Methanation of Carbon Dioxide on Ni(100) and the Effects of Surface Modifiers[†]

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The methanation of CO_2 over Ni(100) was studied with H_2/CO_2 ratios of 4/1 and 96/1 (total pressures of 120 and 97 torr) for temperatures between 450 and 750 K. Large amounts of CO were formed, with activation energies of 21.2 and 17.4-19.7 kcal mol^{-1} for CH_4 and CO formation, respectively. The absolute CH_4 production rates were very close to those seen for methanation of CO. These results support a mechanism with CO and C(a) intermediates. Adsorption of K and/or S resulted in changes in the amounts and rates of CH_4 and CO production, but no change in activation energy. Results showed that the effects of K(a) can compensate for the effects of S(a), and support electronic interaction as responsible for poisoning/promotion effects.

I. Introduction

As compared to the methanation of carbon monoxide, little attention has been paid to the methanation of carbon dioxide. The methanation of CO_2 is reported to proceed with a lower activation energy and a higher rate than the methanation of CO. In general, the same catalysts are active for methanation of both CO and CO_2, although CO_2 gives a higher selectivity for CH_4.[1] While the methanation of CO is generally agreed to proceed via a mechanism which involves adsorbed carbon, C(a),[2-8] there are two major mechanisms proposed for the methanation of CO_2. The first mechanism was originally proposed by Bahr[9] and involves transformation of the CO_2 to CO prior to methanation. The other mechanism was originally proposed by Medsford[10] and involves pathways not requiring the transformation of CO_2 to CO first, with the possibility that much of the reaction takes place in the gas phase rather than on the catalyst surface. Recently, a great deal of support has been given to the model involving a CO intermediate.[3,8,11-21]

Small amounts of promoters and poisons complicate the description of practical catalytic systems. One of the most common promoters is potassium, which is normally added to change selectivity. For Fischer-Tropsch catalysts, the K serves to increase the yields of heavier hydrocarbons and olefins.[22-24] In addition to species added intentionally, catalysts may become poisoned by the presence of impurities in the system. One of the most common poisons, particularly for methanation catalysts,[25] is sulfur, normally coming from H_2S impurities in the gas streams. The poisoning effects of S are particularly severe for Ni.[25-28] Many studies on well-defined systems have recently been performed for both K[22-24,30-39] and S[25-28,31,40-48] in attempts to understand the roles and mechanisms of promoters and poisons.

Single-crystal planes of Ni have been shown to be reasonable models of practical catalysts for methanation.[6,49-51] The work reported here continues in this direction, by studying the methanation of CO_2 over Ni(100) under well-defined conditions. We also report on the effect of surface modifiers, K and S, on this reaction. In addition, we observe the effects on the reaction when both S and K are adsorbed at once.

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II. Experimental Section

These experiments were performed in a high-pressure reactor/ultrahigh-vacuum surface analysis chamber. The Ni(100) single-crystal sample was a disk, oriented and polished on both sides. The sample was heated resistively with the temperature measured by a W/5% Re-W/26% Re thermocouple. The sample was mounted on a motor-driven bellows assembly for rapid horizontal translation between the analysis and reaction chambers. Both reaction and analysis chambers were ion pumped, with base pressures in the 10^{-10}-torr range. The analysis chamber was equipped with a double pass cylindrical mirror analyzer and coaxial electron gun for AES analysis, LEED optics, a quadrupole mass spectrometer, and an ion sputtering gun. The reaction chamber could be filled up to 2 atm (0.5-L volume) with high-purity H_2 (Matheson, 99.99999%) and CO_2 (Matheson, 99.9999%) from an ion-pumped high-vacuum manifold. The gas pressures were measured with a capacitance manometer in the pressure range 0.01-1000 torr. The gas-phase composition in the reaction chamber could be measured by extraction of a small portion (~1%) of the reaction mixture into a gas chromatography (GC) sample loop. The GC was equipped with SF96/Poropak and 5A sieve columns with FID detection. In order to measure CO and CO_2, the GC was also equipped with a Ni methanator. The detector sensitivity was calibrated with standard gas mixtures. The sample could be translated from the reaction to the analysis chamber in <5 min, including pump down, after a reaction.

The Ni(100) crystal was cleaned by oxidation in 1×10^{-6} torr of O_2 for 5 min at ~1450 K. The crystal was then reduced in 10 torr of H_2 for 5 min at ~750 K. This procedure produced a crystal with no contamination observable by AES. After initial cleaning, small amounts of C(a) could be removed by briefly heating the crystal to ~1400 K. The back of the crystal and the crystal mount were deactivated by dosing with ~30 L of H_2S with the crystal at ~600 K. The front of the crystal was then sputtered free of S(a) followed by annealing to ~1400 K. This procedure has been shown to deactivate the unsputtered parts of the crystal and crystal mount, so that the observed reaction products arise only from the front of the crystal.[22,27] This was necessary for the K studies, since K could only be dosed onto the front of the crystal.

The S(a) was deposited by dosing H_2S at ~600 K, until the desired level of S(a) was obtained. Coverages of S(a) were calibrated as described previously.[27,40,52] The K(a) was dosed as K^+ from a zeolite ion source as described previously.[53] The crystal was maintained at ~600 K during deposition to remove any surface damage caused by the incident 200-eV ions. All coverages for K(a) were calibrated as described previously,[22] where the deposition was found to be uniform across the front surface. The best method found for dosing a surface with both S(a) and K(a) was to dose S(a) first, to a level above that desired. The subsequent dosing of K^+ caused sputter depletion of the S(a) as the K(a) was accumulated.

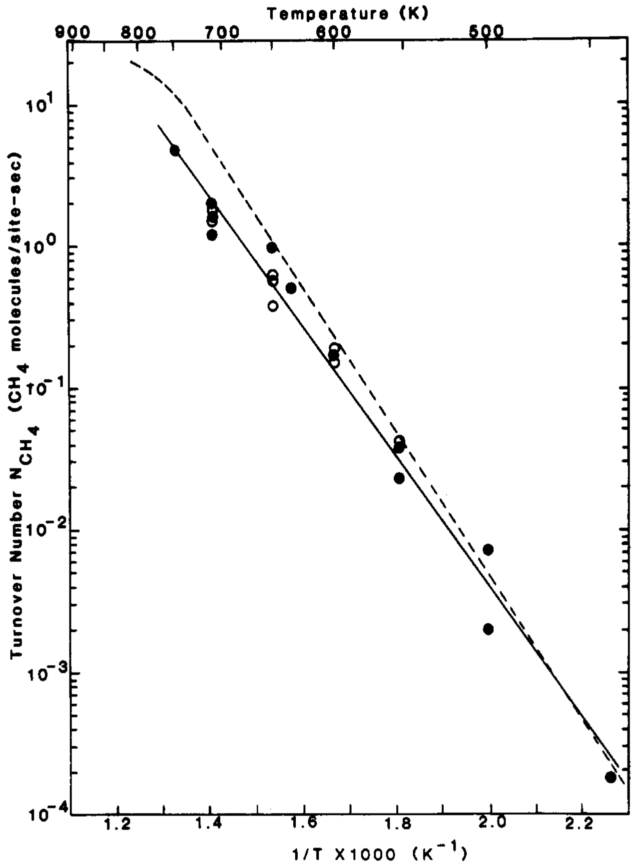

Figure 1. Arrhenius plot for CH_4 production from H_2/CO_2 = 4/1 at 120-torr total pressure (filled-in circles) and from H_2/CO_2 = 96/1 at 97-torr total pressure (open circles). The solid line gives an activation energy of 21.2 kcal mol^{-1}. The dashed line shows the CH_4 production from H_2/CO = 4/1 at 120-torr total pressure, with an activation energy of 24.7 kcal mol^{-1}.

