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Short contact time oxidative dehydrogenation of propane

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Abstract

Short contact time oxidative dehydrogenation of propane has been investigated over a Pt/10%Rh gauze catalyst and a catalyst consisting of VMgO supported on a monolithic substrate. The main focus has been on obtaining information about the roles of homogeneous and heterogeneous reactions by comparing the behavior of the two catalysts with blank runs with no active catalyst in the reactor. The reaction was studied at temperatures ranging from 500 to 950°C and with propane/oxygen ratios between 1.1 and 2.3 at atmospheric pressure. It was observed that ethene, methane and synthesis gas (with a hydrogen/carbon monoxide ratio close to 1.0) were the main products at high conversions of propane. Propene becomes increasingly more important at lower conversions, especially in the presence of an active VMgO catalyst. Very low selectivities to ethene and high selectivities to carbon oxides were obtained with the VMgO catalyst at low conversions of propane ($<20\%$). At high temperatures and high conversions no significant effect of the presence of neither the noble metal catalyst nor the VMgO catalyst was found. Small amounts of ethyne, propyne and benzene were always observed in the product gas. The conversion of oxygen and the selectivity to carbon oxides were higher over the Pt/10%Rh gauze and the VMgO catalyst than in the empty reactor, particularly at the lower conversions of propane. One important role of both catalysts seems to be to ignite and to facilitate the internal production of heat for the gas phase formation of alkenes. The effect of varying the flow rate on the performance of the VMgO catalysts indicates that the heterogeneous reactions are subject to transport limitations as would be expected at these conditions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propane; Oxidative dehydrogenation; Pt/10%Rh gauze catalyst; Monoliths; VMgO catalyst

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1. Introduction

Steam cracking of hydrocarbon feedstocks is the main commercial process for producing lower alkenes such as ethene and propene [1]. Alkene formation is favored by short contact times and in consequence by high temperatures. Propene and the C_4 alkenes are also produced commercially by catalytic dehydrogenation [2] as well as by catalytic cracking in oil refineries [3].

It has recently been shown [4–6] that high yields of C_2–C_4 alkenes can be obtained by oxidative dehydrogenation of alkanes at very short contact times using noble metal impregnated monoliths or noble metal gauze catalysts. Short contact time oxidative dehydrogenation has the attractive potential of being performed in very small-sized reactors, as well as the possibility of autothermal operation. It has been proposed [5] that the catalytic reactor operates by rapid chemical heating followed by rapid quenching to avoid homogeneous reactions.

Previous experimental studies of the partial oxidation of methane on Pt and Pt–Rh gauzes [7,8] at similar conditions have indicated that the reactions in fact mainly proceed on the catalyst surface. However, ethane and propane are more reactive than methane

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and it should therefore be expected that these components are more strongly affected by homogeneous reactions. For the interpretation of experimental results at these conditions it is important to have as detailed information as possible about the temperatures in the reactor. In addition to the catalyst and the gas phase temperature, this also includes the pre- and post-catalytic zones. Unfortunately, reliable temperature measurements at high temperatures are always very difficult. An in-house modeling study indicates that very short residence times in the gas phase at high temperature conditions are sufficient to affect the reactant conversion to a very large degree.

Experimental results documenting the importance and dominance of the homogeneous pathway for the alkene formation during the oxidative dehydrogenation of ethane have recently been published [6,9,10].

The aim of the present work has been to explore the potential of the short contact time reactor for oxidative dehydrogenation of propane. The nature and the extent of surface and gas phase reactions at the short contact time conditions were of particular interest. The previous results obtained with Pt and Pt/10%Rh gauze catalysts show that these catalysts are important for the ignition of the combustion reactions and thereby for an extremely rapid heating of the reactants. It was concluded that the noble metal gauze is catalyzing the combustion reactions, while the dehydrogenation reactions mainly proceed homogeneously in the gas phase [10]. It was also observed that the gauzes deteriorated rapidly at these conditions [6,10] and this lack of stability makes it interesting to study alternative catalytic systems.

