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Interinfluence between Reactions on the Catalyst Surface and Reactions in the Gas Phase during the Catalytic Oxidation of Methane with Air

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Direct catalytic oxidation of CH_4 with air was studied using a wire-mesh reactor and a quartz tube reactor. Two types of nickel-containing catalysts (nickel and Monel 400 alloy) in the form of wire-mesh were used. The wire-mesh reactor features the minimisation of the thermally induced gas-phase reactions by rapidly quenching the products leaving the mesh catalyst surface. The wire-mesh reactor can be used as a differential reactor for the study of both exothermic and endothermic reactions, with the reactions on the catalyst surface not controlled by heat transfer. Increasing total gas flow rate passing through the mesh catalyst caused not only increases in overall reaction rates but also changes in the product selectivities. With the reduction of the thickness of the gas film around the catalyst wires, the coupling of the CH_3 radicals desorbed from the catalyst surface becomes an important route of C_2H_6 formation during the catalytic oxidation of CH_4 with air, even at 950°C. The reactor has proved to be a powerful tool in understanding the reactions on the catalyst surface without the complications caused by the reactions in the gas phase. Comparison of the results from the wire-mesh reactor with those from the quartz tube reactor indicates that the reactions in the gas phase inhibited the reactions on the catalyst surface. The interinfluence between the surface-catalysed reactions and the gas-phase reactions must be considered in evaluating the intrinsic reactions on the catalyst surface. © 2001 Academic Press

Key Words: **direct catalytic oxidation; methane; natural gas; catalysis; wire-mesh reactor.**

1. INTRODUCTION

Catalytic oxidation of natural gas has been extensively studied for the production of synthesis gas (syngas, CO, and H_2) and other valuable chemicals (1–4). The direct catalytic oxidation of methane with air/oxygen is a very complicated reaction system involving reactive radicals. Some products from the catalytic oxidation of CH_4 can be a result of the coupling of the surface-catalysed and gas-phase reactions involving these radicals (5–7). For example, a significant portion of C_2H_6 observed is produced from the coupling of the surface-generated CH_3 radicals in the gas phase at 670°C (8). More recently, a micro wire initiation (MWI) method has been proposed whereby a Ni–Cr wire heated electrically to high temperatures in the CH_4/air mixture initiates the reactions in the gas phase at very low temperatures to form methanol (9) and acetone (10).

When a pellet-supported catalyst is used in the catalytic oxidation of methane with air at high temperatures, the reaction system becomes even more complicated. Because the radicals are very reactive at high temperatures, transport limitations of these radicals may be “irreducible”: the pellet size at which the internal concentration gradients would be negligible is much smaller than the minimal pellet size imposed by pressure drop considerations (11, 12). This is in contrast to the classical consideration of the transport limitation of the reactants and products. The understanding of the intrinsic reactions on the catalyst surface, important for the development of suitable commercial catalysts, is thus impossible with the pellet catalysts at high temperatures.

Further complications in the understanding of the reaction system with the pellet catalyst may arise from the fact that the methane oxidation products (e.g., CO_2 and H_2O) can also react with methane on the catalyst surface at high temperatures. The reaction between CH_4 and O_2 takes place concurrently with the reaction between CH_4 and the CH_4 oxidation products on the catalyst surface inside the pores of the catalyst (pellet or other forms). Furthermore, when a conventional fixed-bed (packed-bed) reactor is used, the direct CH_4/O_2 reaction as well as the reaction between CH_4 and the CH_4 oxidation products can also take place in the gas phase at high temperatures. Little attention has been paid to the influence of the CH_4/O_2 reactions on the catalyst by the catalytic and homogeneous gas-phase reactions between CH_4 and its oxidation products. As a result, it is even difficult to know the main primary reaction products of the CH_4/O_2 reactions. Therefore, in spite of the significant recent progress in the production of syngas from the catalytic oxidation of natural gas using monolith-supported noble metal catalysts (13–17) or other catalysts (18–24), debates still exist about the exact reaction mechanisms involved. For example, when Pt, Rh,

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and Ni coated on ceramic monoliths or Al_2O_3 beads (in a fluidised-bed reactor) were used to catalyse the oxidation of methane with oxygen utilising very short contact times, the contributions by the homogeneous gas-phase reactions were found not to be significant (2, 15, 25). However, when supported Ni catalysts were used to catalyse the oxidation of CH_4 with O_2 in a heated quartz tube reactor, it was found (26) that the formation of syngas proceeded mainly through the complete oxidation of CH_4 to CO_2 and H_2O followed by the reforming of CH_4. The direct oxidation of CH_4 to CO was only possible at very low O_2 partial pressures (<1 kPa) when the Ni surface was reduced (26).

The purpose of this study is to gain information about the intrinsic reactions on Ni-based catalysts during the direct catalytic oxidation of CH_4 with air at high temperatures where the use of a pellet catalyst would have resulted in the "irreducible mass-transport phenomena" mentioned above. We have used a wire-mesh reactor where the catalyst in the form of a mesh is heated directly by passing an electrical current through the mesh. The contact time is on the order of submilliseconds, with the products leaving the mesh catalyst quenched rapidly. We have also carried out experiments using a quartz tubular reactor with the same meshes but heated in a furnace. The comparison of the results from the two reactors gives information about the interinfluence between the reactions on the catalyst surface and those in the gas phase during the catalytic oxidation of methane with air.

