The Reversed-flow Gas-chromatography Technique applied to the Kinetics of the Methanation of Carbon Monoxide

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The reversed-flow gas-chromatography technique has been applied to the methanation reaction of carbon monoxide over two Ni/Al₂O₃ catalysts. A continuous feed by diffusion of carbon monoxide was used, ensuring a continuous change in its concentration with time over the catalyst bed. An integrated rate equation has been derived, permitting the calculation from experimental data of the rate constant and the order of the reaction with respect to carbon monoxide. This was done for a wide range of fractional conversions to methane at each temperature. Arrhenius activation parameters were computed for each reaction order. The latter changes with temperature discontinuously, but does not change with CO concentration at the same temperature. This is explained by the fact that the method is a pulse technique under steady-state conditions. The findings are compared with recent results in the literature, agreeing with some of them but not with others. They are, however, consistent with a conventional reaction mechanism, assuming a non-homogeneous catalytic surface. A rate equation for the formation of methane, based on this mechanism, has been derived and is used to explain the experimental data, especially the change of reaction order with respect to carbon monoxide with temperature. The ratedetermining step is the hydrogenation of CH or CH₃ groups.

The kinetics and mechanism of carbon monoxide methanation over various catalysts, particularly with nickel as the active constituent, continue to be of interest since the discovery of the reaction in 1902 by Sabatier and Senderens.¹ The main reasons for this interest are connected with the formation of methane-rich fuels having low CO contents, the removal of carbon monoxide traces from hydrogen-rich gases of ammonia plants and the transformation of coal into substitute natural gas. However, despite numerous kinetic investigations of this reaction, some of which are very recent and thorough,²⁻⁹ its mechanism still remains obscure. This is mainly due to the kinetic behaviour of the reaction; its order with respect to CO changes with temperature and partial pressure of CO in a complex way,^{7, 8, 10} whereas the order with respect to H₂ appears to be independent of temperature and close to unity.^{2, 7, 8, 10} The complexity of the reaction orders is also reflected in the decrease in activation energy with increasing reaction temperature.^{2, 7, 11}

It occurred to us that additional information on the kinetics of the methanation reaction could be obtained by means of the new technique of reversed-flow gas chromatography (r.f.g.c.), which has already been applied with success to the study of the detailed kinetics of various surface-catalysed reactions^{12–19} and other related phenomena.^{20–29} The method, which has been reviewed recently,³⁰ is used with various experimental arrangements depending on certain characteristics of the reaction. In the present case, where one reactant (H₂) is used in a great excess over the other as a carrier gas, and the second reactant (CO) is not retained on the catalytic bed for a sufficiently long time, but is eluted together with the products, the experimental setup outlined in fig. 1 was employed. This arrangement offers the following advantages over traditional techniques used in heterogeneous catalysis, outlined below.



Fig. 1. Schematic representation of the experimental arrangement for studying the kinetics of carbon monoxide methanation over alumina-supported nickel. TC is a thermal conductivity detector.

(1) It is a very simple arrangement; instead of using flowmeters, mixing chambers, saturators and similar devices to introduce the reaction mixtures into the catalyst bed, a column L void of any solid material is filled with one reactant (CO) using a gas-tight syringe (or with a mixture of two reactants), and this reactant is allowed to diffuse slowly onto the catalyst retained within a short section near the junction of columns L and l'+l.

(2) The diffusion feed described above ensures the presence of reactants over the catalyst bed for a long time period, resembling that of a continuous flow, but with the concentration (and hence the partial pressure) of carbon monoxide changing continuously with time, according to the diffusion laws.

(3) Reversing the flow of the carrier gas by means of the six-port valve for a short time period t' (smaller than the retention time of reactant and products on column l' and l)³⁰ causes a sampling of all substances present at x = l'. The chromatographic material filling l separates these substances, revealing their relative concentrations after passing through the catalyst bed in the form of extra peaks (sample peaks), as shown in fig. 2. From these sample peaks the fractional conversion of reactants to products can be calculated many times during a single diffusion feed. From these conversions, covering a wide range, the rate constant and the order of the reaction can be found for an extending range of partial pressures, in a single experiment lasting only a few hours.

(4) The catalytic bed can be treated either as a differential reactor or in an integral mode as was done in the present work (see Results section).