The experimental procedure is briefly outlined below. The crystal cleanliness was verified by AES. The surface modifiers were dosed to the level desired and the coverages were monitored by AES. The crystal was positioned in the reaction chamber and heated to the desired temperature in the reaction mixture for the desired time. During the reaction, samples of the gas phase were extracted and analyzed by gas chromatography to monitor product formation and reactant depletion. The reaction chamber was then evacuated and the crystal returned to the analysis chamber. After a brief heating to ~600 K to remove adsorbed CO, the AES spectrum was again taken.

III. Results

1. Methanation on the Clean Ni(100) Surface. The methanation of CO_2 on the clean Ni(100) surface was studied for H_2/CO_2 ratios of 4/1 and 96/1 with total

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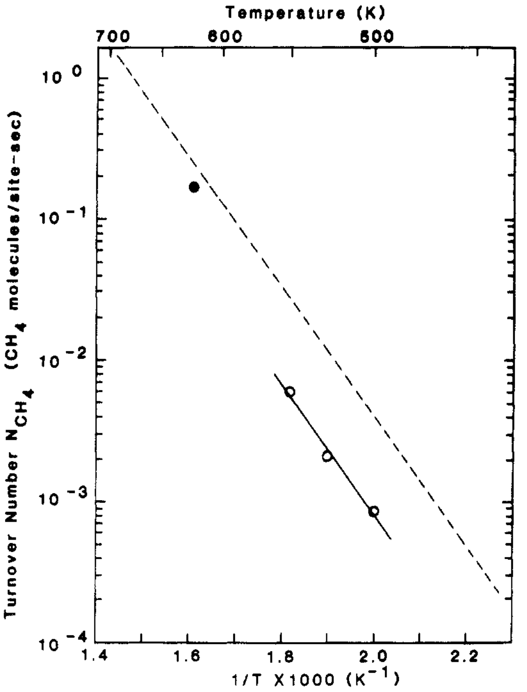

Figure 2. Comparison of the CH_4 production rate obtained in this study (dashed line) to other well-characterized Ni catalysts. The open circles are for 3% Ni/SiO_2 with H_2/CO_2 = 4/1 (combined pressure of 52.5 torr) in N_2 with a total pressure of 1050 torr.[15] The closed circle is for a Ni catalyst with H_2/CO_2 = 3.7/1 with a total pressure of 760 torr.[14]

pressures of 120 and 97 torr (constant H_2 partial pressure of 96 torr). The CH_4 production is shown in Figure 1, in Arrhenius form. Rates for both H_2/CO_2 ratios lie on a single line which yields an activation energy of 21.2 kcal mol^{-1}. The methanation of CO reported in earlier work[6,52] (H_2/CO = 4/1 and 120-torr total pressure) proceeds with a slightly higher activation energy of 24.7 kcal mol^{-1}. As shown in Figure 1, there is also a very close correspondence of the absolute rates of methane formation for the two reactions with a crossover of rates at ~460 K.

When we used AES analysis, the only species detected on the surface after reaction were C(a), O(a), and S(a). The S(a) level was low (<0.01 monolayer, ML) and arose either by slow diffusion from the bulk or more likely by slow migration from the back of the crystal. Here 1 ML = one adsorbed atom per substrate surface atom. This level of S(a) gives $S_{152}/Ni_{848} = 0.04$, where subscripts indicate the kinetic energy of the respective AES signals. The C(a) and O(a) were products of the reaction and were present at typical levels of 0.22 ML ($C_{272}/Ni_{848} = 0.09$) and ~0.15 ML ($O_{503}/Ni_{848} = 0.02$), respectively. The coverage of C(a) was calibrated as by Goodman et al.,[6,54] and the coverage of O(a) was estimated by relative sensitivities for C and O as determined by AES measurements of CO(a). In previous work for methanation of CO on Ni(100)[6,52,54] ~0.10 ML of C(a) and no O(a) were seen after reaction. This is in contrast to Rh(poly) where CO methanation deposits detectable amounts of both C(a) and O(a), while CO_2 methanation deposits only C(a).[55] For supported Rh,[17] a lower C(a) coverage is also seen for CO_2 methanation relative to CO. It is quite likely that in the present case a substantial part of the 0.22 ML of carbon is associated with the oxygen, e.g., carbonates, and thus may be inactive. We propose, as discussed below, that the coverage of "active" carbon is less than the 0.10 ML found for the H_2/CO reaction.[6]

TABLE I: Comparison of Activation Energies for Methanation of CO_2 on Various Ni Catalysts

catalyst	E_A, kcal/ mol^{-1}	temp, K	P_{TOT}, torr	H_2/CO	ref
Ni (100)	21.2	430-710	120	4/1	a
Ni (100)	21.2	550-710	97	96/1	a
Ni/Al_2O_3	25.3	473-503	760	454-41/1	62
Ni/Cu films	21.6[b]	523	0.58	5/1	3
Ni/SiO_2	19.1	500-550	1050[c]	4/1	15
NiB(P-1)	17.0	413-498	760	3/1	70
Raney Ni	12.9	413-498	760	3/1	70
Ni-P-1	33.0	573-623	760	3/1	70
D-Ni	22.9	498-563	760	3/1	70

[a] This work. [b] Average of the values given as a function of % Cu. [c] 52.5 torr of H_2 and CO_2 in N_2 to give a total of 1050 torr.

Figure 2 shows the comparison of our work (dashed line) with two of the small number of studies conducted on well-characterized supported Ni catalysts. The open circles are for a 3% Ni/SiO_2 catalyst with H_2/CO_2 = 4/1 (combined pressure of 52.5 torr) diluted in N_2 to give a total pressure of 1050 torr.[15] The filled-in circle shows the CH_4 production rate for a Ni catalyst with H_2/CO_2 = 3.7 and total pressure of 760 torr.[14] On the Ni/SiO_2 catalyst,[15] the activation energy for CO_2 methanation was lower than that for CO by 3.8 kcal mol^{-1} and the rates crossed at 525 K, both in excellent agreement with our values. Table I lists the activation energies obtained for CO_2 methanation on a variety of Ni catalysts.

Figure 3 shows how the partial pressures (A) and turnover numbers (B) varied with time for H_2/CO_2 = 96/1 at 552 K. Figure 3A shows very little conversion of CO_2 during the 1.5-h reaction time. The production of CH_4 is linear over this same time period. Interestingly, large amounts of CO are also produced, with the formation rate dropping as a function of reaction time. This is demonstrated more clearly in Figure 3B, which shows the turnover numbers for CO and CH_4 as a function of reaction time.

Figure 4, A and B, shows the partial pressures and turnover numbers for reaction at 710 K. Compared to the reaction at 552 K, there is extensive conversion of CO_2, the CO partial pressure approaches a constant value, and the methane formation rate steadily decreases. After 2-h reaction time, the turnover numbers for CO and for CH_4 were very similar. Figure 4A also shows the value for the sum of the partial pressures of CO_2, CO, and CH_4 as a function of time. Within the scatter, the sum remains essentially constant, indicating a good mass balance for carbon. The reaction was also followed at 600 and 650 K and similar curves were observed. Results are summarized in Table II. We note that CH_4 production increases at the expense of CO production as the temperature is increased.

