JOURNAL OF CATALYSIS **143**, 308–313 (1993)

The Methanation of CO and CO_2 over a Rh/Al_2O_3 Catalyst Using a Pulsed-Flow Microreactor

The dry reforming of methane (*1, 2*) (see Eq. (1)) represents an interesting route to utilising two of the cheapest known sources of carbon, CO_2 and CH_4, and may be a way of using CO_2 produced in large scale industrial processes (selective oxidations for instance). At present the dry reforming reaction takes place at high temperatures (>973 K) and little is known about the mechanism. The reverse reaction, which we call dry methanation (*3, 4*) (Eq. (2)), is simpler and operates at lower temperatures. We decided to investigate the methanation reactions (Eqs. (2) and (3)) in order to gain information about the reverse reactions and, in particular, dry reforming. Hydrogenation of CO_2 (*5–7*) (Eq. (4)) was also investigated, so that CO and CO_2 could be compared for their respective methanation capabilities. Further Rh shows unique properties for CO hydrogenation when promoted with certain metal oxides and can show very high selectivity for ethanol under such circumstances, this area of work having been recently reviewed (*8*). This study also ties in with a wider body of work at Liverpool which is investigating oxygenate synthesis of this type.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (1)$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \quad (2)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (3)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (4)$$

The experiments were carried out using a pulsed-flow microreactor, described elsewhere (*9, 10*), capable of pulsing a gas into a stream of other gases. Figure 1 shows a schematic diagram of the equipment. The gases are supplied by B.O.C. as C.P. grade (minimum purity 99.995%) and can either pass through the catalyst bed as single gases/mixed gases, or pass through the pulsing system. The gas flows are set using Brooks mass-flow controllers. The pulsing system consists of a computer-controlled pneumatically operated six-port sampling valve and the sampling loop volume is 0.5 ml. When the loop is opened the gas is pushed through into the other flowing gases. The loop is open for 5 sec, but the reactant gas volume is eluted into the system in ~1 sec. Since the observed peaks are ~3 sec in width at minimum there is clearly some mixing as the pulse joins the main flow of gas. Furthermore there is little (20% maximum) negative effect on the gases in the mainstream as evidenced by (in this case) the He/H_2 signal. The pulse is also more a Gaussian shape rather than a square shape, nevertheless the pulse is sufficiently narrow that transient measurements can be carried out successfully. To briefly summarize the effects which may be anticipated in product pulses: fast surface reactions will result in product lineshapes similar to the input pulse, whereas slow surface reactions will result in a lineshape which has (a) a peak evolution shifted in time from the reactant and (b) the product pulse will be broadened. These effects are described in more detail elsewhere (*10, 11*).

The combined gases flow through a low volume catalytic system (total volume post pulsing ~4 ml, catalyst bed volume ~0.5 ml), passing over the catalyst bed which is a strainless-steel tubular reactor of 3 mm I.D. and the bed length is ~6 cm. A sheathed

0021-9517/93 $5.00

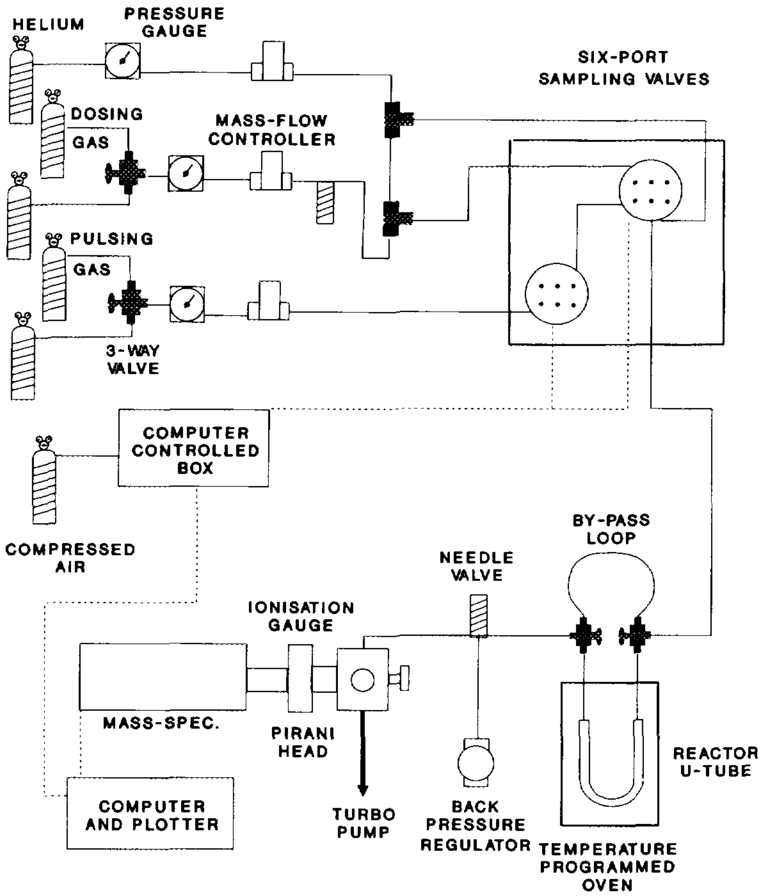

FIG. 1. Schematic diagram of the pulsed flow microreactor.