Oxide catalysts have been extensively studied for the oxidative dehydrogenation of propane [11] and the VMgO system has been shown to be one of the more promising [12,13]. The studies of the oxidative dehydrogenation of light alkanes over oxide catalysts have normally been performed at longer contact times and lower temperatures than in the present study. In order to obtain better knowledge about the role of different types of catalysts at the very short contact time conditions, it was considered of interest to compare the properties of the VMgO catalyst and the noble metal gauze.

2. Experimental

The VMgO catalyst was prepared by the following procedure: A washcoat of 13 wt.% γ-Al_2O_3 was deposited on cylindrical pieces of extruded monoliths (cordierite from Corning: 400 cells/in^2, diameter: 15 mm, length: 10 mm) using Disperal P2 from Condea. After washcoating the monoliths were calcined in flowing air at 550°C. The precoating with γ-Al_2O_3 was necessary in order to increase the porosity of the cordierite surface in such a way that the VMgO phase could subsequently be deposited and stabilized on the monolith substrate. The VMgO slurry was prepared according to [12] and impregnated on the washcoated monolith followed by a second calcination in air at 600°C. The final VMgO loading was about 1 wt.% of the total mass (V:M:O = 1:3:6 on molar basis). No additional pretreatment was performed prior to the catalytic experiments.

The oxidative dehydrogenation of propane was studied in a quartz reactor with an inner diameter of 15 mm at atmospheric pressure and high temperatures (600–1050°C). The experimental set-up has been described in detail elsewhere [7]. The VMgO coated monolith (10 mm long) was stacked between two cordierite monolith pieces without washcoat and catalyst (both having a length of 10 mm) acting as radiation shields above and below the catalyst. The reactor was heated in an electrical furnace and the axial temperature profile was measured by a moveable thermocouple (chromel–alumel type in a quartz well). The normal position of the catalyst was close to the reactor inlet, providing sufficient residence time for the (in situ) preheating of the reactant/argon mixture while also aiming at minimizing the contributions from gas phase reactions. At the reactor outlet two water-cooled condensers were installed for removal of water from the product stream. The reactants were diluted in argon to lower the partial pressures and for flexibility concerning variation of the feed composition. The total flow rate was 2000 N ml/min unless otherwise mentioned. The flows of propane, air and argon were 308, 769 and 923 N ml/min, respectively, giving a propane/oxygen ratio in the feed of 1.9. The conversions and product selectivities were calculated from on-line GC analysis of the “dry-gas” reactor effluent [7]. Blank runs in the empty reactor and runs with only the washcoated (γ-Al_2O_3 without the VMgO phase) monolith between the uncoated monoliths were also performed as well as runs with only the uncoated monoliths.

The Pt/10%Rh gauze catalyst (from K.A. Rasmussen, Hamar, Norway) was woven from 60 μm diameter wires into 1024 meshes/cm^2. The gauze was cut into 15 mm diameter circular pieces and stacked between the uncoated cordierite pieces.

The residence time is rather difficult to define since the reaction mixture is exposed to high temperatures in front of as well as behind the monoliths. There were large axial temperature gradients inside the reactor, especially in the presence of the catalysts. In addition, measurements of the surface and, in particular of the gas phase temperatures are very uncertain at these rather severe conditions. The axial temperature profile was also strongly depending on parameters such as the furnace temperature, the flow rate and the feed composition. The residence time was therefore calculated from the volumetric flow rate at normal conditions (25°C, 1 bar). The void volume of the catalytic reactor section (the coated cordierite monolith) is well defined. The residence time was calculated to 0.15 s in the empty reactor with a feed of 2000 N ml/min. With the three pieces of cordierite present in the reactor, the residence time was calculated to 0.12 s giving a residence time in the coated cordierite in the middle of 0.04 s. The residence time with the Pt/10%Rh gauze catalysts was calculated to 0.0002 s.

3. Results and discussion

The experiments were carried out by increasing stepwise the furnace temperature and measuring the reactor temperature by the moveable thermocouple and the product gas composition by the on-line GC. With the VMgO coated monolith a sudden increase in the reactor temperature was observed at a furnace temperature of 550–600°C as shown in Fig. 1. The temperature increase caused by ignition could be as high as 200–300°C. The Pt/Rh gauze catalyst showed the same behavior as the VMgO catalyst indicating that these catalysts act as very efficient combustion catalysts.