Many previous studies have noted the formation of CO during the methanation of CO_2.[3,13-16,19,20,56-58] The results for Ni/SiO_2,[16] which are in excellent agreement with this work for the activation energy and rate of CH_4 production, also show that relatively large amounts of CO are present when the steady-state rate is measured, i.e., 0.29 torr at

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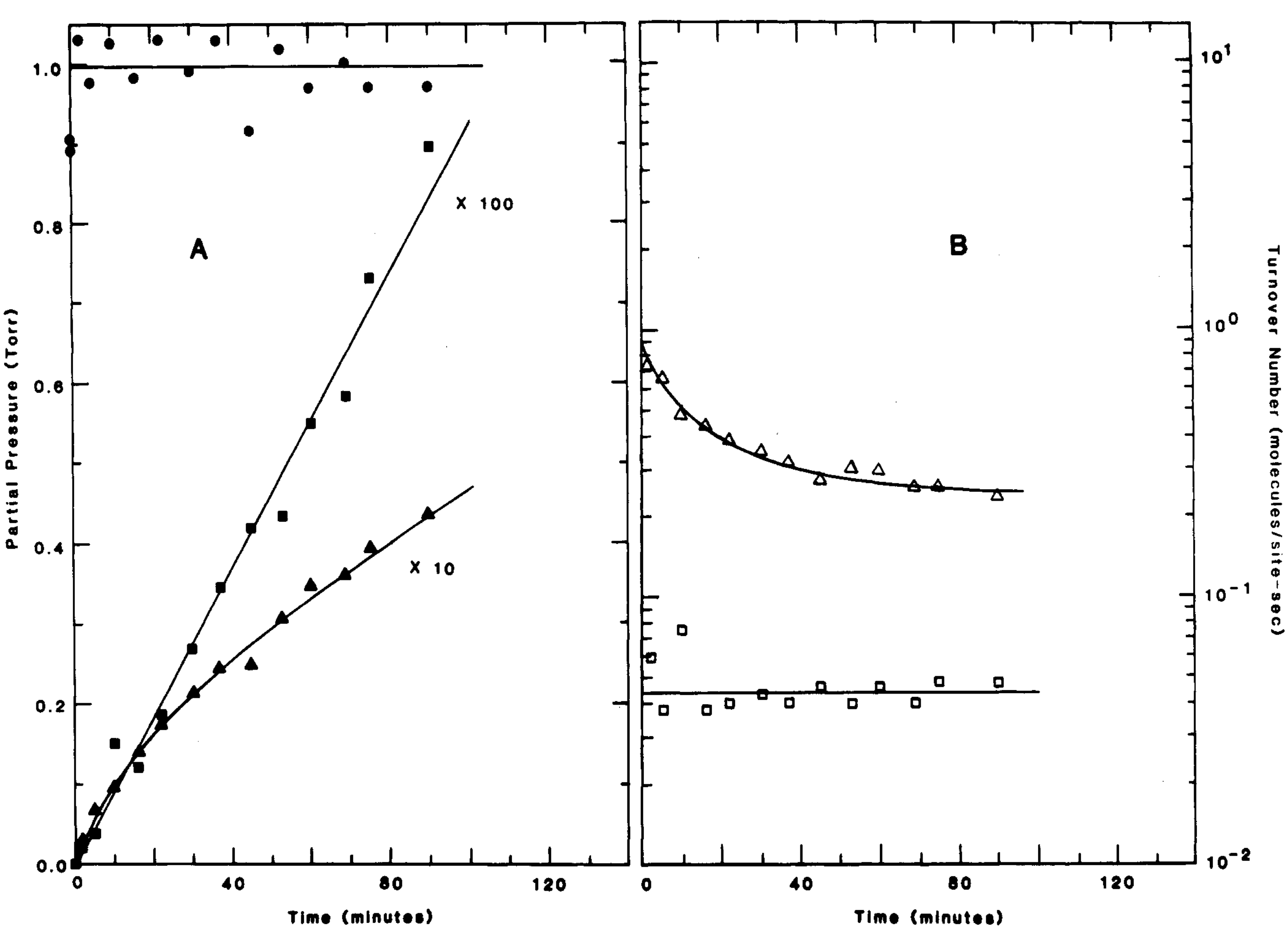

Figure 3. (A) Partial pressure of CO_2 (filled-in circles), CO (filled-in triangles), and CH_4 (filled-in squares) as a function of time for reaction at 552 K with H_2/CO_2 = 96/1 and 97-torr total pressure. Note the scaling factors for CO and CH_4. (B) Turnover numbers for CO (open triangles) and CH_4 (open squares) as a function of reaction time for the same conditions.

550 K. Araki and Ponec[3] also find amounts of CO in excellent agreement with our data, for reaction at a total pressure of 0.58 torr over Ni and Ni-Cu alloy films. We also note that the adsorption of CO_2 on Ni/SiO_2[12] in the absence of H_2 gives rise during desorption to large amounts of CO. The amounts of CO observed on a variety of catalysts for CO_2 methanation are summarized in Table II.

Figure 5 shows Arrhenius plots for CO production at different reaction times for H_2/CO = 96/1 and 97-torr total pressure. The filled-in circles represent extrapolated (t = 0) initial rates while the open circles represent the rates at times equal to those used in determining the activation energy for CH_4 production. The points lie on two separate lines, with activation energies of 17.4 and 19.7 kcal mol^{-1}, respectively. It is of interest to note the very close similarity of activation energies of formation of CO and CH_4 (1.5 kcal mol^{-1} difference) at equivalent reaction times.

2. *Effects of Surface Modifiers.* Figure 6 shows the methanation rates for H_2/CO_2 = 4/1 with a total pressure of 120 torr when the Ni(100) surface was precovered with 0.12 mL of K(a) (K_{250}/Ni_{848} = 0.27). The solid line shows the results for the clean surface. The points for the K-covered surface fall on it, indicating no K-related change in either the methanation rate or activation energy. The K(a) coverage was stable over the course of the reactions. The levels of surface species following reaction were: C = 0.12 ML (C_{272}/Ni_{848} = 0.05), O = 0.50 ML (O_{503}/Ni_{848} = 0.07), and S = 0.005 ML (S_{152}/Ni_{848} = 0.02). Relative to the reaction on the clean surface, there was a decrease for both S(a) and C(a) and an increase for O(a). It is interesting to note that the C(a) coverage is reduced by an amount almost identical with the K(a) coverage, possibly indicating that K(a) directly blocks C(a) adsorption sites. No higher hydrocarbon species were seen during reaction for either the clean or the K-covered surface. A previous study of the effects of adsorbed K on the methanation of CO on Ni(100) (H_2/CO = 4/1 with total presusre of 120 torr)[22] found no change in activation energy but increased selectivity to higher hydrocarbons, increased residual C(a) coverage, and a lower rate of methane production.

As for the clean surface, the CO_2 depletion and CH_4 and CO formation were followed in detail at 600 K for H_2/CO_2 = 96/1 and 97-torr total pressure. At this temperature there was only limited conversion of CO_2. Figure 7A shows the partial pressures of CH_4 (circles) and CO (triangles) as a function of reaction time for the surface precovered with 0.06 ML of K(a) (K_{250}/Ni_{848} = 0.13) (filled-in symbols) and 0.10 ML of K(a) (K_{250}/Ni_{848} = 0.23) (open symbols). The dashed lines show the partial pressures for the clean surface (average of many points, with the points omitted for clarity). Both CO and CH_4 partial pressures are increased by the presence of preadsorbed K, with CO affected more strongly than CH_4. Both precoverages of K(a) give equivalent enhancement of CO partial pressure, whereas, for CH_4, the smaller K(a) precoverage gives a larger enhancement. Figure 7B shows the turnover numbers for CO (triangles) and CH_4 (circles). As in Figure 7A, the clean-surface values are indicated by the dashed lines. The CO and CH_4 production rates for the K(a) precovered surface can be fitted by curves which have shapes identical with those for the clean surface. The rate of CO produc-