thermocouple is situated in the catalyst bed, and the whole reactor is housed in a fan circulation Pye 104 oven capable of heating the bed to 773 K. The exit gases are split, some to vent, the remainder passing down a heated line to the mass spectrometer system. In turn most of the gas from that line by-passes the mass spectrometer itself and the latter "sniffs" a small portion of it. The mass spectrometer (V.G. QX200) is driven by in-house software which enables it to run in the multiplexed mode, monitoring up to six different masses. The direct output from the mass spectrometer is shown in Figs. 2 and 3.

The catalyst used was a Johnson–Matthey 5% $Rh/Al_2O_3(\gamma)$ with a metal surface area of 12–15 m^2/g of catalyst and a Rh particle radius of ~10 Å. It was diluted with four parts by weight of α-alumina, making a 1% total Rh loading. The catalyst (0.5 g), after being pressed and sieved into grains of between 500 and 1000 μm, was loaded into the U-tube reactor and reduced *in situ* at 673 K under flowing hydrogen for about 3 h; subsequent shorter reductions preceded each experiment. The normal experimental procedure involved passing hydrogen in helium (1:80) with a total gas flow rate of 40 ml/min over the catalyst and periodically pulsing 0.5 ml of CO or CO_2 into the stream. The temperature was raised from room temperature to ~703 K over 15 min.

Figures 2a and 2b show a temperature-programmed pulsed reaction experiment (TPPR) and reveal a fascinating evolution