2. EXPERIMENTAL

2.1. *Mesh Catalysts and Gases*

Two types of nickel-containing catalysts (nickel and Monel 400 alloy) in the form of mesh were used in this study. Their properties as supplied by the manufacturer (Goodfellow, UK) are given in Table 1. The meshes were first washed with a mixture of CH_3OH and $CHCl_3$ to remove grease and then used without any further treatment.

Chemical purity grade (>99.99%, Matheson) methane and instrument grade (BOC) air were used without any further treatment.

TABLE 1

Properties of Mesh Catalysts Used in This Study

	Wire diameter (mm)	Number of wires per inch	Open area (%)	Elemental composition
Nickel	0.25	26 × 26	55	Ni : 100%
Monel 400	0.25	40 × 40	37	Ni : 65% Cu : 33% Fe : 2%

2.2. *Oxidation of Methane with Air*

Two reactor systems were used to study the catalytic oxidation of CH_4 with air. The first one was a tubular reactor heated externally with an electric furnace. The reactor was made of a quartz tube with an inner diameter of 2.0 cm and a length of 40 cm. The flow rates of CH_4 and air were controlled with mass flow controllers separately and are reported as the flow rates at 25°C and 1 bar throughout the paper. Methane and air were premixed before being fed into the reactor from the bottom. A piece of catalyst mesh with a diameter just slightly larger than 2.0 cm was pushed into the middle of the quartz tube. The thermal expansion of the metal mesh when heated, being more than that of the quartz, further ensured that the mesh catalyst did not move during an experiment. No other support was used to fix the mesh catalyst in the quartz tube. As a thermocouple may serve as a catalyst for the reactions between CH_4 and O_2, the mesh temperature when the reaction rates were measured was monitored with a thermocouple attached to the external wall of the quartz tube at the same position as the mesh catalyst inside the quartz tube. To ensure that the measured temperature was close to the true temperature of the mesh catalyst, prior experiments were carried out where a thermocouple was inserted into the reactor and touched the mesh catalyst under actual experimental conditions with CH_4/O_2 mixture flowing through the reactor. The reading from the thermocouple touching the mesh inside the reactor was close to (within ± 2°C) the reading from the thermocouple attached to the external wall of the quartz reactor. The length of isothermal zone varied with the total flow rate of the CH_4/air mixture. At a total flow rate of 8.0 L min^{-1}, the temperature of the gas mixture, measured with a thermocouple inside the reactor, increased steadily along the length of the reactor and the mesh catalyst was found to be just at the highest temperature region at 950°C.

The second reactor system used in this study was a wire-mesh reactor. It was similar to that used for the study of coal pyrolysis, and a detailed description of the reactor may be found in the literature (27–29). As depicted in Fig. 1, a single layer of mesh catalyst was stretched between two electrodes and heated directly by means of an alternating current. The heating electrodes as well as other parts in contact with or close to the mesh were cooled with flowing water (27–29). Except from the mesh catalyst itself, all other parts of the reactor remained almost at room temperature even after very long holding time at high mesh temperatures. Care was taken to ensure the same amount of mesh (total area of 3.1 cm^2, including the open area) was used in the quartz tube reactor and in the wire-mesh reactor. The temperature of the mesh in the wire-mesh reactor was measured with two K-type thermocouples made of thin wires (diameter: 51 μm), one placed in the centre of the mesh and the other near the edge. Unlike many reactors used in the past,

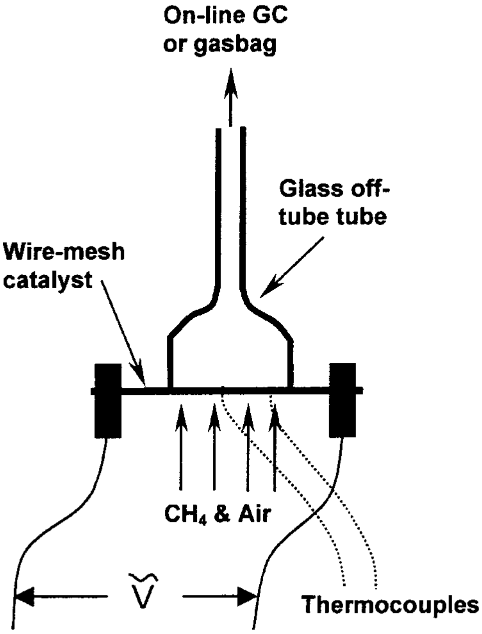

FIG. 1. A schematic diagram showing the operation of the wire-mesh reactor used in this study.

the temperature of the mesh catalyst where reactions took place was accurately measured. As described in detail elsewhere (27–29), the mesh was a part of the thermocouple. The potential of the thermocouple measured was the sum of two potentials: the potential of the junction between the Ni/Cr wire and the mesh and the potential of the junction between the mesh and the Ni/Al/Mn/Si wire. This configuration ensures that the temperature measured with the thermocouple is the temperature of the mesh. The readings from the two thermocouples (normally well within ±10°C) were monitored with a computer-based system. The average of the two readings was taken as the temperature of the mesh and was used to control the heating of the mesh with a computer-based PID control system. The reactor was operated as a differential reactor: the conversion level of CH_4 was generally very low (<2%). Therefore, the reactions on the catalyst surface were not controlled by heat transfer phenomena.

