JOURNAL OF CATALYSIS 62, 349–356 (1980)

A Kinetic Study of the Methanation of CO_2 over Nickel–Alumina

RUSSELL MAATMAN AND SJOUKE HIEMSTRA

Department of Chemistry, Dordt College, Sioux Center, Iowa 51250

Received July 16, 1979; revised October 18, 1979

The methanation rate of CO_2 over nickel–alumina was studied under differential reactor conditions between 210 and 315°C at a total pressure of 1 atm, with He used as diluent in some experiments. The rate was one-half order in both reactants. When the H_2/CO_2 ratio was varied, the rate exhibited a maximum in the H_2-rich region. Based on these observations, a reaction mechanism in which there are 2 slow steps, either of which can be rate determining, is suggested. The site-density criterion for allowable rate-determining steps was also used. This criterion was applied to 15 steps and only 7 meet the criterion. The 2 steps postulated to be slow are among the 7. The activation energies for the reactant mixtures which were 30, 50, and 70% in H_2 (using no diluent) were found from Arrhenius plots to be 21.4, 19.1, and 21.9 kcal/mole, respectively.

INTRODUCTION

In the catalyzed hydrogenation of CO_2 either CH_4 or CO can form, according to the following reactions:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O,$$

$$CO_2 + H_2 \rightarrow CO + H_2O.$$

The methanation reaction, the Sabatier reaction, occurs in a lower temperature range than the second reaction, the water gas shift reaction. The most frequently used catalysts are transition metals, such as Ni, Fe, Co, and Ru, either pure or supported.

We have studied the kinetics of the methanation reaction catalyzed by nickel–alumina for the purpose of elucidating the reaction mechanism. Even though many kinetics studies of this reaction are in the literature, there were two reasons for carrying out this work: (i) Most of the studies reported have been carried out using an excess of H_2. We have, however, also studied the CO_2-rich region, enabling us to determine the dependence of the rate on the concentration of H_2 as well as CO_2; only a few previous workers have looked at this latter question. In addition, we have made tentative conclusions about the mechanism from the observation that the maximum rate apparently occurs when there is more H_2 than CO_2 in the system. (ii) Another reason for studying this system was to obtain data which would enable us to use the site-density criterion in the elucidation of the mechanism. This criterion, used by various workers and described in detail in earlier work (*1*), enables one to eliminate postulated rate-determining steps that require a physically impossible number of active sites.

To minimize back reaction and other complications associated with high conversion, we carried out the reaction under differential reactor conditions.

EXPERIMENTAL

Materials

The catalyst was Houdry $NiO–Al_2O_3$, 42% NiO, with a surface area of 180 m^2/g. Just prior to use the catalyst was reduced in the reactor with H_2 at 450°C for 1 hr. Nitrogen was used to flush the reactor. All the gases used—H_2, CO_2, He, and N_2—passed through a Drierite column before entering the reactor. In addition, O_2 was previously removed from H_2 by a catalytic converter and from N_2 by a bed of hot, reduced copper. No product of the CO_2–H_2 reaction could be detected in any of the gases used.

0021-9517/80/040349-08$02.00/0

Procedure

Carbon dioxide and H_2 flowed into a conventional differential reactor, which consisted of a 25-cm heated horizontal Pyrex tube of 24 mm i.d., after being preheated to the catalyst temperature. They reacted over 0.0500-g 100 to 200-mesh reduced catalyst on a glass tray 5 cm long situated in the middle of the reactor. Helium was used whenever a diluent was needed; nitrogen interfered in the gas chromatographic analysis. The total pressure was always 1 atm and the total flow rate was always about 100 ml min^{-1}. Conversion was usually less than 5% of the limiting reactant. By means of a gas sampling valve, effluent samples were taken at 15-min intervals, starting 30 min after the beginning of the run, and analyzed using a 12-ft Porapak Q column at 26°C. The rate for a run was taken to be the average of the four samples taken between 30 and 75 min after the beginning of the run. Catalyst decay was not observed during that period. It was in some cases possible—as proven by comparison with fresh-catalyst results—to use the same catalyst for the following run, usually after rereduction. Otherwise, fresh catalyst was used.

