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On the Mechanism of CO and CO_2 Methanation over Ru/Molecular-Sieve Catalyst

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Disproportionation of CO and reduction of CO_2 on Ru/molecular-sieve catalyst and the subsequent hydrogenation of the species formed has been studied in the temperature range 400 to 575 K using a through-flow microcatalytic reactor. The results indicate that CO disproportionates on the catalyst to give "active" carbon and CO_2; the active carbon thus formed reacts with H_2 to give CH_4. Unlike CO, CO_2 becomes chemisorbed on the catalyst and is subsequently reduced by H_2 to give CH_4 through the intermediate formation of active carbon. The time and temperature dependence of the reactivity of the carbon has been studied in detail and a mechanism of catalytic methanation of CO and CO_2 through the formation of active carbon intermediate has been proposed.

1. INTRODUCTION

Several authors have reported that interaction of CO with Ni produces carbon which can be subsequently methanated by hydrogen (*1–3*). These studies were, however, carried out under conditions of low pressure ranging from 1 to 10^{-4} Torr (1 Torr = 133.3 N m^{-2}) in contrast to the high pressures used in practical catalytic methanation. Regarding dissociation of CO on ruthenium, contradictory results have been reported. Goodman *et al.* (*4*) and Madey and Menzel (*5*) found no decomposition of CO on Ru(110) and Ru(001) surfaces at low pressures while Singh and Grenga (*6*) have reported the formation of varying amounts of carbon along different poles of a ruthenium single crystal. While preparing this manuscript we came across the recent work of Rabo *et al.* (*7*) on disproportionation of CO at a pressure of 2.8 kg cm^{-2} on silica gel-supported Co, Ni, Ru, and Pd metals. In this paper we report the results of a study on the disproportionation of CO and reduction of CO_2 on Ru/molecular-sieve catalyst and the time and temperature dependent reactivity of carbon thus deposited. This work was aimed at achieving a better understanding of the catalytic methanation of CO and CO_2 which is an important step in the conversion of coal to fuel gases.

2. EXPERIMENTAL

2.1 Catalyst

The catalyst was prepared by impregnating 60 to 80 mesh molecular sieve (13×) with an aqueous solution of $RuCl_3$ followed by drying in air at 375 K and reduction in H_2 at 625 K for 18 hr. The catalyst contained 1.8 wt% of Ru. The surface area of catalyst as measured by BET method using N_2 gas was found to be 293 ± 5 m^2 g^{-1}. The metal surface area of catalyst was evaluated using the fol-

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lowing temperature-programmed desorption method. After activating the catalyst in H_2 at 600 K it was cooled to room temperature and was maintained for 1 hr in a H_2 stream. H_2 was then replaced by He carrier gas (820 ml/V/hr) and after keeping in He flow for 8 hr the catalyst was heated to 825 K at a linear rate of 24 K min^{-1}. The amount of H_2 thus released was evaluated by gas chromatography and was found to be 15 ± 1 mmol/g corresponding to a metal surface area of 13 ± 1 m^2/g. In a separate experiment the effluent was periodically sampled during the entire cycle of desorption and was analyzed by gas chromatography. It was confirmed that the effluent contained no other gas except H_2.

The catalyst column consisted of a 0.4-cm-i.d. stainless-steel U-tube filled with 2.2 ml of the catalyst. The column was enclosed in a heater assembly and maintained at the desired temperature with an accuracy of ±0.5 K. At the start of each experiment the catalyst was heated at 600 K in an oxygen stream for 30 min and then reactivated by heating at the same temperature in a flowing stream of H_2 for 1 hr. No loss of Ru was observed as a result of this reactivation.

2.2 Gas Chromatographic Analysis

(*a*) *Efficiency of the catalyst.* To determine the efficiency of the catalyst, 40 μl of CO, CO_2, or a mixture of both was injected into a H_2 carrier gas stream flowing over the catalyst (flow rate 820 ml/V/hr at $\sim$1.23 kg cm^{-2}) and the methane yields were evaluated at different temperatures between 375 and 575 K. For quantitative analysis of methane, the catalyst column was connected in series with a gas chromatographic column of Porapak-Q and a thermal conductivity detector.