The same mass flow controllers as those for the quartz tube reactor (see above) were used to control the flow rates of CH_4 and air entering the wire-mesh reactor. The well-mixed CH_4/air mixture passed through the mesh catalyst (see Fig. 1). The gas mixture was at room temperature before it came into contact with the mesh catalyst in the wire-mesh reactor. Depending on the percentage of the open area (transparency) of the mesh, only a portion of reactant gas mixture was heated up very rapidly through heat transfer from the hot mesh wires as well as chemical heating. At high flow rates, a significant portion of the gas mixture bypassed the mesh through the apertures without good contact with the hot wires and was heated to a very limited extent. These cold gas molecules mixed rapidly with the hot product molecules leaving the mesh wires, resulting in the extremely rapid quenching of the reaction products. Therefore, the gas-phase reactions due to activation by high temperature, both before and after passing through the mesh, can be expected to have taken place to a negligible extent. Numerous studies on the pyrolysis of coal and other solid fuels (e.g., see Refs. 27–30) have proved this feature of the wire-mesh reactor: the reactions as a result of high temperature in the gas phase are minimised. This is further proven by the results to be presented below in this paper.

As the mesh in the wire-mesh reactor was heated directly with an alternating current, the reactor can be used as a differential reactor for both exothermic and endothermic reactions. This feature has allowed us to study the oxidation of methane at very low temperatures even without the need to preheat the CH_4/air mixture. In contrast to autothermal reactors (15, 16), there is no need to start the reactions with other gas mixtures.

In all experiments reported here, the mesh catalyst was heated slowly (1 $K\,s^{-1}$ in the wire-mesh reactor and similar heating rates in the quartz tube reactor) from room temperature to the required temperature after the reactors had been well purged with reaction gas mixture. Fresh mesh catalyst was used for each experiment.

With both the quartz tube reactor and the wire-mesh reactor, concentrations of O_2, H_2, CO, and CO_2 were measured online with an HP 5890 gas chromatograph (GC) equipped with a HeyeSep DB column (15 ft × 1/8 in.) and a thermal conductivity detector (TCD). Concentrations of hydrocarbons in the products were measured with the same GC using its flame ionisation detector (FID), following the sampling of the product gas into gasbags. Efforts were also made to quantify methanol and formaldehyde by passing the product gas through ice-cooled bubblers containing water, followed by analysis with an HP 6890 GC–MS. The yields of CH_3OH and H_2CO were found to be very low. Due to the use of high concentrations of CH_4 in the feed (e.g., $CH_4/air = 4$) without dilution with inert gas and the differential nature of the reactors, direct measurement of the CH_4 concentration was difficult. The conversion of CH_4 was calculated from the sum of all carbon-containing species in the product. The consumption or formation rates of various species were calculated by considering the total gas flow rate and the concentration of the species. Thus, the relative errors in the reaction rates tend to be bigger at higher gas flow rates (with smaller GC peaks) than at lower flow rates.

3. RESULTS AND DISCUSSION

3.1. *Temporal Behaviour of the Catalysts*

Figure 2 shows the consumption rate of O_2 and formation rates of CO, CO_2, H_2, and C_2 hydrocarbons as a function of

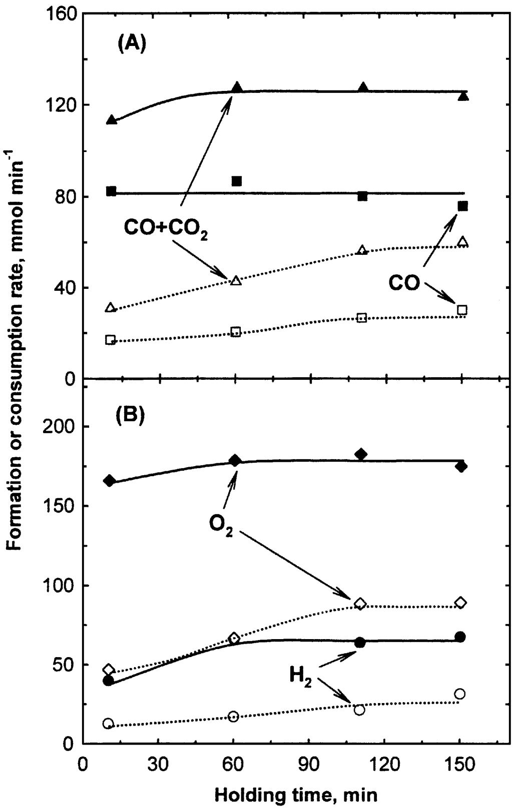

FIG. 2. Consumption rate of O_2 and formation rates of CO, H_2, and CO_2 as a function of holding time at 950°C in a wire-mesh reactor at a total gas flow rate of 8.0 (open symbols and dotted lines) or 15.5 L min^{-1} (solid symbols and solid lines). CH_4/air molar ratio = 4. Catalyst: nickel mesh.

