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Partial oxidation of light paraffins to synthesis gas in short contact-time reactors

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Abstract

The reaction pathways of ethane and propane partial oxidation to synthesis gas were investigated over a Pt/γ-Al_2O_3 and a Rh/α-Al_2O_3 catalyst. An annular reactor was used for this purpose at high space velocities and at temperatures below 700 °C in order to avoid homogeneous reactions. Under fuel-rich conditions, the Pt-based catalyst produced CO and H_2 at high temperatures (>550 °C), while CO_2 and H_2O were the only reaction products at lower temperatures. The formation of CO and H_2 was consistent with direct oxidation reactions, since contact time had no effect on the product distribution, and secondary reactions (steam and dry reforming) showed negligible activity. The Rh/Al_2O_3 catalyst was also active and selective in the partial oxidation of light hydrocarbons, but in this case the production of hydrogen and CO was strongly dependent on contact time, and steam reforming was important even at short contact times. It was concluded that, over rhodium, both direct and indirect routes were probably involved in the formation of CO and H_2. The main difference between the two noble metals thus seemed to be that Pt mainly produced CO and H_2 by means of O_2 (direct routes), while over Rh the light paraffins were converted to CO and H_2 by means of O_2 and H_2O (direct + indirect routes).

This could explain the remarkably different behavior of the two systems when tested in high temperature autothermal reactors ($T >$ 700 °C). Under adiabatic conditions, the partial oxidation of light paraffins led to large amounts of gas-phase olefinic products over Pt, whereas high selectivities to synthesis gas were found over Rh. The mechanistic results suggest that this different behavior could be due to the varying capability of Pt and Rh surface reactions to compete with homogeneous reactions.

Keywords: Catalytic partial oxidation; H_2 from C_2–C_3 paraffins; Olefins from C_2–C_3 paraffins; Pt/γ-Al_2O_3 catalyst; Rh/α-Al_2O_3 catalyst; Short contact time

1. Introduction

Partial oxidation is presently considered an alternative to steam reforming for the generation of H_2 from fossil fuels in decentralized applications [1,2]. An important example is the generation of H_2 for stationary or mobile fuel cells; other applications have also been proposed such as H_2 injection into gas-turbine combustors for flame stabilization [3] or on-site H_2 production for metallurgical treatments. While methane is the fuel of choice for stationary applications, liquid hydrocarbons (LPG, gasolines and diesels) are preferred for mobile applications [4,5].

The partial oxidation of methane to CO/H_2 mixtures has been discussed in the literature and several catalysts were proposed, including all the Pt-group metals [6]. The extensive work of Schmidt and co-workers on short contact-time reactors [7–11] showed that Rh has high activity and selectivity, superior to that of other noble metals. The use of rhodium leads to the conversion of methane/O_2 mixtures to CO and H_2 at contact times of few milliseconds under adiabatic conditions (i.e. at temperatures higher than 800 °C). Other authors reported similar results [12–14].

The partial oxidation of ethane and propane to CO and H_2 has not been studied to the same extent [15], although ethane and propane are important components of natural gas and major constituents of LPG.

Previous works suggested that the partial oxidation of ethane at high temperature and short contact time over Pt-supported catalysts leads to the production of ethylene and water [16]. Under similar operating conditions, the use of Rh instead of Pt gave rise to a lower production of ethylene, but a large amount of synthesis gas. Recent studies reconsidered those data and showed that the oxidative conversion of ethane to ethylene and water

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in short contact-time autothermal reactors in the presence of Pt is mainly the result of a homogeneous process [17–20].

In previous works, the authors reported the results of experiments in an isothermal short contact-time reactor; they proposed that, under fuel-rich conditions, Pt is uniquely active in the oxidation of light paraffins to CO_X, H_2O and H_2 [21]. Ignition of fuel-rich feed streams was observed at nearly 250 °C with the unique production of CO_2 and H_2O up to 500 °C. Higher temperatures induced the production of CO and H_2 and their selectivities increased significantly with temperature. It was confirmed, however, that, in an autothermal reactor, the onset of gas-phase reactions result in a less important role of the catalytic reactions and in the preferential formation of ethylene.