(*b*) *Disproportionation and methanation.* To evaluate disproportionation of CO and reduction of CO_2 on the catalyst surface and to study subsequent hydrogenation of the species produced, gases were separately injected into a He carrier gas stream passing through the catalyst bed (at 820 ml/V/hr and 1.23 kg cm^{-2} pressure) using the experimental set up described earlier (*8*). With this set-up, using sampling valves and injection ports connected in series to the catalyst chamber and gas chromatographic column, gases could be injected with any desired sequence and at different time intervals and the analysis of effluent gases could be automatically carried out.

High-purity CO, CO_2, and He from Airco and electrolytically generated H_2 from an Elhygen generator were used throughout this study to avoid impurity contamination.

2.3 Electron Spin Resonance Studies

For the identification of species formed in the interaction of CO and CO_2 on the catalyst, *in situ* ESR investigations were carried out using a Varian X-band spectrometer. About 125 mg of catalyst was kept in the spectrometer cavity in a flow-through Pyrex tube assembly fitted with greaseless joints and stopcocks through which pure and dry He was continuously flushed. The gases could be injected into the stream independently or together without disturbing the assembly. The ESR tube was maintained at the required temperature using a Varian variable temperature accessory. Before each experiment fresh catalyst was taken and was reactivated *in situ* at 600 K by replacing He with H_2.

3. RESULTS

3.1 Methanation Efficiency of the Catalyst

Figure 1 shows the efficiency of the catalyst for methanation of CO, CO_2, and a mixture of CO + CO_2 (1:2 v/v) in the presence of excess H_2. The methane peaks observed in CO_2 and CO + CO_2 experiments below 450 K were comparatively broad and tailing. It may be noted from

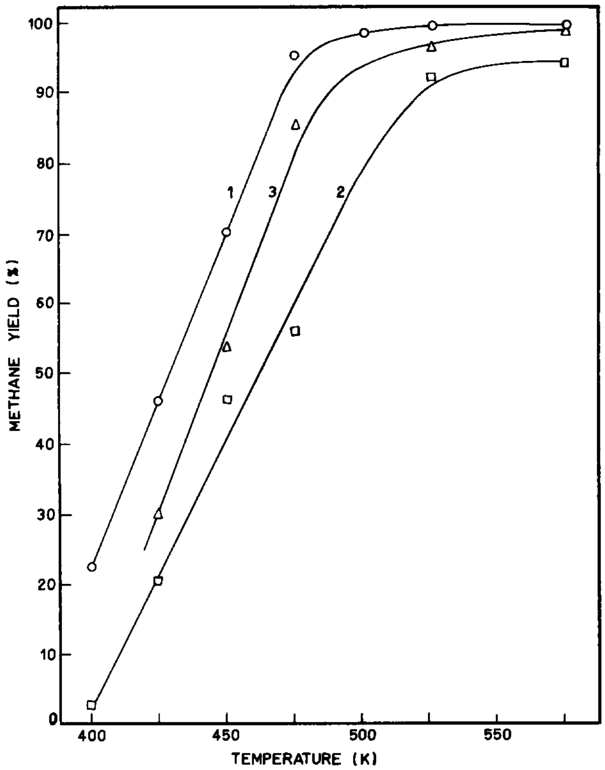

FIG. 1. Methanation efficiency of Ru/molecular-sieve catalyst at different temperatures for CO (curve 1), CO_2 (curve 2), and premixed CO + CO_2 (v/v 1:2) (curve 3) in presence of excess hydrogen.

Fig. 1 that methane is observed in the effluent even at ~400 K and the catalyst is highly efficient for methanation of CO, CO_2, and also a mixture of CO and CO_2.

3.2 Disproportionation of CO, Reduction of CO_2, and Subsequent Methanation

(*a*) *Carbon monoxide.* (i) When CO alone (46 μl, diluted with 405 μl of He) was injected into the He carrier passing through the catalyst, two peaks were observed in the gas chromatograms, one due to unreacted CO and the other due to CO_2. The percentage conversion of CO to CO_2 increased with temperature and beyond 575 K no CO could be detected in the effluent. These results are given in Table 1A.