The conversion of oxygen and propane together with the reactor temperature as measured at the exit of the coated monolith are shown as a function of the furnace temperature in Fig. 1. With a catalyst present in the reactor, a hystheresis behavior in the reactor temperature was observed as shown in Fig. 1 for the VMgO system. The ignition/extinction behavior proceeds as follows: When the furnace temperature was increased before ignition the reactor temperature was lower or close to the furnace temperature. Upon ignition there was a rapid temperature increase inside the reactor. At temperatures higher than the ignition temperature, the difference between the recorded reactor temperature and the furnace temperature decreased with increasing furnace temperature. When the furnace temperature again was reduced, the extinction occurred at a furnace temperature significantly lower than the ignition temperature as shown in Fig. 1. After extinction the catalyst temperature was again equal to the furnace temperature. Of course, the extinction temperature depends on the heat loss from the reactor. In fact, at certain conditions the reactor can be operated autothermally meaning that no external heat input is necessary after ignition.

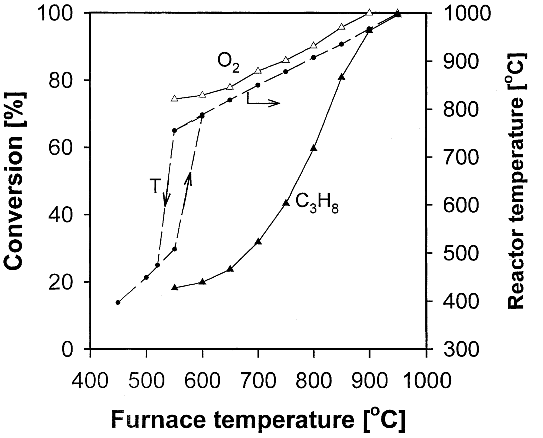

Fig. 1. Conversion of propane and oxygen and observed catalyst exit temperature for the VMgO catalyst as a function of the furnace temperature. Feed (N ml/min): C_3H_8 (308); air (769); Ar (923). Total flow rate: 2000 N ml/min.

As expected, the ignition temperature depends on the feed rate. At a total flow of 2000 N ml/min the ignition occurred at about 20–30°C higher furnace temperatures than with a total flow of 1000 N ml/min. Furnace temperatures below extinction gave no detectable conversion of propane.