The aim of the present work was a better understanding of the reaction pathway for the production of synthesis gas from ethane and propane over Pt and of the reason why, at high temperature, homogeneous reactions prevail. By similarly analyzing the reaction mechanism over a Rh-supported catalyst, an answer was searched to the open question of why such competition between heterogeneous and homogeneous reactions apparently does not occur over Rh-catalysts, which favor the selective production of CO/H_2 mixtures even at high temperatures. As well as these fundamental aspects, the study of the partial oxidation of ethane and propane may provide the means to interpret and exploit the partial oxidation of liquid or liquefied hydrocarbons for mobile H_2 generation.

2. Experimental

2.1. Catalysts

The catalysts used in this study were a commercial 5% Pt/γ-Al_2O_3 (Engelhard) used in previous studies [19] and a 0.5% Rh/α-Al_2O_3, prepared according to the procedure developed by Basini et al. [22], a catalyst of proven activity in the partial oxidation of methane to CO and H_2 [13]. In spite of the different noble metal loadings, these materials were used as reference catalysts, since they are representative of the two classes of materials leading preferentially to the autothermal production of olefins and syngas, respectively. In fact, a negligible effect of Pt loading was found by Huff and Schmidt [16] who performed experiments on 2.3 and 4.7% Pt/Al_2O_3 monoliths and obtained equally high selectivities to ethylene. Also, the performances of the Rh/Al_2O_3 catalyst herein used were similar to those reported for Rh-supported monoliths at higher (5%) Rh loading [16]. Still, the comparison herein addressed is qualitative, and not quantitative. A dedicated study on the effect of catalyst composition (nature of the support, noble metal loading and methodology of metal deposition) on partial oxidation to syngas is presently on-going.

2.2. Reactors for short contact time tests

The reaction mechanisms of the partial oxidation of ethane and propane over Pt and Rh catalysts were studied by means of an isothermal annular reactor. The catalyst is present as a thin, short layer, deposited onto a tubular ceramic support, which is inserted into a quartz tube; the gas stream flows between the two tubes in the laminar regime (hydraulic diameter of the annular duct = 4.25 mm), and high flow rates can be realized with virtually no pressure drop. Experiments of partial oxidation in the annular reactor were performed below 700 °C, a range in which previous studies suggested that homogeneous reactions (probed by the appearance of ethylene in the product mixture) do not occur [19]. Concerning the tests with water addition, preliminary blank experiments confirmed the absence of gas-phase reactions within the same range of temperature.

Tests under nearly adiabatic conditions at a few milliseconds residence time were performed in an insulated reactor [19] wherein the catalyst is supported over Fecralloy fibers, which are packed in a quartz reactor between two guard beds of ceramic particles (heat shields). External insulation prevented dispersion in the radial direction. Deposition of the catalysts over the ceramic and metallic supports was achieved by standard washcoating [23].

3. Results

3.1. Partial oxidation of light paraffins over Pt

3.1.1. Effects of temperature and contact time

Previous tests in the annular reactor [24] showed that ethane partial oxidation started at about 250 °C with formation of CO_2 and H_2O. Production of CO began at around 500 °C, while the initial formation of H_2 began above 550 °C; at higher temperatures, the productivity and selectivity of CO and H_2 increased with increasing temperature. Product distribution did not depend on contact time in the range of flow rate investigated. Fig. 1 reports these results; CO C-selectivity and H_2 H-selectivity are plotted as functions of temperature and space velocity (note that CO_2, CO, H_2O and H_2 were uniquely observed in the product mixtures). At the reference temperature of 650 °C, CO C-selectivity and H_2 H-selectivity were always 35 and 15%, respectively, despite the fact that the GHSV varied from 0.3 to 3.0×10^6 L (NTP)/kg-cat/h (a significant range, considering that the conversion of oxygen also changed from 90 to 30%). Contact time did not affect the product distribution, suggesting that all the reaction products (CO_2, CO, H_2O and H_2) are primary products of the ethane oxidation over Pt.

This hypothesis was verified by testing the activity of the catalyst in those secondary reactions (such as steam and