Mass and Heat Transfer

To determine whether or not our measured rates were limited by mass transfer in the pores, we applied the criterion of Weisz and Prater, who showed that a catalytic reaction is not diffusion limited if

$$(R_p{}^2/D_e)(1/c)(dn_v/dt) < 1,$$

where R_p is the particle radius; D_e the gas diffusion constant applicable to the oxide pores, 1–3% of D, the ordinary diffusion constant; c the concentration of that gas; and (dn_v/dt) the observed rate per unit volume of catalyst (*2*). Thus, if the criterion is met when we take the largest values of the quantities in the numerator and the smallest values of the quantities in the denominator of the left side of the inequality, then the criterion is met for all conditions used. Our highest rate was 3×10^{-5} mole CH_4 cm^{-3} s^{-1} (assuming the catalyst particle density to be about 1 g cm^{-3}), measured at 315°C with $p_{CO_2} = 0.3$ atm. For these conditions, $c_{CO_2} = 6.2 \times 10^{-6}$ mole cm^{-3}; also, D_{CO_2}, taken to be about 0.32 cm^2 s^{-1} (*2*), is the smallest of the diffusion constants of the molecules of the reaction. To minimize the denominator, we let $D_e = 0.01\,D$. For our largest particles (100 mesh), $R_p \approx 0.013$ cm. Then the left side of the inequality is only ~0.24 in this extreme case. We conclude that there was no diffusion limitation in the pores.

Nor was heat transfer a problem. To calculate the temperature differential within the pores we used the method developed by Prater, who showed that

$$T - T_s = -(\Delta H D_e/K)(c_s - c),$$

where T is the temperature in the pores where the concentration of reactant is c, T_s and c_s are the corresponding values at the surface, ΔH is the heat of reaction, and K is the thermal conductivity of the catalyst (*3*). Our "worst case" is for the 315°C, 30% CO_2–70% H_2 case described above. Thus, the conversion here was about 15%, far above the most of the conversions (usually below 5%), corresponding to (if a linear approximation can be made) 3% conversion per cm for the 5-cm catalyst bed. Let us consider rows of particles lying perpendicular to the direction of gas flow. Assuming the bed is loosely packed and all particles are 100 mesh, the size for which there would most likely be a problem, each row occupies about 0.05-cm bed length. Therefore, the conversion per row is ~0.15% (i.e., 0.05 × 3%). It follows that the "average" reactant concentration difference between the surface and the center of the particle is ~0.15%. If we assume that there is a linear decrease in concentration between the surface and the center, the reactant concentration is 0.3% (i.e., 2 × 0.15%) less in the center than at the surface of the particle. Therefore, in our "worst case,"

$(c/c_s) = 0.997$. ΔH is -38 kcal $mole^{-1}$. The D values for CO_2 and H_2 at 315°C are 0.32 and 1.81 $cm^2\ s^{-1}$, respectively (2), and we take a weighted value of 1.36 $cm^2\ s^{-1}$ for a 70–30% mixture. Then, taking the largest estimated value of D_e, i.e., 3% of D, we have $D_e = 0.041\ cm^2\ s^{-1}$. We do not have a K value for our catalyst, and so we use the value 5.3×10^{-4} cal $s^{-1}\ cm^{-1}\ deg^{-1}$, the value Prater used for a similar material, Pt/Al_2O_3. As given above, $c = 6.2 \times 10^{-6}$ mole cm^{-3} at these conditions. Then, for this "worst case," $T - T_s$ is 0.05°C. Our other runs were such that $(T - T_s)$ was much smaller, and so it seems that the intraparticle temperature differential was not large enough to cause difficulty.