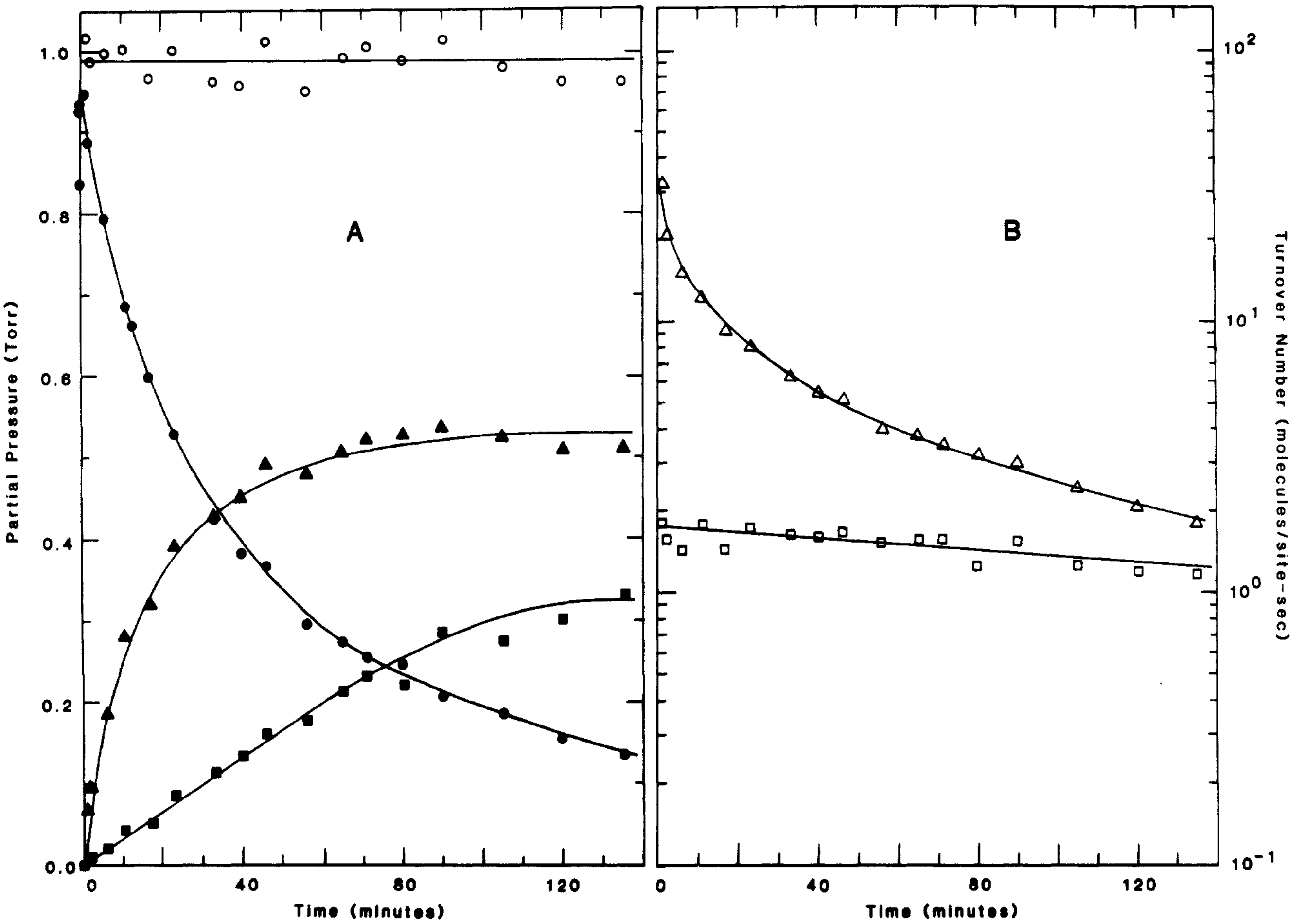

Figure 4. (A) Partial pressure of CO_2 (filled-in circles), CO (filled-in triangles), and CH_4 (filled-in squares) as a function of time for reaction at 710 K with H_2/CO_2 = 96/1 and 97-torr total pressure. The open circles show the sum of the partial pressures of CO_2, CO, and CH_4 as a function of time. (B) turnover numbers for CO (open triangles) and CH_4 (open squares) as a function of reaction time for the same conditions.

tion is up by a factor of 4.7 for both K(a) precoverages, while the rate of CH_4 production is up by factors of 3.5 and 2.1 for K(a) precoverages of 0.06 and 0.10 ML, respectively. There is a negative dependence of CH_4 production rate on CO_2 partial pressure. The enhancement with $\theta_K \sim 0.1$ ML and p_{H_2} = 96 torr decreases as the CO_2 pressure increases. With p_{CO_2} = 24 torr (Figure 6) adding 0.1 ML of K(a) gave no enhancement but, when p_{CO_2} = 1 torr, 0.1 ML of K(a) enhanced the methanation rate by a factor of 2.1.

The same procedure was used to examine the effects of precoverage with 0.05 ML of S(a) (S_{152}/Ni_{848} = 0.20) under the same conditions (H_2/CO_2 = 96/1, 97-torr total pressure and 600 K). Figure 8 shows that both the CO and CH_4 partial pressures are inhibited by the preadsorbed S. The rate of CO production is down by a factor of 2.0 while the rate of CH_4 production is down by a factor of 5.1.

For both K(a) and S(a) precoverages, there are no drastic changes in the shapes of the pressure and rate profiles indicating a simple enhancement or inhibition of the rate of production for both CO and CH_4. We also note that S(a) inhibits, while K(a) enhances, production of CO and CH_4. With preadsorbed K, CO production is enhanced more than CH_4 production while preadsorbed S inhibits CH_4 production more strongly than CO production.

In order to further investigate the opposite effects of preadsorbed S and K, this reaction was studied on a surface precovered by both 0.05 ML of S(a) (S_{152}/Ni_{848} = 0.19) and 0.08 ML of K(a) (K_{250}/Ni_{848} = 0.18). Both S(a) and K(a) coverages were stable during the course of the reaction. As compared to clean Ni(100), the production of CO (Figure 9) is up by a factor of 4.4, very close to the enhancement seen when the surface is pretreated with K(a) alone. The production of CH_4 is up by a factor of 1.2, very close to the value resulting from the difference of twice the enhancement by the preadsorbed K and the inhibition by the preadsorbed S (i.e., almost a coverage-weighted average). Thus, K(a) is able to totally overcome the inhibition of CO production by S(a), while the resulting CH_4 production rate is some coverage-weighted average of the individual effects.

IV. Discussion

1. Methanation on the Clean Surface. Recent results[3,8,11-21] support the idea that the methanation of CO_2 proceeds via a CO intermediate on a wide variety of catalysts. The close agreement in this study of activation energies and absolute rates of CH_4 formation from CO_2 and CO under identical reaction conditions all lend support to this mechanism. Furthermore, from these studies it is clearly seen that the initial rates of CO_2 reduction to CO far exceed the methanation rates, indicating that this reduction step is not rate determining. The slowing of the rate of CO_2 conversion to CO as the reaction proceeds is apparently a consequence of the surface becoming saturated with CO, which blocks sites for CO_2 reduction. This mechanism is also consistent with CO_2 adsorption studies.[12,18,60,61] The fact that addition of CO to CO_2 and H_2

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TABLE II: Comparison of Relative Amounts of CO and CH_4 Formed during Methanation of CO_2 on a Variety of Catalysts

catalyst	temp, K	total press., torr	conversion of CO_2, %	production of CO %[b]	production of CO torr	production of CH_4 %[b]	production of CH_4 torr	ref
Ni(100)	552	97	5	83	0.042	17	0.009	a
	600	97	13	84	0.11	16	0.021	a
	650	97	43	79	0.34	21	0.090	a
	710	97	78	68	0.53	32	0.25	a
Ni/SiO_2	500	1050	3.9	9	0.037	70	0.29	15
	525	1050	8.6	5	0.045	77	0.69	15
	550	1050	11.2	25	0.29	70	0.82	15
Ni	623	760	14	45	10.1	55	12.2	14
Ni	573	760	46	2	2.3	98	114	20
	673	760	50	2	2.6	98	124	20
	773	760	46	13	15.1	87	101	20
3.7% Cu/96.3% Ni	573	760	5	80	10.1	20	2.5	20
	673	760	32	84	68.1	16	13.0	20
	773	760	67	58	90.4	42	71.3	20
Ni film	523	0.58		84		16		3
Ni/Cu alloys[c]	523	0.58		95		5		3
Ni	533-672	760	3-70	<3.5	<3.7	>97	>4.4	56
Ni/SiO_2[d]	398	760		46				12
	443	760		56				12
	523	760		78				12
MoO_2	623	760	28	94	42	6.5	2.9	14
MoS_2	623	760	1.8	86	2.6	14	0.40	14
Mo	623	760	18	96	27	3.5	0.99	14
Mo-C-4	623	760	31	77	38	20	9.9	14
Mo-N	623	760	21	99	33	0.91	0.30	14
Fe	623	760	>27	>68	>30	>22	>9.5	14
Ru/Al_2O_3	443-503	760	10-15	<2		>98		13
Ru/Al_2O_3	497	16264	81	3.7	250	90	6166	57
Rh/Al_2O_3	443-548	760		<1		>99		17
Rh/TiO_2	443-548	760		<1		>99		17
Rh/MgO	443-548	760		12		88		17

[a] This work. [b] % of converted CO_2 showing up as CO or CH_4. [c] For % Cu >10 the relative amounts are constant. [d] These values are for CO_2 adsorption at the indicated temperature, with desorption of CO and CO_2.