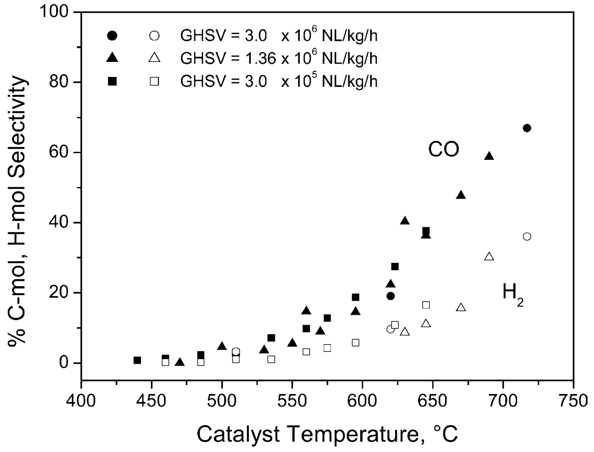

Fig. 1. Effect of temperature and gas hourly space velocity on CO C-selectivity and H_2 H-selectivity from ethane partial oxidation over Pt/Al_2O_3 in annular reactor. Ethane/O_2 feed ratio = 1.

dry reforming), which could, in principle, contribute to the formation of CO and H_2.

3.1.2. *Steam reforming vs. partial oxidation at short contact time*

Activity tests were performed to compare the relative rate of steam reforming and partial oxidation over the Pt-supported catalyst. Since the injection and vaporization of water upstream from the reactor presented difficulties, given the large size of empty volumes of the annular reactor, an alternative solution was adopted; it consisted of synthesizing the desired amount of water right in the reactor. For that purpose, a feed stream of ethane/O_2/H_2 in N_2 was used, and the relative concentration of oxygen and hydrogen was varied so that an equivalent feed of ethane/water/H_2 or ethane/oxygen/water reacted over the catalyst. In practice, the experiments were performed with a relatively long catalyst layer (5 cm, corresponding to about 50 mg of catalyst) with a total flow rate of 0.6 L (NTP)/min, after having verified that 0.5 cm was sufficiently long to convert hydrogen and oxygen into water under the same conditions (temperature, flow rate, and concentration) as those of the steam reforming tests. As shown in Fig. 2a, it was thus assumed that H_2O production occurred at the beginning of the catalyst layer, while most of the rest of the catalyst layer was exposed to a H_2O-enriched feed stream.

Fig. 3a presents the results of reference partial oxidation tests, in which only ethane/O_2/N_2 with respective molar concentrations of 3/3/94 were fed. The usual features of partial oxidation are shown, with the unique formation of CO_2 and water at lower temperatures, and a decrease in CO_2 and an increase of CO at higher temperatures. Above 700 °C a small contribution from gas-phase reactions was indicated by the production of ethylene (not reported in the figure). As expected, H_2 was also produced in small amount. Fig. 3b reports the results of partial oxidation tests in the presence of steam. In these experiments, the reacting mixture was enriched by H_2O (ethane/oxygen/H_2O/N_2 = 3/3/3/91) by feeding a corresponding amount of H_2 and O_2 to the reactor. The results of the experiments corresponded to those of the reference tests; the addition of water did not affect the chemistry of the reaction. The water that had been produced via H_2 combustion was present in the same amount in the outlet stream, and contributed almost nothing to the conversion of ethane or the productivity of CO. A third set of experiments was performed by feeding ethane/O_2/H_2 in the relative amounts corresponding to the equivalent reacting mixture of C_2/H_2O = 3/3 (Fig. 3c); the expected amount of water was observed in the outlet mixture but no conversion of ethane was realized. These data further support the conclusion that, at high space velocity, the role of steam reforming is negligible over Pt.

3.1.3. *Dry reforming and reverse water gas shift at short contact time*

The high temperature decrease in the CO_2 selectivity during the partial oxidation of ethane is due to the onset of CO formation, as well as to a net decrease in the production of CO_2. The possibility that reactions occur with CO_2 as a reactant was, therefore, considered. Tests of partial oxidation,

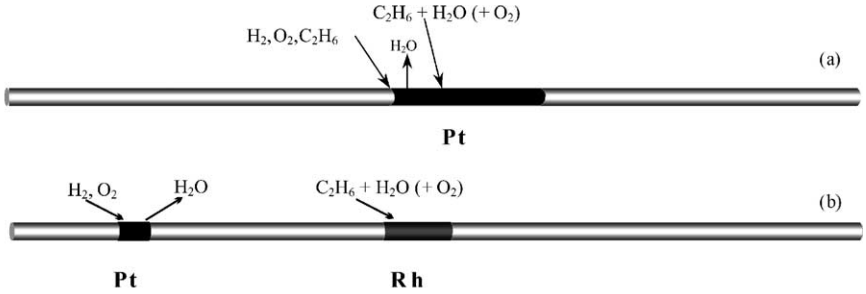

Fig. 2. Tests of partial oxidation with H_2O or steam reforming over Pt were realized by co-feeding ethane, O_2 and H_2 and by using a long catalyst layer (5 cm, 10 times longer than the length required for H_2 oxidation). Tests of partial oxidation with H_2O or steam reforming over Rh were realized by co-feeding ethane, O_2 and H_2 and by using a double catalyst layer reactor, wherein an initial Pt layer kept outside the furnace converted H_2 and O_2, while a second Rh layer was heated by the furnace and converted ethane or propane with H_2O (and O_2).

