve if the paraffins are anaerobically converted with oxygen from a solid oxygen carrier.

A problem in many high-temperature oxidation processes is the tendency to over-oxidize the reactant. This has also been an important issue in studies concerning the catalytic partial oxidation of methane. In this field, recent research has shown that combustion reactions can be suppressed by feeding oxygen to the active sites by solid diffusion rather than by gas phase adsorption [9]. Cerium oxide is a good dynamic oxygen reservoir and has the capability to easily store and release oxygen [10,11]. Cyclic operation of promoted cerium oxide with cycles of methane and oxygen has been shown to give higher synthesis gas yields at lower temperatures than what can be obtained from steady-state operation at similar conditions [12,13]. In this system oxygen is transported slowly to the catalytic surface by diffusion in the bulk of the solid. Several other researchers have also studied the dynamics of the methane–cerium oxide reaction to produce synthesis gas [14–16].

The reaction between other light paraffins and solid oxygen carriers was therefore also considered interesting both in context of olefin production, but also with possible applications for syngas production. This study deals with the

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gas–solid reaction between ethane and cerium oxide to form ethylene and/or synthesis gas. The effect of promoting the cerium oxide with noble metals (Pt, Rh, Ru) was also studied.

2. Experimental

2.1. Catalyst preparation and characterization

The materials were prepared by incipient wetness impregnation of about 20% CeO_2 on γ-Al_2O_3. The γ-Al_2O_3 material was supplied by Alfa Aesar in pellets and crushed down to particles in the size 300–710 μm. The γ-Al_2O_3 was impregnated with $Ce(NO_3)_3{\cdot}6H_2O$ dissolved in distilled water, dried at 150 °C and calcined in air at 600 °C for 10 h. The materials were reimpregnated with either 0.5 wt% Pt ($Pt(NH_3)_4(NO_3)_2$), Rh ($Rh(NO_3)_3$) or Ru ($Ru(NO)(NO_3)_3$) and calcined again in air at 600 °C for 10 h. Detailed characterization (BET, XRD, H_2-TPR) of the material samples has recently been published [12]. The surface area decreased from about 198 to 158 m^2/g by impregnation of 20 wt% CeO_2 on the γ-Al_2O_3. XRD analysis identified both the phases CeO_2 and γ-Al_2O_3. H_2-TPR showed that addition of small amounts of promoters such as platinum or rhodium largely affected the reducibility of the CeO_2 phase.

2.2. Reactor setup and experimental procedure

Reactions with ethane and oxygen with the various materials were carried out by injecting 0.25 Nml ($\sim$10 μmol) of reactant pulses into a steady flow of He (50 Nml/min) that passed over the material samples (0.50 g) which were placed inside an electrically heated quartz reactor. Downstream of the reactor, the He flowed continuously directly into a packed Porapak Q column (2.1 m, 1/4 inch) that was held isothermal at 70 °C. A thermal conductivity detector and in certain cases a Gaslab 300 mass spectrometer were placed at the exit of the column. The total pressure in the reactor was always 1.8 bar. All lines downstream of the reactor were heated to avoid condensation upstream of the packed column. The reactor was a quartz tube with an inner diameter of 3 mm. This gave a linear gas velocity of 0.22 m/s at 700 °C (1.8 bar) and a contact time between the reactant gases and the material samples (void fraction 0.4) of about 0.26 s. Complete separation and analysis (12–15 min) of the products from a reactant pulse was allowed before a new pulse was injected. The materials were studied in cycles of multiple pulses of oxygen and subsequently multiple pulses of ethane. The materials were then reoxidized in a series of oxygen pulses before again starting new series of ethane pulses. Carbon deposition was studied in the above-described procedure by measuring the formation of carbon oxides while pulsing oxygen over the used samples. Carbon accumulation was also estimated from the product material balance when pulsing ethane over the material samples. The amount of coke presented in the figures is based on such material balance calculations.

