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Transient Studies of Low Temperature Catalysts for
Methane Conversion

directed by

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BRIEF SUMMARY OF PROGRESS

This report summarizes results related to a new approach using fast flow low residence time to the production of synthesis gas from methane. A series of experiments were conducted over Rh supported on TiO_2 catalysts to determine the effect of operating variables on the catalyst activity prior to ignition.

SUMMARY OF PROGRESS.

Previous results showed that a 3% Rh/ TiO_2 catalyst was active for the partial oxidation of methane to synthesis gas at temperatures significantly lower than those previously reported in the literature. Schmidt and coworkers [1] have shown that Rh deposited on a monolith support operating at millisecond residence times exhibits high selectivity to CO and H_2 and high methane conversion. The operation of the Rh monolith catalyst requires that ignition be carried out at high temperatures of about 600 °C using ammonia oxidation to ignite the catalysts and avoid excursions into the explosive methane/oxygen mixtures. The 3% Rh/ TiO_2 catalyst ignites at much lower temperatures which permits the direct ignition of the methane oxygen mixture under safer conditions than reported by Schmidt and coworkers. In order to study the effect of the operation variables on the activity and selectivity of the 3%Rh/ TiO_2 catalysts we conducted steady state experiments at low conversion prior to ignition. Experiments were also conducted at high conversion after ignition.

Figure 1. shows the methane conversion and selectivity at various short residence times and 400°C. The numbers correspond to the flowrate. The CO selectivity is high and it decreases as the residence time increases. These results indicate that both CO and CO_2 are produced and that CO is converted to CO_2 in a series type reaction. The effect of temperature versus reaction temperature at 500 cc/min of total flowrate (res. time 0.01) are shown in Fig. 2. Here the behavior is contrary to what is expected from a series reaction in that the CO selectivity increases with temperature with the corresponding decrease in CO_2 selectivity. This behavior is contrary to that of a series reaction. In this case, the conversion is limited by the oxygen flowrate, however, a five fold increase in the oxygen flowrate from 4 to 20 cc/min only changes the selectivity by a few %.

The effect of the oxygen to methane ratio is shown in fig. 3. It can be seen that the conversion increases as the oxygen concentration increases but the selectivity remains fairly constant, again indicating that under this low conversion conditions the series reaction of CO being converted to CO_2 is not the main reaction pathway.

Transient TPD on a reacted catalysts and pulse experiments indicated that the only product desorbed and produced in these experiments is CO₂ revealing again that it is the primary product of the reaction and that CO is the secondary product. Such mechanistic proposal is the opposite to the one proposed by Schmidt, but it agrees with results reported by the group of Baerns in Germany [2].