It may be observed from these data that at temperatures above 500 K the yield of CO_2 was essentially half of the amount of CO consumed in the reaction.

After the initial elution of CO and CO_2 as mentioned above, the effluent was periodically monitored to check for any slow desorption of CO and CO_2 from the catalyst. For this purpose a high-sensitivity gas chromatographic method was used which could detect CO and CO_2 at levels as low as $\sim 10^{-3}$ μl ($\sim 4 \times 10^{-11}$ mol) (*9*). It was observed that though no CO was present in the effluent, a small quantity of CO_2 was continuously released, the extent of release decreasing gradually with time. The desorption of CO_2 continued for about 90 min when the catalyst was kept at 400 K whereas at 575 K no significant amount of CO_2 was detected in the effluent after the initial burst release of CO_2 (Table 1A). Raising the temperature of the catalyst after injecting CO at a lower temperature hastened the desorption rate of CO_2 while CO was still not found in the effluent.

(ii) If, following CO injection, H_2 (2 ml) was subsequently injected (referred to hereafter as the first H_2 injection), a peak due to methane was observed. At this stage, if additional H_2 injections at intervals of 2 min were made, further methane formation with a progressive decrease in peak height was observed, the actual yield being dependent on the catalyst temperature. When the time gap between CO and the first H_2 injection was increased, the methane yields were found to decrease progressively. Typical examples of the variation of methane yields for successive H_2 injections are shown in Fig. 2 for two time intervals of 10 and 40 sec between CO and first H_2 injection. It may be observed from this figure that the number of H_2 injections necessary to effect complete conversion of methane precursor to methane decreases with increasing catalyst temperature.

The effect of delaying the first H_2 injection on total yield is shown in Fig. 3 for different temperatures of the catalyst. The methane values given in this figure were calculated by adding up individual CH_4 yields from all successive H_2 injections until no more methane was detected and the values thus obtained for the 10-sec

TABLE 1

Yields of Eluted CO_2 (Unadsorbed) on Injection of CO (46 μl)/CO_2 (40 μl) over Catalyst at Different Temperatures

Temperature of catalyst (°K)	(A) CO experiments		(B) CO_2 experiments
	Yield of eluted CO (unreacted) (μl)	Yield of CO_2 (μl)	Yield of eluted CO_2 (μl)
400	13.0	0	0
425	12.8	2.8	0
450	12.0	7.0	10.5
475	11.5	9.0	23.0
500	—	—	31.1
525	10.2	16.4	35.4
550	—	—	38.0
575	1.5	22.0	40.0

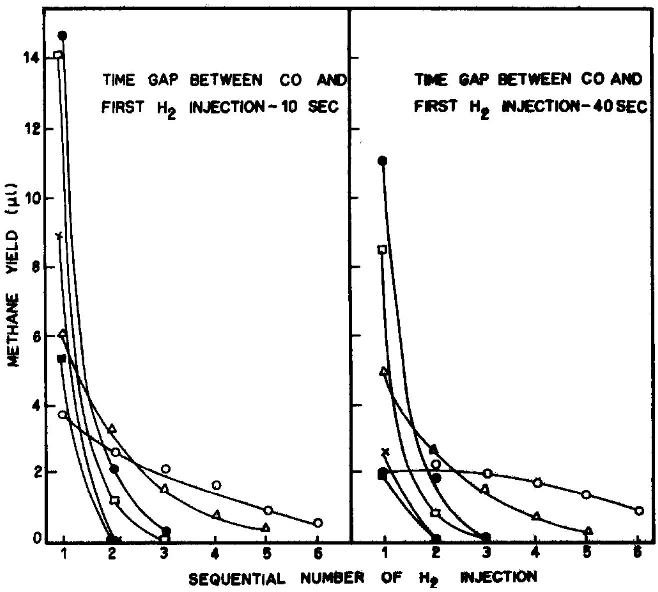

FIG. 2. Methane yields obtained at different temperatures on injection of 46 μl of CO on Ru catalyst followed by successive injections of 2 ml H_2. ○, 400 K; △, 425 K; ●, 450 K; □, 475 K; ×, 525 K; ■, 575 K.