holding time at 950°C. A nickel mesh catalyst (Table 1) was used. Considering the slow heating rate of the mesh catalyst (see Experimental section) and the high CH_4/air ratio of 4 used in the experiments, it was surprising to note that the catalyst activity actually continued to *increase* for about 100 min after the mesh had reached the required temperature. It seemed that the catalyst activity stabilised more rapidly at higher flow rates. As shown in Fig. 2, the catalyst activity stabilised after 60 min of holding time at a flow rate of 15.5 L min^{-1}. With a flow rate of 8.0 L min^{-1}, the stabilisation only happened after 110 min. Similar behaviour was also seen with nickel mesh in the quartz tube reactor as well as with the Monel 400 mesh catalyst in both reactors in this study. In the catalytic oxidation of alkanes with a Pt/Rh mesh, Goetsch and Schmidt (31) also noted that long holding times were required to achieve stable conversions and selectivities.

In many past studies using Ni-based catalysts, catalytic activity was often observed to decrease with increasing holding time in the stream of reactants containing CH_4. In fact, this has represented a major problem with the use of Ni-based catalyst in the production of syngas from the oxidation of methane. For example, Tsipouriari and co-workers (26) observed that many supported Ni catalysts rapidly deactivated within a short period of time (e.g., <30 min) even in the stream of CH_4/O_2 heavily diluted with inert gas (94%), apparently due to coke formation (26, 32). In our study, the mesh catalysts before and after reactions were examined with scanning electron microscopy (SEM) and associated energy-dispersive X-ray (EDX) microanalysis facility. The mesh catalyst was found to have roughened after reaction, including the appearance of small cracks/holes mostly on the cross points on both sides of the mesh. Similar phenomena were also seen with the Monel catalyst. No strong evidence was found for the formation of coke on the main smooth mesh surface with the preliminary EDX analysis. To our surprise, our EDX analysis showed evidence of coke formation only inside the cracks/holes. It seemed that, even under our experimental conditions of high space velocities, the oxygen was depleted inside the cracks/holes to allow for the formation of coke. Further investigation is being carried out.

Each reaction rate reported hereafter in this paper represents an average of two or three rates measured after the reaction rates had reached steady-state values. As shown in Fig. 2, the steady-state values were normally attained after a holding time of 60 or 110 min at the reaction temperature.

3.2. *Effects of Total Gas Flow Rate on the Reaction in the Wire-Mesh Reactor*

When the Monel mesh was used as the catalyst in the wire-mesh reactor and the mesh temperature was lower than 850°C, an increase in gas flow rate from 1.5 to 3.2 L min^{-1} did not result in any change in the measured reaction rates. This observation indicates that the reactions were not limited by mass transfer under these experimental conditions. However, at mesh temperatures higher than 850°C, the reaction rates were found to be very sensitive to changes in total gas flow rate (contact time), as shown in Fig. 3 for a mesh temperature of 950°C in the wire-mesh reactor. When Monel mesh was used as the catalyst in the wire-mesh reactor, the main products were found to be CO, H_2, CO_2, H_2O, and C_2H_6. The sum of CO, CO_2, and C_2H_6 formation rates is considered as an approximation of the CH_4 reaction rate. Therefore, the data in Fig. 3 suggest that the overall CH_4 consumption rate was controlled by the mass transfer of CH_4 from the bulk gas phase onto the mesh surface when the total gas flow rate was lower than ~8 L min^{-1}. At flow rates higher than 8 L min^{-1}, the overall CH_4 consumption rate was controlled by the reactions on the surface. The slight declines of the CH_4 consumption rate (as the sum of CO, CO_2, and C_2H_6 in Fig. 3) at higher flow rates may be due to the formation of trace tary/soot materials, which was observed only at flow rates higher than 8 L min^{-1}.

The data in Fig. 3 also indicate that increases in total gas flow rate at a fixed CH_4/air ratio of 4 have resulted not only in increases in the overall reaction rates but also in

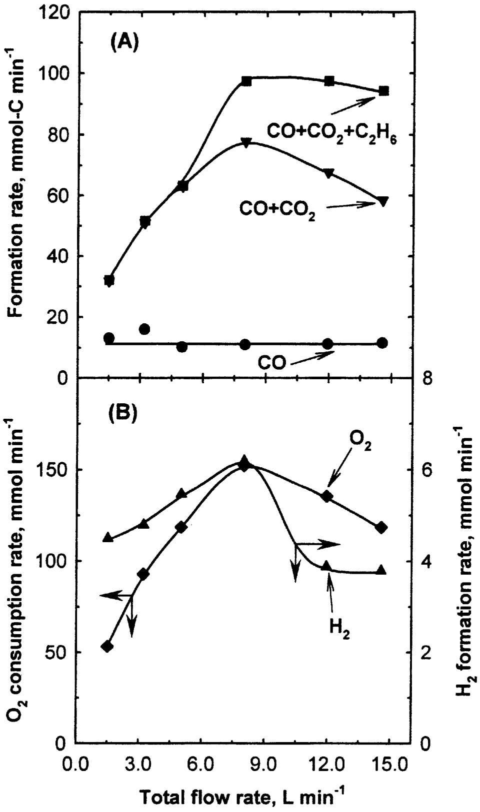

FIG. 3. Reaction rates at 950°C as a function of total gas flow rate during the catalytic oxidation of CH_4 with air in the wire-mesh reactor with the Monel mesh as the catalyst. CH_4/air = 4.

changes in product selectivities. While there was little C_2H_6 produced when the flow rate was lower than ~5 L min^{-1}, C_2H_6 became one of the major products at high flow rates. The formation of C_2H_6 was at the expense of the formation of CO_2 and H_2.

