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Partial oxidation of methane to synthesis gas at very short contact times

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Abstract

Catalytic partial oxidation of methane has been studied over Pt, Pt/Rh, Pt/Ir and Pd gauze catalysts at contact times in the range 0.00021–0.00033 s. The experiments were carried out at 1 bar and 700–1100°C using a single gauze in a quartz reactor heated in an electric furnace. The feed consisted of CH_4, O_2 and inert (Ar) and with different ratios between CH_4 and O_2. High selectivities to CO were observed at high temperatures. However, the selectivity to H_2 was always rather low (below 30% in most cases) at these conditions with incomplete conversion of O_2. Alloying the Pt gauze with Rh improves the selectivity to synthesis gas as well as the time on stream behaviour. The effect of the CH_4/O_2 ratio depends on the gauze. The selectivity to synthesis gas decreased with increasing amount of O_2 on the Pt gauze whereas the opposite effect was observed on a Pt/Rh gauze. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Synthesis gas; Methane; Gauze catalysts; Partial oxidation

1. Introduction

Two different routes exist for the conversion of methane to fuels and chemicals, either via synthesis gas or directly to C_2 hydrocarbons or methanol. Commercial processes for methane conversion are all based on synthesis gas. Steam reforming is the dominant process for production of synthesis gas [1]. However, oxidation reactions are generally much faster than steam reforming suggesting that synthesis gas could be produced in smaller reactors by using O_2 instead of steam.

It is usually observed that the catalytic partial oxidation of methane consists of two steps: Total oxidation of part of the methane followed by H_2O and CO_2 reforming [2]. However, different proposals exist regarding the formation of primary products in the catalytic partial oxidation of methane [3–6]. A large research effort is presently being carried out on the catalytic partial oxidation of methane to synthesis gas [7].

Since the reforming reactions are slower than the oxidation reactions it should be possible to study the partial oxidation without being influenced to any large extent by secondary reactions at very short contact times. In fact, by using gauze catalysts it has been shown that the partial oxidation can be studied at such conditions [3,8]. High temperature reactions at extremely short contact times are also interesting in many

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other applications [9]. The present work was initiated in order to study the behaviour of different gauzes on the partial oxidation of methane.

2. Experimental

The following metal gauzes (supplied by K.A. Rasmussen) were used: Pt, Pt/5%Rh, Pt/10%Rh, Pt/10%Ir and Pd. The gauzes were woven from metal wires with different diameters. The Pt/10%Rh and the Pt/5%Rh gauzes were woven into 1024 meshes/cm^2 from wires with a diameter of 60 μm and the Pt gauze (256 meshes/cm^2) was made from a 90 μm wire. Experiments have also been carried out with a Pt gauze of the same size as the Pt/Rh gauzes (Fig. 1(a) and (b)). The Pt/10%Ir and the Pd gauzes had 250 meshes/cm^2 (120 μm wire) and 256 meshes/cm^2 (180 μm wire), respectively. Before use the Pt/10%Rh gauze has a surface area of 0.005 m^2/g [10]. Since the different gauzes had different mesh sizes (and wire diameters) it means that the reactor volume and the space times are not exactly the same at a constant feed rate.

The experiments were carried out in a conventional flow apparatus using a quartz reactor with a circular gauze held between two cylindrical pieces of a ceramic monolith (Cordierite from Corning, 400 cells/in.^{2}). The diameter of the gauze, the monolith pieces and the reactor was 15 mm. The quartz reactor was placed inside a furnace. The gauze temperature was measured by a moveable thermocouple inside the reactor, and controlled by careful regulation of the furnace temperature. In addition to the moveable thermocouple, an optical pyrometer was also used to measure the gauze temperature. The two methods gave almost identical values.

The products were analysed by gas chromatography. Prereduction of the gauze was carried out in situ with H_2 at 600°C for $1\frac{1}{2}$ h. The gauze was then heated to 920°C in argon atmosphere. The methane and oxygen diluted in argon were introduced, and the ignition caused the gauze temperature to rise to above 1000°C. The gauze was then cooled to the desired temperature by temporarily turning off the heat and venting the furnace if necessary.

3. Results and discussion

Experiments were initially performed without any catalyst present and also without the two pieces of