In our system heat transfer away from the particles was also satisfactory. At our highest rate, 3.5×10^{-5} mole $CH_4\ g^{-1}\ s^{-1}$ at 315°C, the heat produced by 0.0500-g catalyst is 6.5×10^{-2} cal s^{-1} for a reaction in which $\Delta H = -38$ kcal $mole^{-1}$. But that part of the reactor immediately adjacent to the 5-cm catalyst tray produced ~25 cal s^{-1} at 315°C. Thus, the reaction produced only 0.3% as much heat as the furnace. These calculations convince us that bulk heat transfer was good enough to insure a reasonably uniform particle-to-particle temperature.

RESULTS AND DISCUSSION

Reaction Mechanism

We carried out all runs between 210 and 315°C and therefore only the low-temperature reaction, the methanation reaction, occurred. Our results are summarized in Figs. 1–6. Figure 1 shows the reaction rate as a function of p_{H_2} and $p_{H_2}^{1/2}$, with $p_{CO_2} = 0.3$ atm; in Fig. 2 the rate is given as a function of p_{CO_2} and $p_{CO_2}^{1/2}$, with $p_{H_2} = 0.3$ atm. In Fig. 3, $p_{H_2} + p_{CO_2} = 1$ atm; the rate is given as a function of p_{CO_2}. Least-mean-squares Arrhenius plots of the rates using 30–70, 50–50, and 70–30% CO_2–H_2 mixtures, at a total pressure of 1 atm but without a diluent, are shown in Figs. 4–6. The activation energies are, respectively, 21.4, 19.1, and 21.9 kcal/mole.

In spite of the rather large deviations (shown by the error bars) of Figs. 1 and 2, it seems that one can conclude that the rate is more nearly linear in $p^{1/2}$ than p in both figures. Thus, our results suggest that the rate is one-half order in both H_2 and CO_2. Also, our results indicate that our conditions were such that for neither Fig. 1 nor Fig. 2 was the partial pressure of either reactant large enough so that the rate depended entirely on the partial pressure of the other reactant. Thus, rate vs $p_{H_2}^{1/2}$ is

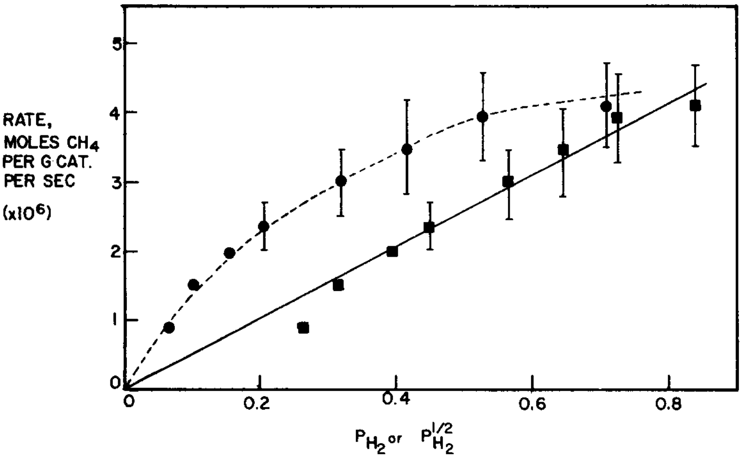

FIG. 1. Rate as a function of p_{H_2} (●) and of $p_{H_2}^{1/2}$ (■). Conditions: $p_{CO_2} = 0.3$ atm; total pressure is 1 atm, with He diluent; $T = 250$°C. Points with average deviation error bars are the averages for three to nine runs.