3. Results and discussion

In this experimental procedure, the hydrocarbon feed and the gas phase oxygen were never present in the reactor at the same time. This excluded the possibility of homogeneous reactions between the oxygen and ethane. The previous study with methane showed that neither gas phase reactions nor coke formation occurred without an activating or oxygen-containing material present in the reactor. Ethane can, however, more easily than methane undergo thermal decomposition also in absence of gas phase oxygen. A blank run with one pulse of ethane through the empty reactor at 700 °C revealed that this indeed was the case with a yield of ethylene of 17%. This must be kept in mind when considering the results obtained with the different materials present in the reactor.

The reaction between ethane and unpromoted CeO_2/γ-Al_2O_3 was studied at temperatures up to 700 °C. One pulse of ethane was injected over the sample at each temperature. The temperature was raised to a new level and the samples were reoxidized with pulses of oxygen before a new pulse of ethane was injected. This procedure was also performed with the noble-metal-promoted material samples: Pt/CeO_2/γ-Al_2O_3, Rh/CeO_2/γ-Al_2O_3, Ru/CeO_2/γ-Al_2O_3. The results in figure 1 clearly show that the presence of these noble metals enhances the conversion of ethane at lower temperatures. Yield is here the number of micromoles of a compound in the reactor exit resulting from an inlet pulse of 10 μmol of ethane. Missing carbon atoms in the product gas can be found from the material balance and shows the amount of carbon accumulated on the material samples. The main gaseous product from only one pulse of ethane over the fresh materials at all temperatures was carbon dioxide. Rhodium was apparently the most active promoter at low temperatures.

The oxygen dynamics of the cerium oxide phase itself is most likely unaffected by the noble metals since these are believed to be situated on top of the ceria phase in separate particles. The role of the promoter was expected to be the heterogeneous activation of ethane and to transfer oxygen from the CeO_2 phase to the sites where the activated hydrocarbon species were situated. Figure 1 therefore indicates that ethane activation is rate determining at low temperatures. No conversion of ethane was observed over the unpromoted CeO_2/γ-Al_2O_3 sample at 400 °C whereas all promoted samples gave full ethane conversion at this temperature.

Repeated pulsing of ethane over preoxidized samples were expected to give more information about the dynamic behavior of the materials. Both the oxygen transport in cerium oxide and the hydrocarbon activation on the promoters could be possible rate-determining steps. The relative influence from these processes on the dynamic behavior of the materials was therefore expected to be largely dependent on the reaction temperature. Multiple-pulse experiments were performed both at low (500 °C) and high (700 °C) temperatures. The results from repeated pulsing of ethane (>20