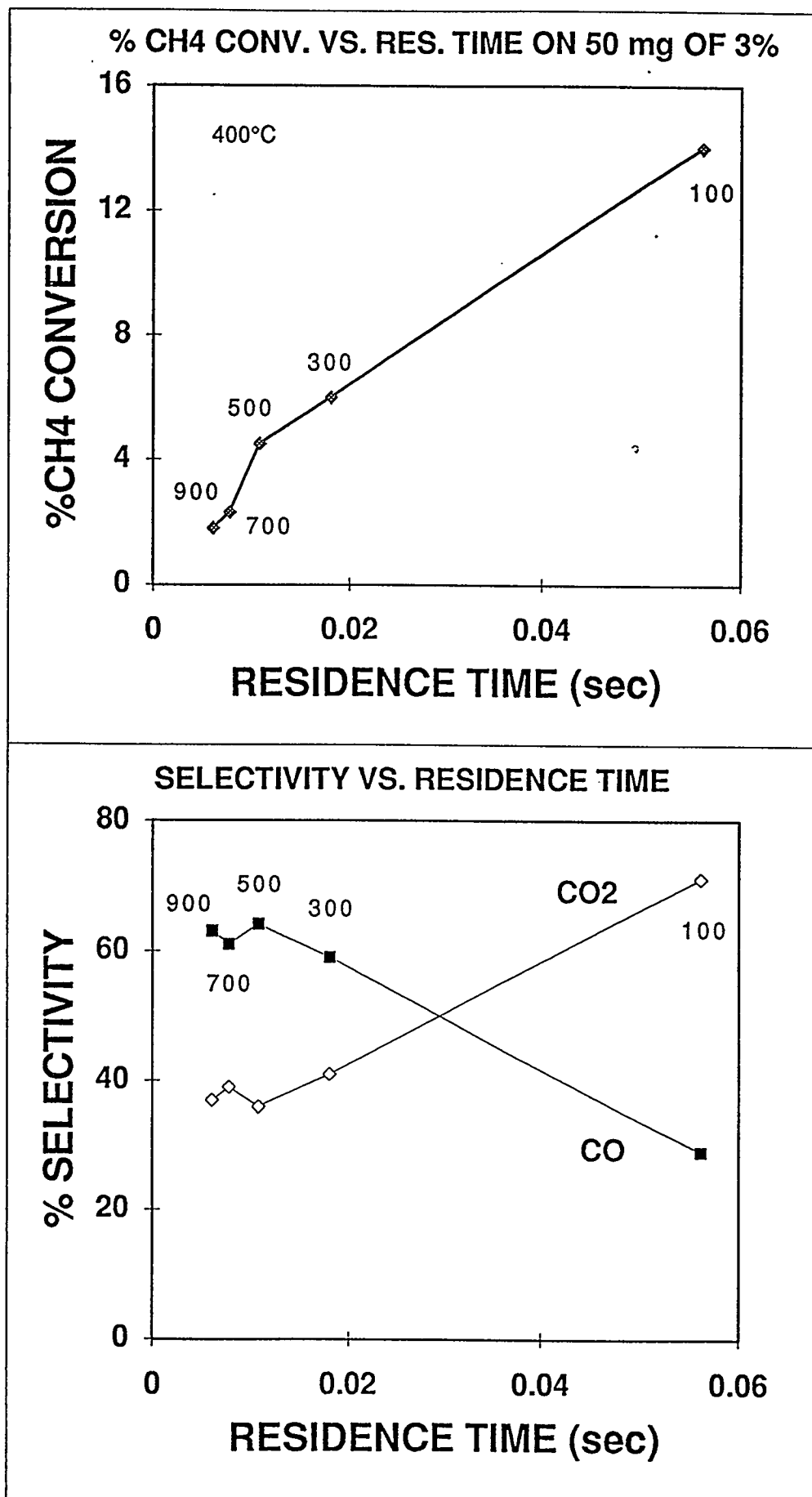
Based on the results of the effect of oxygen on conversion a high methane to oxygen ratio was used (500 cc/min CH₄ and 250 cc/min O₂). Under these conditions an ignition type behavior is observed at about 310°C and then the temperature increase dramatically to about 750°C and stabilizes at this value. At ignition, methane conversion reaches 55% , O₂ conversion is 100% and CO selectivity is about 85%. The formation of large amount of water is also observed. The catalyst is very stable and does not show any indication of deactivation. Experiments conducted on a 3% Rh/ZrO₂ and 3% Rh/Al₂O₃ show that the ignition temperature increases to 310 and 450°C respectively. Hence the catalysts support is important in determining the ignition temperature of the catalyst. After ignition the reaction is limited by diffusional transport and the catalyst has no effect on conversion.

Pulse experiments were conducted at high flowrates by injecting pulses of CH₄ with oxygen concentrations of 25%, 50%, 75% and 100%. Under these pulse conditions only at 25% oxygen concentration all oxygen is consumed. However no ignition type behavior is observed at higher oxygen concentrations. The major product detected is CO₂ and some CO is observed at higher O₂ concentrations.

There are several mechanistic issues as well as several reactor design issues to be studied based on the results summarized above. Regarding the mechanism, we plan to conduct isotopic experiments to determine if CO or CO₂ is the primary product. With respect to reactor design, the difficulty of this reaction is the fact that it is rather easy to reach the explosive limit and a new reactor design is required to ensure that the explosive limit is never reached. As this project is ending, additional time is required to complete these studies.

1. Hickman, D.A., Haupfear, E.A., and L.D. Schmidt, Catalysis Letter 17, 23 (1993)
2. Walter, K., Buyevskaya, O.V., Wolf, D., and M. Baerns, Catalysis Letters, 29, 249 (1994).