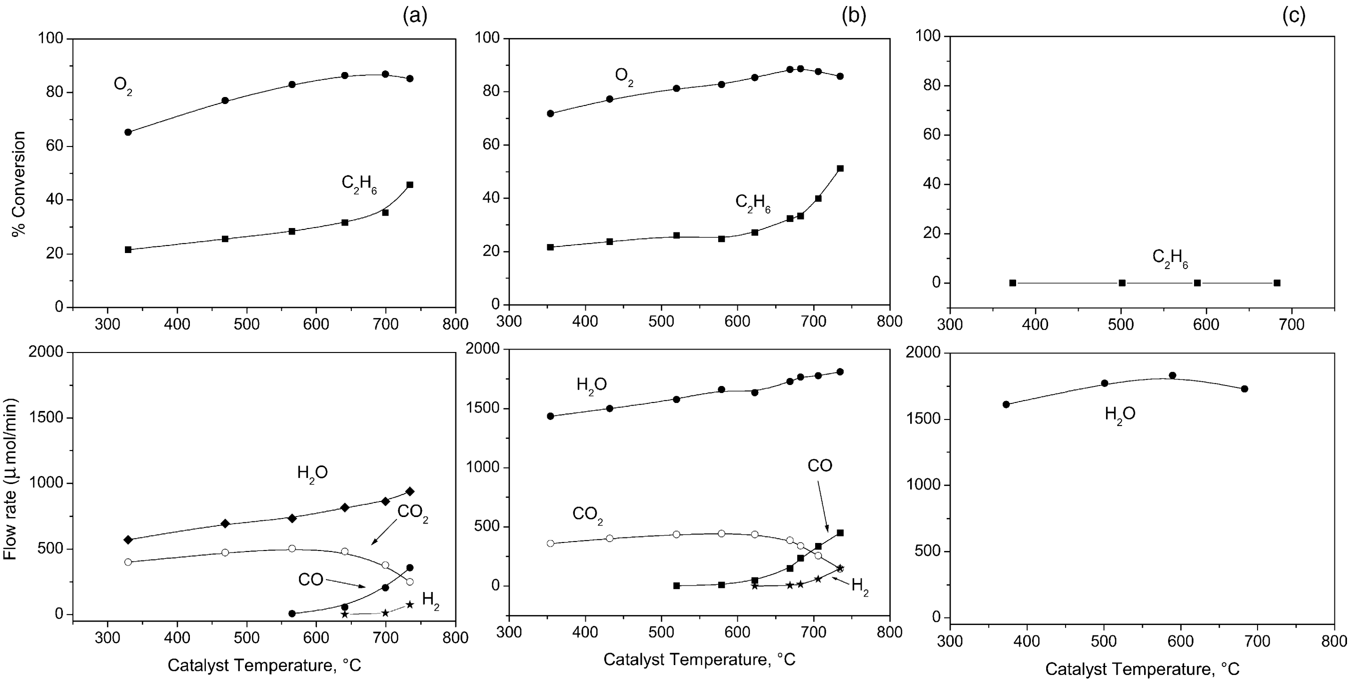

Fig. 3. Comparison of Pt performances under three cases of feed compositions: (a) ethane/O_2/N_2 = 3/3/94; (b) ethane/O_2/H_2O/N_2 = 3/3/3/91; (c) ethane/H_2O/H_2/N_2 = 3/3/5/89. Total flow rate = 0.6 L (NTP)/min. Catalyst load = 50 mg.

with and without addition of CO_2 to the feed stream, were performed to verify the role of dry reforming in the production of synthesis gas (conditions as in Fig. 3a). The results are not reported here. Ignition of the ethane/O_2 mixture did not change in the presence of a large amount of CO_2 (three times that observed during the single ethane/O_2 feed test). This suggests that CO_2 adsorption on the catalyst surface was negligible. In the whole range of applied temperatures, the conversion of ethane and oxygen did not change after the addition of CO_2. The concentration of CO_2 in the outlet stream corresponded to the "natural" amount produced plus the amount of CO_2 injected into the reactor. At the higher temperature, at which the decrease in the CO_2 yield had been observed, the same trend (but higher concentrations) was found in the presence of co-fed CO_2.

