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The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals

II. The Kinetics of the Methanation Reaction over Supported Metals

M. A. VANNICE

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

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The methanation reaction over supported Group VIII metals has been found to provide an example where a catalytic property, in this case activity, can be correlated with a physically measurable property, such as the heat of adsorption for CO. Also, a pronounced compensation effect exists for this reaction. One model for the methanation reaction, assuming a uniform surface, not only explains these observed relationships but also accounts for the experimental rate equation determined for each metal catalyst. The assumption of surface nonuniformity was made in a second kinetic model. This model also describes the data and provides the same conclusions and catalytic trends as the first model.

INTRODUCTION

Although a number of past studies have investigated the kinetics of methanation over different metal surfaces, few of these kinetic studies were conducted at low conversions and no kinetic information has been gathered on well-characterized metal surfaces to allow the calculation of *specific activities*. This situation, coupled with the wide range of experimental conditions employed in these past studies, makes it impossible to compare directly the kinetic behavior of these different catalysts. These earlier investigations pertained only to Ni, Co, Fe and Ru, and although a variety of kinetic expressions have been forwarded to describe the methanation reaction over these metals, no studies have investigated this reaction over the remaining Group VIII metals.

The first part of this investigation (*1*) provided a detailed study of the catalytic behavior of supported Group VIII metals in the H_2/CO synthesis reaction. Since the methanation reaction was the only significant reaction found to occur over *all* these metal surfaces, it was investigated in more detail. For the first time accurate kinetic data have been obtained for all the Group VIII metals, except Os, using well-characterized supported metal catalysts in a differential reactor.

It is desirable to know the kinetic behavior of the Group VIII metals not only to allow meaningful comparisons between these metals but also to allow the possible deduction of some of the chemistry that is occurring on the metal surface. A sequence of elementary steps that is consistent with experimental data can result in new insight into the catalytic process. This paper provides a model for the methanation reaction that is applicable to all the Group VIII metals and creates a unifying picture of methane formation on these metal surfaces.

EXPERIMENTAL METHODS

All the kinetic data used in this study were obtained at 1 atm total pressure. A steady-state, flow microreactor was operated at low conversions, usually $\leq 5\%$, to provide initial rate data. Such data, taken from a differential reactor, is free from problems that typically plague integral reactors, such as heat and mass transfer effects, product inhibition, and secondary reactions.

Both CO and H_2 chemisorption measurements were made to determine the metal surface area of these supported catalysts. A typical glass high-vacuum adsorption unit was used.

The 4.75% Pd/SiO_2 catalyst was prepared by the incipient-wetness technique using 2.2 ml of aqueous $PdCl_2$ solution/g SiO_2. The 0.5% Pd/H-Y molecular sieve was prepared by techniques described by the Union Carbide Corp.

Further details concerning reactor operation, chemisorption techniques, catalyst preparation, and materials used are provided in the preceding paper (*1*).

RESULTS

The chemisorption data and kinetic parameters are listed in Tables 1 and 2 in the preceding paper (*1*). The pertinent information is listed again in Table 1 along with data from two additional supported Pd catalysts. The chemisorption data characterizing these two Pd catalysts are provided in Table 2. Again metal dispersion values are calculated. Methane formation was the only significant synthesis reaction which occurred on these Pd catalysts in agreement with the results found earlier (*1*). The kinetic parameters listed were obtained by expressing the methanation reaction in the form of a power rate law:

$$N_{CH_4} = A e^{-E_m/RT} P_{H_2}{}^{X} P_{CO}{}^{Y}. \qquad (1)$$

DISCUSSION

From past studies it has been found that the synthesis reaction in general and the methanation reaction in particular are frequently close to zero order in CO concentration and near first order in H_2 concentration over a specified pressure range (*2–4*). From this data, therefore, it has been assumed that the catalyst surface is nearly completely covered with strongly adsorbed CO while the more weakly bound hydrogen competes for adsorption on the small number of available metal sites remaining. This model has been pro-

TABLE 1

SYNTHESIS KINETICS OF SUPPORTED METALS[a]

Catalyst	CH_4 formation @ 275°C; turnover No. × 10^3	E_m (kcal/mole)	X	Y	A (molecules/site · sec)
5% Ru/Al_2O_3	181	24.2 ± 1.2	1.6 ± 0.1	-0.6 ± 0.1	5.7×10^8
15% Fe/Al_2O_3	57	21.3 ± 0.9	1.14 ± 0.10	-0.05 ± 0.07	2.2×10^7
5% Ni/Al_2O_3	32	25.0 ± 1.2	0.77 ± 0.04	-0.31 ± 0.05	2.3×10^8
2% Co/Al_2O_3	20	27.0 ± 4.4	1.22 ± 0.18	-0.48 ± 0.28	9.0×10^8
1% Rh/Al_2O_3	13	24.0 ± 0.4	1.04 ± 0.1	-0.20 ± 0.1	5.2×10^7
2% Pd/Al_2O_3	12	19.7 ± 1.6	1.03 ± 0.05	0.03 ± 0.09	1.2×10^6
1.75% Pt/Al_2O_3	2.7	16.7 ± 0.8	0.83 ± 0.01	0.04 ± 0.01	1.6×10^4
2% Ir/Al_2O_3	1.8	16.9 ± 1.7	0.96 ± 0.02	0.1 ± 0.08	1.4×10^4
4.75% Pd/SiO_2	0.32	26.9 ± 1.8	0.71 ± 0.05	0.15 ± 0.07	2.0×10^6
0.5% Pd/H-Y Zeolite	5.9	21.2 ± 3.1	0.84 ± 0.12	0.30 ± 0.15	5.7×10^5