(5) It is apparent from fig. 2 that the method uses pulses of reactants created by the flow reversals, but these pulses are superimposed on an initial concentration line of reactant and product(s), constituting a continuous flow of substances over the catalyst





Fig. 2. Sample peaks of CO and CH₄ obtained by reversing the flow for t' = 30 s, at 489 K, 37 min after introducing carbon monoxide in the diffusion column L. The catalyst was 5% Ni/Al₂O₃, the chromatographic material molecular sieve 5A (80–100 mesh), and the carrier gas hydrogen $(\dot{V} = 0.75 \text{ cm}^3 \text{ s}^{-1}).$

bed. Thus it has all the advantages of both a pulse technique and a continuous feeding of the reactant, and because this feeding is due to slow gas diffusion, steady-state conditions over the catalyst are soon and easily established. In other words, the method is a pulse technique under steady-state conditions. This should lead to kinetic information that is not masked by adsorption effects of reactants and products on the catalyst surface.

As a catalyst in the present study alumina-supported nickel was used, with two different nickel loadings.

Experimental

Materials

The catalytic support was alumina Ho 425 of Houdry Katalysatorenwerke with a specific surface area of 150 m² g⁻¹. The catalysts used were prepared by the classical method of dry impregnation of the alumina with an aqueous solution of Ni(NO₃)₂ \cdot 6H₂O (Merck *pro analysi*). After drying at 373 K in air for 24 h they were reduced at 503 K for 1 h and at 758 K for 14 h in flowing hydrogen at a space velocity of 2000 h⁻¹. In all cases the change of temperature from ambient to 373 K, then to 503 K and to 758 K was made with a heating rate of 1 K min⁻¹. The loading of the active phase, expressed as Ni was 2 and 5% (w/w).

The hydrogen used in the reduction of the catalysts and as a carrier gas in the kinetic experiments was purchased from Linde A. G. (Greece) and had a purity of 99.99%. The carbon monoxide (99.69% pure) was obtained from Matheson gas products.

The chromatographic materials used in column l' + l were molecular sieve 5A (80–100 mesh) of Matheson, Coleman and Bell, Chromosorb 102 (100–120 mesh) of Applied Science Laboratories, and silica gel (100–120 mesh) of B.D.H.



Fig. 3. Gas lines and important connections of the set-up used to study the kinetics of the reaction $CO+3H_2 \rightarrow CH_4+H_2O.$

Apparatus and Procedure

The experimental setup for the application of the r.f.g.c. technique consists basically of a conventional gas chromatograph modified so that it accommodates inside its oven the r.f.g.c. cell, connected to the carrier gas inlet and the chromatographic detector through a four- or six-port valve (*cf.* fig. 1). Fig. 3 shows the details of the apparatus used in the present study. All three branches of the cell *L*, *l'* and *l* were of stainless-steel chromatographic tube with i.d. 4 mm. The diffusion column *L* (100 cm long) was empty. Sections *l'* and *l* were each 115 cm long and were both filled with chromatographic material, except for a short length (5 mm) of *l* near the junction with *L* which contained 53 or 107 mg of 5 or 2% (w/w) Ni/Al₂O₃, 80–100 mesh catalyst, respectively. This part of column *l* was heated with a separate heating element and its temperature was measured with a separate thermocouple. The variations during each run were < 1 K.

The pressure drop along column l' was the same as that along column l and was measured with a mercury manometer. It was found that the catalyst bed was under a pressure of 2.015 atm[†] during all experiments.

Conditioning of the catalyst was carried out *in situ* at 713 K for 16 h, under a carrier gas (H₂, 0.75 cm³ s⁻¹) flowing in direction F (*cf.* fig. 1) and with 30 cm³ CO at atmospheric pressure injected with a gas-tight syringe into column L. The temperature of the chromatographic oven was 346 ± 1 K in all experiments.

Following the above conditioning, and after the chromatographic signal had decayed to a negligible height, a new 30 cm³ volume of CO at atmospheric pressure was slowly injected into the column L. After ca. 10 min a continuous concentration-time curve decreasing slowly is established in the recorder owing to both the reactant CO and the products. This can be taken as the steady-state condition for the catalyst. Then, the carrier gas flow is reversed from the F- to the R-direction (cf. fig. 1) by turning the six-port

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valve from one position (solid lines) to the other (dashed lines). After 30 s of backward flow the carrier gas was again turned to the original F-direction. Because the time t'elapsing between two successive reversals of the flow (one from the F- to R-direction and one back to the F-direction) is less than the retention time on columns l' and l of the substances giving rise to the chromatographic signal, a symmetrical 'sample peak' for each substance follows the restoration of the gas flow to its original direction,³⁰ as shown in fig. 2. The above procedure of the flow reversals was repeated many times at each temperature, giving rise to a series of sample peaks which correspond to different partial pressures of CO over the catalyst and different fractional conversions of reactants to products. The pressure change in tube L and over the catalyst at each flow reversal was negligibly small, owing to the same pressure drop along columns l' and l and to the time interval t' being short.