Experiments were also performed in which CO_2 and H_2 in N_2, with a respective molar composition of 3/3/94, were fed at the same total flow rate as that in the partial oxidation tests. There was no appreciable conversion of reactants. Only when the flow rate was decreased by a factor of 3, measurable conversions of CO_2 were observed at increasing temperature; CO and H_2O were detected in the product mixture. It was thus concluded that the decrease in the CO_2 flow rate, which is a characteristic feature of the partial oxidation process over Pt at $T > 500\,°C$, was due to a net decrease in the production rate of CO_2 rather than to a consecutive consumption. Dry reforming or reverse water gas shift, in particular, do not explain the effect. This also supports the hypothesis that at sufficiently high temperature the consumption of O_2 was shifted towards partial oxidation products.

3.1.4. *Effect of ethane/O_2 feed ratio*

Fig. 4 shows the results of partial oxidation experiments at ethane/O_2 feed ratios from 1/0.5 to 1/2.6. Note that the stoichiometric ethane/oxygen molar ratio for deep oxidation

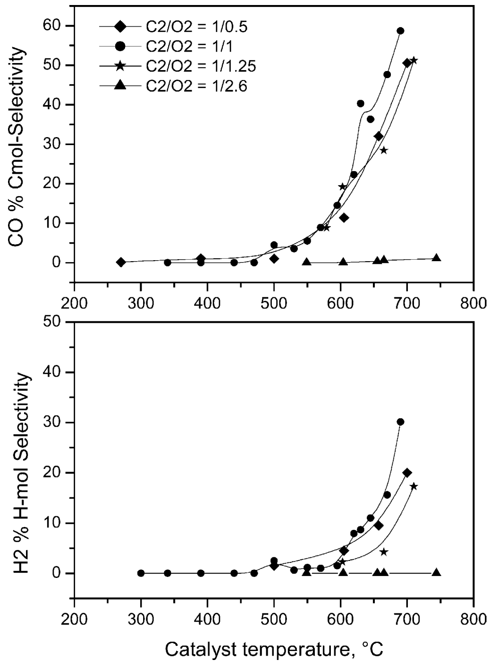

Fig. 4. Effect of ethane/O_2 feed ratio on CO and H_2 selectivities in the partial oxidation of ethane over Pt/Al_2O_3 catalyst. Feed composition: 3% ethane with variable O_2 concentration in N_2. Total flow rate = 1 L (NTP)/min. Catalyst load = 50 mg.

is 1/3.5. The results show that, as long as the oxygen concentration was lower or slightly higher than the ethane concentration, H_2 and CO were produced at high temperatures. However, with the feed ratio 1/2.6, H_2 and CO did not form, while CO_2 and H_2O were the only reaction products at all temperatures. This suggests that the desorption of the partial oxidation products from the Pt surface can only occur successfully at extremely low surface concentrations of oxygen (a condition that is favored in the annular channel by inter-phase mass transfer limitations [23,25]), but cannot compete with the rapid oxidation to CO_2 and H_2O when the concentration of O_2 in the bulk and at the wall increases.

3.1.5. Propane partial oxidation

Results of tests of propane partial oxidation were largely in line with those obtained with ethane [26].

3.2. Partial oxidation of light paraffins over Rh

3.2.1. Effect of contact time

An analogous investigation of the partial oxidation of ethane and propane was performed over the Rh/Al_2O_3 catalyst. Preliminary experiments on the effect of temperature were reported elsewhere [24]. The data, collected under selected operating conditions, were compared with the Pt data. Also in the case of Rh, the conversion of ethane (or propane) and O_2 first started at about 300 °C with the initial, main production of CO_2 and H_2O; above 500–550 °C, higher yields of CO and H_2 were observed compared to Pt. Fig. 5 gives the results of partial oxidation experiments of ethane, in which the flow rate was varied at constant catalyst loading (about 15 mg), feed composition (ethane/O_2/N_2 = 3/3/94), and temperature (640 °C). The GHSV varied from 0.66 to 8.0×10^6 L (NTP)/kg-cat/h. The conversions of both reactants changed significantly within the range of investigated flow rates. At increasing contact time and increasing conversions, the selectivity to the partial oxidation products reached a minimum and then increased significantly, which clearly indicated the existence of a more complex reaction mechanism than that observed over Pt. In particular, this suggested that, over the Rh catalyst, several reactions were involved in the production and consumption of CO and H_2. The range of GHSV explored in the experiments over Pt corresponds to the region of lower flow rates, at which a strong effect of contact time was observed over Rh.