[a] $r_{CH_4} = A e^{-E_m/RT} P_{H_2}{}^{X} P_{CO}{}^{Y}$.

TABLE 2

Characterization of Pd Catalysts

Catalyst	CO uptake (μmole/g)		H_2 uptake (μmole/g)		% Dispersion used sample	
	New	Used	New	Used	CO[a]	H_2
4.75% Pd/SiO_2	–	84.8	–	58	38	26
0.5% Pd/H-Y Zeolite	49	8	–	–	34	–

[a] Assuming bridged bonding.

posed for Fe surfaces and has been discussed in detail by Dry and co-workers (*5*). The reported kinetic equations describing the methanation reaction are summarized in Table 3. However, many of these studies were conducted at high conversions which at best complicate the kinetic analysis and at worst can invalidate it. It might be noted here that even in the more recent studies, specific activities were not measured so that it is not possible to compare directly the activity data from different authors. It is clear that a wide variety of kinetic expressions exists, even for the same metal, presumably due to the wide variety of experimental conditions used, but also possibly to differences in pretreatment procedures.

Carbon monoxide is known to chemisorb strongly on transition metals (*19*) and if the metal surface is saturated with CO or an adsorbed CO–H_x complex during reaction conditions, the rate of reaction might be expected to be dependent upon the strength of the metal–adsorbate bond. It is reasonable to assume that the strength of the CO complex–metal bond will vary on different metals in a manner paralleling the variation in the CO chemisorption bond strength on these same metals. If this is so, the heats of adsorption of CO on the Group VIII metals should provide a relative measure of the adsorbate-metal bond strength of the CO surface species present during the synthesis reaction. Values for heats of adsorp-

TABLE 3

Kinetics of the Synthesis Reactions over Various Metals

Metal	Temp range (°C)	Pressure range (atm)			Proposed rate equation	E_a (kcal/mole)	Ref.
		H_2	CO	Total			
Ru	220–260	16.1	5.3	21.4	$r_{(3H_2+CO)\ \text{usage}} = kP_H^{1.33} P_{CO}^{-0.13}$	–	(*6*)
Ru	175–275	1	5.35×10^{-4}	1	$r_{CH_4} = kP_H{}^0 P_{CO}{}^1$	37.2	(*7*)
Ru	20–160	$2\text{-}5 \times 10^{-2}$	$1.3\text{-}13 \times 10^{-2}$	$1\text{-}16 \times 10^{-2}$	$r_{CH_4} = kP_H{}^2 P_{CO}{}^0$	9	(*8*)
Fe (nitrided)	240	–	–	7.8–21.4	$r_{(H_2+CO)\ \text{usage}} = P_{\text{total}}^{0.94}$	–	(*9*)
Fe (promoted)	225–265	6–12	1–8	10–20	$r_{CO\ \text{usage}} = kP_H{}^1 P_{CO}{}^0$	16.8	(*2*)
Co	170–190	–	–	1–7.8	$r_{(H_2+CO)\ \text{usage}} = k$	–	(*10*)
Ni	135–175	~1	$4\text{-}30 \times 10^{-4}$	1	$r_{CH_4} = kP_{CO}{}^0$	16.2	(*11*)
Ni	170–210	~1	$2\text{-}24 \times 10^{-3}$	1	$r_{CH_4} = kP_{CO}{}^1/(1 + KP_{CO})^2$	10.1	(*12*)
Ni	200–294	1–15	0.1–0.75	1–15	$r_{CH_4} = kP_H^{0.15}/(1 + K \times P_{CO}/P_H)^{1/2}$	18–28	(*13*)
Ni	25–300	$0\text{-}8 \times 10^{-2}$	$0\text{-}8 \times 10^{-2}$	$7\text{-}19 \times 10^{-2}$	$r_{CH_4} = kP_H^{1.4} P_{CO}^{-0.9}$	20	(*14*)
Ni	243	1–100	0.01–1	1–100	$r_{CH_4} = kP_{\text{total}}^{0.5}$	24–26	(*15*)
Ni	300–350	–	–	1	$r_{CH_4} = kP_{CO} P_H{}^3/(A + BP_{CO} + CP_{CO_2} + DP_{CH_4})^4$	–	(*16*)
Ni	250–300	–	–	0.1–1	$r_{CH_4} = kP_H^{0.9} P_{CO}^{-0.2}$	36	(*17*)
Ni	261–281	–	–	1–21.4	$r_{CH_4} = kP_{\text{total}}^{0.3}$	29–32	(*18*)