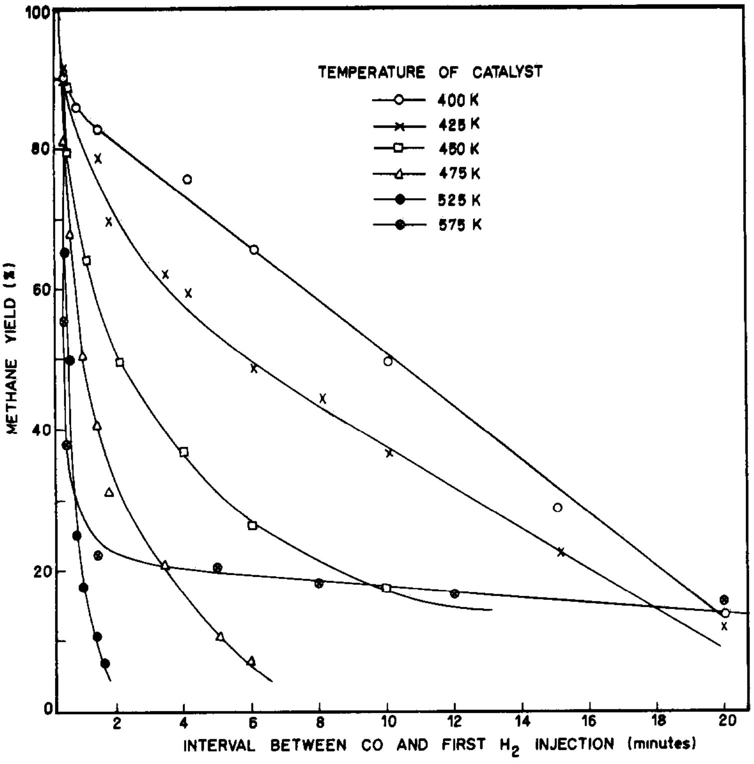

FIG. 3. Effect of the time interval between CO and first H_2 injection on the total methane yield.

time gap study at different temperatures were assumed to be 100% for comparative evaluation of the data. It is of interest to note that although at 400 K methane formation was observed for time intervals as long as 20 min, above 525 K no measurable amount of methane was detected if the time interval exceeded 2 min. At 575 K, however, anomalous behavior was observed in that methane continued to be formed for time intervals up to 30 min.

The time-dependent decrease in the number of methane precursor species as shown by Fig. 3 for different temperatures can be resolved into at least two stages, one a fast component and the other a slow one. At temperatures above 500 K the first stage decay is apparently very fast and is unobservable within our experimental limits and hence only one step is observed. On the contrary, at lower temperatures (e.g., 400 K) the decay is dominated by the slowly decaying stage.

(*b*) *Carbon dioxide.* The experiments as given in Section 3.2a were repeated with CO_2 in place of CO. When 40 μl of CO_2 was injected into the He stream, a part of the CO_2 was initially adsorbed on the catalyst and the rest was eluted immediately. The amounts of CO_2 eluted immediately after injection of 40 μl CO_2 for different temperatures of the catalyst are given in Table 1B.

The adsorbed CO_2 was found to be released slowly (Section 3.2a), the amount decreasing with time. At 400 and 425 K, an induction period of about 3 min was observed for the start of CO_2 desorption and thereafter the release of CO_2 continued for about 90 min. At temperatures above 550 K no significant quantity of CO_2 was observed after the initial release (Table 1B).

When H_2 was injected after CO_2 injection at different time gaps ranging from zero time (simultaneous H_2 injection) to as long as 25 min, methane formation was observed. Further H_2 injections at 2-min intervals (without introducing additional CO_2) again gave rise to CH_4 formation, the yields depending on catalyst temperature. Typical examples of methane yields thus obtained on successive H_2 injections for different CO_2–first H_2 injection time gaps are given in Fig. 4A–F. The horizontal lines in these figures indicate limiting percentage methane yields obtained for each of the successive H_2 injections. Thus, the distance between abscissa and the first line indicates the CH_4 yield on first H_2 injection, the distance between the first and second lines that for second H_2 injection, and so on. At 400 K, no measurable CH_4 was observed when H_2 (2 ml) was injected simultaneously with CO_2 or 10 sec after CO_2 injection. The first horizontal lines above the abscissa of Fig. 4A in these two cases refer to CH_4 yields for the second H_2 injection.