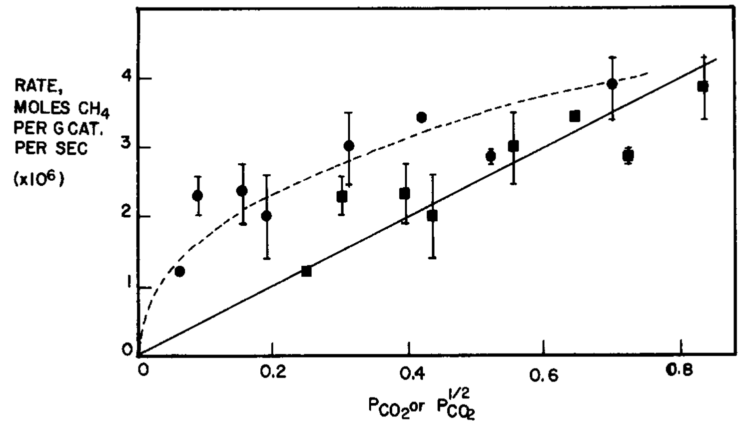

FIG. 2. Rate as a function of p_{CO_2} (●) and of $p_{CO_2}^{1/2}$ (■). Conditions: p_{H_2} = 0.3 atm; total pressure is 1 atm, with He diluent; T = 250°C. Points with averge deviation error bars are the averages for two to eight runs.

linear in Fig. 1 as p_{CO_2} is held constant at 0.3 atm. One point on this curve is for $p_{H_2} = p_{CO_2} = 0.3$ atm, and this point is also on the curve of Fig. 2, a curve which seems to indicate that the rate is linear in $p_{CO_2}^{1/2}$. It would seem that we could not have such results if either of the steps we refer to as rate limiting was much more rapid than the other.

Our conclusion that the reaction is one-half order in each reactant does not depend entirely on our own results. An order of one-half for CO_2 has been reported for nickel and nickel-supported catalysts (*4*, *5*). Under certain conditions, however, Vlasenko and co-workers found that the reaction over a nickel–chromia catalyst is first order in CO_2 (*6*). Dwyer and Somorjai reported turnover numbers for CO_2 sites on an Fe catalyst, thus implying that with their operating conditions the reaction is zero order (*7*). However, such a finding is not unreasonable; their experiments were carried out at a p_{CO_2} value of 4.5 atm, much higher than our maximum of 0.7 atm. Others have implied an order of one-half for H_2. For example, Shultz, Karn, and Anderson reported a rate which was one-half order in total pressure (*8*).

To understand further the relation between the two slow reactions, we now turn to Fig. 3. (Both reactant partial pressures are variables in Fig. 3 and therefore only one point of Fig. 1 and one of Fig. 2 are included in this figure.) The curve of Fig. 3 suggests the possibility that the maximum rate occurs in the H_2-rich region. Since the average deviation, indicated by the error bars, was large here also, we checked our conclusion about the maximum rate using the more reliable constant-pressure plots of Figs. 4–6. The least-mean-squares equations for the three plots of Figs. 4–6, each for 14 or 15 points, are

$$\ln(\text{rate}) = -1.10 \times 10^4(1/T) + 8.80,$$

$$\ln(\text{rate}) = -0.959 \times 10^4(1/T) + 5.88,$$

$$\ln(\text{rate}) = -1.08 \times 10^4(1/T) + 8.07,$$

for 30, 50, and 70% CO_2, respectively. The corresponding 250°C rates are calculated to be 4.9×10^{-6}, 3.9×10^{-6}, and 3.4×10^{-6} mole CH_4/g cat-sec; that is, the rate is greatest in the H_2-rich region.