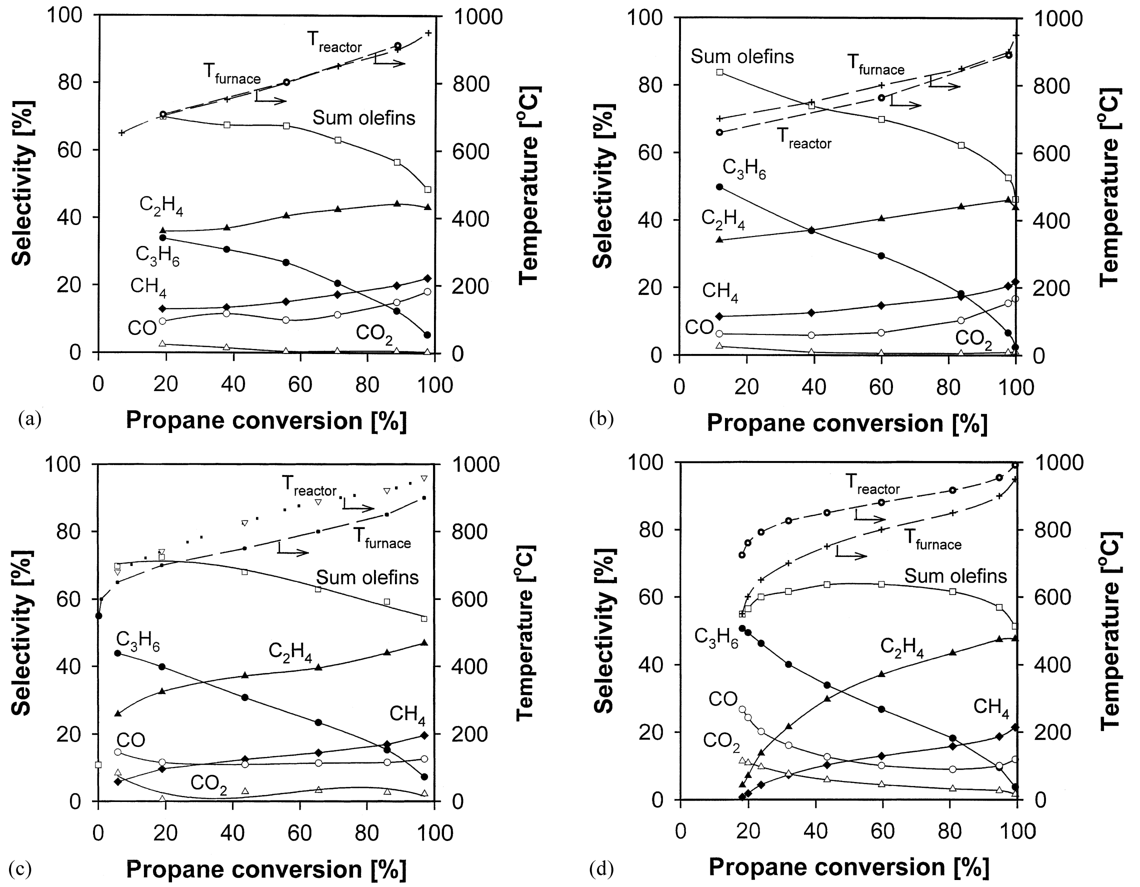

Fig. 2. Product selectivities and reactor/furnace temperatures as a function of the propane conversion. Feed (N ml/min): C_3H_8 (308); air (769); Ar (923). Total flow rate: 2000 N ml/min. (A) The empty reactor; (B) the uncoated monolith; (C) the monolith; (D) the monolith impregnated with VMgO.

With the blank runs using the inert reactor configurations (empty reactor, the reactor with uncoated monoliths and the reactor with one monolith washcoated with Al_2O_3) no ignition was observed even at high temperatures. The induction time for ignition of the gas phase reactions is longer than the actual residence time at these relatively low temperatures.

The effect of varying the furnace temperature, the oxygen concentration in the feed and the total flow were studied for the different reactor configurations. The product selectivities as function of the conversion of propane at various furnace temperatures (500–900°C) are given in Fig. 2A for the empty reactor, in Fig. 2B for the reactor with only the cordierite monoliths, in Fig. 2C for the reactor with one of the monoliths washcoated with γ-Al_2O_3 and Fig. 2D contains the results for the reactor with the washcoated cordierite monolith impregnated with VMgO. The results obtained using the Pt/10%Rh gauze catalyst are shown in Fig. 3. In Fig. 4 the conversion of oxygen for all the different reactor configurations is given and the temperature profiles through the reactor with the different configurations are given in Figs. 5 and 6.

Provided that only homogeneous reactions occur, a well-described correlation between selectivity and conversion of propane exists [14,15]. The comparison of Fig. 2A and B shows the small effect of placing only the monolith pieces in the reactor. Compared with

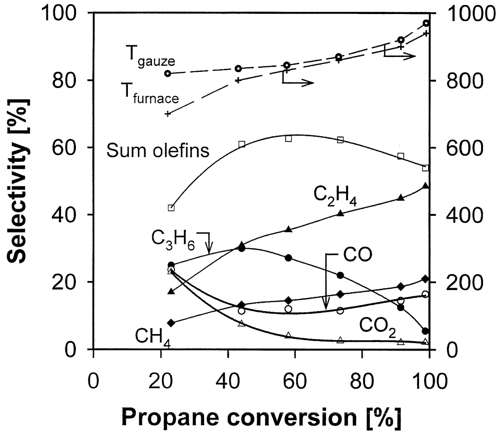

Fig. 3. Product selectivities and reactor/furnace temperatures as a function of the propane conversion over the Pt/10%Rh gauze catalyst. Feed (N ml/min): C_3H_8 (264); O_2 (156); Ar (1580). Total flow rate: 2000 N ml/min.

the empty reactor the monoliths reduce the measured temperature profile in the reactor and cause a small reduction in the selectivity to carbon monoxide with a corresponding increase in the selectivity to propene. The monoliths have an overall void fraction of about 76% and this leads to a slightly reduced residence time. In addition, the monolith pieces act as radiation shields for the thermocouple as demonstrated in Fig. 5. Fig. 4 shows that this configuration also gives the lowest conversion of oxygen. Fig. 2C shows the results obtained using the washcoated monolith. The most pronounced effect is on the temperature profile as shown in Fig. 5. A significantly higher temperature throughout the whole reactor is observed due to the higher conversion of oxygen. The product distribution (Fig. 2C) seems to be more similar to the empty reactor configuration (Fig. 2A) than in the case of the