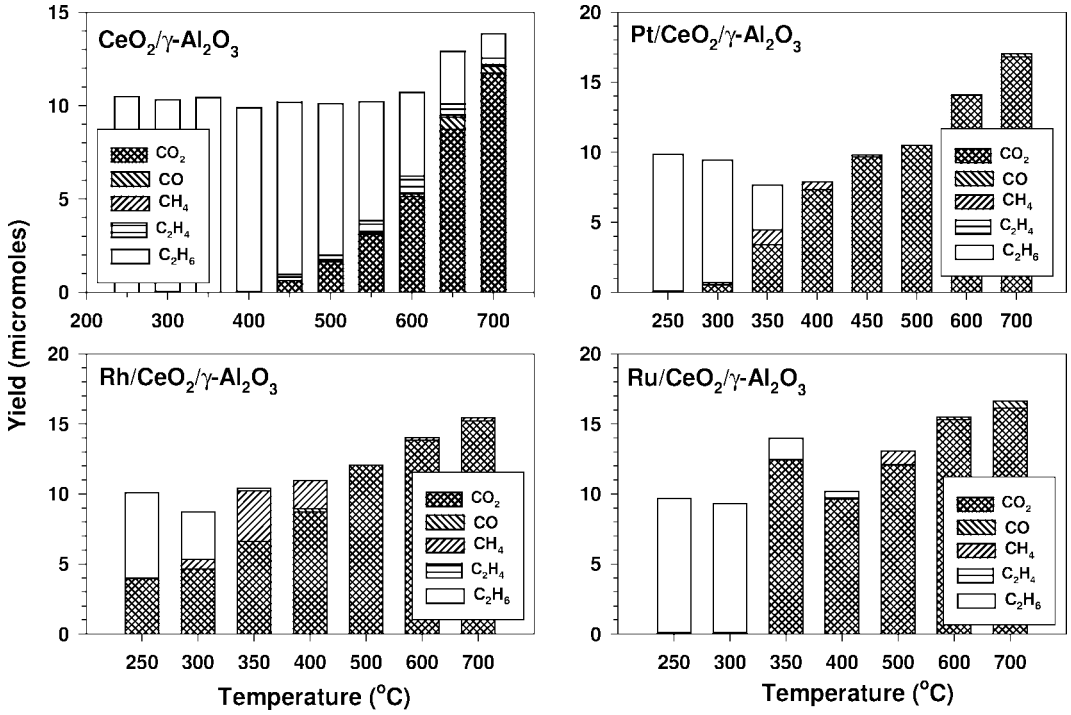

Figure 1. Molar yields from one pulse of ethane over 0.5 g of 20 wt% CeO_2/γ-Al_2O_3, 0.5 wt% Pt/CeO_2/γ-Al_2O_3, 0.5 wt% Rh/CeO_2/γ-Al_2O_3 and 0.5 wt% Ru/CeO_2/γ-Al_2O_3 at various temperatures. The samples were oxidized in oxygen before each pulse of ethane at all temperatures.

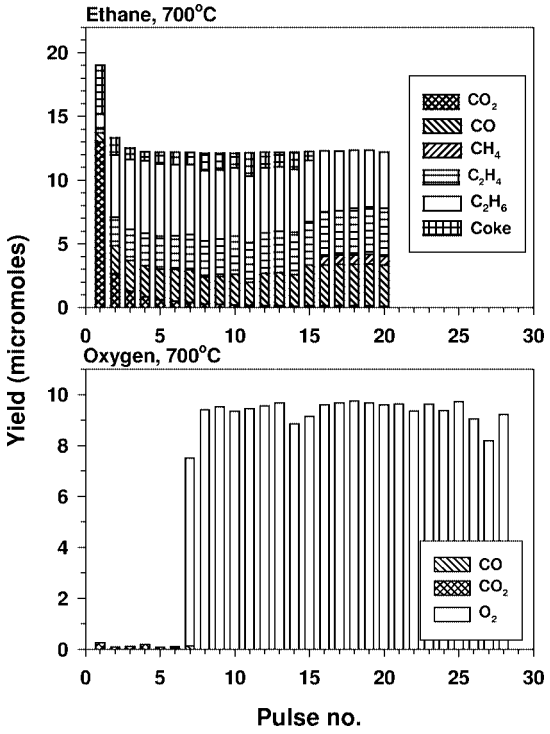

Figure 2. Molar yields from multiple pulses of ethane followed by multiple pulses of oxygen over 20 wt% CeO_2/γ-Al_2O_3 at 700 °C.

following pulses) over CeO_2/γ-Al_2O_3 followed by repeated pulsing of oxygen (>20 pulses) at 700 °C is shown in figure 2. The results from identical experiments performed both at 500 and 700 °C over the promoted material samples are shown in figures 3, 4 and 5. The degree of reduction of the CeO_2 phase in all material samples was calculated from the amount of oxygen-containing molecules coming off the material samples during the experiments presented in figures 2–5 and are given in table 1. Water is not shown in the figures since hydrogen accumulation severely influenced its material balance, but is still taken into account in the calculation of the apparent oxidation state of cerium oxide after the reduction.