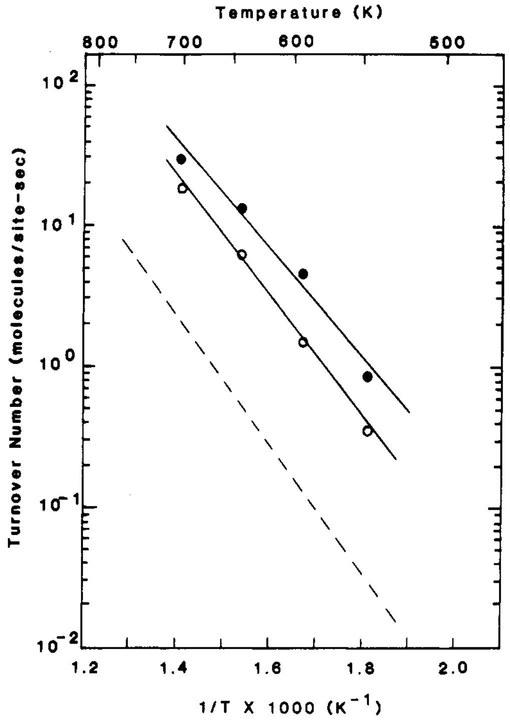

Figure 5. Arrhenius plot for CO production from H_2/CO_2 = 96/1 at 97-torr total pressure. The filled-in circles represent the extrapolated initial rates of CO production, with an indicated activation energy of 17.4 kcal mol^{-1}. The open circles represent the rates of CO production at times equivalent to those used to find the activation energy for CH_4 production. The latter points yield an activation energy of 19.7 kcal mol^{-1}. The dashed line shows the rate of CH_4 production (activation energy of 21.2 kcal mol^{-1}).

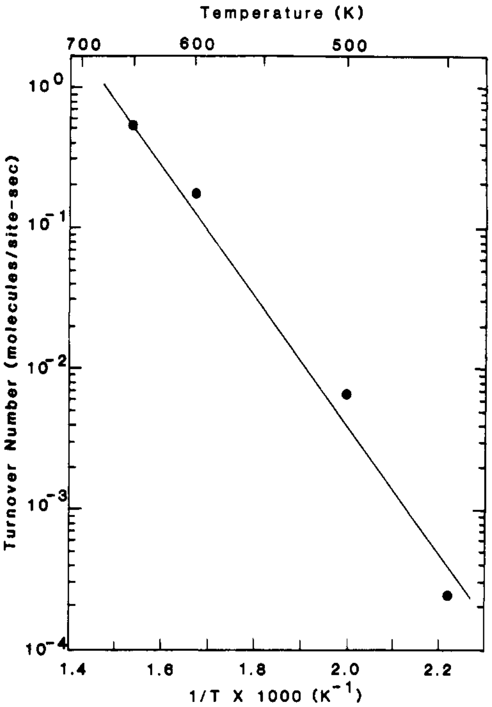

Figure 6. Arrhenius plot for CH_4 production from H_2/CO_2 = 4/1 at 120-torr total pressure. The points for the surface covered by 0.12 ML of K fall on the solid line which is for the clean surface, indicating no change in activation energy (21.2 kcal mol^{-1}) or CH_4 production rate.

mixtures reduces the rate of CH_4 formation[17] and CO_2 conversion to CO[63] is consistent with this model, assuming that the rates will drop with CO pressures in excess of the equilibrium pressures (i.e., negative order in CO) as is generally observed. This model also accurately predicts,

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(63) E. J. Gibson and C. C. Hall, *J. Appl. Chem.*, 4, 494 (1954).

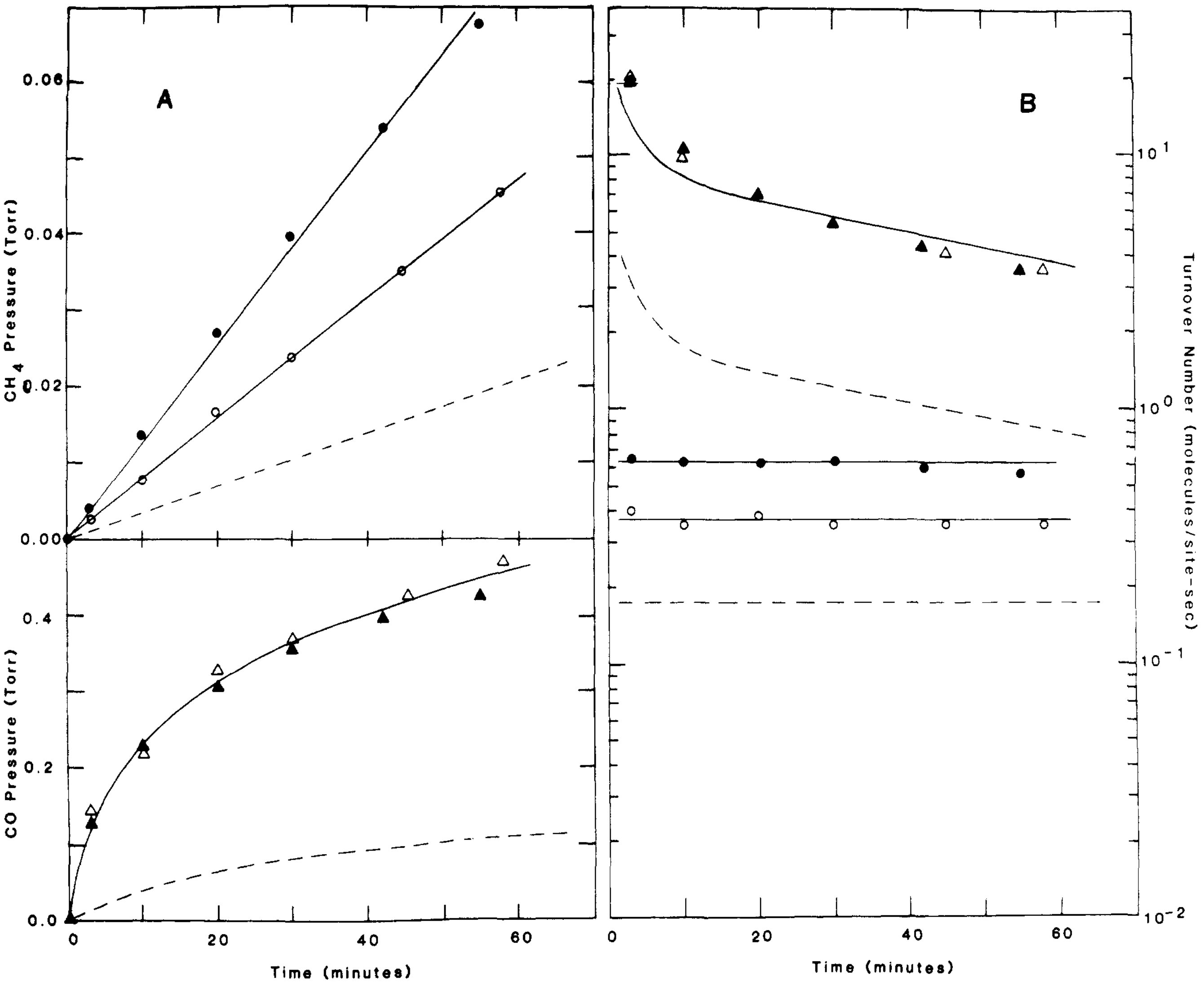

Figure 7. (A) Partial pressure of CO (triangles) and CH_4 (circles) as a function of time for reaction at 600 K with H_2/CO_2 = 96/1 (97-torr total pressure) and K precoverages of 0.06 (filled-in symbols) and 0.10 (open symbols) ML. The dashed lines are for an equivalent reaction on the clean surface. (B) Turnover numbers for CO (triangles) and CH_4 (circles) as a function of reaction time with K precoverages of 0.06 (filled-in symbols) and 0.10 (open symbols) ML. The dashed lines are for the clean surface.

as observed experimentally,[16,62-64] that CO_2 methanation in $H_2/CO/CO_2$ mixtures should be inhibited until all CO in excess of the equilibrium amount is converted to CH_4.