Because the thermal activation of CH_4 in the gas phase in the wire-mesh reactor was negligible (see above), the activation of CH_4 on the catalyst surface was the initial step in the consumption of CH_4 in the wire-mesh reactor. Clearly, C_2H_6 is a product from the coupling of CH_4. The fact that C_2H_6 was only observed at high flow rates (see Fig. 3) means that C_2H_6 was formed in the gas phase as a result of the coupling of two CH_3 radicals desorbed from the catalyst surface. Campbell and co-workers (8) also observed the desorption of CH_3 from the catalyst surface and the coupling of CH_3 radicals in the gas phase to form C_2H_6, although their study was at 670°C, much lower than the temperature of 950°C in this study.

The mesh wires were surrounded by a gas film. The absence of C_2H_6 as a main reaction product at lower gas flow rates indicates that CH_3 radicals were not able to diffuse into the cold bulk gas stream before they were consumed in the gas film to form other products such as CO_2 and H_2O. At very low gas flow rates (e.g., 1.5 L min^{-1}), the radicals and/or their coupling products (e.g., C_2H_6) had enough time in the hot thick gas film around the catalyst to be readsorbed onto the catalyst and react with O-containing adspecies to form CO_2 and H_2O. Little C_2H_6 was observed (see Fig. 3). With increasing gas flow rate (e.g., up to 5 L min^{-1}), the thickness of the gas film necessarily decreased and there was increasingly more oxygen and CH_4 supplied to the mesh, leading to the generation and desorption of more radicals. These radicals still had long enough time in the hot region around the catalyst wires for them to be oxidised to CO_2 and H_2O. The net result was the observed increases in CO_2 yield. With further increases in the total gas flow rate (beyond 5 L min^{-1}, Fig. 3), the thickness of the gas film around the mesh wires further decreased. The radicals could diffuse through the thin gas film into the cold gas phase to form C_2H_6 (Fig. 3) before they were destroyed to form CO_2 and water. The configuration of the wire-mesh reactor means that the increases in gas flow rate also resulted in the products leaving the catalyst wires to be quenched more rapidly because more reactant mixture passed through the holes of the mesh remained at low temperatures. The relative coverages of O_2-derived species and CH_4-derived species on the catalyst surface are governed by the partial pressures of O_2 and CH_4, respectively. The escape of CH_4-derived radicals (e.g., CH_3) into the gas phase without further reactions with the O-containing adspecies on the catalyst surface resulted in the decreases in the consumption of O_2 (Fig. 3). In other words, the desorption of CH_3 radicals competed with the reactions between CH_3 and O-containing adspecies on the catalyst surface, leading to the observed decreases in the reaction rate of O_2.

The data in Fig. 3 indicate that the escape of CH_3 radicals from the catalyst surface into the gas phase to form C_2H_6 was accompanied by the decreases in the yields of H_2 as the gas flow rate was increased from ~8 to ~15 L min^{-1}. Therefore, H_2 was mainly a product of the reactions involving CH_x (and O-containing) species on the catalyst surface. The increases in the yield of H_2 with increasing gas flow rate from 1.5 to 8.0 L min^{-1} were also due to the increased reaction rates of CH_4- and O_2-derived species on the catalyst surface as mentioned above. As the formation of CO was not affected by changes in gas flow rate, CO was formed only on the catalyst surface and was not consumed in the film. Experiments at a CH_4/O_2 ratio of 0.5 under otherwise identical conditions to those in Fig. 3 showed that CO formation was negligible. It is therefore believed that CO was formed only on certain sites on the Monel surface. These sites were likely to be the (reduced) nickel sites, in agreement with the observation of high CO formation rates with the nickel mesh (Fig. 2).

For the nickel mesh catalyst in the wire-mesh reactor at the same temperature of 950°C, increases in gas flow rate also lead to the increases in the reaction rates (see Fig. 2). However, even at a very high total flow rate of 15.5 L min^{-1}

(the upper flow limit of the mass flow controllers used in the current setup), the reaction system was still controlled by the mass transfer resistance across the film, even for the consumption of the reactants and the formation of stable products (see Fig. 2). Experiments were carried out with nickel meshes of less open area percentages, therefore allowing for shorter contact time for a given flow rate, than that shown in Table 1. The experimental results confirmed that, at very short contact time, C_2H_6 was the major reaction product.