It may be noticed from Fig. 4 that there is a gradual variation in methane yields from successive H_2 injections, the variation being dependent on catalyst temperature and CO_2–first H_2 injection time interval. For example, at 400 and 425 K the methane yield obtained on first H_2 injection increases with increasing CO_2–first H_2 time gap. At 450 K, it first shows an increase and then decreases, while at higher temperatures it decreases progressively with increasing time gap. Similarly, a gradual variation in ratio of CH_4 yields obtained on first and second H_2 injections [referred to as CH_4(I) and CH_4(II), re-

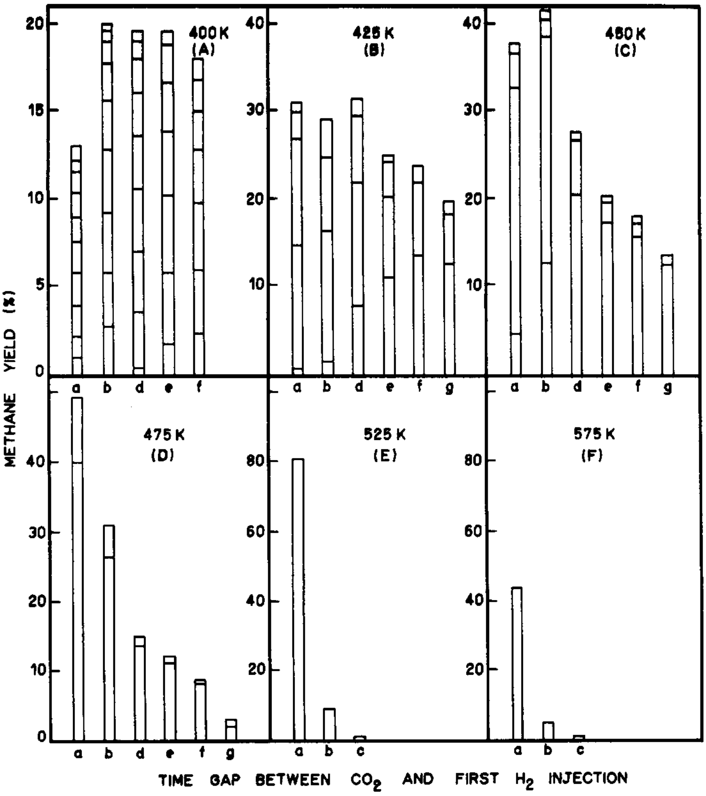

Fig. 4. Methane yields obtained at different temperatures on injection of 40 μl of CO_2 on Ru catalyst followed by successive injections of 2 ml H_2 (see Section 3.2b for details). a to g refer to CO_2–first H_2 injection time gaps of O (simultaneous CO_2 and H_2), 10 sec, 40 sec, 1 min, 5 min, 10 min, and 25 min, respectively.

spectively] may be noted. At 400 K CH_4(I) is less than CH_2(II) for time gaps up to 10 min, while at 425 and 450 K this behavior was observed for time intervals up to 1 min and 10 sec, respectively. At 475 K CH_4(I) was higher than CH_4(II) for all time gaps studied and above 500 K the first H_2 injection resulted in conversion of nearly all chemisorbed CO_2 to CH_4. At temperatures above 525 K for CO_2–first H_2 interval of more than 40 sec no significant CH_4 yields were observed.

(c) When the sequence of CO or CO_2 and H_2 injections was reversed, i.e., when H_2 (2 ml) injection was followed after 8 sec (to prevent premixing of gases) by CO or CO_2 injection, CH_4 was not detected in the effluent at all the temperatures studied. When CO or CO_2 and H_2 were simultaneously injected into the He flowing over the catalyst, the yields of eluted CO_2 were less than those shown in Table 1 and at temperatures greater than 500 K negligible amounts of eluted CO_2 were observed.