Formate species have also been seen for mixtures of CO_2 and H_2. Even though the interaction of adsorbed formate and H_2 can produce CH_4,[65] this species is generally throught to be inactive.[13,17,66] If a CO intermediate is assumed, the methanation of CO_2 then most likely proceeds via C(a), as in CO methanation.[2-8] However, this raises the questions of why the selectivity to CH_4 is greater and why the activation energy is generally lower for methanation of CO_2. These effects have been attributed to a lower coverage of C(a) for CO_2, as compared to CO methanation.[8,17] This has been observed for supported[17] and polycrystalline[55] Rh catalysts. Although we find higher *total* carbon coverages resulting from CO_2 methanation as compared with CO, much of this carbon likely is associated with oxygen, and therefore not active. Although a quantitative assessment is difficult, we believe, as discussed below, that the "active" surface C(a) level is lower in the case of CO_2 methanation. This supports the suggestion[12,16] that the selectivity to methane is due to low equilibrium partial pressures to CO and thus an effectively high H_2/CO ratio.

Assuming a mechanism with CO and C(a) intermediates, an important question to address is that of which step is rate limiting. The adsorption of CO_2 has previously been assumed to be rate limiting[56,62] and is supported by the observation that CO_2 adsorption is activated.[12,18] However, the higher initial specific rates for CO production, relative to CH_4, together with the lower activation energy, as seen here, suggest that neither the adsorption of CO_2 nor its conversion to CO is the rate-limiting step. This is supported by work on Ni/SiO_2 which indicates that the amounts of CO formed are controlled by equilibrium restrictions rather than kinetics.[15,16] Breaking of the C–O bond to form C(a), as suggested previously,[12,16,18] and the hydrogenation of the C(a) must also be considered. Under various conditions, one or the other of these is generally believed to be rate limiting for the methanation of CO.[4,22,49,54] We propose that the kinetics for CO_2 methanation, as for CO methanation,[54] are controlled by a delicate balance of the C(a) formation step and its removal by surface hydrogen. For relatively high partial pressures

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[64] V. M. Vlasenko, G. E. Yuzefovich, and M. T. Rusov, *Kinet. Katal.*, **6**, 938 (1965).

[65] F. Solymosi, T. Bansagi, and A. Erdohelyi, *J. Catal.*, **72**, 166 (1981).

[66] F. Solymosi, A. Erdohelyi, and M. Kocsis, *J. Catal.*, **65**, 428 (1980).

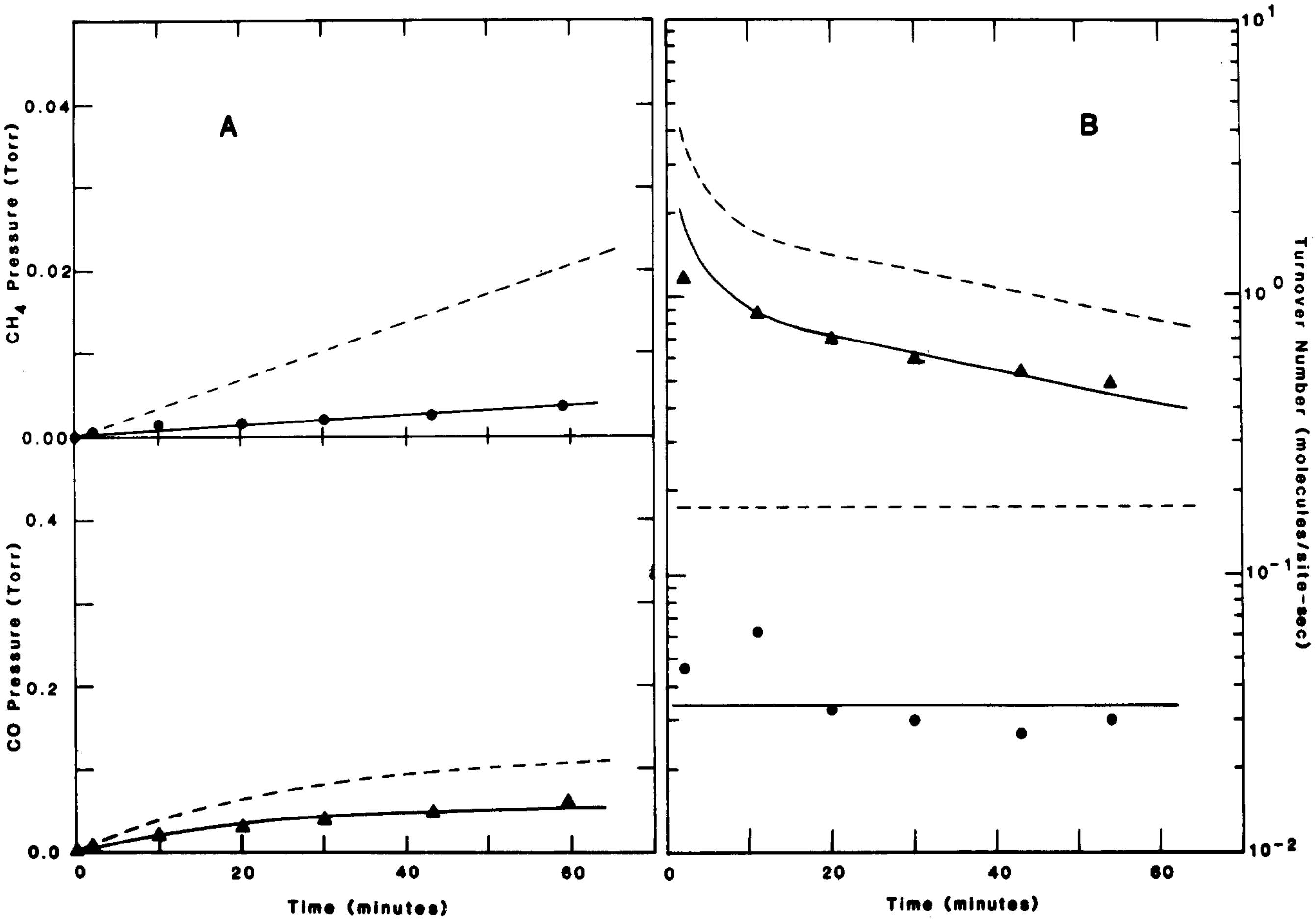

Figure 8. (A) Partial pressure of CO (triangles) and CH_4 (circles) as a function of time for reaction at 600 K with $H_2/CO_2 = 96/1$ (97-torr total pressure) and a S precoverage of 0.05 ML. The dashed lines are for an equivalent reaction on the clean surface. (B) Turnover numbers for CO (triangles) and CH_4 (circles) as a function of reaction time. The dashed lines are for the clean surface.

of CO_2, i.e., H_2/CO_2 ratios of 4/1 and total pressures of 120 torr and higher, the hydrogenation of C(a) appears to be rate limiting because promotion of C(a) formation by K(a) (discussed in section IV.2) under these conditions produces essentially no change in the overall kinetics. For these reaction conditions the kinetic parameters for the methanation of CO and CO_2 are virtually identical. Since the measured carbon coverage is higher in the case of CO_2 (0.22 vs. 0.10 ML), we suggest that, for CO_2 methanation, there is a significant coverage (~0.12 ML) of inactive carbon, perhaps present as oxygenates. In passing, we note that for these reaction conditions the resultant equilibrium CO partial pressure is sufficiently high that C(a) formation is *not* rate limiting.