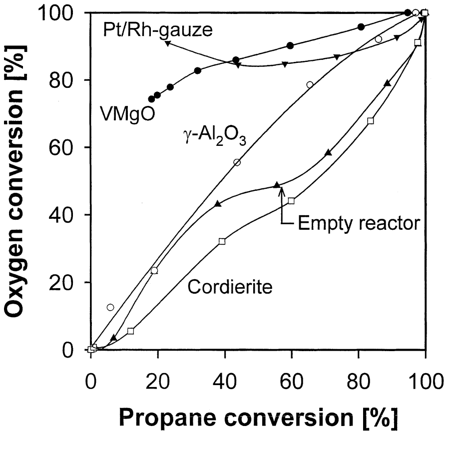

Fig. 4. Conversion of oxygen as a function of the conversion of propane. Feed (N ml/min): C_3H_8 (308); air (769); Ar (923). Total flow rate: 2000 N ml/min.

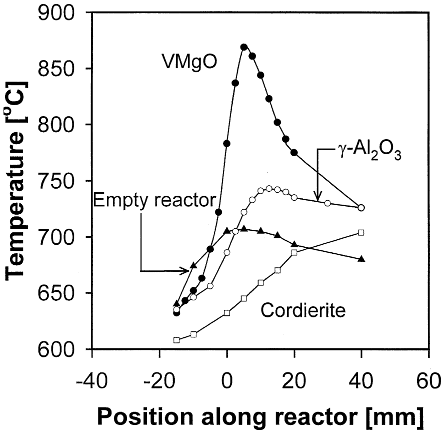

Fig. 5. Axial temperature profiles for the empty reactor, the reactor with the uncoated monolith, the washcoated monolith and the monolith impregnated with VMgO. The inlet of the active monolith was placed at position zero. Furnace temperature: 700°C. Feed (N ml/min): C_3H_8 (308); air (769); Ar (923). Total flow rate: 2000 N ml/min.

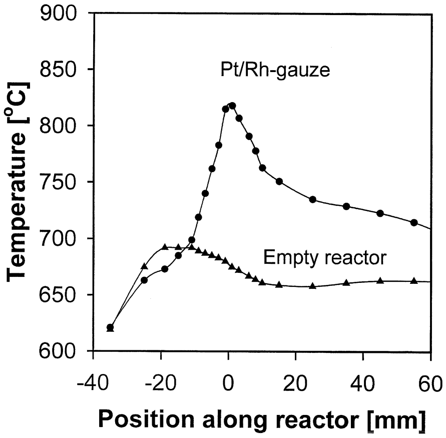

Fig. 6. Axial temperature profiles for the reactor with the Pt/10%Rh gauze catalyst and for the empty reactor. The gauze was placed at position zero. Furnace temperature: 700°C. Feed (N ml/min): C_3H_8 (264); O_2 (156); Ar (1580). Total flow rate: 2000 N ml/min.

uncoated monolith (Fig. 2B) but the differences are not large. The selectivity to carbon oxides is somewhat higher and the propene selectivity is lower. The oxygen conversion is also generally higher compared with the empty reactor and with the uncoated monoliths. This is in good agreement with the findings reported by Huff and Schmidt [16].

However, the presence of the active VMgO phase or the Pt/Rh gauze catalyst changes the behavior of the system quite significantly. Fig. 4 clearly shows that both catalysts decouple the oxygen conversion from the propane conversion indicating formation of carbon oxides. The conversion of oxygen is very high even at low conversion of propane. As expected, the gauze catalyst is a more efficient combustion catalyst at low conversions of propane. The temperature profiles reported in Figs. 5 and 6 are quite different for the reactors containing either the VMgO catalyst or the Pt/Rh gauze catalyst compared to the other systems. The peak temperatures for the two catalytic systems are more than 100°C higher compared with the inert reactor configurations.