The results with pure CeO_2/γ-Al_2O_3 show that the product distribution from the oxidation of ethane depended strongly on the degree of reduction of the cerium oxide phase. When the material was fully oxidized, the main product was carbon dioxide. As the material was being reduced by ethane, more and more carbon monoxide and ethylene was formed. The ethylene yield in pulse no. 20 was about 34%, which is significantly higher than was observed in the empty reactor (yield = 17%). Only traces of H_2O were found in the products after the first pulse of ethane. The material balance from the pulsing of ethane showed that there was some accumulation of carbon on the material sample. Very small amounts of carbon oxides were formed in the regeneration with pulses of oxygen. This discrepancy can be explained by a slow coke gasification between the reactant pulses. Similar discrepancies were found during identical experiments with methane [12]. The regeneration in oxygen therefore showed that very little permanent carbon deposition had occurred on unpromoted cerium oxide and that the oxygen conversion was complete until the material sample was saturated after about 7 pulses.

The same experiments with the promoted samples (in figures 3–5) show large differences from the unpromoted ma-

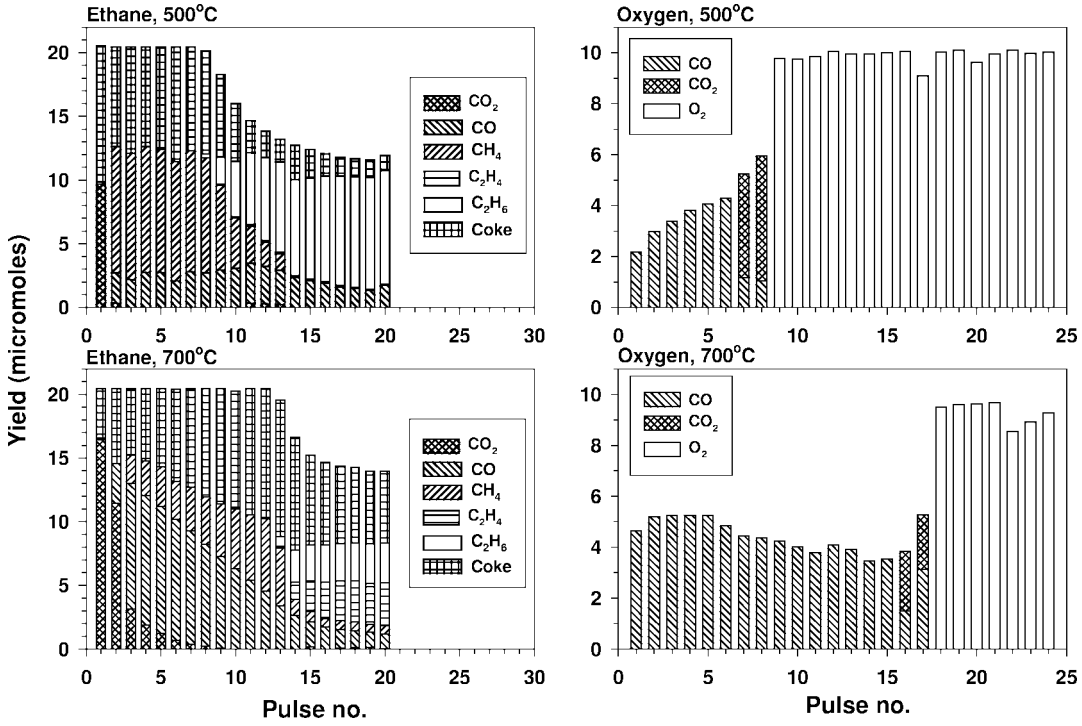

Figure 3. Molar yields from multiple pulses of ethane followed by multiple pulses of oxygen over 0.5 wt% Pt/CeO_2/γ-Al_2O_3 at 500 °C (upper charts) and at 700 °C (lower charts). The amount of coke is calculated using the material balance from each pulse.