At low CO_2 partial pressure, i.e., H_2/CO_2 ratios of 96/1 and total pressures of 97 torr and lower, we believe that the C(a) formation step is rate limiting. Under these conditions the equilibrium CO partial pressure is insufficient to maintain the CO dissociation at a rate comparable to the C(a) hydrogenation step; thus, the reaction is limited in C(a). Promotion of CO dissociation by K(a) (discussed in section IV.2) results in a substantial increase in the overall reaction rate. As above, these results are consistent with an active carbon level that is significantly lower (<0.10 ML) than the total level. A recent study on Ni/SiO_2,[16] using H_2 pressures < 100 torr, CO_2 pressures < 20 torr, CO pressures < 4 torr, and temperatures between 500 and 600 K, concludes a mechanism identical with that proposed here, except C(a) formation is believed to be strictly rate limiting.

2. *Effects of Surface Modifiers.* There are four primary reasons for the addition of K promoters to Fischer–Tropsch catalysts: (1) increase synthesis activity; (2) shift selectivity toward higher hydrocarbons; (3) increase olefin yields; and (4) increase rate of C formation.[23] These effects have been observed for well-defined surfaces of Fe(poly)[24] and Ni(100).[22] It is believed that the selectivity to higher hydrocarbons is a result of poisoning of the CH_4 production and simultaneous promotion of the chain-lengthening and olefin-producing steps.[22,35,36,39] No previous studies have been done for K promotion of CO_2 methanation on well-defined catalysts. However, on Co–Cu catalysts, K increases the selectivity to higher hydrocarbons from CO_2,[36] and CO_2 is bound more strongly to Fe catalysts in the presence of K.[35,37,38] Adsorption studies on Fe catalysts[35] and on single-crystal planes of Fe,[30,31] Pt,[32] and Ni[33] show that CO is held more strongly when K is present and the CO dissociation probability is increased relative to the clean surface. These effects are generally attributed to the increased back-bonding between the transition metal and CO, made possible by the added electron density donated by the K(a). In addition, K(a) has been shown to increase the adsorption energy of H_2 on Fe(100)[31,34] and Fe(111).[34]

Even though we observed no higher hydrocarbon formation in this study, the rates of CH_4 and CO production are affected by the presence of K(a). The rate of CO production, for $H_2/CO_2 = 96$ and a total pressure of 97 torr, is enhanced by a small amount of K(a), with further additions of K(a) giving no additional enhancement. In contrast, on Al_2O_3[67] at higher temperatures and CO_2 pressures, the activity for water-gas shift, starting with CO_2

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(67) Y. Amenomiya and G. Pleizier, *J. Catal.*, **76**, 345 (1982).

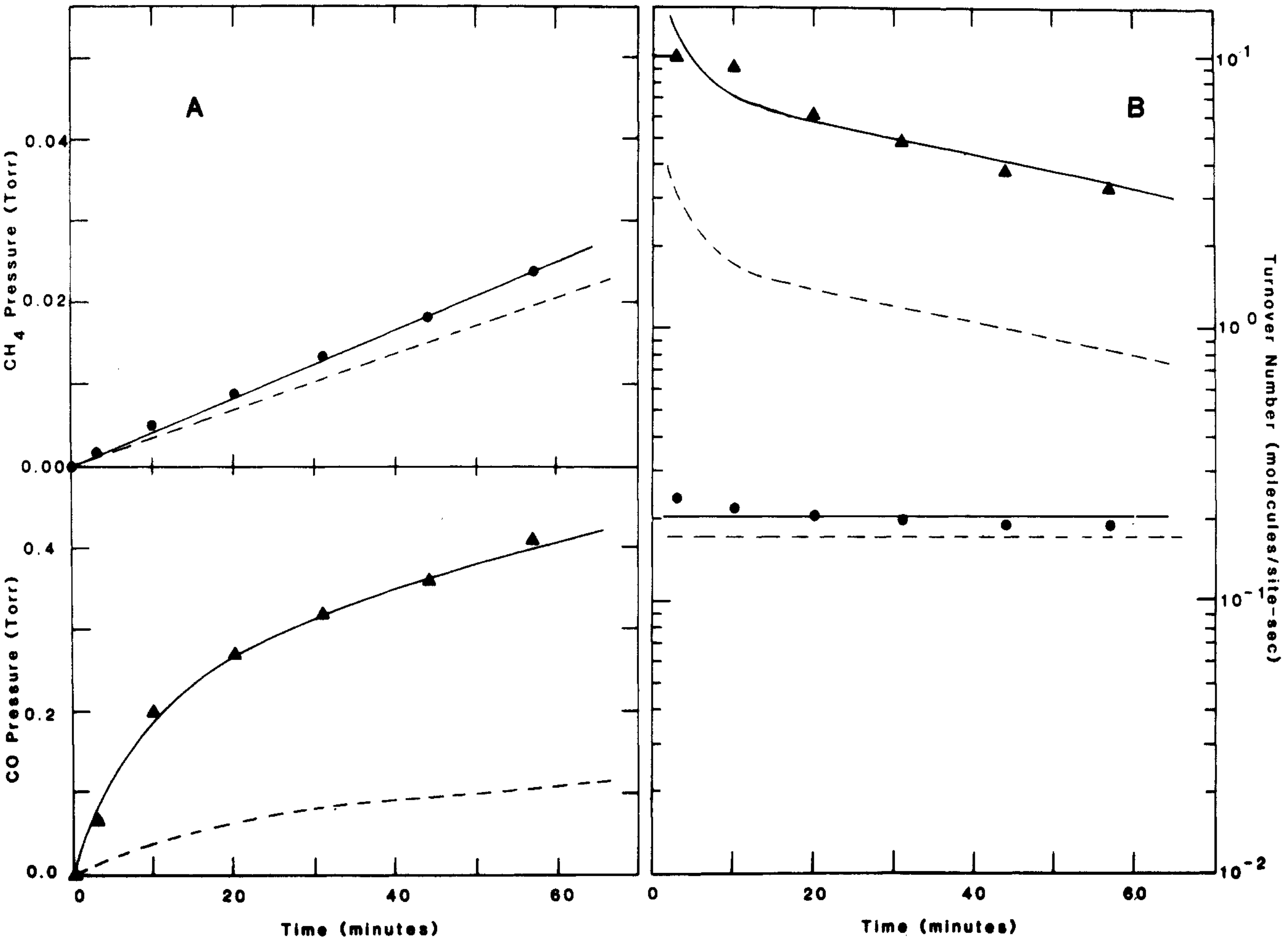

Figure 9. (A) Partial pressure of CO (triangles) and CH_4 (circles) as a function of time for reaction at 600 K with H_2/CO_2 = 96/1 (97-torr total pressure) and with precoverage of both S (0.05 ML) and K (0.08 ML). The dashed lines are for an equivalent reaction on the clean surface. (B) Turnover numbers for CO (triangles) and CH_4 (circles) as a function of reaction time. The dashed lines are for the clean surface.

and H_2, increases continuously with K coverage. In our experiments CO production may be limited by equilibrium considerations, as indicated above. The conversion of CO_2 to CO is thought to occur via a formate-like intermediate.[67-69] The K serves as a site for the formate but lowers its stability relative to the clean surface.[67] Production of CH_4 is negative order in CO_2 pressure and, above 0.06 ML, in K(a) coverage; thus, the fastest CH_4 production occurs with low CO_2 pressures and low K(a) coverages. The mechanism reported above is consistent with these results. At low coverages, the K(a) increases the rate of active C(a) buildup as noted above, and, assuming this is the rate-limiting step for the reaction at these conditions, the CH_4 production rate increases. As the K(a) coverage increases or the CO_2 pressure increases, the surface carbon level reaches, and then exceeds, an optimum level. The reaction rate likewise increases until the optimum surface carbon concentration is reached, and then levels off.