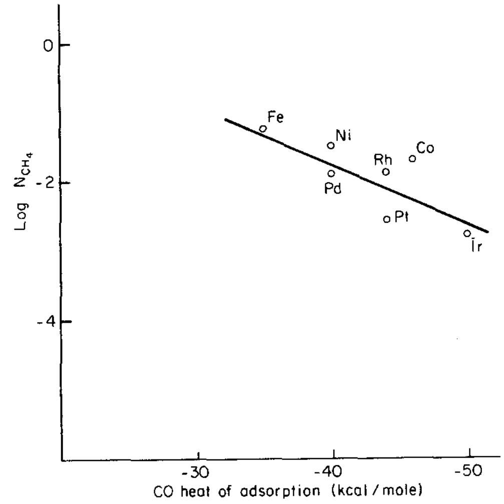


FIG. 1. Correlation between methanation activity and ΔH_a for CO.

tion, ΔH_a, were obtained from the open literature (*19,20*). When the rate of methane formation is plotted as a function of the heat of adsorption for CO, a definite trend exists as shown in Fig. 1. A similar plot occurs for the total conversion of CO. This correlation resembles the right half of a "volcano plot," a concept first forwarded by Sabatier and whose significance has been discussed elsewhere (*21*). This concept would predict that as CO adsorption becomes progressively weaker on other transition metals, the rate will reach a maximum then begin to decline.

It is also apparent that a pronounced compensation effect exists for the methanation reaction as shown in Fig. 2. The preexponential factor varies by 5 orders of magnitude as the activation energy changes by 10 kcal/mole. The slope of this plot is equal to $1/R\ \theta$ where θ is the isokinetic temperature at which rates on all the metal surfaces are equal. The value of $\theta = 436°\mathrm{K}$ lies outside the experimental temperature range used in this study which is strong evidence that the compensation effect is not an experimental artifact (*22*).

A comprehensive kinetic analysis must not only be able to explain these two correlations and confirm the partial pressure dependencies, but it must also be consistent with information existing in the open literature. For instance, Vlasenko *et al.* (*11*) and Van Herwijnen *et al.* (*12*) have shown that the reaction products, CH_4 and H_2O, do not inhibit the rate of CH_4 formation. A number of investigators have attempted to determine the nature of the surface complex, both during the synthesis reaction and at temperatures lower than required to initiate reaction, by employing infrared spectroscopy, CO–H_2 coadsorption measurements, and flash-desorption

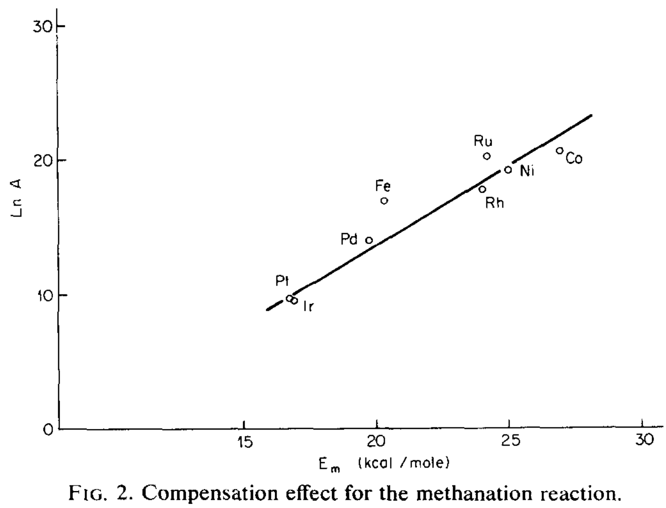


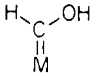
FIG. 2. Compensation effect for the methanation reaction.

TABLE 4

CO-H_2 SURFACE COMPLEXES ON DIFFERENT METALS

Metal	Proposed surface complex	Authors	Ref.
Ru	CHOH	McKee	(*8*)
Pt	CHOH	Baldwin and Hudson	(*23*)
Ni	CHOH	Vlasenko and Yuzefovich	(*24*)
Ni	CO	Blyholder and Neff	(*25*)
Co	CHOH	Gupta *et al.*	(*26*)
Fe	CHOH	Kölbel *et al.*	(*27*)
Fe	CHOH	Subramanyam and Rao	(*28*)
Fe	CHOH	Blyholder and Neff	(*29*)

techniques. The conclusions from these studies are represented in Table 4. It is clear that the most likely species is of the form CHOH and is generally assumed to be adsorbed in the enol form (*24*):



However, Blyholder and Neff (*25*) used ir to follow changes in the surface species on Ni as the temperature was raised to reaction temperatures in a CO-H_2 atmosphere. Although adsorbed CO was seen, no other stable CO surface species was found to appear (*25*). Finally, McKee (*8*) has shown that no H_2O is formed unless CH_4 is concurrently formed.