3.3 ESR Studies

(*a*) *Carbon monoxide.* A fresh catalyst sample, regenerated *in situ* and maintained under a continuous flow of He, did not give any ESR signal except a very broad background. At this stage, when CO was injected into the He carrier gas stream, the signal shown by curve a in Fig. 5 appeared. If subsequent to CO injection, H_2 was passed over the catalyst at temperatures less than 470 K, the ESR signal height was found to fall by ~30% (Fig. 5b). This reduced signal remained unaffected on further passage of H_2 over the catalyst. At higher temperatures (>470 K) the reduction in ESR signal on H_2 injection was not observable due to reasons explained later.

The magnetic field at which signals a and b in Fig. 5 appeared coincided with that from a standard pitch sample (Fig. 5c). The *g* value of signals a and b was found to be 2.0036 using DPPH as reference.

(*b*) *Carbon dioxide.* When CO_2 was injected into He carrier gas flowing over the catalyst, no signal was observed at all temperatures between 400 and 600 K. However, when CO_2 injection was followed by injection of H_2 at catalyst temperatures less than 500 K, an ESR signal similar to that shown in Fig. 5a was observed.

4. DISCUSSION

4.1 Disproportionation of CO and Reduction of CO_2

(*a*) *Carbon monoxide.* ESR signals of evaporated carbon films, chars, and other carbons consist of a single symmetric line with a free-electron *g* value (*10, 11*). Since the *g* value and line width of the ESR signals observed on injection of CO over the catalyst correspond with those from the pitch standard, it may be reasoned that signals a and b of Fig. 5 are due to carbon deposited over the catalyst surface. Gas chromatographic evidence clearly indicates that CO_2 is formed when CO reacts over the catalyst. Quantitative formation of CO_2 from CO at 525 and 575 K (Table 1A) further confirms that the only species that can be left behind on the catalyst, at least at these temperatures, is carbon. From these observations it can be concluded that CO disproportionates on Ru surface to give C and CO_2

$$2CO \rightarrow C + CO_2 \qquad (1)$$

Another possible route for the formation of CO_2 could be oxidation of CO if a part of the Ru is present as oxide. However, on varying the period of reduction in H_2 from 2 to 30 hr while preparing catalyst samples and from 1 to 6 hr while regenerating (Section 2.1), no significant variation in CO_2 yield from CO was observed. Also, in experiments using catalyst which was not sintered in O_2 before regeneration, the yields of CO_2 remained unchanged. It is evident, therefore, that the route for the formation of CO_2 from CO in our experiments is disproportionation only.

(*b*) *Carbon dioxide.* The ESR results (Section 3.3b) indicate that, unlike CO, CO_2 does not directly decompose on the catalyst surface but when H_2 is passed over adsorbed CO_2, carbon is formed. Since no significant amount of CO_2 remained adsorbed at temperatures above 500 K (Table 1), no ESR signal was observed at these temperatures when H_2 was injected after CO_2 (Section 3.3b). The formation of carbon on H_2 reduction of CO_2 may be due either to direct reduction of CO_2 to carbon or to reduction via CO formation. If CO is formed as an intermediate it may immediately disproportionate to give carbon.

4.2 The Reactivity of Deposited Carbon

The ESR signal of carbon was reduced on subsequent H_2 injection (Fig. 5). This suggests that deposited carbon reacts directly with H_2 and gas chromatographic data confirm that the reaction product is methane. Since the reduced ESR signal persists even after continuous passage of H_2 for hours (Section 3.3a) it would appear that the carbon atoms formed on decomposition are of two types, namely, ones which are reactive to H_2 and others which are not. At reaction temperatures above 470 K the carbon signal was not reduced on subsequent passage of H_2. These results suggest that the carbon atoms formed on disproportionation of CO or reduction of CO_2 are initially "reactive" and convert with time and temperature to an inactive form. At temperatures above 470 K, the conversion of active carbon to its inactive form would have been completed by the time the ESR signal was recorded in our experiments. This conclusion is supported by gas chromatography evidence.