Unlike K(a), S(a) is a very strong poison for Fischer-Tropsch and methanation catalysts, particularly Ni.[25-28] The effects of S contamination are complex,[71] but generally addition of only a few ppb of H_2S to the feed gases, or a low coverage of preadsorbed S, reduces the methanation rate by orders of magnitude. However, the activation energy for the reaction is not changed,[26-28] small coverages of S(a) increases the coverage of C(a) during reaction,[27] and the relative amounts of heavier hydrocarbons increase.[25,29]

Adsorbed S reduces the electron density in the metal[46-48] and reduces back-bonding between the metal and CO. In turn this reduces the CO dissociation probability, as observed on Ni(111),[41,42] Ni(100),[27,40] and Fe(100).[31,48] The presence of S(a) blocks CO adsorption and also causes the appearance of more weakly bound CO.[27,31,40,42-45] It has been seen that CO_2 adsorption is less strongly affected by S poisoning, relative to CO on Fe catalysts.[38] It has also been observed that S(a) reduces the coverage of adsorbed H_2.[27,31] Geometric site blocking is often invoked to explain effects[26,28] although electronic effects have also been invoked to explain the observation that low coverages of S(a) affect ~10 binding sites.[27,42] Detailed studies of methanation on Ni(100) have shown that low coverages of S(a) reduce the rate of C(a) hydrogenation while high coverages of S(a) reduce the rate of C(a) formation.[27]

In our results the formation of CO is inhibited by S(a), possibly, by the reduced formation of formate species. The production of CH_4 is much more strongly inhibited and is consistent with a reduction of the rate of C(a) formation as suggested by the CO adsorption studies noted above. Previous studies on Ni(100) have suggested that for small coverages of K(a)[22] and S(a)[27] the rate-limiting step for methanation of CO is the hydrogenation, not the formation, of C(a). However, in all of these studies the partial pressures of CO used were much higher than those encountered in this study.

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(68) Y. Amenomiya, *J. Catal.*, 57, 64 (1979).

(69) D. C. Grenoble, M. M. Estadt, and D. F. Ollis, *J. Catal.*, 67, 90 (1981).

(70) Y. Okamoto, E. Matsunaga, T. Imanaka, and S. Teranishi, *J. Catal.*, 74, 183 (1982).

(71) R. J. Madon and H. Shaw, *Catal. Rev.—Sci. Eng.*, 15, 69 (1977).

To our knowledge, there are no previous results for CO or CO_2 hydrogenation in well-defined systems with poisons and promoters used at the same time. However, previous studies on Fe catalysts have shown that addition of K increases the resistance of the catalysts to S poisoning.[71,72] Our results show that CO formation proceeds in the presence of both K(a) and S(a) as if the S(a) were absent. As noted previously, the effect on CH_4 production seems to be a coverage-weighted average of the individual effects of S(a) and K(a). This supports the idea that the effects of S(a) and K(a), separately and together, reflect the changes of electron density in the metal rather than any direct, local-site effects, at least for CH_4 formation. Much more study, however, should be directed into this area to gain a better understanding of these processes.

V. Summary

The activation energy for CH_4 formation from CO_2 at total pressures of 97 and 120 torr over a Ni(100) single-crystal surface is 21.2 kcal mol^{-1}. The activation energy and absolute rates for CH_4 formation from CO_2 are very close to the values seen from CO under identical reaction conditions. Rapid formation of large amounts of CO was seen, with the activation energy for formation increasing from an initial value of 17.4 to a steady-state value of 19.7 kcal mol^{-1}. The results support a mechanism where CO_2 is converted to CO and then to C(a) before hydrogenation.

Preadsorption of K and/or S gives rise to no drastic changes in reaction mechanism. At $H_2/CO_2 = 96/1$ and a total pressure of 97 torr, the adsorption of K increases the rate of production of both CO and CH_4, affecting CO more strongly, but the overall activation energy is unchanged. The adsorption of S decreases the rate of production of both CO and CH_4, affecting CH_4 more strongly. The adsorption of both K and S shows that the K(a) can compensate for the effects of S(a). The production of CO is increased up to the level seen when K(a) is alone on the surface while the production of CH_4 reflects a coverage-weighted average of the individual effects of K(a) and S(a). This supports an electronic interaction model for the effects of S(a) and K(a), rather than local bonding effects.

Registry No. Carbon dioxide, 124-38-9; nickel, 7440-02-0; methane, 74-82-8; potassium ion, 24203-36-9; sulfur, 7704-34-9.

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[72] R. B. Anderson, F. S. Karn, and J. F. Shultz, *J. Catal.*, 4, 56 (1965).

Infrared Multiphoton Photochemistry of Hexafluorobenzene Studied by Time-Resolved Visible Luminescence Spectroscopy[1a]

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C_6F_6 gas (0.15–3 torr) was irradiated with IR pulses at 1023 cm^{-1}, where C_6F_6 absorbs strongly, and the time evolution of the visible/near-UV luminescence spectrum was examined. IR pulse fluence ranged mostly from 100 to 900 J cm^{-2}, and square-pulse equivalent intensity from 2 to 18 GW cm^{-2}. By use of a plasma shutter to truncate IR pulses after ~60 ns, luminescence evolving during irradiation could be clearly distinguished from that emitted subsequently. Kinetic measurements at 360 nm showed that luminescence begins shortly (10–20 ns) after the start of the IR pulse. After pulse truncation, the initial decay of luminescence comprises two first-order lifetimes, $\tau_A \approx 15$ ns and $\tau_B = 575 \pm 75$ ns. Time-resolved spectroscopy shows that the 575-ns emission agrees closely with a well-characterized emission, previously assigned to C_3, seen in carbon furnaces and fuel-rich oxyacetylene flames. During the period 1.8–18.8 μs after the IR pulse, time-resolved spectra are dominated by broad-background emission, with sharp superposed intensity peaks assignable to C_2 Swan bands. The broad-background emission during this period agrees with blackbody radiation spectra for temperatures decreasing from 3640 to 3440 K. The luminescence yield for the background emission varies as the square of the initial C_6F_6 pressure. Final reaction products are mostly C_2F_4(g) and a black solid ("fluorocoal") of approximate composition $(C_2F)_n$. It is suggested that the final products indicate *not* how the parent molecules decompose but how the fragments formed from them reassemble afterward as the gas temperature returns to ambient.

Introduction

It was found early in the history of infrared laser chemistry with pulsed CO_2 lasers that at very high intensities, of the order of 10^9 W cm^{-2}, absorbing gas molecules decompose rapidly and small fragments appear, some of them in excited electronic states.[2,3] For example, irradiation with focused IR beams at appropriate wavenumbers produced SiF* from SiF_4 ($\Delta E > 460$ kcal mol^{-1}),[2,5] C_2* from C_2H_4 ($\Delta E > 240$ kcal mol^{-1}),[3,5] and CN*, C_2*, and CH* from CH_3CN.[3] In these experiments, the characteristic luminescence from the electronically excited

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[1] (a) We thank the Edith C. Blum Foundation and the National Science Foundation for grants which provided partial support. (b) Present address: M.T.D., Code 6540, Naval Research Laboratory, Washington, DC 20375; S.S., Department of Chemistry, Technion-IIT, Haifa 32000 Israel.

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[5] Sources for thermochemical and spectroscopic data are the following: (a) "JANAF Thermochemical Tables", 2nd ed.; National Bureau of Standards: Washington, DC, 1971; *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* No. 37, 1141 pages. (b) Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules"; Van Nostrand-Reinhold: Princeton, NJ, 1979; pp 112, 138, 140, 154. (c) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

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