The selectivities of the main products are also quite different from the inert reactor configurations (Figs. 2A, B, D and 3). First of all, at low conversions the selectivities to carbon oxides are higher for both catalysts and the selectivity to ethene and methane are lower. The VMgO catalyst gives almost no formation of ethene and methane at the lowest conversions of propane ($<20\%$). This is strikingly different from all the inert reactor configurations and also for the Pt/10%Rh gauze. However, the selectivity to propene is much higher with the VMgO catalyst at low conversions than with the Pt/10%Rh gauze catalyst. At a propane conversion of 20% the selectivity to propene is 50% with the VMgO catalyst and only 23% with the gauze. At high conversion of propane the differences between the performance of the different reactor configurations are rather small.

The catalysts also have an influence on the production of some of the byproducts. The observed ethyne selectivity was low at all conversions. The ethyne formation was least affected by the catalysts, but strongly favored by high reaction temperatures and approached almost 4% selectivity at reaction temperatures above 850°C. The ethyne selectivity depends also on the residence time. Trace amounts of propyne were observed in the empty reactor, increasing with the conversion of propane towards a selectivity of approximately 0.5% at complete conversion. However, in the presence of both the γ-Al_2O_3 washcoat and the VMgO catalyst, the selectivity to propyne was rather high (3%) at low conversions and decreasing with increasing conversion of propane. Propyne was formed even at the lowest temperatures and conversions in the presence of the VMgO catalyst. The formation of ethyne and propyne was expected at these high temperature conditions [17,18]. However, the presence of alkynes is unwanted in a process for light alkane dehydrogenation since they have to be removed in a separate selective hydrogenation step. Alkynes, although in small amounts, were indeed observed at all conversions in this study.

The formation of higher hydrocarbons (C_{4+}) was not significantly affected by the presence of neither γ-Al_2O_3 nor the VMgO catalyst. C_{4+} products were hardly detectable at low furnace temperatures, reaching a maximum selectivity of about 5% at a temperature of 900°C and decreasing with even higher temperatures. The maximum C_{4+} selectivity was observed at a propane conversion of 50% in the empty reactor. With the γ-Al_2O_3 washcoat and the VMgO catalyst present in the reactor, the C_{4+} selectivity reached a maximum level at a conversion of propane of 80%. This is also in good agreement with the relationship between the propane conversion and product selectivities observed over Pt/10%Rh gauze catalyst [10]. One effect of the gauze was to shift the C_{4+} maximum to a slightly higher conversion level.

The results presented in Figs. 2–6 lead to the conclusion that the presence of the VMgO catalyst and the Pt/10%Rh gauze affected the system most significantly at low conversions of propane. The catalysts obviously enhanced the internal production of heat by favoring in situ combustion, especially for the gauze catalyst. At these conditions, the selectivities to ethene and methane were lower and the selectivities to propene and carbon oxides were higher, in particular for the VMgO catalyst. Only minor effects of the catalysts were observed at higher temperatures and conversions.

The total flow rate was varied at a constant feed composition and a constant furnace temperature of 600°C. This temperature level was chosen to ensure an influence of the active catalyst on the reaction. Fig. 7 indicates that the conversion of propane and the

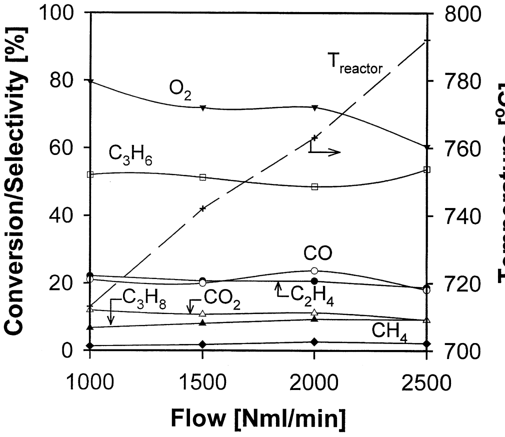

Fig. 7. Effect of total flow rate on the conversion, selectivity and catalyst outlet temperatures over the VMgO catalyst. Furnace temperature: 600°C, propane/oxygen ratio: 1.9.