Due to the nonuniform heating of the gas stream passing through the mesh, the actual contact time between the gas and the mesh catalyst is difficult to calculate. For a total gas flow rate of 8.0 L min^{-1}, the contact time in the case of the Monel mesh catalyst, calculated by dividing the wire diameter by the average gas velocity passing through the mesh, is between 50 and 220 μs at a mesh temperature of 950°C. The upper limit corresponds to the assumption of gas temperature at 25°C and the lower limit corresponds to the assumption of gas temperature of 950°C. Similarly, the contact time for a total gas flow rate of 14.5 L min^{-1} is between 30 and 120 μs. Clearly, these contact times (bulk gas velocities) are difficult to achieve within the pores of a pellet catalyst. More importantly, radicals desorbed from the active sites inside a pore of the pellet catalyst will likely be adsorbed on the neighboring sites inside the pore. The diffusion within the pores of a catalyst pellet is similar to that through the gas film around the catalyst wires at low gas flow rates in this study. Therefore, the radicals or the coupling products inside a catalyst pellet have little chance to escape into the gas phase. The true intrinsic reactions on the catalytic sites inside a catalyst pellet cannot be observed at high temperatures. Thus, the wire-mesh reactor is a powerful tool for understanding the intrinsic reactions whose reaction rates are so fast that the use of a pellet catalyst would result in the limitation by the ”irreducible” mass-transport phenomena (11, 12).

3.3. Comparison between the Reactions in the Wire-Mesh Reactor and Those in the Quartz Tube Reactor

At high temperatures, where noncatalytic homogeneous gas-phase reactions take place easily, the evaluation of the intrinsic catalyst activity using a quartz tube reactor such as the one used in this study is very difficult. The overall rates measured in the quartz tube with catalyst may have significant contributions from the reactions in the gas phase. A set of data are shown in Fig. 4 where the overall reaction rates from the quartz tube reactor with Monel mesh are compared with those from the empty reactor without any mesh catalyst (blank experiments). As was noted in the Experimental section, the consumption rate of CH_4 was calculated as the sum of all detectable carbon-containing species. Care must be exercised in looking at the data from the blank experiments shown in Fig. 4. It was found that some catalyst might have been lost from the Monel mesh and deposited on the quartz wall at 950°C. It is likely that the data from blank runs representing the gas-phase reactions may contain slight contributions from the reactions on the reactor wall even though the flow inside the reactor was mainly laminar. For this reason, the data for blank experiments in Fig. 4 were taken immediately following the experiments with the corresponding mesh catalysts.

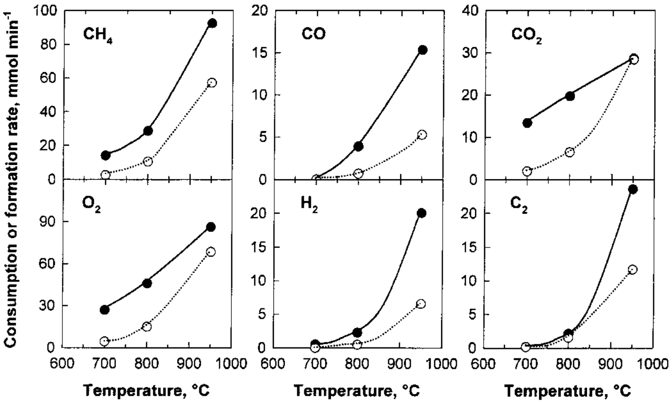

FIG. 4. Product distribution from the oxidation of CH_4 with air (CH_4/air = 4) in the quartz tube reactor with (solid symbols and solid lines) or without (open symbols and dotted lines) Monel mesh catalyst as a function of temperature. The total gas flow rates were 3.2 L min^{-1} at 700 and 800°C and 8.0 L min^{-1} at 950°C, respectively.

For the data shown in Fig. 4, different flow rates were used for experiments at different temperatures. This was to ensure that the mass transfer (for reactants and stable products) was not the limiting step and also that the products could be accurately quantified. As was explained above, a flow rate of 3.2 L min^{-1} was enough to ensure that the overall reaction rates were controlled by the reactions on the Monel mesh catalyst in the wire-mesh reactor when the mesh temperature was lower than ~850°C. The use of a flow rate of 8 L min^{-1} at 800 and 700°C would have resulted in products of very low concentrations in the exit of the reactor, making the accurate quantification of products impossible. Under the conditions of the same mesh temperature and the same total gas flow rate measured at ambient conditions, the actual gas linear velocity would be higher in the quartz tube reactor than in the wire-mesh reactor. This is because all gas was heated up in the former case and only a portion of the gas was heated close to mesh temperature in the latter case. Therefore, the data in Fig. 4 were all obtained when the consumption rate of CH_4 was controlled by the reactions at the catalyst surface.

As C_2H_4 was not observed as an important product in the wire-mesh reactor (see Fig. 3) and only observed in the quartz tube reactor, C_2H_4 is believed to be a product of the dehydrogenation of C_2H_6 in the gas phase. The yields of C_2H_6 and C_2H_4 were therefore lumped together and shown as “C_2” in Fig. 4. It is noted from Fig. 4 that the reaction