With these constraints in mind, a number of kinetic sequences were examined which incorporated the breaking of the carbon–oxygen bond as the slow step. This seems reasonable since this bond is very strong for CO (256 kcal/mole) (*30*). Only two sequences have been found which are consistent in all respects with the results from this study and evidence from previous studies.

The first approach assumes a uniform surface and is similar to that frequently used by Sinfelt (*31*). It is the simpler of the two models, which is one of its merits. It involves the assumption of a rate determining step (RDS) with all preceding steps being in quasi-equilibrium. Only the chemistry involved in the RDS need then be assessed in detail. The second approach attempts to determine the effect of surface nonuniformity and employs an approach discussed by Boudart (*32*). However, either approach results in the appearance of the same trend of catalytic behavior through the transition metals and reveals a similar interaction between adsorbed hydrogen and the CO-H_2 surface intermediate.

In the first approach it is assumed that the rate determining step (RDS) is the final hydrogenation of the CO-H_2 surface complex to complete the rupture of the C-O bond and that all preceding steps are in quasi-equilibrium. The following sequence of elementary steps is proposed:

$$CO \xleftrightarrow{K_{CO}} CO_{(ad)}, \qquad \text{(I)}$$

$$H_2 \xleftrightarrow{K_{H_2}} H_{2(ad)}, \qquad \text{(II)}$$

$$CO_{(ad)} + H_{2(ad)} \xleftrightarrow{K_1} CHOH_{(ad)}, \qquad \text{(III)}$$

$$CHOH_{(ad)} + y/_2H_{2(ad)} \xrightarrow{k_2} CH_{y(ad)} + H_2O, \qquad \text{(IV)}$$

$$CH_{y(ad)} + H_2 \xrightarrow{\text{rapid}} CH_4, \qquad \text{(V)}$$

where the last step proceeds very rapidly and does not influence the kinetics of the reaction. This may be simplified to the following representation.

$$H_2 + CO \xleftrightarrow{K} CHOH_{(ad)}, \qquad \text{(IIIa)}$$

$$CHOH_{(ad)} + y/_2H_{2(ad)} \xrightarrow{k_2} CH_{y(ad)} + H_2O, \qquad \text{(IV)}$$

plus step V.

From step IIIa, if $CHOH_{(ad)}$ is assumed to be the most abundant surface intermediate, its surface coverage, θ_c, can be represented by

$$\theta_c = \frac{KP_{CO}P_{H_2}}{1 + KP_{CO}P_{H_2}},$$

which may be approximated over a specified range of pressure by

$$\theta_c \approx (KP_{CO}P_{H_2})^n. \qquad (2)$$

If the surface is covered predominantly by strongly adsorbed CHOH species, then the sites available for hydrogen adsorption will be

$$1 - \theta_c = \theta \approx (KP_{CO}P_{H_2})^{-1}, \qquad (3)$$

and the fraction of the total surface covered by hydrogen will be

$$\theta_{H_2} = \frac{\theta K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2}} \approx \theta K_{H_2}P_{H_2}, \qquad (4)$$

if $K_{H_2}P_{H_2} << 1$ which is the situation when hydrogen is weakly adsorbed. This approach is similar to that discussed by Kemball (*33*). The rate of methanation from step IV is:

$$r_{CH_4} = k_2\theta_c\theta_{H_2}{}^{y/2} \qquad (5)$$

and substituting values from above for θ_c and θ_{H_2} we get

$$r_{CH_4} = k_2K^{n-y/2}K_{H_2}{}^{y/2}P_{CO}{}^{n-y/2}P_{H_2}{}^{n}. \qquad (6)$$

By using a power rate law of the form shown by Eq. (1) in the Results section, the values of X and Y have been determined for different catalysts and are listed in Table 1. By equating (1) and (6), we see that

$$Ae^{-E_m/RT} = K^{n-y/2}K_{H_2}{}^{y/2}k_2, \qquad (7)$$

$$X = n, \qquad (8)$$

and

$$Y = n - y/2. \qquad (9)$$

From step IV, it is clear that y must be an integer from 1 to 4 if the RDS is to involve either a 2-body or 3-body interaction. The interaction of more than 3 species is highly improbable. Since n is defined by the experimental value of X, an integral value of y is chosen to give a calculated value of Y in best agreement with the experimental value. The results of this approach are shown in Table 5. It appears that the number of H atoms interacting in the rate determining step increases with increasing ability of the metal to produce higher molecular weight species. Here ruthenium reveals the unique catalytic behavior it has shown in earlier studies.