If it is indeed true that the rate is greater when $p_{H_2} > p_{CO_2}$, then the slow dissociative adsorption of H_2 is more important in determining the overall rate than the slow dissociative adsorption of CO_2. The H_2 reaction could be more important because this reaction is somewhat slower (although not much slower, as noted above) than the CO_2 reaction; or, it could be more important because the H_2 reaction must occur more

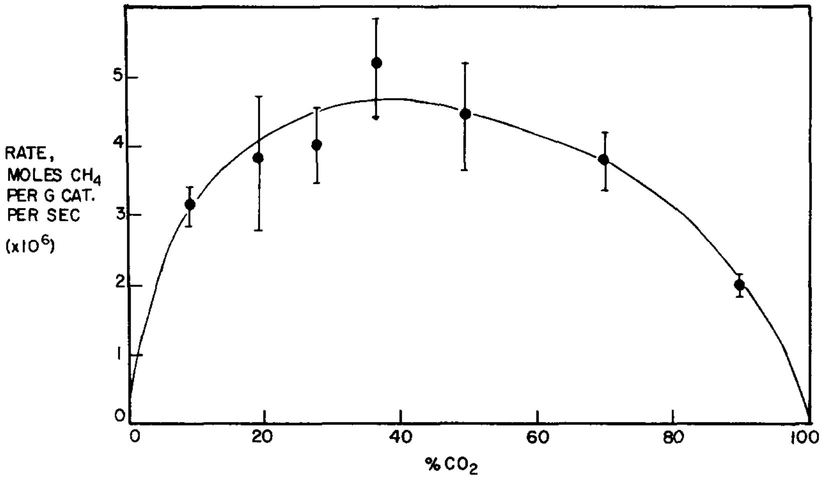

FIG. 3. Rate as a function of percentage CO_2 in CO_2–H_2 mixtures; no diluent; total pressure 1 atm; T = 250°C. Each point is the average for 2–12 runs; the error bars indicate the average deviations.

than once for each time the CO_2 reaction occurs. The first possibility—that the H_2 reaction is slower than the CO_2 reaction—seems unlikely from the point of view of ordinary chemical considerations. Rather, the second possibility, in which it is postulated that the hydrogen reaction must occur more often than the CO_2 reaction (that is, the H_2 reaction has the greater stoichiometric number), seems to be more likely.

We therefore propose the following mechanism, using some of the suggestions of Dwyer and Somorjai for CO_2 hydrogenation over Fe (7), where A′ and A are surface sites:

$$H_2 + 2A' \rightarrow 2HA' \quad (1)$$

$$CO_2 + 2A \rightarrow OCA + OA \quad (2)$$

$$2HA' + OCA \rightarrow H_2O + 2A' + CA \quad (3)$$

$$2HA' + OA \rightarrow H_2O + 2A' + A \quad (4)$$

$$H_2 + CA \rightarrow H_2CA \quad (5)$$

$$H_2 + H_2CA \rightarrow CH_4 + A. \quad (6)$$

We assume that steps (1) and (2) are much slower than steps (3)–(6). We do not make any assumptions about the nature of bonding in any of the intermediates in step (1)–(6). For example, we do not have evidence that adsorbed CO ("OCA") or a carbide ("CA") exists in our system.

If steps (1) and (2) are both slow with respect to steps (3)–(6), then the reaction is one-half order in both reactants, provided that (i) the coverage is relatively low and (ii) slow dissociation follows rapid adsorption. Steps (1)–(6) add up to the stoichiometric methanation reaction, provided that step (1) is multiplied by two: the slow step (1) must occur twice each time slow step (2)

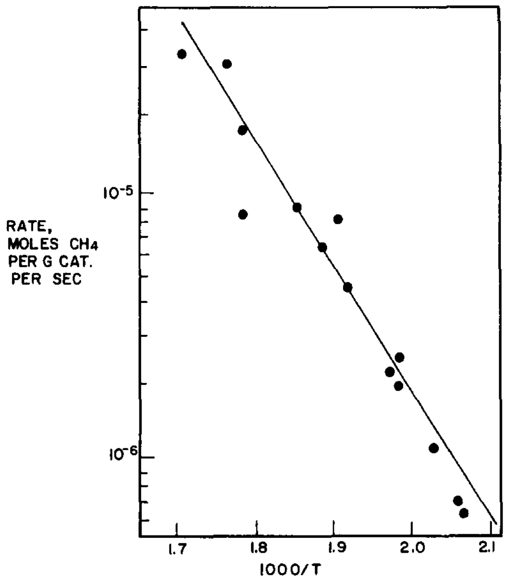

FIG. 4. Arrhenius plot for 30% CO_2–70% H_2 mixture.