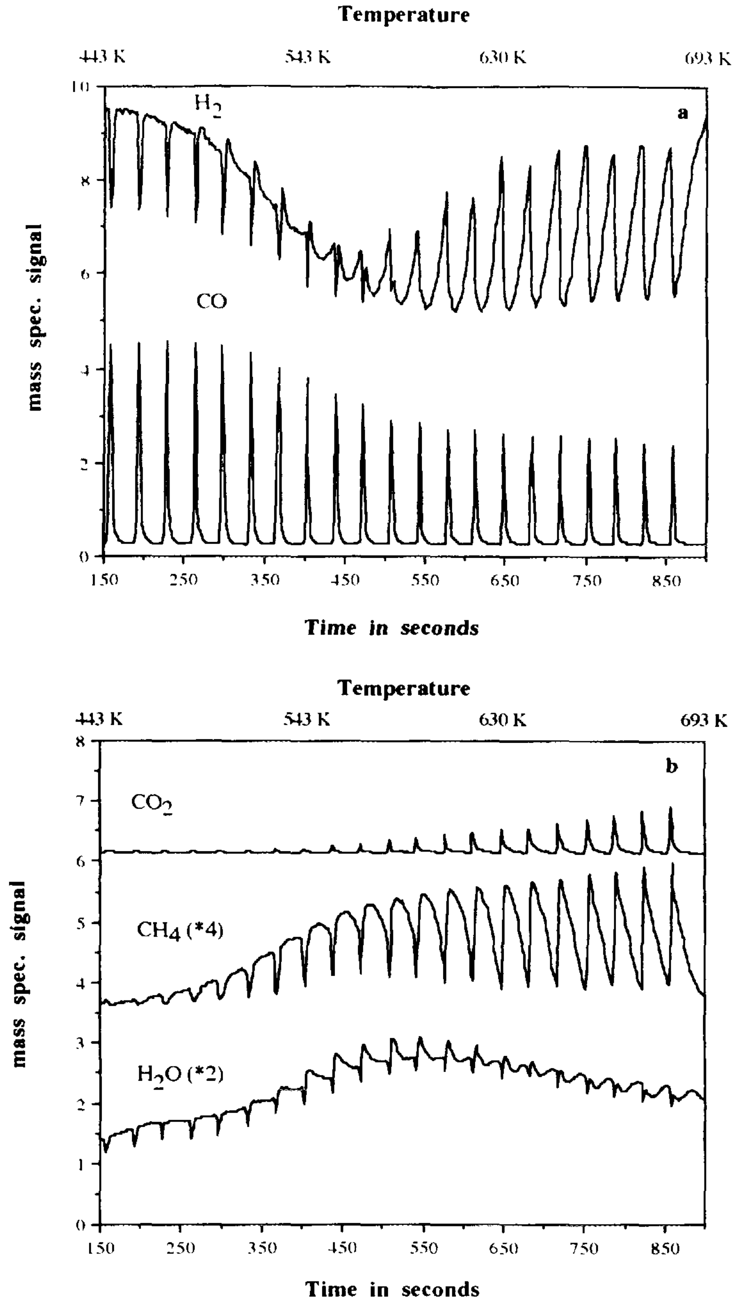

FIG. 2. Pressure–time profiles for a continuous flow of H_2 in He with periodic pulses of CO into the stream, all passing over the Rh/Al_2O_3 catalyst. At the same time the temperature of the reactor is ramped, yielding the profiles of reactant consumption and product evolution shown. Conversion of CO is low below 500 K and reaches ~50% at high temperatures. At high temperature, the mechanism is almost entirely dry methanation, while wet methanation is the route below 600 K under these conditions. The individual mass signals are offset for clarity.

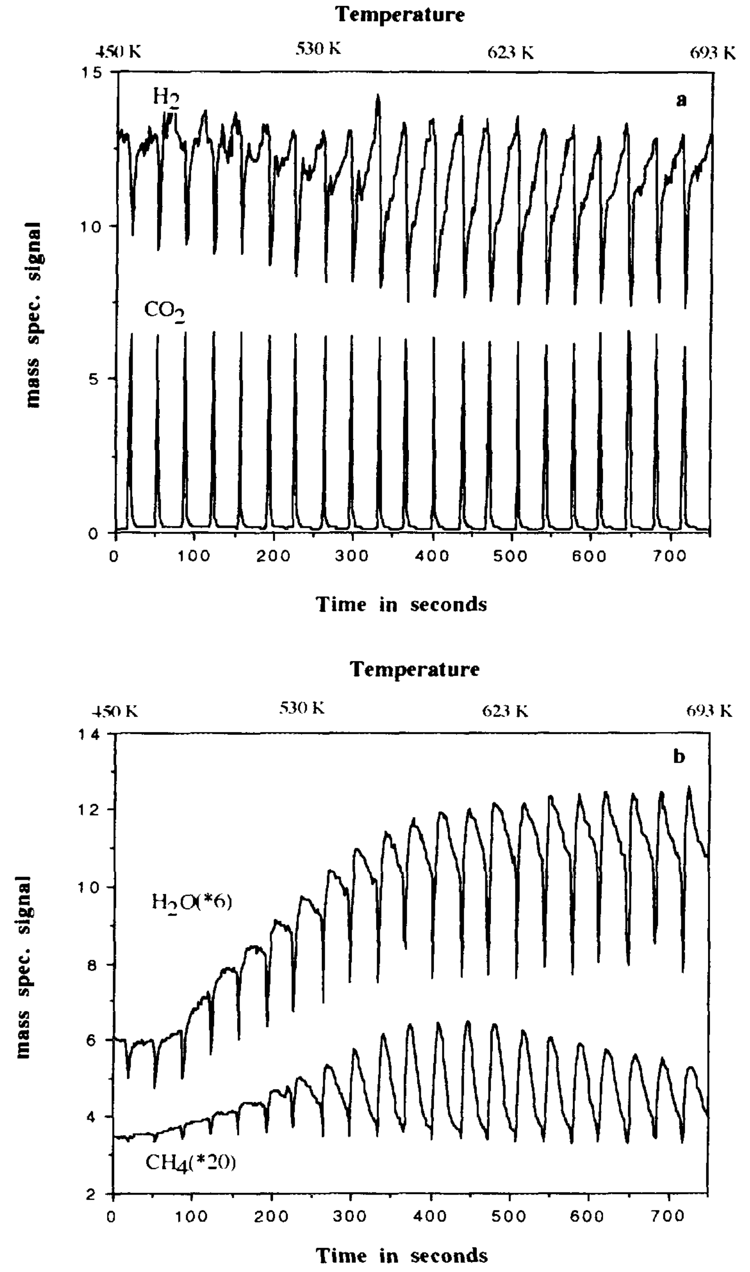

FIG. 3. As for Fig. 2, but with CO_2 as the pulsed gas and in this case only wet methanation is allowed.

of reactivity with temperature. Hydrogenation of $C_{(ads)}$ began very slowly at ~450 K and increased in rate with a rise in temperature, reaching a maximum integral production of CH_4 at ~630 K (Fig. 2b). The methane peaks are very broad at low temperatures and the evolution is incomplete at the next CO injection. As the temperature increases the surface hydrogenation becomes faster, the CH_4 peak narrows and at

>675 K the reaction is essentially completed during the interval between pulses. It is noticeable that there is a dip in CH_4 production at the time of the CO pulse, probably because the incoming CO displaces hydrogen from the surface. At higher temperatures this is not so noticeable because the steady state hydrogen coverage is lower. Hydrogenation of O(ads) began slowly at ~443 K and reached a maximum at ~603 K, but above this temperature the reaction stoichiometry was changed from wet methanation (Eq. (3)) to dry methanation (Eq. (2)). The production of CO_2 began at ~523 K and increased with temperature, CO_2 formation was more rapid than both CH_4 and H_2O, as evidenced by the lineshape. As CO_2 production increased, there was a simultaneous drop in both CH_4 and H_2O production. By 623 K, the competition between H_2 and CO for adsorbed dissociated oxygen was won by the latter, whereas at lower temperatures H_2 dominated the reaction.