Calculations and plots were made with a New-Brain microcomputer and a Hewlett-Packard 9825A desk-top computer with a 9872B plotter.

Results

Derivation of the Integrated Rate Equation

The general chromatographic equation describing the elution curve and the sample peaks in the r.f.g.c. method has been published many times^{16, 17, 19, 21, 22, 25, 30} and is not repeated here. We only mention that the height of each sample peak above the continuous chromatographic signal (taken as baseline) is proportional to the concentration of the substance giving rise to this peak, at the junction x = l' (cf. fig. 1) and at the time of the flow reversal. In the present case, however, this would be true in the absence of catalyst, while with the catalytic bed present at the entrance of column section l, the sample peaks at the detector, like those of fig. 2, are due to substances present at the exit of the bed, *i.e.* after passage of the carbon monoxide sample peak at x = l'through the catalyst. The only product detected in measurable amounts was methane. The water, expected as a second product, was presumably retained on the molecular sieve 5A used as chromatographic material in columns l' and l. By using chromosorb 102 and silica gel in place of molecular sieve 5A, the formation of carbon dioxide, ethane and higher paraffins was sought, but none was observed in detectable amounts. This finding is in fair agreement with the results of Klose and Baerns,⁸ who found small concentrations of ethane, traces of higher paraffins and a negligible formation of carbon dioxide. Also relevant here is the finding of Baetzold³¹ that Co and Fe form long chains, whereas Ni is a methanation catalyst. The material used in subsequent kinetic runs was molecular sieve 5A, and the catalytic fractional conversion x of reactants to products was calculated from the methane and the carbon monoxide sample peaks detected after each flow reversal. The areas f under the sample peaks were used, instead of their heights, because, owing to the different retention times of CO and CH_4 on column *l*, the two peaks had different widths at their half-heights. Therefore, the conversion x was calculated by the relation

$$x = 0.76 f_{\rm CH_4} / (0.76 f_{\rm CH_4} + f_{\rm CO}) \tag{1}$$

0.76 being the response of the thermal conductivity detector for CH_4 relative to that for CO, under the experimental conditions used.

As mentioned in the Introduction, x can be approximately considered as a differential conversion, but we preferred to treat it accurately as an integral conversion. The equation relating the rate constant k to the fractional conversion of carbon monoxide to products is derived as follows. The specific reaction rate $r_{\rm m}/{\rm mol} \ {\rm kg^{-1}}_{\rm catalvst} \ {\rm s^{-1}}$ is

$$r_{\rm m} = \frac{\mathrm{d}x}{\mathrm{d}\tau_{\rm m}} = \frac{\mathrm{d}x}{\mathrm{d}(1/v_{\rm m})} = \frac{\mathrm{d}x}{\mathrm{d}(W/v)} \tag{2}$$

where $\tau_{\rm m}$ is the space time of the reactor, $v_{\rm m}$ the reactor's space velocity (mol kg⁻¹_{catalyst} s⁻¹), v the feed rate (mol s⁻¹), and W the catalyst's weight (kg).

Integration over the entire catalyst bed, taking into account the fact that during a flow reversal cycle the feed rate v remains practically constant, gives

$$\int_{0}^{x} \frac{\mathrm{d}x}{r_{\mathrm{m}}} = \int_{0}^{W} \mathrm{d}\left(\frac{W}{v}\right) = \frac{W}{v} = \frac{W}{\dot{V}c_{0}} \tag{3}$$

where \dot{V} is the volume flow rate (in m³ s⁻¹) of the reacting mixture (carrier gas H₂ and CO) and c_0 the extra concentration (in mol m⁻³) of carbon monoxide in the mixture created by the flow reversal at x = l', *i.e.* at the entry of the catalytic bed.

Since hydrogen is used in great excess as a carrier gas, only the order of the reaction n with respect to carbon monoxide is considered, so that the rate equation is of the form

$$r_{\rm m} = kc^n = kc_0^n (1-x)^n \tag{4}$$

where k is the rate constant $(m^{3n} \text{ mol}^{1-n} \text{ kg}^{-1}_{\text{catalyst}} \text{ s}^{-1})$. Substituting the r.h.s. of eqn (4) for r_m in eqn (3) and integrating one obtains, after rearrangement,

$$k = \frac{\dot{V}c_0^{1-n}}{W(1-n)} [1 - (1-x)^{1-n}].$$
(5)