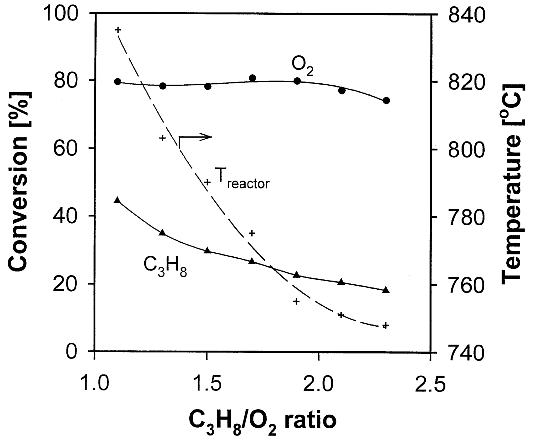

Fig. 8. Effect of the propane/oxygen ratio on the conversion and the reactor temperature for the VMgO catalyst. Feed (N ml/min): C_3H_8 (308); air (641–1282); Ar (1051–410). Total flow rate: 2000 N ml/min. Furnace temperature: 600°C.

selectivities to alkenes remain fairly constant in the investigated flow range and that the conversion of oxygen and the selectivities to carbon oxides decreased somewhat upon an increase in the flow rate. The temperature measured at the catalyst exit increased by approximately 80°C when increasing the flow rate from 1000 to 2500 N ml/min (Fig. 7).

A factor that generally complicates the kinetic interpretation of the results from catalytic high temperature oxidative systems is the presence of transport limitations. Both heat and mass transport limitations have been documented to be very important during the partial oxidation of methane over gauze catalysts at similar conditions as in the present work [19,20]. As mentioned, the heat production increased as a result of increased flow rate. It was stated above that the effect of the catalyst was mainly to supply heat by in situ combustion. The variations in the flow rate therefore indicate that the exothermal catalytic combustion processes are subject to transport limitations.

The propane/oxygen ratio was varied in the range 1.1–2.3 at a constant feed rate (2000 N ml/min), furnace temperature (600°C) and propane partial pressure (0.15 bar). Fig. 8 shows that the propane conversion and especially the catalyst exit temperature decreases strongly with increasing propane/oxygen ratio. The major effect was observed on the selectivities to propene, ethene and methane as shown in Fig. 9. The selectivities to carbon oxides were fairly constant. The selectivity to propene increased with increasing propane/oxygen ratio, whereas the selectivity to ethene and methane decreased. This shift in product distribution can partly be explained by the change in temperature. The relation between conversion and selectivity, as shown in Fig. 9, is qualitatively similar to what is shown in Fig. 2D where only the external furnace temperature is varied. The yield of carbon oxides increased from about 6 to 14% over the range studied, which is in good agreement with

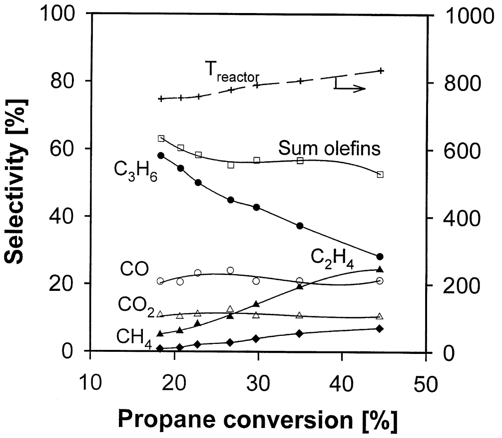

Fig. 9. Product distribution and the reactor temperature for the VMgO catalyst as a function of propane conversion. The results were obtained at various propane/oxygen ratios as given in Fig. 8.

the increase in the catalyst exit temperature. This is a strong indication that the partial pressure of oxygen mainly affects the reactor temperature, which then affects the alkene formation. The above result therefore indicates that alkenes and methane are produced mainly in homogeneous reactions.

It appears that the VMgO catalysts play the same role as the Pt and Pt/Rh gauze catalysts for this system [10]. The production of carbon oxides was clearly enhanced by the Pt/10%Rh gauze and the VMgO catalysts, thus efficiently providing more energy for the homogeneous reaction. However, the VMgO catalyst gives a much better propene selectivity at low conversion levels than the Pt/10%Rh catalyst.

