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Catalytic partial oxidation of methane to synthesis gas

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Abstract

The partial oxidation of methane to synthesis gas has been studied using several different catalytic systems: Fixed-bed, a monolithic type catalyst, and a Pt gauze. The monoliths were impregnated with Ni and Pd (5 wt.% metal) whereas 5% Ni/Al_2O_3 was used in the fixed-bed reactor. The experiments were carried out at 500–800°C, 1 bar and with space times in the range of 0.14–0.0002 s. The measured temperature profiles for both the fixed-bed and the monolithic reactor indicate that the reaction consists of a total combustion of some of the methane followed by the endothermic reforming reactions and the water–gas shift reaction. Selectivities close to equilibrium composition were obtained in most cases except at the very low space times. Only small amounts of H_2 were observed in the product gas from the Pt gauze catalyst.

1. Introduction

Steam reforming is the preferred commercial process for production of synthesis gas from methane [1]. However, interest has recently focused on alternative methods such as partial oxidation and different combinations of steam reforming and partial oxidation [2]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^0_{298} = 206 \text{ kJ/mol}$$

$$CH_4 + 1/2O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H^0_{298} = -36 \text{ kJ/mol}$$

Partial oxidation gives a H_2/CO ratio suitable for the Fischer–Tropsch synthesis and for the production of methanol [2].

Partial oxidation has been the subject of a number of recent studies [3–7]. Yields of CO and H_2 close to equilibrium values have been reported and the results indicate that the partial oxidation consists of an initial combustion followed by H_2O and CO_2 reforming and water–gas shift. However, it has also been concluded that the selectivity depends on the catalyst [8–10]. In addition, high selectivities to CO and H_2 even at low temperatures have been reported [11], although reexamination of these results shows that it most probably is the result of inadequate temperature measurements [12,13].

The present work deals with the partial oxidation of methane in different catalytic systems: Supported catalyst particles, monolithic catalysts and gauze catalysts. Monoliths have been proposed as a suitable system for partial oxidation [6,14,15]. The main objective with the gauze catalyst was to study the reaction at very short space times.

2. Experimental

The experiments have been carried out in a conventional flow apparatus using either a quartz

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reactor or a steel reactor into which the catalysts were placed. The fixed-bed microreactor had an internal diameter of 6 mm whereas the reactor for the monoliths and the gauze catalyst was made according to the size of the catalysts. The supported Ni catalyst was made by wet impregnation of γ-Al_2O_3 (Akzo, Alumina 000-1 1/2) with $Ni(NO_3)_2 \cdot 6H_2O$ (Merck). The monoliths (cordierite supplied by Corning, 400 cells/sq. in) were cut into cylindrical pieces with a diameter of 15 mm and a length of 23 mm or less. The monoliths were wash-coated (γ-Al_2O_3) before impregnating with $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) or $Pd(NO_3)_2$ (Johnson Matthey). The gauzes were woven from a Pt wire of 60 μm diameter (1024 meshes/cm^2) and cut into 15 mm diameter circles. The catalyst consists of only one layer of the Pt gauze. All the catalysts were calcined in air at 500–550°C and finally reduced with H_2 at 600°C for 1.5 h.

The catalytic experiments were performed at 500–800°C, 1 bar and with space times (τ) between 0.14 and 0.0002 s (referred to 1 bar and 0°C). The CH_4/O_2 ratio was kept constant and equal to 2 and the feed was always diluted with He. The reactor was heated by an electrical furnace and the reactor was placed in the isothermal part of the furnace. The axial temperature profile was measured at the center of the catalysts by a moveable thermocouple. (Chromel–Alumel protected by a quartz tube.) Conversion and selectivities were obtained by on line GC analysis of the reactor effluent using nitrogen as an internal standard. Light gases were analyzed on a 3 m Carbosieve S-2 column using a TCD detector and the hydrocarbons could be separated on a 30 m GS-Q column and detected by FID.