TABLE 5

ASSUMPTION OF C–O BOND BREAKING AS RDS PROVIDES EXCELLENT AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL *Y* VALUES

Catalyst	$X = n$	y	Ycalc	Yexp
Pd/SiO_2	0.7	1	0.2	0.2
Pd/H-Y Zeolite	0.8	1	0.3	0.3
Ni/Al_2O_3	0.8	2	−0.2	-0.3
Ir/Al_2O_3	1.0	2	0	0.1
Pd/Al_2O_3	1.0	2	0	0
Pt/Al_2O_3	0.8	2	−0.2	0
Rh/Al_2O_3	1.0	2	0	−0.2
Fe/Al_2O_3	1.1	2	0.1	-0.1
Co/Al_2O_3	1.2	3	−0.3	−0.5
Ru/Al_2O_3	1.6	4	−0.4	−0.6

This kinetic model is not only consistent with data in the open literature but also explains the kinetic parameters determined in this study. It is perhaps surprising that one sequence of steps can explain the methanation reaction on all these metal surfaces but the consistency of this model certainly supports this conclusion. The dependence of the rate on the CO heat of chemisorption and the compensation effect are readily explained by this approach. It is reasonable to assume that the bond strength of the metal–CHOH surface complex is directly related to the strength of the CO bond on the metal surface. Therefore as ΔH_a for CO decreases, θ_c is also expected to decrease and the portion of the surface available for hydrogen adsorption increases. This increases θ_{H_2} as shown in Eqs. (2) and (3) thereby tending to equalize the relative surface coverages of the two reactants $CHOH_{(ad)}$ and $H_{2(ad)}$. It has been shown that the rate of a bimolecular reaction on a uniform surface is maximized when the coverages of the two

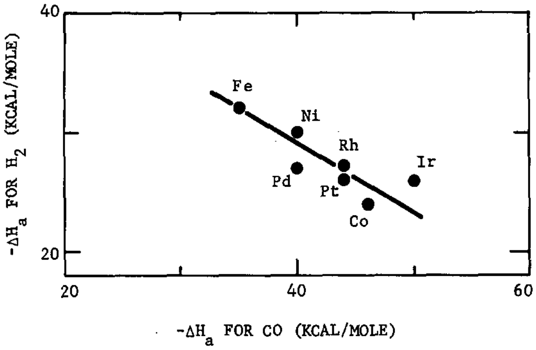


FIG. 3. Variation of H_2 chemisorption with CO chemisorption on group VIII metals.

species are equal (*34*). On this basis any variation which tends to equalize θ_c and θ_{H_2} will result in an increase in the rate. The change in CO heat of adsorption on these metal surfaces is such a variation and Fig. 1 reflects its influence on the rate.

A general trend appears to exist with the Group VIII metals which supports this picture. The metals which adsorb CO the most strongly adsorb H_2 the most weakly as indicated in Fig. 3 from data available in the literature (*19,35,36*). When the specific activities in the synthesis reaction are plotted versus the heat of adsorption for H_2, as in Fig. 4, a correlation opposite to that for CO is seen. Although the dependence on H_2 is not so pronounced as with CO it is clear that, excepting Ru, an increase in the strength of adsorption for H_2 correlates with an increase in the activity. The H_2 chemisorption data for Ru may not be comparable to the other data anyway, since it was obtained for Ru/SiO_2 whereas all other data were obtained on unsupported metals. However, it is the only value available in the literature. Again this behavior resembles one half of a volcano plot, this time the left side. The closer the heats of adsorption of H_2 and CO, the more competitive will be H_2 with CO for adsorption sites and the more equal will be the surface coverages of these two gases.

To explain the compensation effect, we begin by looking at Eq. (7). Since $K = K_{H_2}K_{CO}K_1$ and $k_2 = e^{S\ddagger/R}e^{-E\ddagger/RT}$ we equate

$$Ae^{-E_m/RT} = K_1^{n-y/2}K_{CO}^{n-y/2}K_{H_2}{}^{n}e^{S\ddagger/R}e^{-E\ddagger/RT}, \tag{10}$$

where $S\ddagger$ is the entropy of activation and $E\ddagger$ is the activation energy in the RDS. Both K_{CO} and K_{H_2} are equilibrium adsorption coefficients and are represented by

$$K_i = e\left(\frac{\Delta S^0_{a,i}}{R} - \frac{\Delta H^0_{a,i}}{RT}\right) \tag{11}$$

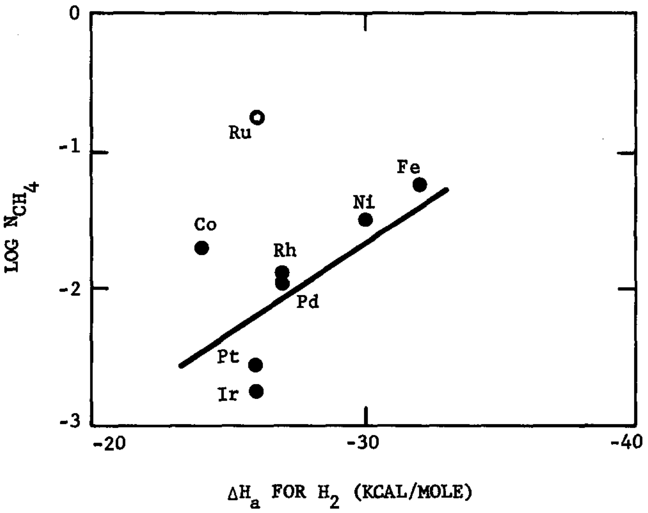


FIG. 4. Correlation between activity and H_2 chemisorption.