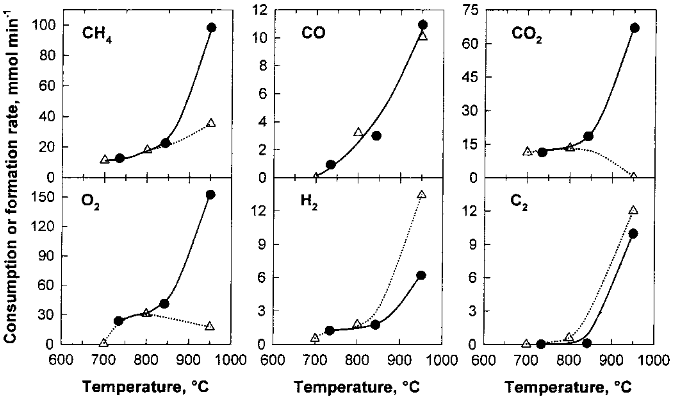

FIG. 5. Comparison of the calculated reaction rates on the Monel mesh catalyst in the quartz tube reactor (open symbols and dotted lines) with those determined in the wire-mesh reactor (solid symbols and solid lines). The total gas (CH_4/air = 4) flow rates were 3.2 (mesh temperatures of 700 and 800°C) and 8.0 L min^{-1} (mesh temperature of 950°C).

rates, both with and without the catalyst, increased very significantly with increasing temperature. While the gas-phase reactions only contributed to the formation of CO_2 at 700°C, the formation rates of all species (CO, CO_2, H_2, C_2H_6, and C_2H_4) at 950°C in the gas phase (blank experiments) were of the same magnitude as those from the experiments with Monel mesh catalyst. This clearly indicates that the contributions by the gas-phase reactions cannot be ignored. In particular, the O_2 consumption rate and CO_2 formation rate were almost identical with or without the catalyst.

An attempt was then made to calculate the "net" reaction rates due to Monel mesh in the quartz tube reactor by subtracting the rates in the blank experiments from the overall reaction rates with Monel mesh catalyst. These calculated reaction rates are shown in Fig. 5 together with the reaction rate in the wire-mesh reactor. The same amounts of mesh catalyst were used in the experiments in both reactors. At temperatures up to the 800–850°C region, the reaction rates in both reactors were the same (within experimental error). At higher temperatures, the calculated rates on the Monel mesh in the quartz tube were much lower than the reaction rates in the wire-mesh reactor. It was surprising to note that the formation rates of CO were the same in both reactors. This further confirms our conclusion drawn above that the catalytic formation of CO took place only on the Monel catalyst surface and was not affected by any reactions in the gas film around the catalyst. As was explained above, the same gas flow rate (measured at room temperature) was used in the experiments in both reactors; therefore, the real contact time in the quartz tube reactor was much shorter than in the wire-mesh reactor. The gas film around the catalyst surface was much thinner in the quartz tube reactor than in the wire-mesh reactor. In agreement with the data shown in Fig. 2, this thinned gas film has led to somewhat higher C_2 yield in the quartz tube reactor, particularly considering that much less CH_4 was consumed on the mesh catalyst in the quartz tube reactor than in the wire-mesh reactor. Part of the H_2 in the quartz tube reactor was associated with the formation of C_2H_4, which was nearly absent in the products from the wire-mesh reactor.

This temperature of about 800–850°C is the onset temperature for significant gas-phase reactions, as can be seen from Fig. 4. Comparison of the data in Figs. 4 and 5 indicates that the homogeneous gas-phase reactions initiated by high temperature ($>$850°C) in the quartz tube reactor have inhibited the catalyst activity, as is evident from the drops in the calculated consumption rates of CH_4 and O_2. In particular, the *calculated* formation rate of CO_2 on the mesh catalyst in the quartz tube reactor was nearly zero at 950°C. Similar behaviour was also observed with the nickel mesh catalyst, as shown in Fig. 6. Due to the limitation in the flow rate of the current setup, it was not possible to ensure that reaction system with Ni mesh was only controlled by chemical reactions on the catalyst. However, the comparison in Fig. 6 is considered to be valid. This is because the true flow rate at the reaction temperature was higher in the quartz tube reactor than in the wire-mesh reactor. Even so, the calculated reaction rates were still lower in the quartz tube reactor than in the wire-mesh reactor.

While the exact reaction mechanisms for this inhibition of the reactions on the catalyst surface by the reactions in the gas phase remain unclear, we believe that this inhibition is mainly caused by the competitive adsorption of gas-phase reaction products (including radicals) with the fresh reactants (CH_4 and O_2). As can be seen from Fig. 4, considerable amounts of CO_2 and C_2 were formed from the homogeneous gas-phase reactions, particularly at temperatures higher than 850°C. Mass balance calculation also suggested that a significant amount of H_2O was also formed

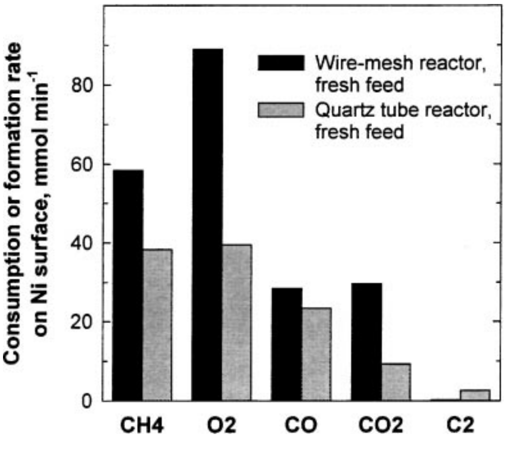

FIG. 6. Comparison of the calculated reaction rates at 950°C on nickel mesh catalysts in the quartz tube reactor with those determined in the wire-mesh reactor. The total gas (CH_4/air = 4) flow rate was 8.0 L min^{-1}.