3. Results and discussion

3.1. Fixed-bed reactor

Control experiments with empty quartz reactors with and without supports have been carried out

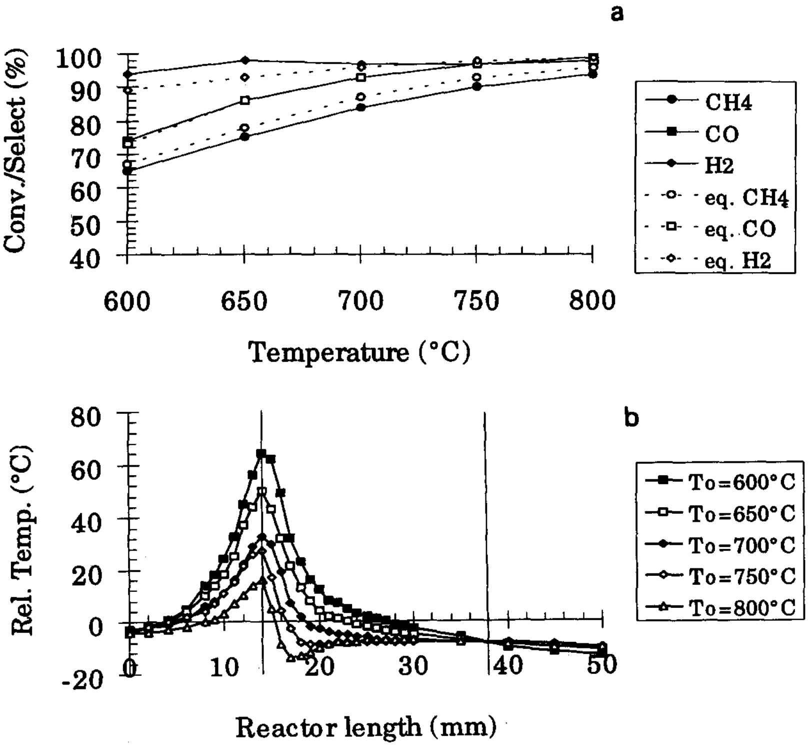

Fig. 1. (a) Conversion and selectivities over the 5 wt.% Ni/Al_2O_3. Feed CH_4:O_2:He = 2:1:7, τ = 0.14s. (b) Temperature profiles over the Ni/Al_2O_3 relative to the furnace temperature, T_0. The catalyst bed is placed between the vertical lines.

Table 1
Conversion (η) of CH_4 and selectivities (S) of CO and H_2 over Ni and Pd monoliths at furnace temperature T_0=600°C. Feed $CH_4:O_2:He=2:1:4$ and space time $\tau=0.07$ s. Equilibrium calculations (eq.) are based on bed exit temperatures: T_{exit}=650°C for the Ni monolith and T_{exit}=630°C for the Pd monolith.

	5 wt% Ni monolith	5 wt% Pd monolith
η CH_4	80	73
eq. η CH_4	76	71
S CO	84	84
eq. S CO	85	80
S H_2	93	87
eq. S H_2	92	90

previously [15]. These experiments demonstrated that the conversion of CH_4 is low at temperatures below 800°C without a catalyst present. In order to obtain an active catalyst, the Ni system had to be reduced prior to the experiments or exposed to the feed gas at high temperatures ()850°C). The conversion of CH_4 and the selectivities of CO and H_2 in the fixed-bed microreactor using 5% Ni/Al_2O_3 are shown in Fig. 1a, and the corresponding temperature profiles in Fig. 1b.

For each experiment the equilibrium composition was calculated based on the bed exit temperature. These calculations are based upon thermodynamic data for total oxidation, steam reforming and the water–gas shift reaction [16]. Simultaneous gas phase equilibria were calculated. When comparing experimental results with calculated values the problems related to the temperature measurements should be emphasized. The selectivity follows very closely the equilibrium values although some deviations are observed. The temperature profiles (Fig. 1b) show that the peak temperature appears exactly at the bed inlet. The temperature profile indicates that at these space times the reaction consists of a total oxidation of some of the methane followed by the endothermic reforming reactions and the water–gas shift reaction. The conversion of O_2 is almost complete at all temperatures reported in Fig. 1a. It is also observed that a lower furnace temperature gives a higher temperature peak showing that more CO_2 is formed at lower temperatures and that the reforming reactions are slower. The constant temperatures towards the outlet of the catalyst bed indicate that equilibrium is achieved.