where $\Delta S^0_{a,i}$ and $\Delta H^0_{a,i}$ are the entropy and enthalpy of adsorption, respectively, for species i. Therefore, if the logarithms of both sides of Eq. (10) are taken, it can be shown that $\ln A$ is a linear function of ΔS^0_a such that

$$\ln A = 1/R\ [S\ddagger + n\Delta S^0_{a,\mathrm{H_2}} + (n - y/2)\Delta S^0_{a,\mathrm{CO}} + a] \quad (12)$$

and E_m is a function of ΔH^0_a such that

$$E_m = E\ddagger + n\Delta H^0_{a,\mathrm{H_2}} + (n - y/2)\Delta H^0_{a,\mathrm{CO}} - b. \quad (13)$$

Since CHOH is assumed always to be the primary surface species, K_i is assumed to change little, therefore a and b are constants. The important point to emphasize here is the relationship of $\ln A$ only to the entropies of adsorption whereas E_m is a function only of the heats of adsorption. All that is required to produce a compensation effect like the one observed is a linear relationship between $\Delta S^0_{a,i}$ and $\Delta H^0_{a,i}$. Boudart *et al.* (*37*) have shown that a general correlation does exist between the entropy and enthalpy of chemisorption such that

$$-\Delta S^0_{a,i} = c\Delta H^0_{a,i} + d. \quad (14)$$

By substituting this relationship into Eq. (13) and the result into Eq. (12), it can be shown that $\ln A = -E_m + B$ which accounts for the compensation effect observed for the methanation reaction.

In the second kinetic model, it is assumed that the catalytic surface is nonuniform and the methanation reaction can be described by a series of irreversible steps. Two general types of adsorption sites are assumed to exist. The first type of site, designated S, constitutes the majority of the metal surface sites and adsorbs only CO. This is in agreement with the literature studies mentioned earlier which have shown that CO adsorbs much more strongly than H_2 and covers most of the surface sites (*8,19*). Hydrogen then adsorbs only on the remaining sites, designated as $*'$ sites. Again assuming that the slow process is the rupture of the C–O bond and that the reaction may be described by 2 irreversible catalytic steps, the approach discussed by Boudart (*32*) can be utilized. The chemistry involved is very similar to that assumed in the first model.

The following steps are proposed to describe the methanation reaction:

$$* + \mathrm{H_2} \xleftrightarrow{K_{\mathrm{H_2}}} *\text{-}\mathrm{H_2}, \quad (\mathrm{VI})$$

$$\mathrm{S + CO + H_2 \xrightarrow{k_1} S\text{-}CHOH}, \quad (\mathrm{VII})$$

$$\mathrm{S\text{-}CHOH} + y/2(*\text{-}\mathrm{H_2}) \xrightarrow{k_2} \mathrm{S\text{-}CH}_y + * + \mathrm{H_2O}, \quad (\mathrm{VIII})$$

$$\mathrm{S\text{-}CH}_y + \mathrm{H_2} \xrightarrow{\text{rapid}} \mathrm{CH_4 + S}. \quad (\mathrm{IX})$$

Implicit in this approach is the assumption that the equilibrated step does not feel the surface nonuniformity, an applicable assumption here for H_2 chemisorption, and that step IX occurs very rapidly to regenerate an S site. The fraction of the total number of surface sites, L, present as S sites which adsorb CO will be

$$\frac{S}{L} = \theta_s = \frac{K_{\mathrm{CO}}P_{\mathrm{CO}}}{1 + K_{\mathrm{CO}}P_{\mathrm{CO}}} \quad (15)$$

and the fraction present as sites available for H_2 adsorption, $*'$, will be

$$1 - \theta_s = \theta_* \simeq (K_{\mathrm{CO}}P_{\mathrm{CO}})^{-1} = \left(e^{\frac{\Delta S^0_{a,\mathrm{CO}}}{R}} e^{\frac{-\Delta H^0_{a,\mathrm{CO}}}{RT}} P_{\mathrm{CO}}\right)^{-1}, \quad (16)$$

where K_{CO} is the equilibrium adsorption coefficient for CO, then $L\theta* = *' = * + *\text{-}\mathrm{H_2}$. For hydrogen chemisorption, the surface concentration of $[*\text{-}\mathrm{H_2}]$ will be