This equation holds for all values of n other than 1. In the latter case the integration of eqn (3) gives¹⁹

$$k = \frac{\dot{V}}{W} \ln \frac{1}{(1-x)}.$$
(6)

If the reaction were first-order, the calculation of k by means of eqn (6) would require only the fractional conversion x, the weight of the catalyst W and the hydrogen flow rate \dot{V} , corrected at the catalytic bed temperature and pressure with the help of the relation

$$\dot{V} = \dot{V}_{\text{meas}} \frac{T_1}{T_2} \frac{p_2}{p_1}$$
(7)

where V_{meas} is the measured flow rate and the subscripts 1 and 2 refer to the bed and the environment, respectively. However, for orders $n \neq 1$ eqn (5) must be used and this requires the additional quantity c_0 , *i.e.* the concentration of carbon monoxide at x = l'(cf. fig. 1). This is not the total concentration of CO at this point, but only the extra concentration above the continuous baseline, created by the flow reversal and giving rise to the two sample peaks of fig. 2, *i.e.* to the measured conversion. According to the theory of r.f.g.c,³⁰ the flow reversal for time t' creates a square concentration function at x = l' of width t' and height c_0 , twice that corresponding to the existing baseline [cf. fig. 3A in ref. (30)]. The area under this square sample peak is $c_0 t' V$ mol, and this should be proportional to the total area f_{tot} under the sample peaks of fig. 2, as these are recorded by the detector system:

$$f_{\rm tot} = f_{\rm CO} + 0.76 f_{\rm CH_4}.$$
 (8)

Since, however, f_{tot} is measured in mV s or in cm s (as in the present case), the sensitivity S_c in cm m³ mol⁻¹ of the thermal-conductivity detector is required to transform f_{tot} in mol. Thus

$$c_0 t' \dot{V} = \frac{f_{\text{tot}}}{S_c} \dot{V} \text{ mol}$$
(9)

and, if from this relation $f_{tot}/S_c t'$ is substituted for c_0 in eqn (5), we obtain

$$k = \frac{V f_{\text{tot}}^{1-n}}{(1-n) W(S_{\text{c}} t')^{1-n}} [1 - (1-x)^{1-n}].$$
(10)

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Table 1. Fractional conversions x of CO to CH_4 , mean rate constants k, and orders n with respect to CO, for the methanation reaction over 50° (w/w) Ni /AIO of various features

Table 2. Fractional conversions x of CO to CH_4 , mean rate constants k, and orders n with respect to CO, for the methanation

		$k/10^{-3}$ m ³ⁿ mol ¹⁻ⁿ				$k/10^3 \text{ m}^{3n} \text{ mol}^{1-n}$	
T/K	$10^{2}x$	kg ⁻¹ catalyst s ⁻¹	и	T/K	$10^{2}x$	kg ⁻¹ catalyst S ⁻¹	u
433	1.8-5.8	6.1 ± 0.4	-0.50	473	4.3-22.5	14.6 ± 0.8	-0.20
439	4.7 - 30.0	10.3 ± 0.3	0.50	478	5.5-23.8	16 ± 1	-0.20
451	6.8-73.9	27.3 ± 0.9	-0.45	483	3.1-32.2	21 ± 2	-0.20
457	3.5-46.3	29 ± 2	-0.50	488	4.7-43.3	26 ± 1	-0.20
460	6.3-73.2	50 ± 2	-0.50	493	3.8-25.4	38 ± 8	-0.20
469	9.3-88.7	83 ± 10	-0.55	498	5.1-45.7	47 ± 4	-0.24
469	6.5-87.4	91 ± 5	-0.45	503	8.4-48.4	48±3	-0.16
470	13.7-88.0	80+9	-0.50	508	8.7 - 67.0	46土3	0.0
476	4.2-66.4	104 ± 5	-0.50	508	9.7-44.8	47±3	0.0
477	2.7-18.6	118 ± 5	-0.50	509	11.3-61.9	52 ± 1	0.0
479	15.7-85.9	151 ± 19	-0.50	513	10.0-39.3	53 ± 3	0.0
483	3.0-64.9	137 ± 19	-0.50	519	13.3-76.5	52 ± 3	0.2
488	8.0-51.2	83 ± 3	0.00	523	15.9-65.3	53 ± 3	0.2
489	30.7-93.1	103 ± 33	0.00	528	22.1-78.5	64 ± 3	0.2
493	13.4-56.3	58 ± 9	0.52	533	27.5-71.5	67 ± 3	0.2
498	17.2-44.6	73 ± 10	0.40	538	32.2-73.0	81 ± 3	0.2
499	52.2-95.3	66 ± 22	0.60	543	33.6-73.9	87 ± 6	0.2
500	63.0-91.0	86 ± 11	0.60	548	34.8-73.3	102 ± 12	0.2
503	22.5-59.9	77 ± 9	0.52	553	34.4-76.9	116 ± 12	0.2
508	21.7-70.7	80 ± 12	0.50	558	45.4-79.6	131 ± 9	0.2
513	21.1-67.1	94 ± 19	0.50	563	41.7-85.7	151 ± 17	0.2
518	36.9-53.1	101 + 7	0.50	568	44.1-88.9	163 ± 15	0.2
523	37.0-79.0	127 ± 21	0.50	573	59.4-95.9	197 ± 12	0.2
^a The erro fidence lim	rs given with tl its.	ne mean k values represe	ent 95% con-	^a The erro fidence lin	rs given with th its.	le mean k values repr	esent 95% con-