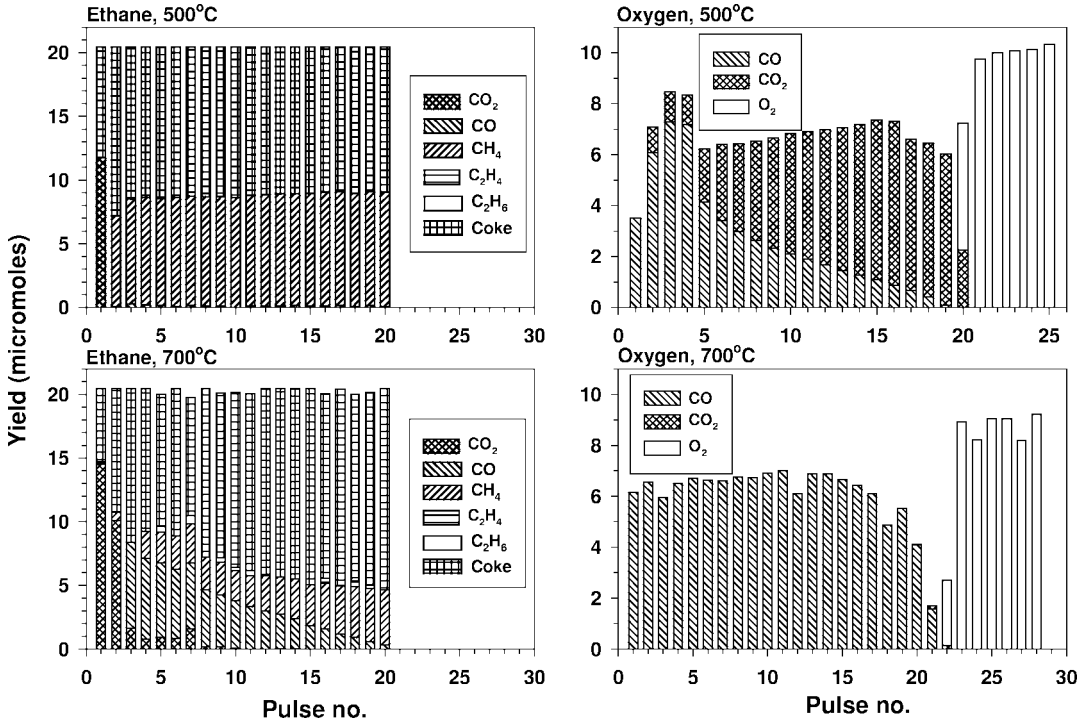

Figure 4. Molar yields from multiple pulses of ethane followed by multiple pulses of oxygen over 0.5 wt% Rh/CeO_2/γ-Al_2O_3 at 500 °C (upper charts) and at 700 °C (lower charts). The amount of coke is calculated using the material balance from each pulse.

terial sample, and also differences between the noble-metal-promoted samples. Firstly, much more carbon was deposited on the promoted samples compared with the one without a noble metal promoter. Secondly, much more methane was formed with all the promoted samples, and particularly so at 500 °C with rhodium as promoter. Carbon oxides were also formed in large amounts from all fresh samples. The yield switched from carbon dioxide to more and more carbon monoxide as the material samples were being reduced. The yields of ethylene were very low compared to those obtained