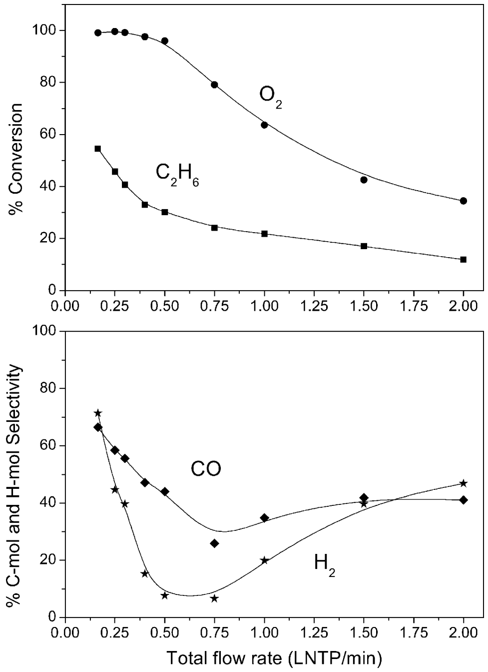

Fig. 5. Effect of contact time on CO and H_2 selectivities in the partial oxidation of ethane over Rh/Al_2O_3 catalyst. Catalyst load = 15 mg, feed composition: ethane/oxygen/N_2 = 3/3/94. $T = 640$ °C.

Assuming that the loss of H_2 and CO selectivity observed at an intermediate flow rate was due to the consecutive oxidation to CO_2 and water, with O_2 still present over the catalyst layer, then the formation at short contact time is in line with a fast direct mechanism of partial oxidation. The pronounced increasing trend at longer contact times was associated with additional contributions of secondary reactions such as steam and dry reforming.

3.2.2. Steam reforming vs. partial oxidation at short contact time

The contribution of steam reforming to CO and H_2 production was verified by comparing their productivity when the feeds consisted of alkane/O_2/N_2, alkane/O_2/H_2O/N_2, and alkane/H_2O/N_2. Again, the injection of H_2O was realized by feeding calibrated amounts of H_2 and O_2 to the reactor, and letting them react over a short Pt layer deposited upstream of the Rh layer (Fig. 2b). Fig. 6 shows the results of the three sets of experiments realized with propane. The addition of H_2O to the fuel-rich stream enhanced both the conversion of propane and the productivity of CO and H_2 (Fig. 6b vs. 6a). Furthermore, in the presence of propane and H_2O without extra-O_2 (Fig. 6c, case of excess H_2 in the feed) propane was still converted to CO and H_2 above 600 °C.

Similar results were obtained from tests of ethane steam reforming. The reaction was active at temperatures higher than 500 °C. Thus, while secondary reactions were negligible over Pt, they played an important role in the kinetics of CO and H_2 formation over Rh. Further work is in progress and will be discussed in detail in a separate paper.

3.3. Partial oxidation of light paraffins in an autothermal reactor in the presence of Pt and Rh

In previous papers, the authors discussed the results of experiments of ethane and propane partial oxidation in an autothermal reactor in the presence of a Pt/Al_2O_3 catalyst. After ignition, the temperature of the reactor stabilized at