Fig. 4. Arrhenius plots for the methanation of carbon monoxide over Ni/Al₂O₃ catalysts. The four plots correspond to different reaction orders *n* with respect to CO. The n = -0.5 plot includes two -0.45 and one -0.55 points; the n = 0.5 plot includes two points with order 0.60 and one with 0.40; the n = -0.2 plot includes one point with order -0.24 and one with -0.16. The various symbols refer to the coordinate and the abscissa scales on which they are written: •, n = -0.5; \blacksquare , n = -0.2; \Box , n = 0.2; \bigcirc , n = 0.5.

The sensitivity S_c (= 19.8 cm m³ mol⁻¹) of the thermal conductivity detector was easily found by injecting a known volume of CO into the column L and allowing it to diffuse into column l in the absence of catalyst. By making flow reversals and measuring the height h(cm) of the sample peaks as a function of time, the diffusion coefficient of CO into H₂ was calculated as described elsewhere.^{21, 30} From the value of the intercept of the relevant plot the factor S_c was calculated.

Calculation of Rate Constants and Orders of the Reaction

In each kinetic run at a given temperature, the variables of eqn (10) are f_{tot} and x. These are loaded into the computer, together with the constants V, W and t', and the values of k are calculated by means of a suitable program, for various values of n. Of these, we chose that n value which gave the smallest variation in the k values. As a criterion for this variation were taken the 95% confidence limits of the mean k values.

Tables 1 and 2 compile the range of conversions, the mean k value and the order n of the reaction at various temperatures for two catalysts of different Ni content.

Activation Parameters of the Reaction

These have been determined from conventional Arrhenius plots, using in each plot rate constants pertaining to the same reaction order. Thus four plots are given in fig. 4,

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catalyst	n	$E_{\rm a}/{\rm kJ}~{ m mol}^{-1}$	$\frac{\ln (A/m^{3n} \text{ mol}^{1-n})}{\text{kg}^{-1}_{\text{catalyst}} \text{ s}^{-1}}$
5% (w/w) Ni/Al ₂ O ₃	-0.5	112±5	26 ± 1
	+0.5	47±7	9 ± 2
2% (w/w) Ni/Al ₂ O ₃	-0.2	89 <u>+</u> 8	18 ± 2
	+0.2	62 ± 2	11.2 ± 0.4

Table 3. Activation energies E_a and frequency factors A for the methanation of carbon monoxide over two Ni/Al₂O₃ catalysts^a

^a The \pm values are standard errors.

corresponding to orders -0.5, -0.2, 0.2 and 0.5. These Arrhenius plots are presented in graphical form to show that activation energies and frequency factors remain constant within the range of temperatures of the same reaction order. Table 3 collects the activation parameters found.

Discussion and Conclusions

Some of the findings in the present work agree with certain recent results of other workers. Some are in contrast with them, and some others are new and have not been previously reported. Both the new results and those in disagreement with the previously published ones refer to the quantitative behaviour of the reaction, rather than qualitative trends. Let us discuss some major points.

The order of the reaction n with respect to carbon monoxide has been reported many times and has recently been shown^{7, 8, 10} to change with the partial pressure of CO and with the temperature. In the present work the order n changes with temperature, but not with the concentration c_0 of CO in the gas mixture at the same temperature. In each kinetic run c_0 changes about ten-fold, corresponding to the conversion ranges of tables 1 and 2, but this leads to a single value for the rate constant k and a single value for the order n. The simplest explanation of this lies probably in what has been pointed out under point (5) in the Introduction. As regards the change in n with temperature, the most noticeable finding is its discontinuous change, whereas in the literature^{7, 10} a continuous change is reported in about the same temperature ranges. Moreover, the usual finding was that n is negative, increases with temperature and tends to zero at high temperature, whereas here positive values of n are found at high temperatures (cf. tables 1 and 2). Our results are consistent with the following rather conventional reaction mechanism, assuming a non-homogeneous catalytic surface with independent adsorption sites \bullet and * for H and CO, C, O, CH_x species, respectively:

$$\operatorname{CO}(g) + * \rightleftharpoons^{K_1} \operatorname{CO} *$$
 (11)

$$CO* + * \rightleftharpoons C* + O* \tag{12}$$

$$H_{2}(g) + 2 \bullet \rightleftharpoons^{K_{3}} 2H \bullet$$
 (13)

$$C* + H_{\bullet} \rightleftharpoons^{K_4} HC* + \bullet$$
 (14)

$$HC* + H_{\bullet} \xrightarrow{k_1} H_2C* + \bullet$$
 (15)

$$H_2C* + H_{\bullet} \rightleftharpoons^{K_5} H_3C* + \bullet$$
 (16)

$$H_{3}C*+H \bullet \xrightarrow{k_{2}} CH_{4}(g)+*+ \bullet$$
 (17)

$$O^* + 2H_{\bullet} \xrightarrow{k_3} H_2O(g) + * + 2\bullet.$$
(18)

Two of the carbon hydrogenation steps, eqn (14) and (16), are chosen as fast equilibria, whereas steps (15) and (17) are assumed to be slow. This choice has been based on the calculations of Baetzold,³¹ who found that the activation energy for steps (14) and (16) is zero, while that of steps (15) and (17) is 63 and 88 kJ mol⁻¹, respectively.

Steady-state kinetics based on the above mechanism lead to the following equation for the rate of formation of CH_4 , as explained in the Appendix:

$$r_{\rm CH_4} = \frac{k' c_{\rm H_2}}{(1 + K_3^{\frac{1}{2}} c_{\rm H_2}^{\frac{1}{2}})^{\frac{3}{2}}} \frac{c_{\rm CO}^{\frac{3}{2}}}{1 + K' c_{\rm CO}^{\frac{1}{2}} + K_1 c_{\rm CO}}$$
(19)

where c_{H_2} and c_{CO} are gas-phase concentrations (partial pressures p_{H_2} and p_{CO} could also be used) and k' and K' are given by the relations:

$$k' = (k_1 k_3 K_1 K_2 K_4)^{\frac{1}{2}} K_3$$
(20)

$$K' = \left(\frac{k_3 K_1 K_2}{k_1 K_4}\right)^{\frac{1}{2}} \left(\frac{1}{1 + K_3^{\frac{1}{2}} c_{\mathbf{H}_2}^{\frac{1}{2}}}\right)^{\frac{1}{2}}.$$
(21)

Since H_2 is used as carrier gas in all experiments and the gas concentration of CO in it is relatively low, the first fraction on the r.h.s. of eqn (19) can be considered as constant k'' at constant temperature, and by further division of both terms of the remaining fraction by $c_{CO}^{\frac{1}{2}}$ eqn (19) becomes

$$r_{\rm CH_4} = \frac{k''}{c_{\rm CO}^{-\frac{1}{2}} + K' + K_1 c_{\rm CO}^{\frac{1}{2}}}.$$
 (22)

The reaction order as a function of temperature, starting from a negative value of n at low temperatures, passing through zero and ending with the respective positive value at high temperatures, as shown in table 1 and 2, can now easily be explained with the help of eqn (22). According to this rate equation, the apparent experimental order of the reaction depends on the relative magnitudes of the three terms in the denominator. At low temperatures the equilibrium constant K_1 for the CO adsorption may become sufficiently large to make the term $K_1 c_{CO}^{\frac{1}{2}}$ predominate over the other two terms, $c_{CO}^{-\frac{1}{2}}$ and the composite constant K', which can be neglected. This limiting case then leads to an order $n = -\frac{1}{2}$ with respect to c_{CO} . As eqn (21) shows, K' consists of two factors, namely a ratio of rate and equilibrium constants which may decrease as the temperature rises, and a hydrogen adsorption factor $1/(1+K_3^{\frac{1}{3}}c_{H_2}^{\frac{1}{2}})^{\frac{1}{2}}$ which increases with increasing temperature. It is thus possible that, as the temperature rises, K' increases, passing through a maximum and then decreases. At the temperature of the maximum K' value, this would predominate over the other two terms in the denominator of eqn (22), giving zero-order kinetics. Finally, at high enough temperatures both K' and $K_1 c_{CO}^2$ may become negligible compared with $c_{CO}^{-\frac{1}{2}}$, thus leading to an order $n = \frac{1}{2}$. The discussion above explains the reaction orders of table 1, and also the discontinuity in the variation of order with temperature around the value n = 0, because this value corresponds to the maximum value of K'.