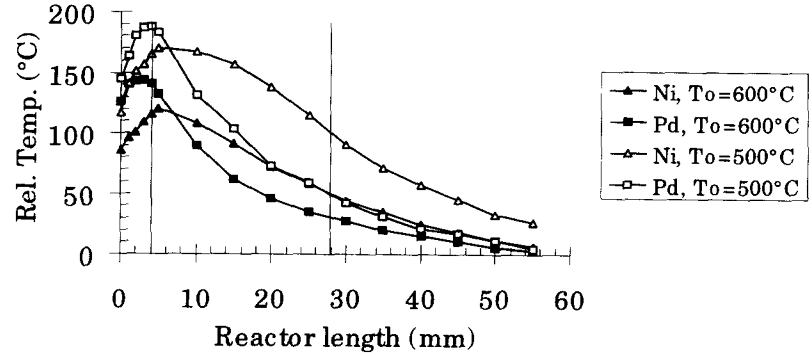

Fig. 2. Temperature profiles over 5 wt.% Ni and Pd monoliths relative to the furnace temperature, T_0. The monolith is placed between the vertical lines.

3.2. Ni and Pd supported monolithic catalysts

Comparisons between Ni and Pd impregnated monoliths using a steel reactor are shown in Table 1. Although previous experiments [15] have pointed to the possible catalytic activity of the reactor wall, it is believed that most of the observed differences could be related to different behaviour of the Ni and Pd monoliths.

The results given in Table 1 show that the product distribution follows the calculated equilibrium values. It should be emphasized, however, that the calculated equilibrium composition is very dependent on the temperature at these low temperatures. However, as shown in Fig. 2 the temperature profiles over the Ni and Pd catalysts at furnace temperatures of 500°C and 600°C are different. The feed gas seems to ignite more rapidly on the Pd catalyst than on the Ni catalyst. (The

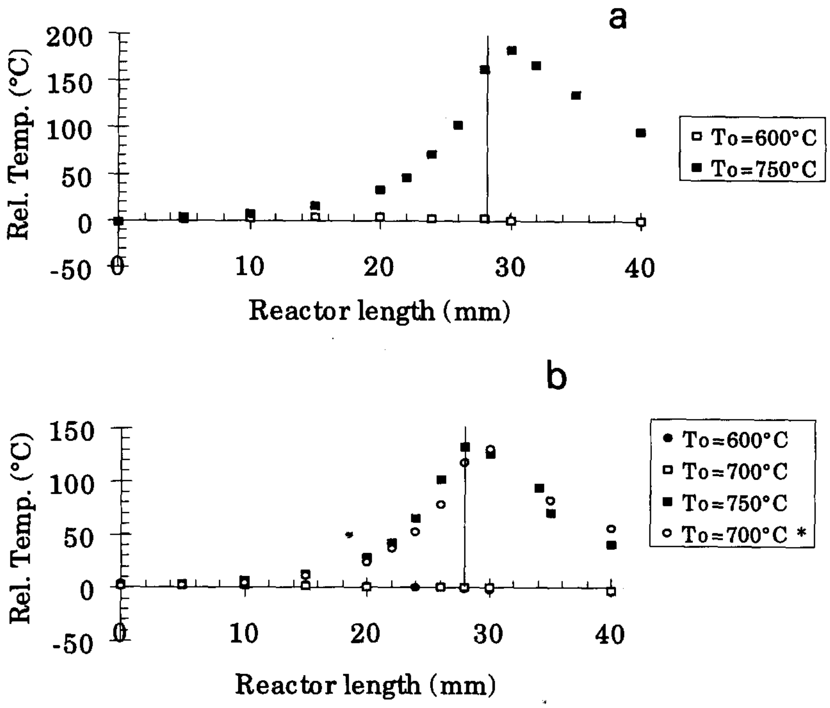

Fig. 3. (a) Temperature profile over the Pt-gauze relative to the furnace temperature, T_0. The vertical line marks the position of the gauze. $\tau=2\times10^{-4}$ s. (b) Temperature profile over the Pt-gauze relative to the furnace temperature, T_0. The vertical line marks the position of the gauze. $\tau=4\times10^{-4}$ s.