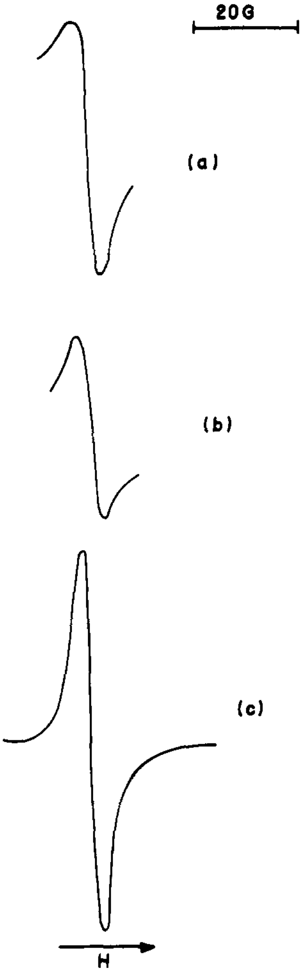

FIG. 5. ESR signals from Ru catalyst (a) after injection of CO and (b) after subsequent H_2 injection (c) pitch sample.

These results are in agreement with the work of Rabo *et al.* (*7*) who found that about 15% of surface carbon deposited on Ru/SiO_2 at 670 K reacted with H_2 to give 81% methane and 19% ethane. Wentrcek *et al.* (*2*) have reported the conversion of active carbon to a graphitic form on Ni catalyst.

4.3 Methane Formation

The decrease in methane yields observed with increasing time gap between CO–first H_2 injection and CO_2–first H_2 injection

TABLE 2

Quantity of Carbon and CO_2 Available on Catalyst Surface after Injection of 46 μl of CO (11 × 10^{17} Molecules) and the Yield of CH_4 on Subsequent H_2 Injections for Various CO–First H_2 Time Intervals.[a]

(1) Catalyst temperature (K)	(2) Number of carbon atoms formed from retained CO (×10^{17})	(3) Number of adsorbed CO_2 molecules (×10^{17})	(4) Total number of CH_4 molecules[b] for different CO–first H_2 time intervals				
			6 sec (×10^{17})	10 sec (×10^{17})	1 min (×10^{17})	5 min (×10^{17})	10 min (×10^{17})
400	4.09	4.09	2.33	2.31	2.10	[illegible]70	1.19
425	4.11	3.42	3.19	2.99	2.56	1.49	1.11
450	4.21	2.48	4.56	4.12	2.64	1.23	[illegible].73
475	4.27	2.04	4.60	3.83	1.94	0.29	—
525	4.44	0.37	2.87	2.18	0.39	—	—
575	5.51	0.06	2.28	1.39	0.38	0.29	0.22

[a] Volume of CO and CO_2 initially eluted as in Table 1A.

[b] Calculated by adding up CH_4 yields obtained from successive H_2 injections [see Section 3.2a(ii)].

(Figs. 2, 3, and 4) can be interpreted in two possible ways:

(a) A fraction of the uneluted CO or CO_2 [including CO_2 produced in Reaction (1)] may remain adsorbed on the catalyst surface and may react with H_2 injected subsequently to give CH_4. Slow desorption of these gases with time would result in reduced CH_4 yields with increasing time interval between CO/CO_2 and H_2 injections. Experiments (Section 3.2) have shown that a part of the injected CO_2 or the CO_2 formed from CO remains adsorbed on the catalyst surface below 550 K and desorbs slowly with time, thus leaving decreasing quantities of adsorbed gas on the catalyst. The formation of CH_4 directly from CO_2 may therefore explain the decrease in CH_4 yields with time. To evaluate the contribution of adsorbed CO_2 towards methane formation in the experiments of Section 3.2a, the number of C atoms and CO_2 molecules retained by the catalyst after initial elution of CO_2 (Table 1A) was calculated and the data are given in Table 2 together with the total methane yields obtained for different CO–first H_2 time intervals. For these calculations it was presumed that CO retained by the catalyst decomposes completely according to Reaction (1). It may be noted from Table 2 that at temperatures above 425 K the numbers of CH_4 molecules formed for time intervals between 6 sec and 1 min (column 4) are much more than the maximum theoretical yield of CH_4 obtainable from adsorbed CO_2 (column 3) even though no desorption of retained CO_2 is taken into account. Therefore it can be concluded that CH_4 is also formed by a route other than direct reaction of CO_2 with H_2.