$$[*\text{-}\mathrm{H_2}] = [*']K_{\mathrm{H_2}}P_{\mathrm{H_2}}/(1 + K_{\mathrm{H_2}}P_{\mathrm{H_2}}) = [*']K_{\mathrm{H_2}}P_{\mathrm{H_2}} \quad (17)$$

if $K_{\mathrm{H_2}}P_{\mathrm{H2}} << 1$ as is the case for weak hydrogen adsorption. As discussed in Ref. (*32*), the rate of the methanation reaction is represented by

$$r_{\mathrm{CH_4}} = \frac{kP_{\mathrm{CO}}P_{\mathrm{H_2}}[*\text{-}\mathrm{H_2}]^{y/2}}{P^m_{\mathrm{CO}}P^m_{\mathrm{H_2}}[*,\ \mathrm{H_2}]^{(y/2)(1-m)}}, \quad (18)$$

where y is the number of H atoms reacting in step VIII and m is a constant from a Brønsted relation where $0 \leqslant m \leqslant 1$ (*38*). Substituting Eqs. (16) and (17) in (18) and simplifying we obtain

$$r_{\mathrm{CH_4}} = k' K_{\mathrm{CO}}{}^{-my/2} P_{\mathrm{H_2}}^{1-m+my/2}\ P_{\mathrm{CO}}^{1-m-my/2}. \quad (19)$$

By equating this equation to the power rate law determined experimentally it is clear that $X = 1 - m + my/2$ and $Y = 1 - m - my/2$. Since X and Y have been measured experimentally, there are 2 equations with 2 unknowns and values of m and y can be obtained algebraically. These values for the Group VIII metals are listed in Table 6. The trend exhibited by this kinetic analysis is nearly identical to that obtained in the first analysis. Again, one sequence of steps accounts for the catalytic behavior over all the metal surfaces and the value of y is smallest for the catalysts most selective to methane and largest for those metals capable of producing substantial quantities of high-molecular-weight products. This scheme is remarkably consistent in the values of m obtained—all are in the vicinity of ½, a value frequently found in other studies (*38*). In addition, all values of y are meaningful since they would be expected to lie between 1 and 4 in order to maintain either 2-body or 3-body interactions. The assumption of surface nonuniformity does not alter appreciably the results obtained from kinetic analysis.

TABLE 6

KINETIC PARAMETERS DETERMINED ASSUMING AN IRREVERSIBLE REACTION OCCURS ON A NONUNIFORM SURFACE

Catalyst	M (a constant in Brønsted relationship)	y (No. H atoms interacting with CHOH)
Pd/SiO$_2$	0.57	1.0
Pd/H-Y Zeolite	0.43	1.3
Pt/Al$_2$O$_3$	0.60	1.3
Ni/Al$_2$O$_3$	0.77	1.4
Ir/Al$_2$O$_3$	0.47	1.8
Pd/Al$_2$O$_3$	0.47	2.1
Rh/Al$_2$O$_3$	0.58	2.1
Fe/Al$_2$O$_3$	0.455	2.6
Co/Al$_2$O$_3$	0.63	2.7
Ru/Al$_2$O$_3$	0.50	4.4

If step VIII is unique, y is expected to be an integer to be physically meaningful and the calculated values of y can be divided into different groups. The first five catalysts in Table 6 have y values near unity, while Pd/Al$_2$O$_3$, Ir, and Rh are clustered around $y = 2$. Fe and Co have a value approaching 3 and Ru, again exhibiting its uniqueness, appears to require 2 hydrogen molecules in step VIII. The variation in y from integral values is most likely due to experimental error in the data, although it is also conceivable that parallel reaction paths could occur in step VIII, each involving a different number of H atoms, thereby averaging the apparent y value to a nonintegral value. It should be emphasized, however, that it is the trend of y values that is of primary interest rather than their individual values.

The compensation effect and the correlation of activity with variations in CO chemisorption are also readily explained by this model using the same arguments as presented earlier. By looking at Eqs. (16) and (17) it is clear that as the coverage of CO (or the CO–H$_2$ complex) decreases, as would be expected by a decrease in heat of adsorption, the coverage of hydrogen will increase, even if the H$_2$ heat of adsorption does not increase. As discussed earlier, this would tend to equalize CO and H$_2$ surface concentrations and produce a rate enhancement. Also, at steady-state the surface concentration of S–CHOH may be so small that spectroscopic tools such as ir cannot detect it, accounting for the failure of Blyholder and Neff (*25*) to observe intermediate CO–H_x species on Ni.