FIG.1



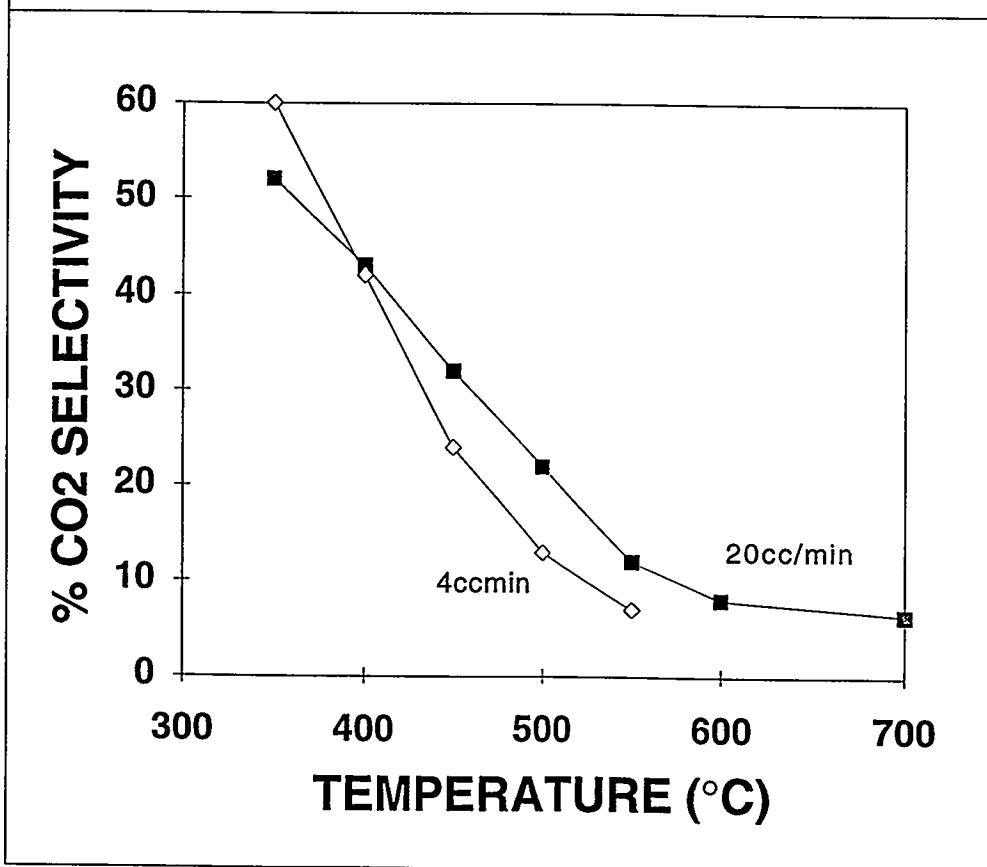
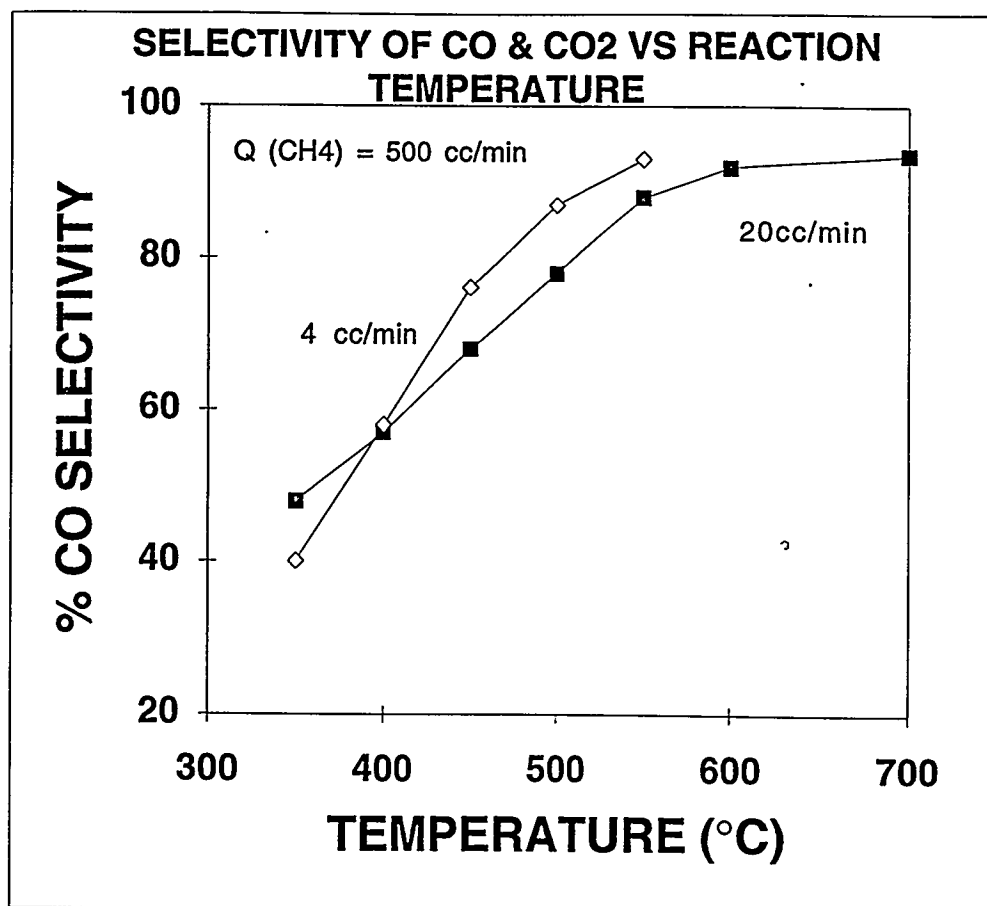


FIG. 3