The results of table 2 can be explained in an analogous manner by a varying contribution of the three terms to the dependence of the denominator of eqn (22) on $c_{\rm CO}$ as the temperature rises, although the orders -0.2 and 0.2 do not correspond to

limiting cases as before, but to intermediate ones. The discontinuity around n = 0 now occurs in a different temperature range, owing to the different adsorptive and catalytic properties of the 2% Ni/Al₂O₃ catalyst from those of 5% Ni/Al₂O₃.

Since the apparent rate constant is composed of different constants in each reaction order, as eqn (22) shows, activation energies and frequency factors should remain constant within the temperature range where the reaction order is kept constant, and should change when the order changes. This is in accord with the results of table 3. Thus, the finding of other workers^{2, 7, 11} that activation energy decreases with increasing temperature is confirmed here, but again with the difference that distinct discontinuities in E_a with T are observed in a narrow T range where n = 0.

The values of activation energy found in the present work $(47-112 \text{ kJ mol}^{-1})$ cover a range similar to that reported by Vannice¹⁰ for different supported nickel catalysts (70–130 kJ mol⁻¹). Sughrue and Bartholomew¹¹ found a decrease in activation energy from 130 to 70 kJ mol⁻¹ with a temperature increase from 473 to 623 K, and accounted for this effect by assuming a change in the rate-determining step or the reaction mechanism. Klose and Baerns⁸ on the other hand explain the change in activation energy with temperature by adopting limiting cases of a general rate equation similar to eqn (19), but applied to a homogeneous surface. As mentioned earlier, Baetzold³¹ calculated an activation energy of $63 \text{ kJ} \text{ mol}^{-1}$ for step (15) in the reaction mechanism and 88 kJ mol⁻¹ for step (17); from these values, together with the respective pre-exponential values and the surface concentrations of CH and CH_3 species, he concluded that the rate-determining step is reaction (17), *i.e.* the hydrogenation of methyl groups. Klose and Baerns⁸ take the reaction $C^* + 2H^* \rightarrow H_2C^* + 2^*$ or step (15) as the rate-determining step. In our mechanism [reactions (11)-(18)] either one of the steps (15) or (17) can be rate-determining, because eqn (19) has been derived assuming steady-state kinetics, as was done in almost all similar studies. Since steps (15) and (17) are consecutive reactions with an intermediate equilibrium, one cannot distinguish by the steady-state approximation which is the slow step. One conclusion is certain, however, that one of the two above steps is much faster than the other. This is because the reversed-flow technique applied here can monitor the reaction rate for a long time period, starting from the time of injection of the reactant CO, and would detect a transient reaction period corresponding to two slow steps in the reaction mechanism.

Another point worth citing is that reported by Dalmon and Martin,⁷ who used the relation

$$E_{\rm a} = E_0 - n_{\rm CO} Q_{\rm CO} \tag{23}$$

with $Q_{\rm CO}$ denoting the isosteric heat of adsorption of CO, to calculate E_0 by extrapolating to $n_{\rm CO} = 0$ the linear plot of $E_{\rm a}$ vs. $n_{\rm CO}$. They found $E_{\rm o} = 71.1$ kJ mol⁻¹, claiming that this represents the true activation energy of the reaction, and because this value is the same as that for surface carbon hydrogenation, they conclude that the rate-determining step is that reaction. Coming now to our results, if one plots the data of table 3 as E_{a} vs. n, a straight line with a correlation coefficient 0.997 and a negative slope is obtained, indicating that eqn (23) formally holds true. Although the estimated value of E_{a} for n = 0is 77.5 kJ mol⁻¹, in fair agreement with that found by Dalmon and Martin, it does not seem to us that eqn (23) offers a plausible explanation for the variation of $E_{\rm a}$ with temperature. This is because, Q_{CO} , as calculated from the slope of the plot mentioned above, equals $65 \pm 4 \text{ kJ mol}^{-1}$, *i.e.* the adsorption is endothermic, a rather improbable fact. Thus the identification of 71.1 kJ mol⁻¹ with the true activation energy of surface carbon hydrogenation may be fortuitous.

As a general conclusion we can say that the new technique of r.f.g.c. used here reveals characteristics of the reaction not observed with other methods. This is due most probably to what has been pointed out in the Introduction, namely that it is simultaneously a pulse and a continuous feed method, extracting all the information expected from a pulse technique under steady-state conditions.