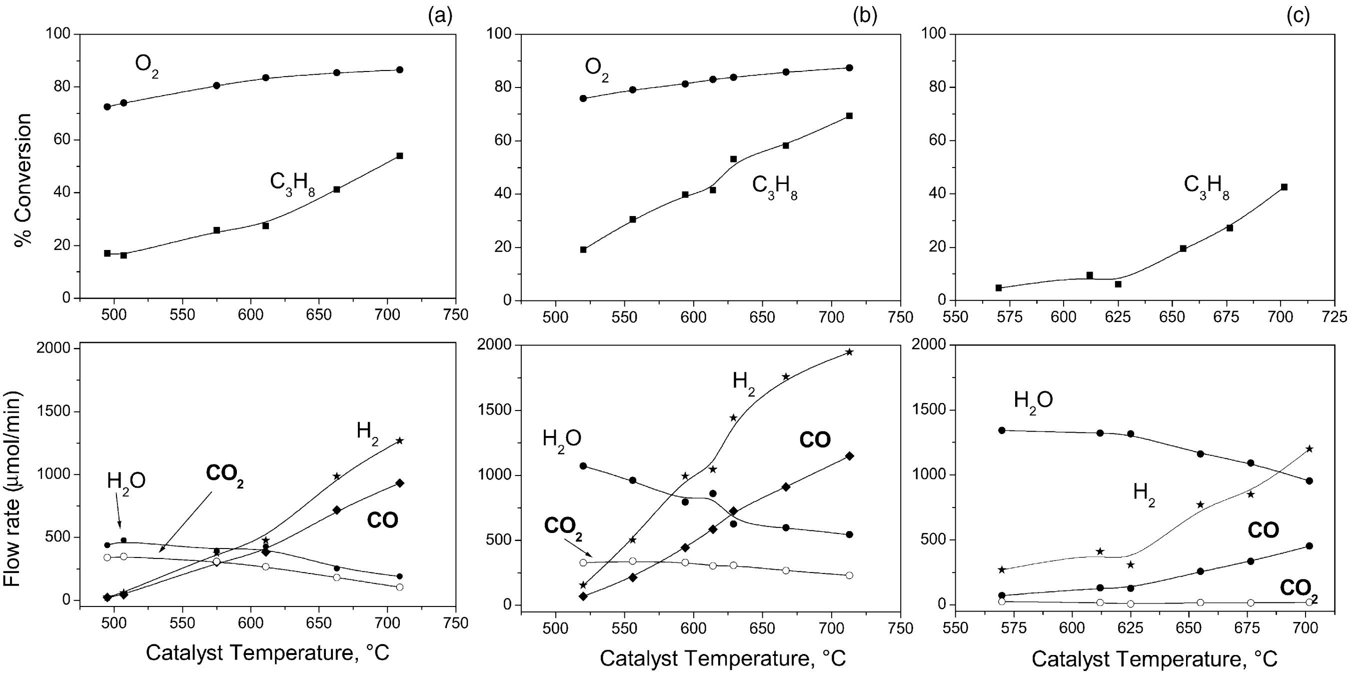

Fig. 6. Comparison of Rh performances under three cases of feed compositions: (a) propane/O_2/N_2 = 3/3/94; (b) propane/O_2/H_2O/N_2 = 3/3/3/91; (c) propane/H_2O/H_2/N_2 = 3/3/5/89. Total flow rate = 0.5 L (NTP)/min. Catalyst load = 50 mg.

values between 700 and 1000 °C (depending on the composition of the feed), and large amounts of olefins were produced (ethylene from ethane/air mixtures and propylene + ethylene from propane/air mixtures). The olefin selectivity increased with increasing hydrocarbon/O_2 feed ratio; over 60% selectivity to ethylene was observed at an ethane/O_2 feed ratio of 1.5. Experimental and theoretical studies clarified that olefins were produced by a homogeneous process that, after a catalytic light-off of the reactor, proceeded spontaneously inside the insulated reactor [19].

Analogous experiments were performed in the autothermal reactor using the Rh-supported catalyst. Table 1 lists some of the results obtained with an ethane/air feed stream, which was preheated at 400 °C to achieve a temperature in the reactor of 1000 °C. It is surprising that almost no ethylene was found in the product mixture, while CO and H_2 were produced with over 90% selectivity. High yields to synthesis gas were also obtained from propane/air mixtures.

4. Discussion

The remarkably different behavior of the Pt and Rh systems in the autothermal partial oxidation of light paraffins can probably be explained by considering the different chemical routes that are catalyzed by the two materials.

Pt-supported catalyst. The kinetic tests in the annular reactor showed that:

- Pt converted the light paraffins to partial and deep oxidation products through direct reactions with O_2. At high temperatures and low surface concentrations of oxygen, the production of CO and H_2 tended to replace the production of CO_2 and H_2O.
- The role of secondary reforming reactions was negligible at short contact time. In particular, the catalyst converted only negligible amounts of paraffin to CO and H_2 when H_2O was the co-reactant.