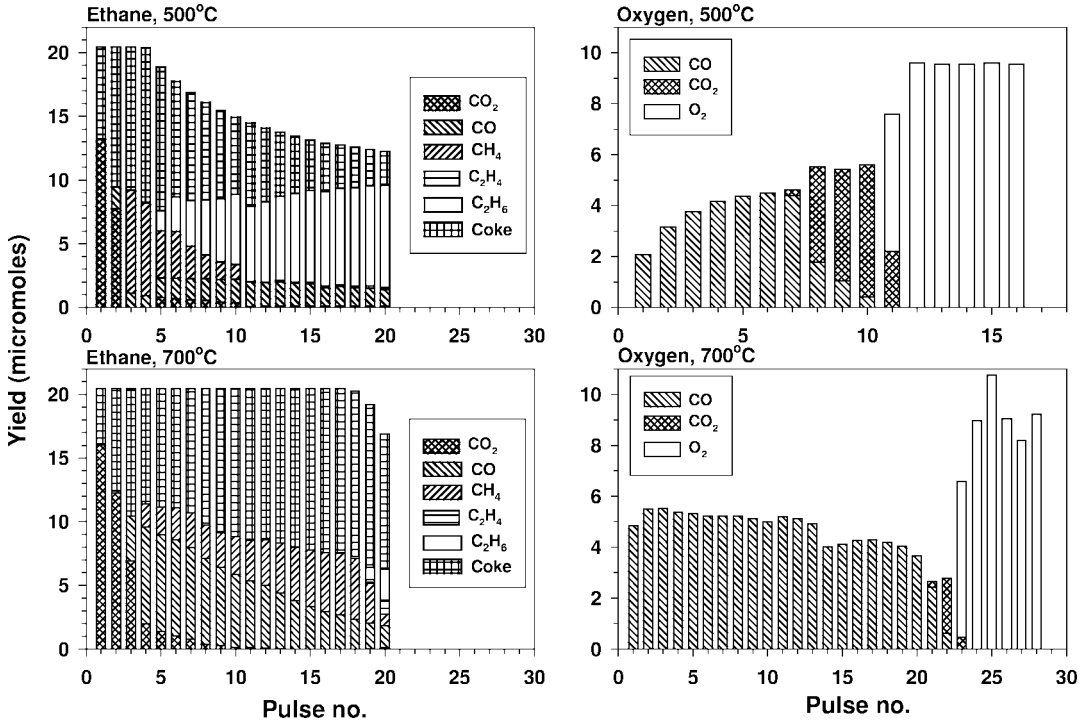

Figure 5. Molar yields from multiple pulses of ethane followed by multiple pulses of oxygen over 0.5 wt% $Ru/CeO_2/\gamma$-Al_2O_3 at 500 °C (upper charts) and at 700 °C (lower charts). The amount of coke is calculated using the material balance from each pulse.

Table 1
Calculated apparent oxidation state for the cerium oxide phase in the different material samples after the experiments presented in figures 2–5.

	CeO_2/γ-Al_2O_3	$Pt/CeO_2/\gamma$-Al_2O_3	$Rh/CeO_2/\gamma$-Al_2O_3	$Ru/CeO_2/\gamma$-Al_2O_3
Stoichiometric coeff. (x in CeO_x) 500 °C		1.88	1.93	1.83
Stoichiometric coeff. (x in CeO_x) 700 °C	1.81	1.66	1.73	1.64

over unpromoted cerium oxide except with partly reduced platinum-promoted cerium oxide at 700 °C, when more than 15% of the oxygen bound in the ceria phase had been removed.

As stated above, the promoters were expected to assist the heterogeneous activation of the hydrocarbon feed. This indeed turned out to be the case and can be seen from the high conversion of ethane for many more pulses of ethane than with the unpromoted samples. The oxygen transport through the promoter metal to the active site was largely different and can be compared by looking at the relative amounts of carbon oxides formed over the different materials. Platinum and ruthenium apparently transported oxygen better than rhodium, particularly at low temperatures. Ethane pulsing over the sample promoted with rhodium at 500 °C gave almost no oxygen-containing products whatsoever. The only products in this experiment were carbon, hydrogen and methane indicating total ethane decomposition. This shows that the mobility of oxygen in rhodium is very poor at 500 °C as compared with platinum and ruthenium. In addition, table 1 shows that the obtained degree of reduction of this material sample at both temperatures was significantly lower than that observed with the other promoted material samples. The results also show that the hydrocarbon dissociation was significantly more severe in presence of all the promoters as compared with unpromoted cerium oxide. As previously reported from the reaction between methane and cerium oxide, very low methane conversion was observed with unpromoted cerium oxide [12]. As expected, the unpromoted cerium oxide was found to be more active towards oxidation of ethane than methane. This can be correlated with the relative C–H bond strengths in ethane and methane. The complete conversion of ethane to C_1 products and coke with promoted cerium oxide also indicates that addition of the noble metal promoters increase not only the activity for C–H bond cleavage, but also C–C bond cleavage.