(A 6)

Appendix

Eqn (19) is derived as follows using the mechanism described by eqn (11)–(18). The equilibrium constants of steps (11), (12), (13), (14) and (16) are given by eqn (A 1), (A 2), (A 3), (A 4) and (A 5), respectively:

$$K_1 = \frac{\theta_{\rm CO}}{c_{\rm CO}\theta *} \tag{A 1}$$

$$K_2 = \frac{\theta_{\rm C} \,\theta_{\rm O}}{\theta_{\rm CO} \,\theta_*} \tag{A 2}$$

$$K_3 = \frac{\theta_{\rm H}^2}{c_{\rm H_2} \theta_{\bullet}^2} \tag{A 3}$$

$$K_4 = \frac{\theta_{\rm HC} \,\theta_{\bullet}}{\theta_{\rm C} \,\theta_{\rm H}} \tag{A 4}$$

$$K_{5} = \frac{\theta_{\mathrm{H}_{3}\mathrm{C}}\,\theta_{\Phi}}{\theta_{\mathrm{H}_{2}\mathrm{C}}\,\theta_{\mathrm{H}}} \tag{A 5}$$

where
$$\theta_{\mathbf{x}}$$
 is the surface fraction of species X.

The reaction rates according to steps (15), (17) and (18) are:

$$-r_{\rm CO} = k_1 \theta_{\rm HC} \theta_{\rm H} \tag{A 6}$$

$$r_{\rm CH_4} = k_2 \theta_{\rm H_3C} \theta_{\rm H} \tag{A7}$$

$$r_{\rm H_{2}O} = k_3 \theta_O \theta_{\rm H}^2. \tag{A 8}$$

The overall mass balance at steady state, neglecting the negligible amounts of products other than methane, requires that

$$-r_{\rm CO} = r_{\rm CH_4} = r_{\rm H_2O}.$$
 (A 9)

The surface balance for sites • is

$$\theta_{\bullet} + \theta_{\rm H} = 1 \tag{A 10}$$

and that for sites*

$$\theta_* + \theta_{\rm C} + \theta_{\rm CO} = 1 \tag{A 11}$$

neglecting the coverage by oxygen and CH_x species.

From the rate eqn $(A \ 6)$ - $(A \ 8)$ and the mass balance eqn $(A \ 9)$ the following relations are easily derived:

$$\theta_{\rm H_3C} = k_1 \theta_{\rm HC} / k_2, \quad \theta_{\rm O} = k_1 \theta_{\rm HC} / k_3 \theta_{\rm H}. \tag{A 12}$$

Multiplying eqn (A 1) by eqn (A 2), dividing the second of eqn (A 12) by (A 4) and further multiplying the two results, one obtains θ_c as a function of c_{co} :

$$\theta_{\rm C} = K'' c_{\rm CO}^{\frac{1}{2}} \theta_* \theta_{\bullet}^{\frac{1}{2}} \tag{A 13}$$

where

$$K'' = (k_3 K_1 K_2 / k_1 K_4)^{\frac{1}{2}}.$$
 (A 14)

The analogous relation of θ_{H} and c_{H_2} is obtained from eqn (A 3):

$$\theta_{\rm H} = K_3^{\frac{1}{2}} c_{\rm H_2}^{\frac{1}{2}} \theta_{ullet} \tag{A 15}$$

whereas θ_{CO} comes from eqn (A 1):

$$\theta_{\rm CO} = K_1 c_{\rm CO} \theta_{\ast}. \tag{A 16}$$

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Now, if $\theta_{\rm C}$, $\theta_{\rm H}$ and $\theta_{\rm CO}$ from eqn (A 13), (A 15) and (A 16), respectively, are substituted into the surface balances (A 10) and (A 11), the expressions giving θ_{\bullet} and θ_* as functions of $c_{\rm H_2}$ and $c_{\rm CO}$ are obtained:

$$\theta_{\bullet} = \frac{1}{1 + K_3^{\frac{1}{2}} c_{H_2}^{\frac{1}{2}}} \tag{A 17}$$

$$\theta_* = \frac{1}{1 + K' c_{\rm CO}^{\frac{1}{2}} + K_1 c_{\rm CO}} \tag{A 18}$$

where K' is given by eqn (21).

Finally, the rate equation of methane formation, *i.e.* eqn (19), results from a combination of eqn (A 6), (A 9) and (A 4) with eqn (A 13), (A 15), (A 17) and (A 18). The same result is obtained if one uses eqn (A 7) and the first part of eqn (A 12) instead of eqn (A 6), or eqn (A 8) and the second part of eqn (A 12).

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