from the gas-phase reactions (not shown in Fig. 4). All of these products have very good adsorption characteristics on the Ni-based catalysts. In fact, nickel is the commercial catalyst for the steam reforming of natural gas in which CH_4 is the main component. Nickel has also been shown to be a good catalyst for the dry reforming of CH_4 with CO_2 (e.g., see Refs. 33 and 34). These molecules (CO_2, H_2O, and C_2) are bigger than CH_4 and O_2 and may occupy more than one active site if adsorbed dissociatively. Therefore, their adsorption on the catalyst surface would greatly decrease the relative coverages of CH_4 and O_2 on the catalyst surface, leading to the observed decreased reaction rates. The situation could be furthermore complicated when the radicals are involved in the system. For example, the desorption of a CH_3 radical from the catalyst surface, known to be taking place under the current experimental conditions (see Fig. 3), could lead to the formation of a C_2H_6 molecule by combining with another CH_3 radical generated in the gas phase. This would mean a way of termination of the nonselective chain reactions in the gas phase. The data in Fig. 5 did show that the selectivity of CO_2, a product of nonselective gas-phase reactions, decreased with the combination of hot gas stream and hot mesh catalyst in the quartz tube reactor. There is also a possibility that other radicals originally generated in the gas phase were consumed on the catalyst surface following their adsorption on the catalyst surface, representing another way of termination of chain reactions in the gas phase.

Experiments were then carried out to test our hypothesis outlined above. The same reactant gas mixture (CH_4/air = 4) was first fed into the empty quartz tube reactor at 950°C to allow gas-phase reactions to take place. The product stream from the exit of the empty quartz tube reactor was cooled to room temperature and then fed into the wire-mesh reactor with the Monel mesh catalyst heated to 950°C. As in the cases of Figs. 5 and 6, the “net” reaction rates on the mesh catalyst were calculated by subtracting the reaction rates in the gas phase in the empty quartz tube reactor from the overall reaction rates determined at the exit of the wire-mesh reactor. The calculated rates are compared with those determined by feeding the original fresh feed (CH_4 and air) directly into the wire-mesh reactor, as shown in Fig. 7. The data in Fig. 7 clearly show that the calculated consumption rates of CH_4 and O_2 as well as the calculated formation rates of CO_2 and C_2 decreased with the passage of the reactant mixture through the empty quartz tube. In agreement with the data in Figs. 5 and 6, the calculated formation rate of CO was affected by this passage only to a very limited extent. The data in Fig. 7 thus support the conclusion that the stable products formed in the gas phase have inhibited the reactions of CH_4 with O_2 on the Monel mesh in the wire-mesh reactor.

Many reaction products from the noncatalytic homogeneous gas-phase reactions and catalytic oxidation of CH_4 are common. The data shown in Figs. 5–7 suggest that the (physical) design of the catalysts for the *direct* catalytic oxidation of CH_4 may need to consider the minimisation of catalyst “poisoning” by its reaction products.

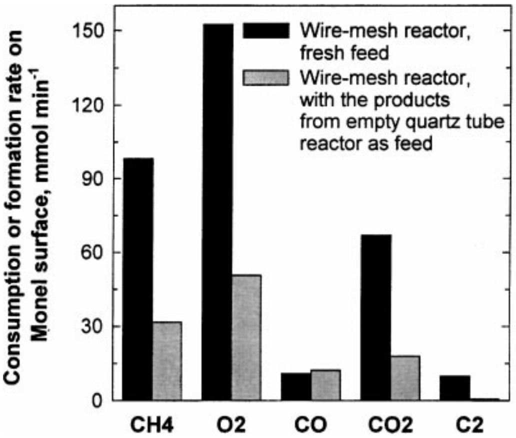

FIG. 7. Comparison of the reaction rates at 950°C on Monel mesh catalysts in the wire-mesh reactor when the gas mixture (CH_4/air = 4) was fed directly into the wire-mesh reactor or was first fed into the empty quartz tube reactor and then into the wire-mesh reactor. Total flow rate was always 8.0 L min^{-1}.

4. CONCLUSIONS

1. The wire-mesh reactor of unique features has proved to be a very powerful tool in understanding the fundamental reactions on the catalyst surface without complications caused by the reactions in the gas phase.
2. For the two Ni-containing mesh catalysts studied, increasing total gas flow rate has caused not only changes in overall reaction rate but also changes in product selectivities from the catalytic oxidation of CH_4 with air. These results demonstrated the importance of eliminating the “irreducible” mass-transport limitations for the understanding of intrinsic reactions on the catalyst surface.
3. For the catalysts studied, the gas-phase coupling of the CH_3 radicals desorbed from the catalyst surface is an important route of C_2H_6 formation at high temperatures.
4. The reactions between CH_4 and O_2 in the gas phase inhibited the reactions on the catalyst surface.
5. The (physical) design of industrial catalysts for rapid reactions needs to consider the interinfluence between the reactions on the catalyst surface and the reactions in the gas phase.

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