4. Conclusions

Ethene is the main product formed from the oxidative dehydrogenation of propane over different catalysts (Pt/10%Rh gauze and VMgO impregnated monoliths) at very short contact time conditions. At high temperatures with almost complete conversion of propane the main products formed are ethene, methane and synthesis gas with a hydrogen/carbon monoxide ratio close to 1. The maximum yield of ethene is about 50% at these conditions. Propene becomes gradually an increasingly important product at lower conversions and more so for the VMgO catalyst than for the Pt/10%Rh gauze. However, at low conversion of propane ($<20\%$) almost no ethene nor methane was observed in the product gas from the reactor with the active VMgO catalyst.

Important byproducts are ethyne and propyne. These products, as well as the higher hydrocarbons (C_{4+}), were especially favored by high reaction temperatures. The formation of propyne was enhanced at low conversions by the VMgO catalyst.

At high temperatures and high conversions very similar results were obtained with all the different reactor configurations studied: Pt/10%Rh gauze, VMgO impregnated monolith, only washcoated (γ-Al_2O_3) monolith, uncoated monoliths and the empty reactor. This result indicates the importance of the gas phase reactions in these systems. At lower conversions the different reactor configurations showed some different behavior. The gauze is a particularly efficient oxygen converter at the lower propane conversions studied. It was seemingly possible to obtain complete conversion of both propane and oxygen with the VMgO catalyst. For the other configurations the oxygen conversion was strongly correlated to the propane conversion.

The role of both catalysts seems mainly to be to ignite and to facilitate the production of internal heat for the gas phase formation of the alkenes. Flow variations with the VMgO catalysts system indicate that the heterogeneous reactions are subject to transport limitations.

Acknowledgements

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References

[1] L.F. Albright, B.L. Crynes, W.H. Corcoran (Eds.), Pyrolysis: Theory and Industrial Practice, Academic Press, London, 1983.
[2] D.E. Resasco, G.L. Haller, Catalysis (London) 11 (1994) 379.
[3] P.B. Venuto, E.T. Habib, Fluid Catalytic Cracking with Zeolite Catalysts, Marcel Dekker, New York, 1979.
[4] M. Huff, L.D. Schmidt, J. Phys. Chem. 97 (1993) 11815.
[5] D.A. Goetsch, L.D. Schmidt, Science 271 (1996) 1560.
[6] R. Lødeng, O.A. Lindvåg, S. Kvisle, H. Reier-Nielsen, A. Holmen, Stud. Surf. Sci. Catal. 119 (1998) 641.
[7] K. Heitnes Hofstad, O.A. Rokstad, A. Holmen, Catal. Lett. 36 (1996) 25.
[8] K. Heitnes Hofstad, O.A. Rokstad, A. Holmen, Catal. Lett. 45 (1997) 97.
[9] A. Beretta, M.E. Gasperini, G. Trepiedi, L. Piovesan, P. Forzatti, Stud. Surf. Sci. Catal. 119 (1998) 659.
[10] R. Lødeng, O.A. Lindvåg, S. Kvisle, H. Reier-Nielsen, A. Holmen, Appl. Catal. A 187 (1999) 25.
[11] H.H. Kung, Adv. Catal. 40 (1994) 1.
[12] H.H. Kung, M.A. Chaar, US Patent No. 4,777,319 (1998).
[13] M.A. Chaar, D. Patel, M.C. Kung, H.H. Kung, J. Catal. 109 (1988) 463.
[14] A. Beretta, L. Piovesan, P. Forzatti, J. Catal. 184 (1999) 455.
[15] A. Beretta, P. Forzatti, E. Ranzi, J. Catal. 184 (1999) 469.
[16] M. Huff, L.D. Schmidt, J. Catal. 149 (1994) 127.
[17] A. Holmen, O. Olsvik, O.A. Rokstad, Fuel Proc. Technol. 42 (1995) 249.
[18] K.L. Hohn, P.M. Witt, M.B. Davis, L.D. Schmidt, Catal. Lett. 54 (1998) 113.
[19] D.A. Hickman, L.D. Schmidt, J. Catal. 136 (1992) 300.
[20] C.R.H. de Smet, M.H.J.M. de Croon, R.J. Berger, G.B. Marin, J.C. Schouten, Appl. Catal. A 187 (1999) 33.