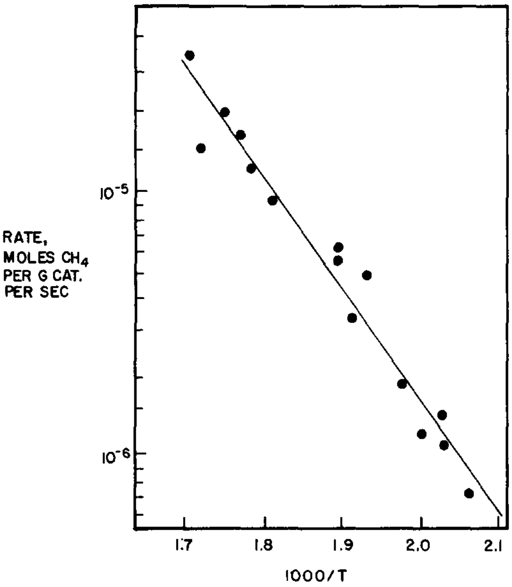

FIG. 5. Arrhenius plot for 50% CO_2–50% H_2 mixture.

occurs. A rate maximum in the H_2-rich region of Fig. 3 is therefore reasonable.

Our conclusions do not enable us to distinguish between steps (3) and (4) and possible alternatives, or steps (5) and (6) and possible alternatives. We can state only that there are surface species of oxygen and carbon which, when hydrogenated, produce water and methane, respectively.

Site-Density Criterion

The site-density criterion can be used to reject some postulated slow steps (*1*). Just as the determination of the order of the reaction enables one to reject certain steps as rate determining, a postulated slow step is possible only if the site density calculated for that step is physically possible. The order and the site-density criteria complement each other.

From transition-state theory for a solid-catalyzed gas reaction,

$$L = C\left(\frac{veE/RT}{kT/h}\right),$$

where L is the site density (or, in some cases, one or two magnitudes less than the site density), v is the reaction rate per unit area of catalyst, E is the activation energy, T is the absolute temperature, R is the gas constant, k and h are the Boltzmann and Planck constants, respectively, and C is a function of the partition function and concentration of reactants and activated complex (*9*). The function C depends upon which step is postulated to be rate determining. When the reaction is gas adsorption not accompanied by dissociation, $C = F/c_g$, where F and c_g are the partition function and concentration per unit volume, respectively, of the reactant gas. (The partition functions of bare and occupied sites as well as the symmetry factors are taken to be close to unity, and they can therefore be neglected.) For adsorption with dissociation, $C = (F/c_g)^{1/2}$; for a surface reaction, $C = 1$. Only the translational and rotational contributions to F need be taken into account; the vibrational contribution is negligible in the catalytic systems normally encountered. We have given elsewhere a fuller description of the calculation methods for many steps, including all those listed in Table 1 (*1*, *10*).

In Table 1 we give the site density for each of 15 postulated slow steps, using our experimental results at three H_2/CO_2 ra-

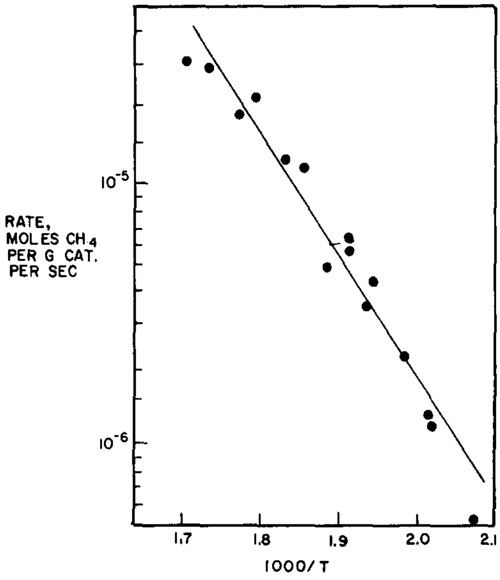

FIG. 6. Arrhenius plot for 70% CO_2–30% H_2 mixture.