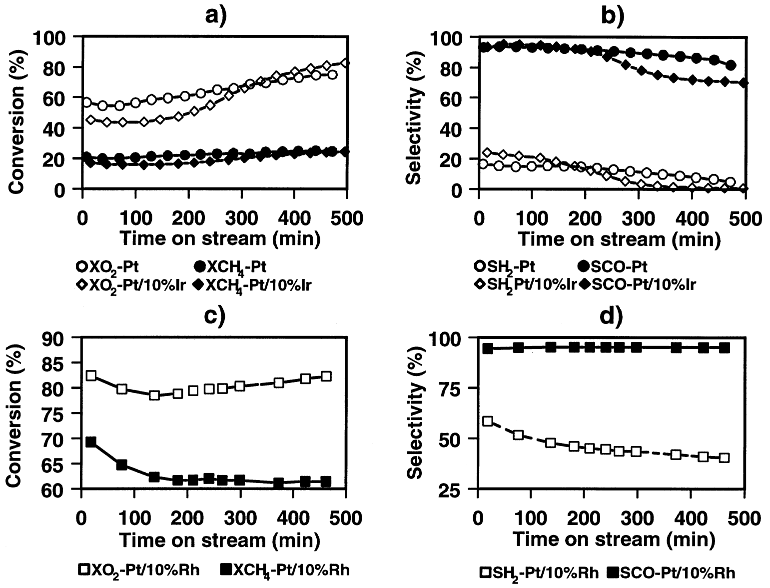

Fig. 1. Effect of time on stream: (a), (b) Conversion (X) and selectivity (S) over Pt (1024 meshes/cm^2) and Pt/10%Ir gauzes at 990°C and CH_4:O_2:Ar feed ratio of 2:1:10. (c), (d) Conversion and selectivity over a Pt/10%Rh gauze at 1100°C and CH_4:O_2:Ar feed ratio of 2:1.6:9.4. The total gas flow is 2000 N ml/min.

cordierite in the reactor but at exactly the same conditions as with a gauze present. Initiation of the methane oxidation without any catalyst requires very high temperatures. The conversion of methane was less than 5% at 1000°C. Small amounts of C_2 were observed with a maximum selectivity to C_2H_6 of 50% at 850°C. CO_2 was the main carbon oxide below 970°C. The cordierite did not influence the conversion of CH_4, but the C_2-formation was higher with the pieces of cordierite in the reactor (maximum selectivity of 75%).

The activity, selectivity and stability of the different gauzes were studied as a function of the temperature and the ratio between CH_4 and O_2 in the feed. The gauzes show different ignition temperatures at a total feed rate of 2000 Nml/min and a feed composition of CH_4:O_2:Ar=2:1:10. The following ignition temperatures were observed: Pt: 800°C, Pt/5%Rh and Pt/10%Ir: 820°C, Pt/10%Rh: 880°C and Pd: 620°C. However, due to the formation of PdO the Pd gauze was not suitable for studying the partial oxidation of methane at high temperature.

The time on stream behaviour of the different gauzes is shown in Fig. 1(a)–(d). The Pt and the Pt/10%Ir gauzes loose syngas selectivity as time on stream increases (Fig. 1(a) and (b)). It was observed that the temperature in the monolith downstream of the gauze increased during an experiment indicating that metal is possibly transported from the gauze to the monolith where it causes secondary combustion of both CO and H_2.

The Pt/10%Rh gauze has been studied at different conditions, e.g. higher temperatures. It is of interest to recognize that a much higher conversion of methane is obtained with the Pt/10%Rh gauze compared with the Pt (and the Pt/10%Ir) gauze, but the conversion of oxygen is about the same after 500 min on stream. A major difference is also observed in the selectivity of hydrogen. However, it must be emphasized that the results for the Pt gauze given in Fig. 1 are obtained at 990°C whereas 1100°C (and a different feed composition) was used for the Pt/10%Rh gauze. The Pt and the Pt–Rh gauzes in Fig. 1 have the same mesh size (1024 meshes/cm^2). No temperature increase was observed downstream of the Pt/10%Rh gauze and it is believed that the decrease in the selectivity of H_2 is caused by a change in the surface properties of the metal rather than metal migration. It is well known from ammonia oxidation that alloying the Pt gauze with Rh increases the stability of the gauze [11].

The conversion and the selectivity of the Pt and Pt/Rh gauzes have been studied at different temperatures and CH_4:O_2 ratios in the feed. The experiments at different temperatures have been carried out in the following way: The gauze was cooled down rapidly after ignition and the temperature was then increased in steps of 100°C to 1100°C, and thereafter reduced in the same way to 700°C. Analysis of the product gas was performed at each temperature level and the results are shown in Fig. 2(a)–(d). The high temperatures were not held for long periods of time and no significant ageing of the catalyst was observed.

Fig. 2 clearly shows that the increase in conversion of methane and oxygen with temperature is very low indicating that the reaction rate is controlled by mass transfer limitations. For the Pt gauze the conversion is almost constant and independent of the temperature. At higher temperatures the linear gas velocity will increase and the space time decrease due to the fact that the experiments have been performed at a constant feed rate. The increased gas velocity means that at higher temperatures larger parts of the reactants may pass through the gauze without having any contact with the metal. The Pt gauze in Fig. 2 has a much more open structure than the Pt/Rh gauzes (256 and 1024 meshes/cm^2, respectively). This will give a less distinct temperature response for the Pt gauze compared with the Pt/Rh gauzes.