Figures 3a and 3b show a similar experiment for CO_2 hydrogenation, although in this case it is clear that the only reducing agent in the gas is H_2. The hydrogenation of $C_{(ads)}$ and $O_{(ads)}$ began at ~453 K as it did with CO hydrogenation. The rate of hydrogenation of $C_{(ads)}$ from CO_2 was quicker than that from CO, as evidenced by the sharper peak shape and reached a maximum at ~613 K, above which temperature, both the rate and yield of CH_4 began to drop. This higher rate from CO_2 is probably due to easier availability of surface hydrogen because of reduced competition in the absence of adsorbed CO and less surface carbon. Adsorbed hydrogen coverage will be a factor in the low temperature rate limiting step of methane production. The production of H_2O increased with temperature up to ~653 K after which it remained constant. There was near 100% selectivity in the hydrogenation of CO_2 to CH_4 and H_2O. This agrees with the stoichiometry (Eq. (4)) and the simple lineshapes illustrate that only one reaction pathway occurs. It is clear that the conversion of CO_2 is much lower than CO, which probably reflects a much lower adsorption and dissociation ability of CO_2 on the surface. We also note that no deactivation of the catalyst occurred over a period of 3 months, indicating that no irreversible coking was taking place. Whilst a direct comparison with dry reforming cannot be made, due to the different temperature regimes, the present experiments would be consistent with the following mechanism for that reaction, which is also consistent with the overall stoichiometry above:

$$CH_{4(ads)} \rightarrow C_{(ads)} + 4H_{(ads)} \quad (5)$$

$$CO_{2(ads)} \rightarrow CO + O_{(ads)} \quad (6)$$

$$C_{(ads)} + O_{(ads)} \rightarrow CO \quad (7)$$

$$4H(ads) \rightarrow 2H_2. \quad (8)$$

The rate of Eq. (7) must be high as no build up of carbon was observed for dry reforming itself (*2*). Steps (5) and (6) are likely to be highly activated processes, but occur at significant rates above 500 K, as evidenced by CH_4 production from CO_2 in Fig. 3 and by H_2 production during pulses of CH_4 alone onto the catalyst, above 550 K.

Work is continuing on these reactions both at Liverpool and Santa Barbara and will be reported in detail in the near future.

ACKNOWLEDGMENTS

The authors thank British Gas plc. for their CASE awards to T.J.C. and A.T.A.

REFERENCES

1. Richardson, J. T., and Paripatyadar, S. A., *Appl. Catal.* **61,** 293 (1990).
2. Ashcroft, A. T., Cheetham, A. K., Green, M. L. H., and Vernon, P. D. F., *Nature* **325,** 225 (1991).
3. Vlasenco, V. M., and Yuzefovich, G. E., *Russ. Chem. Rev.* **38,** 728 (1969).
4. Vandervell, H. D., and Bowker, M., *Appl. Catal.* **30,** 151 (1987).
5. Solymosi, F., and Erdolhely, A., *J. Mol. Catal.* **8,** 471 (1980).
6. Kai, T., Matsumara, T., and Takahashi, T., *Catal. Lett.* **16,** 129 (1992).

7. Ichikawa, S., *J. Mol. Catal.* **53,** 53 (1989).
8. Bowker, M., *Catal. Today* **15,** 77 (1992).
9. Bowker, M., and Law, D., *Catal. Today* **10,** 397 (1991).
10. Kobayashi, H., and Kobayashi, M., *Catal. Rev.-Sci. Eng.* **10,** 139 (1974).
11. Bowker, M., Francis, S., Law, D., and Cassidy, T., submitted for publication.

M. Bowker[1]
T. J. Cassidy[1]
A. T. Ashcroft[2]
A. K. Cheetham[2]

Leverhulme Centre for Innovative Catalysis
Department of Chemistry
University of Liverpool
L69 3BX, United Kingdom

Received January 11, 1993; revised March 26, 1993

---

[1] Also at Surface Science Centre, Liverpool University, L69 3BX, U.K.

[2] Materials Department, University of California, Santa Barbara, CA 93106.