TABLE 1

L Values for Various Postulated Rate-Determining Steps[a]

Step No.	Step[b]	L sites/cm^2)[c]		
		30% H_2–70% CO_2	50% H_2–50% CO_2	70% H_2–30% CO_2
1	Dissoc. ads. of H_2	3×10^{11}	2×10^{10}	4×10^{11}
2	Dissoc. ads. of CO_2	2×10^{13}	3×10^{12}	8×10^{13}
3, 4	Surface reaction	9×10^{7}	1×10^{7}	2×10^{8}
5, 6	Nondissoc. ads. of H_2[d]	8×10^{14}	6×10^{13}	8×10^{14}
7	Nondissoc. ads. of CO_2[d]	5×10^{18}	9×10^{17}	3×10^{19}
8	Act. complex: surface-mobile H_2[e]	4×10^{-4}	3×10^{-5}	4×10^{-4}
9	Act. complex: surface-mobile CO_2[e]	8×10^{-4}	1×10^{-4}	4×10^{-3}
10	Surface sparsely covered with reacting H_2 and CO_2	2×10^{25}	3×10^{24}	6×10^{25}
11	Strongly ads. H_2 reacts with ads. CO_2	3×10^{11}	9×10^{10}	4×10^{12}
12	Strongly ads. CO_2 reacts with ads. H_2	6×10^{3}	3×10^{2}	3×10^{3}
13	Ads. H_2 reacts with ads. CO_2; both appreciably ads.	5×10^{18}	9×10^{17}	3×10^{19}
14	Both H_2 and CO_2 surface mobile; react on fixed sites	6×10^{17}	8×10^{16}	2×10^{18}
15	Like 14, but act. complex retains rotation	1×10^{14}	1×10^{13}	3×10^{14}

[a] Total pressure, 1 atm; no diluent. T, 523°K. See Ref. (*1*) for methods of calculation.

[b] See the text for a description of steps (1)–(6).

[c] Moments of inertia used to calculate the rotational partition functions of H_2 and CO_2, respectively: 4.59×10^{-41} g cm^2, 7.187×10^{-39} g cm^2. Reaction rate, molecules per cm^2, and activation energy, kcal/mole, for the 30–70, 50–50, and 70–30% H_2–CO_2 mixtures, respectively: 1.2×10^{12}, 21.4; 1.3×10^{12}, 19.1; 1.6×10^{12}, 21.9.

[d] Any dissociation which occurs is not part of the rate-determining step considered here.

[e] The physically possible value for L for this step is of the order of unity, not 10^5–10^{17} sites/cm^2. See Ref. (*1*).

tios. Each calculation requires that that step be assumed to be the rate-determining step and that the reaction order be whatever is required by that step. Thus, we do not use our earlier conclusions that steps (1) and (2) are slow and that the reaction is one-half order in each reactant. Six of the steps given in the table are steps (1)–(6); the others, not included in our mechanism, are a priori conceivable rate-determining steps. The range of site densities which are in most cases physically allowable is rather large, partly because some catalysts do indeed have very low site densities (*11*), and partly because there are approximations in the method used. For our purpose, the extremes in the allowable site-density range are 10^5 and 10^{17} sites/cm^2; usually a fully covered surface is considered to have the order of 10^{15} sites/cm^2.

We now compare the site-density calculations in Table 1 with the mechanism we have proposed. The results for the three H_2/CO_2 ratios are so close that we can neglect differences between columns 3, 4, and 5.