In similar experiments with methane, hydrogen was found to accumulate on cerium oxide samples [12]. Analysis of the water formation when producing ethylene from ethane is crucial in order to determine whether or not the dehydrogenation that takes place is oxidative or non-oxidative. Hydrogen was also found to accumulate on the material samples in this study, but only during the first pulse of ethane with all material samples. Thereafter some water came off

the samples in variable amounts but water was never found after more than five pulses of ethane. Production of hydrogen in the subsequent pulses was confirmed with the mass spectrometer. Figures 2 and 3 show that the ethylene yield during the first pulses of ethane was always very low. In the cases where ethylene was observed, the yield always increased with increasing degree of reduction. The Pt-promoted sample gave ethylene far beyond the point where water no longer was formed. This quite conclusively proves that dehydrogenation that takes place at 700 °C with promoted or unpromoted cerium oxide in an anaerobic environment is non-oxidative. Presence of solid cerium oxide can improve the yield above that obtained homogeneously, but this appears to be a result of catalytic dehydrogenation.

The mechanism of catalytic dehydrogenation of ethane to ethylene is different from that of partial oxidation to synthesis gas. Ethylene and hydrogen were observed as products from ethane reacting with the partially reduced unpromoted material. A possible mechanism for this reaction may be:

$$\mathrm{CH_3{-}CH_3} \qquad\qquad \mathrm{CH_2{=}CH_2 + H_2}$$

$$\mathrm{{-}Ce^{3+}{-}O{-} \rightarrow {-}Ce^{3+}(CH_2CH_3)(H)O{-} \rightarrow {-}Ce^{3+}{-}O{-}} \qquad (1)$$

The reaction does not remove oxygen from the surface and water is not formed. The mechanism is here proposed to be of radical nature, although, an ionic mechanism cannot be ruled out.

Oxidation of ethane to carbon oxides and water or hydrogen involves reduction of Ce^{4+} and transport of lattice oxygen in the material. The fully oxidized material is very active for total oxidation of ethane. The partly reduced material is less active for oxidation because the oxygen transport to the sites with adsorbed ethane is restricted. The most important effect of the metal promoters is to increase/facilitate the adsorption of ethane on the surface. The adsorption on the noble metals leads to rapid fragmentation of ethane on the surface.

$$\begin{aligned}\mathrm{CH_3{-}CH_3 + 8{*} &\rightarrow CH_3{-}CH_2{*} + H{*} + 6{*}\\ &\rightarrow CH_y{*} + CH_z{*} + (6-y-z)H{*} + (y+z){*}\end{aligned} \qquad (2)$$

The * represents an active site on the surface. The promoted materials may have active sites both on the surface of the ceria and on the surface of the promoter metals. At lower temperatures the mobility of oxygen from the CeO_2 lattice is slow and the main products will be carbon, hydrogen and methane, e.g.,

$$\mathrm{CH_3{-}CH_3 + 2{*} \rightarrow 2C{*} + H_2 + CH_4} \qquad (3)$$

This becomes a highly selective reaction with the Rh promoter at 500 °C (figure 4).