Table 1
Partial oxidation of ethane in autothermal reactor over Rh/α-Al_2O_3 catalyst[a]

C_2/O_2	T_{max} (°C)	C_2 conversion (%)	C-selectivity (%)			H-selectivity (%)		
			CO	CO_2	$CH_4 + C_2H_4$	H_2	H_2O	$CH_4 + C_2H_4$
0.92	1033	98.5	92.5	5.8	1.7	91.0	7.0	2.0
1.46	870	65.7	92.1	4.1	3.8	92.5	3.9	3.6
1.77	838	53.8	91.4	5.1	3.5	91.5	5.6	2.9

[a] Feed = ethane/air. Total flow rate = 1 L (NTP)/min. Catalyst load = 50 mg. Preheat T = 400 °C. Complete O_2 conversion.

As a consequence, oxidation reactions should be mainly invoked to explain the overall stoichiometry and the product distribution.

In the adiabatic reactor (in which the initial activation of the catalytic oxidations ignites in turn the homogeneous reactions), O_2 is rapidly consumed by the radical process; thus, the capability of the catalyst to convert the hydrocarbons is reduced. Olefins (the products of gas-phase oxidative pyrolysis) then become the major reaction products, while synthesis gas is produced in small amounts only.

Rh-supported catalyst. The kinetic tests in the annular reactor showed that:

- Rh was more selective than Pt in the partial oxidation of light paraffins to CO and H_2.
- The effect of contact time was in line with the existence of both direct partial oxidation reactions (effective at high space velocities) and indirect reactions (effective at lower space velocities) to CO and H_2.
- In particular, Rh was active in converting paraffin/H_2O mixtures into synthesis gas.

As a consequence, both oxidation and steam reforming reactions have important roles in the partial oxidation process.

When the autothermal partial oxidation of ethane was run over Rh no ethylene was observed in the product mixture. This surprising result could, in principle, be explained by considering that Rh can produce CO and H_2 both through a direct pathway by using O_2 and through an indirect pathway by using H_2O. In that case, even when homogeneous reactions (converting an ethane molecule into a probably more reactive ethylene molecule and adding water to the gas phase) take place, the conversion of the C_2 species may still proceed on the catalyst surface through secondary reactions, as long as the contact time (or catalyst load) is sufficiently long.

Thus, Rh would act as a sort of catalytic filter, converting both the feed gases and the gas-phase products into CO and H_2. Indeed, preliminary experiments in which the paraffin feed stream was replaced in part by the corresponding olefin, confirmed that the catalytic partial oxidation of gas-phase products was even faster than that of the paraffin itself.

5. Conclusions

In addition to methane, light paraffins such as ethane and propane can also be converted to CO and H_2 under fuel-rich conditions. Both Pt and Rh are active catalysts for the partial oxidation of light paraffins; in line with the literature on methane partial oxidation, Rh was more active and selective than Pt in the case of ethane and propane, too. Either with Pt and Rh the selectivity to syngas improved with increasing temperature, while deep oxidation only was observed at low temperatures. The same trend was reported in the literature also for methane partial oxidation [8].

The partial oxidation of light paraffins has the advantage of being much more exothermic than the partial oxidation of methane (about 30 kcal per mole of converted ethane compared to 5 kcal per mole of converted methane), so that autothermal operation may be feasible even when air is used instead of pure O_2. This is a desirable feature, especially for the realization of small-scale H_2 generation.

However, one potential limitation of the partial oxidation of light paraffins is that the homogeneous conversion of ethane and propane cannot be avoided at the high temperatures necessary for the autothermal production of synthesis gas, even for extremely short contact times. This is in contrast to the partial oxidation of methane, in which the onset of gas-phase reactions occurs only at higher temperatures.

Homogeneous reactions are known to play the most important role in the conversion of ethane and propane in Pt-containing autothermal reactors. Nevertheless, a highly dispersed Rh/Al_2O_3 catalyst seems to offer the possibility of circumventing the gas-phase process. CO and H_2 were produced selectively, even under conditions which favor the production of olefins. The bulk of data suggests that this could depend on the especially high activity of the Rh-supported catalyst in indirect reactions such as steam reforming.

It is worthwhile mentioning that stable activity was observed during the partial oxidation tests over both Pt and Rh and no direct evidence was available on C formation. It cannot be excluded, however, that in analogy with the partial oxidation of liquid hydrocarbons (wherein coking is a major problem [5]) the partial oxidation light paraffins in autothermal reactors could be accompanied by C-formation, thus requiring a proper tuning of the feed composition (O_2/C ratio, steam addition).

Acknowledgements

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