Step (1): The reaction can be one-half order in hydrogen over a pressure range only if the surface is well below saturation even at the highest pressure used. Therefore, the L value calculated for this step should be appreciably less than the actual site density, and so the value of 10^{10}–10^{11} is quite reasonable.

Step (2): The same conclusion holds for L values of 10^{12}–10^{13} for the CO_2 sites.

Steps (3) and (4): Although these are surface reactions, they are not to be confused with steps (10)–(15) discussed below. The chance that L values as low as 10^7–10^8 are correct is not large. There would certainly be no measurable reaction if such a small number of A and A′ sites were spread uniformly over the surface: species adsorbed on A and A′ would be too far apart to react with each other. This calculation is made assuming no appreciable movement of the activated complex. Any other assumption for the activated complex leads to an even smaller L value (*1, 10*). Also, it is almost certain that steps (3) and (4) would not be one-half order in either reactant over the range of pressure used.

Steps (5) and (6): The L values of 10^{13}–10^{14} are possible, but the steps are ruled out as rate determining because they require that the reaction be first order in hydrogen. The observed order rules out both the first-order adsorption of H_2 and the first-order reaction of H_2 adsorbed on a sparsely covered surface.

Of the steps included in Table 1 but not part of the proposed mechanism, steps (7)–(15), only three need be considered. For step (11) the L values are allowable but it would be required that the reaction be first order in CO_2 and -1 order in H_2. The L values for step (14) could at the outside be allowable; the order for each reactant would probably be less than one but, however, not one-half over the range of pressure used. For Step (15) the L values are reasonable, but the orders would be the same as in Step (14).

In summary, steps (1) and (2) seem to be the most likely rate-determining steps. Since steps (3)–(6) are postulated to be fast steps following the rate-determining steps, they are somewhat speculative. From site-density considerations alone, either step (5) or step (6) could be the rate-determining step; these steps are, however, ruled out on the basis of order. None of the nine steps included in Table 1 but not in the proposed mechanism meets both the order and the site-density criteria.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. Maatman, R. W., *J. Catal.* **43,** 1 (1976).
2. Weisz, P. B., and Prater, C. D., *in* "Advances in Catalysis and Related Subjects" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Eds.), Vol. 6, p. 143. Academic Press, New York, 1954.
3. Prater, C. D., *Chem. Eng. Sci.* **8,** 284 (1958).
4. Muller, J., Pour, V., and Regner, A., *J. Catal.* **11,** 326 (1968); Pour, V., *Collect. Czech. Chem. Commun.* **34,** 45 (1969); Pour, V., *Collect. Czech. Chem. Commun.* **35,** 2203 (1970); Pour, V., *Collect. Czech. Chem. Commun.* **34,** 1217 (1969).
5. Cognion, J. M., and Margeren, J., *Kinet. Katal.* **16,** 1552 (1975).
6. Vlasenko, V. M., Rusov, M. T., and Yuzefovich, G. E., *Kinet. Katal.* **2,** 525 (1961); Golodets, G. I., Vlasenko, V. M., and Yuzefovich, G. E., *Dokl. Akad. Nauk SSSR* **164,** 839 (1965); Vlasenko, V. M., and Yuzefovich, G. E., *Usp. Khim.* **38,** 1622 (1969).
7. Dwyer, D. J., and Somorjai, G. A., *J. Catal.* **52,** 291 (1978).
8. Shultz, J. F., Karn, F. S., and Anderson, R. B., *U.S. Bur. Mines Rep. Invest.* No. 6941 (1967).
9. Glasstone, S., Laidler, K., and Eyring, H., "The Theory of Rate Processes." McGraw–Hill, New York, 1941.
10. Maatman, R. W., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 29. Academic Press, New York, in press.
11. Maatman, R. W., *J. Catal.* **19,** 64 (1970); *Catal. Rev.* **8,** 1 (1973).