(b) The other possible path for methane formation is the reaction of "active" carbon (formed on disproportionation of CO or reduction of CO_2) with H_2. The ESR results support this mechanism (see Section 4.2). The decreasing methane yields as shown in Figs. 2 and 3 can be partly attributed to the decay in the activity of carbon with time and temperature, though the contribution from adsorbed CO_2 toward CH_4 formation at lower temperatures cannot be completely ruled out (see Table 2).

A theoretical study by Goddard *et al.* (*12*) has shown that a chemisorbed C_2 species formed on dissociation of CO on Ni is catalytically active.

The data for the CO_2–H_2 reaction (Fig. 4) show that at 400 and 425 K if the time gap between CO_2 and H_2 injections was less than 1 min, the first H_2 injection resulted in negligible yields of methane while subsequent H_2 injections gave higher methane yields. This and other observations in Section 3.2b may be explained as follows. The first H_2 injection results in reduction of CO_2 to carbon (via CO) which on subsequent H_2 injection will give methane. The ESR results of Section 3.3b support this view. At lower temperatures CO_2 is strongly adsorbed on the catalyst surface (Table 1) and therefore the rate of its reduction to give carbon will be less (*13*) and furthermore the reaction rate of carbon at these temperatures towards H_2 will be slower (Fig. 2). Many injections of H_2 will therefore be required to convert adsorbed carbon dioxide completely to CH_4 (Fig. 4A and B). At higher temperatures the formation of C and its further reaction with H_2 will be accelerated and therefore at these temperatures CH_4 can be produced on the first H_2 injection itself, even though CO_2 is desorbed faster. At temperatures above 525 K no significant amount of CO_2 remains adsorbed on the catalyst (Table 1) and therefore at longer time gaps between CO_2 and H_2 injections no CH_4 formation should be expected. This is in agreement with the results obtained in this study (Fig. 4E and F). The variation in CH_4(I) yield with increasing time gap (Section 3.2b) clearly indicates that reduction of CO_2 on the catalyst surface is a diffusion-controlled process. At lower temperatures, CO_2 probably diffuses with time to such sites where its reduction is facilitated resulting in enhanced CH_4(I) yields with increase in the CO_2–first H_2 time gap.

4.4 Mechanism

A mechanism for the formation of CH_4 on the catalyst from sequential injection of CO and H_2 can therefore be envisaged as follows. The injection of CO on the catalyst results in its disproportionation to C and CO_2. The first H_2 injection results in a C–H_2 reaction and the reduction of a part of adsorbed CO_2 to CO or carbon. The subsequent H_2 injections will again give rise to CH_4 and generate progressively smaller amounts of active carbon. This chain will sustain itself until all adsorbed CO_2 has reacted or so long as carbon retains its activity towards H_2. The observation that no unreacted CO_2 was observed when CO and H_2 were simultaneously injected over the catalyst above 500 K (Section 3.2c) clearly indicates that CO_2 formed on disproportionation of CO is eventually methanated. The different curves in Figs. 2 and 3 thus represent the amount of active carbon available at a particular time and temperature.

The CO_2–H_2 reaction can be envisaged to follow a similar path except for an additional step requiring conversion of CO_2 to CO.

The observation that deposited carbon does not react with preadsorbed H_2 (Section 3.2c) is in agreement with the low-pressure study of Goodman *et al.* (*4*) who found that no CH_4 was formed from coadsorbed H_2 + CO on a clean ruthenium surface. This probably indicates that CH_4 is formed by the reaction of the "active" form of carbon directly with the H_2 in gas phase.

4.5 Formation of Methane from Premixed CO–H_2 and CO_2–H_2

Although various mechanisms involving formation of an HCHO-type intermediate surface complex have been proposed for methanation of both CO and CO_2 (see, for example, Refs. *14–17*), the results reported here suggest that the intermediate formation of "active" carbon and its subsequent methanation should also be considered as a mechanistic route for the formation of CH_4 from mixtures of CO–H_2 and CO_2–H_2. It has been reported in the literature that CO_2 is not methanated in the presence of CO (*18*), though it has been recently suggested (*14*) that this is not necessarily so. Experiments with premixed CO + CO_2 (curve 3, Fig. 1) clearly indicate that methane is formed from both CO and CO_2.

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