At higher temperatures the mobility of lattice oxygen is higher and adsorbed carbon species may oxidize to CO:

$$\mathrm{C{*} + 2CeO_2 \rightarrow CO + Ce_2O_3 + {*}} \qquad (4)$$

If the material is partly reduced it will take some time for lattice oxygen to move to the surface, and in the mean time CO may desorb to the gas phase. The fully oxidized material will immediately oxidize adsorbed CO to CO_2 as experienced with the first ethane pulse:

$$\mathrm{CO{*} + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 + {*}} \qquad (5)$$

Hydrogen atoms on the surface of the promoter metal or the partly reduced CeO_2 may combine to H_2 and desorb to the gas phase. The fully oxidized material will immediately oxidize hydrogen to water:

$$\mathrm{2H{*} + 2CeO_2 \rightarrow H_2O + Ce_2O_3 + {*}} \qquad (6)$$

However, a limited amount of hydrogen may be trapped on the ceria surface for some time in hydroxyl groups:

$$\mathrm{{-}Ce^{4+}{-}O{-}Ce^{4+}{-} + H{*} \rightarrow {-}Ce^{4+}(OH){-}O{-}Ce^{3+}{-} + {*}} \qquad (7)$$

This may explain the deficit in the hydrogen balance, which was observed for the products from the first pulse of ethane.

Regeneration of the used materials in oxygen showed that coke gasification and cerium oxide reoxidation occurred simultaneously. The selectivity to carbon oxides during regeneration in oxygen depended strongly on the temperature. The amounts formed of carbon dioxide were much higher during regeneration of all materials at 500 °C compared with that at 700 °C, where the gasification with near 100% selectivity yielded carbon monoxide. This is in good agreement with the thermodynamics of carbon monoxide disproportionation, which is exothermic and yields carbon dioxide at low temperatures. If carbon dioxide is formed at the inlet of the material bed, it can contribute to gasify carbon further down in the bed at high temperatures. Partly reduced cerium oxide can also be oxidized directly by carbon dioxide [12,17].

The results with unpromoted cerium oxide at 700 °C show that a mixture of synthesis gas and ethylene may be produced from ethane. Such a mixture may be used in a hydrocarbonylation process for production of propionaldehyde. Syngas is the usual feed for the Fischer–Tropsch synthesis. A syngas containing ethylene may also be used as a feed for the Fischer–Tropsch synthesis since it is known that under certain conditions ethylene can contribute to the chain growth.

With the noble-metal-promoted cerium oxide much coke is produced together with hydrogen and carbon monoxide. However, gasification of the coke with oxygen at 700 °C in a separate step yields almost pure carbon monoxide, which can be included in the synthesis gas. Thus, in cyclic operation the overall yield of synthesis gas can be high.

4. Conclusions

The selectivity during anaerobic conversion of ethane with cerium oxide depends strongly on the oxidation state of the cerium oxide. Total oxidation of ethane took place with the fully oxidized cerium oxide. The maximum yield of ethylene from ethane in an anaerobic environment was found to be 34% in presence of the partly reduced oxide, $CeO_{1.8}/\gamma$-Al_2O_3. This yield was significantly higher than that observed in the empty reactor (17%) at identical conditions. The dehydrogenation of ethane to ethylene took place with simultaneous production of carbon monoxide and hydrogen. The dehydrogenation was thus non-oxidative. Ethylene was formed by catalytic dehydrogenation on the partly reduced cerium oxide surface.

The main effect of promoting the cerium oxide with metals such as Pt, Rh or Ru was to increase the rate of ethane conversion with simultaneous reduction of the cerium oxide. The promoters increased the production of coke, methane, hydrogen, water and carbon oxides. This was believed caused by the high activity for C–H and C–C bond cleavage introduced by the noble metal promoters. The yield of synthesis gas (CO and H_2) was higher at 700 °C than at 500 °C and it depended on the promoter and the degree of reduction of the cerium oxide. A maximum carbon monoxide yield of 50% was obtained with Pt as promoter. Addition of Rh as promoter yielded almost exclusively coke, methane, hydrogen and coke at 500 °C.

Regeneration of the used materials in oxygen showed that coke gasification and reoxidation of cerium oxide occurred simultaneously. During regeneration at high temperature (700 °C) a high selectivity to carbon monoxide was obtained.

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