Table 2

Conversion (η) of CH_4 and O_2 and selectivity of CO over a Pt gauze at different furnace temperatures (T_0) and space times (τ). The temperature profiles are given in Figures 3a and 3b. Feed CH_4:O_2:He=2:1:10. The run at 700* °C is performed immediately after the run at 750°C.

T_0 (°C)	τ (s)	η CH_4	η O_2	S CO
600	$2\cdot10^{-4}$	~0	~0	~0
600	$4\cdot10^{-4}$	~0	~0	~0
700	$4\cdot10^{-4}$	0.4	2	~0
750	$4\cdot10^{-4}$	31	91	71
750	$2\cdot10^{-4}$	29	85	84
700*	$4\cdot10^{-4}$	30	88	63

experiments reported in Table 1 are compared for Ni and Pd monoliths at exactly the same conditions.) It should also be noted that the product distribution at 600°C is closer to equilibrium than the corresponding values at 500°C (not shown), and at the same time it is seen that the temperature rise is higher the lower the furnace temperature.

3.3. Pt gauze catalyst

The partial oxidation of methane to synthesis gas has also been studied on a Pt gauze catalyst and the results are reported in Table 2 and in Figs. 3a and 3b. The space time is calculated from the free volume of the gauze and the gas flow-rate.

The gauze catalyst gives the possibility to study the reaction at very short space times. It has been indicated [17] that the partial oxidation of methane to synthesis gas can be studied independent of the reforming and shift reactions by using a gauze catalyst. The results obtained by Hickman and Schmidt [17] on a Pt–10%Rh woven gauze catalyst showed that $CO+H_2$ are the primary products. As shown in Table 2 no products were detected at a furnace temperature of 600°C. Doubling the space time did not have any influence on the reaction. By increasing the furnace temperature to 700°C a small conversion of CH_4 and O_2 could be observed as well as some CO_2 in the product gas. A further increase in the furnace temperature resulted in a sudden temperature increase of more than 150°C above the furnace temperature (Fig. 3a). Increasing the gas flow-rate by a factor of about 2 did not change the activity of the gauze very much. The higher selectivity to CO observed at the lowest space time could indicate that CO is a primary product.

From a thermodynamic point of view the high CO selectivity may be explained by the higher temperature measured at the lowest space time as seen by comparing Figs. 3a and 3b. However, the reactions are far from equilibrium. Only small amounts of H_2 could be detected in the product gas with the Pt gauze catalyst. The total oxidation of H_2 to H_2O is also confirmed by the large temperature increase on the gauze (Figs. 3a and 3b). By reducing the furnace temperature from 750°C to 700°C, the catalyst was still active. At the lowest temperatures (600°C, Table 2) the gauze may be oxidized by the feed and temperatures above 700°C are required in order to reactivate the Pt gauze.

It has been shown by using monoliths that Rh is much superior to Pt in producing synthesis gas at short space times [8]. This is explained by the instability of adsorbed OH on Rh which reduces the formation of H_2O and by the high mass trans transfer characteristics of monoliths at very high flow-rates [17]. The low selectivity to H_2 from the Pt gauze at these very low space times is in accordance with high rates for the surface reaction between $H+O$ and for the abstraction of H from adsorbed CH species by O. Even though H_2 selectivities below equilibrium have been observed at very short contact times using monoliths impregnated with Pt, H_2 was always observed as one of the main products [15]. The difference in product distribution between these two systems is not obvious, but it could be related to the oxidation state of the Pt gauze or support effects on the Pt monolith.

The results show that the gauze catalysts could be a suitable system for studying rapid reactions at very short space times. However, the temperature measurements needed for kinetic studies represent a challenge for these very rapid oxidation reactions at high temperatures.

4. Acknowledgements

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