As expected the selectivity to syngas increases with increasing temperature and at 1000°C the selectivity to CO is more than 95% for the Pt/10%Rh gauze. At these conditions with incomplete conversion of O_2 the selectivity to H_2 is rather low and in addition there is a large difference between the Pt and the Pt/Rh gauzes. It has been reported that Rh-impregnated monoliths are superior to Pt monoliths for the production of syngas, an observation which has been explained by the higher heat of adsorption of oxygen on Rh than Pt [12].

The ratio of CH_4 to O_2 in the feed has been varied from 1.3 to 4 and the results at 900°C for the Pt and Pt/5%Rh gauzes are given in Fig. 3. The results clearly show that for the Pt gauze the conversion of methane decreases and the selectivity to syngas increases with increasing CH_4:O_2 ratio in the feed. However, for the

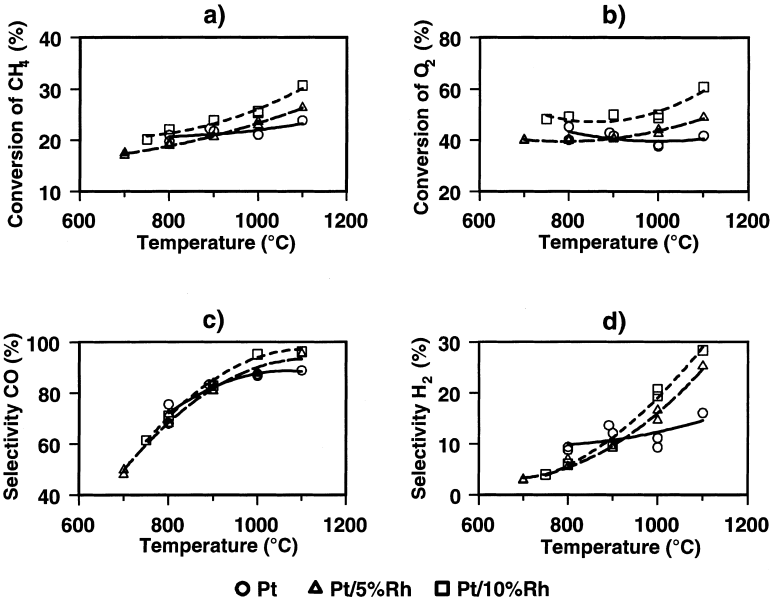

Fig. 2. Influence of gauze temperature on conversion and selectivity over Pt (256 meshes/cm^2) and Pt/Rh gauzes. Total gas flow is 2000 Nml/min and the CH_4:O_2:Ar ratio is 2:1:10.

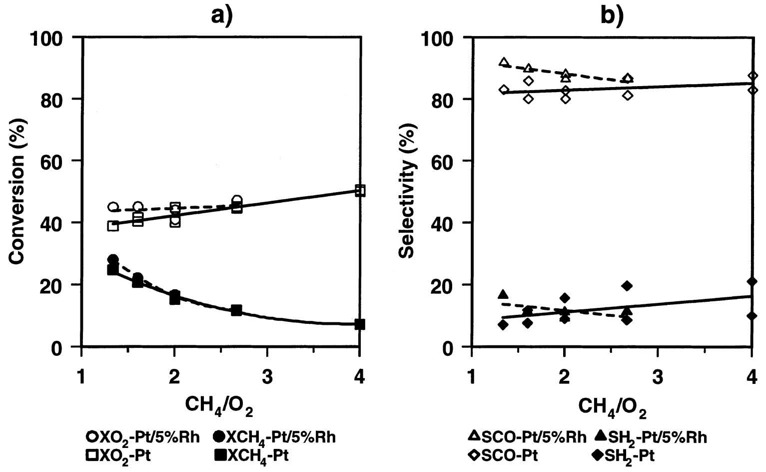

Fig. 3. Conversion (*X*) and selectivity (*S*) over a Pt and a Pt/5%Rh gauze as function of CH_4/O_2 ratio in the feed gas, T=900°C, total gas flow=2000 Nml/min.

Pt/5%Rh gauze the selectivity to syngas decreases with increasing CH_4:O_2 ratio indicating that the higher partial pressure of O_2 changes the oxidation state of the surface or/and the surface composition.

The results presented in Fig. 1(c) and (d) are obtained using a CH_4:O_2 ratio of 2:1.6 in the feed. It has been shown that the steady-state conversion of methane on the Pt/10%Rh gauze at 1100°C increases from 30% with CH_4:O_2=2:1 to 60% using CH_4:O_2=2:1.6.

4. Conclusion

The Pt/Rh gauzes are superior to the Pt gauze as far as syngas selectivity and time on stream stability are concerned. For the Pt/5%Rh gauze the selectivity to CO+H_2 increases with increasing concentration of O_2 in the feed whereas the opposite effect is observed for the Pt gauze. Noble metal gauzes are very effective for combustion of H_2.

Acknowledgements

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