The more recent proposals of a catalytic sequence of steps to describe the methanation reaction are those of Van Herwijnen *et al.* (*12*), Bousquet and Teichner (*14*), Schoubye (*15*) and Vlasenko and Yuzefovich (*24*). Van Herwijnen and co-workers stated only that on Ni the surface reaction, presumably in the RDS, is the interaction of adsorbed H_2 with the CO complex, which they represented as

$$[H_2\text{–}CO]_{(ad)} + H_{2(ad)} \rightarrow CH_{2(ad)} + H_2O_{(ad)}.$$

Bousquet and Teichner proposed a series of 5 irreversible steps to describe the reaction on Ni. These are as follows:

$$H_{2(g)} + S \rightarrow 2H_{(ad)},$$

$$CO_{(g)} + H_{(ad)} \rightarrow x',$$

$$x' + H_{(ad)} \rightarrow x,$$

$$x + H_{2(g)} \rightarrow CH_{2(ad)} + H_2O_{(g)},$$

$$CH_{2(ad)} + H_{2(g)} \rightarrow CH_{4(g)} + 2S.$$

The derived equation, shown in Table 3, did not agree closely with their experimentally determined rate equation, but did have some similarity to it. Schoubye assumed that the dissociation of H_2 on Ni is the RDS and proposed two routes for this to occur. By adding these two rate equation over Ni, Co and possibly Fe, where experimental data. Finally, Vlasenko and co-workers have forwarded the following scheme to describe the methanation reaction over Ni, Co and possibly Fe, where [ ] represents a vacant site:

$$[\ \ ] + e + H_2 \rightarrow [H_2]^-$$

$$[\ \ ] + CO \rightarrow [CO]^+ + e$$

$$[CO]^+ + [H_2]^- \rightarrow [HCOH]^+ + e(\text{RDS})$$

$$[HCOH]^+ + [H_2]^- \rightarrow [CH_2] + H_2O + [\ \ ]$$

$$[CH_2] + [H_2]^- \rightarrow CH_4 + e + [\ \ ].$$

This sequence results in the rate equation obtained in Table 3. All these models deal primarily with Ni surfaces and these authors do not attempt to test the applicability of their models to all the Group VIII metals.

In comparing either of the two kinetic models proposed in this study with these earlier models, it is seen that Van Herwijnen's RDS is very comparable to that envisioned in this study, while the model suggested by Bousquet is more similar to the second model proposed in this work although minor differences involving adsorbed, dissociated H_2 do exist. The results from this study cannot be explained by assuming H_2 dissociation to be the RDS, therefore the kinetic sequences in this study clearly disagree with Schoubye's model. Finally, either catalytic sequence discussed in this paper is simpler than Vlasenko's series of steps because no charge transfer to or from adsorbed species is invoked. In addition, the direction of charge transfer suggested by Vlasenko is opposite to that assumed to occur on Fe surfaces (*6*). Also, their assumption of CHOH complex formation as the RDS does not agree with the kinetics proposed here. The success obtained here in describing the kinetics of methanation by assuming a noncharged CHOH surface intermediate provides support for the kinetic sequence proposed by workers at the U.S. Bureau of Mines to explain the more complicated Fischer–Tropsch synthesis (*4*). The wide applicability of either kinetic model proposed in this study over all the Group VIII metals is strong support for its veracity and provides another example where the assumption of uniform or nonuniform surfaces produces little effect on the final kinetic analysis.

Regardless of the model used, for the first time a detailed kinetic analysis has been proposed for the methanation reaction over *all* the Group VIII metals. Either kinetic model is self-consistent not only with the data generated in this study, but also with data in the open literature, and as a result we are allowed to gain some insight concerning the chemistry of the methanation reaction on metal surfaces. As a result of this investigation, it has been shown that the catalytic behavior of the Group VIII metals, such as specific activity, correlates very strongly with their adsorption properties toward CO and H_2. This study shows that variations in heats of chemisorption produce corresponding changes in the rate of methanation. These differences in heats of chemisorption between the Group VIII metals also results in a compensation effect.

CONCLUSIONS

The catalytic behavior of supported Group VIII metals has been examined using kinetic data obtained in such a way as to allow comparison of specific activities. The kinetic behavior of these metals has been determined under well-defined experimental conditions and the methanation reaction has been described by a power rate law of the form $N_{CH_4} = Ae^{-E_m/RT}P_{H_2}^{x}P_{CO}^{y}$. These data were obtained at low conversions to minimize or eliminate heat and mass transfer problems thereby providing accurate kinetic data without the difficulties encountered at high conversions.

A correlation has been found between the specific activity of these transition metals in the synthesis reaction and the strength of the adsorbed CO–metal bond, determined by heats of adsorption. This correlation provides a linear relationship between one of the catalytic properties of a metal and a physically measurable parameter of that metal. The activity is highest when the strength of the CO–metal bond is lowest. An opposite trend exists when rates are compared to the heats of adsorption for H_2. The presence of a pronounced compensation effect can also be attributed to these variations in chemisorption properties.

Kinetic modeling of the methanation reaction has shown that two sequences of elementary steps accurately describe the experimental data and are also consistent with data in the open literature. One model assumes a uniform surface while the other takes into account nonuniformity of the metal surface. Either model gives a consistent picture of the methanation reaction over all the Group VIII metals and results in the appearance of a similar trend—the greater the metal's capability to produce higher molecular weight species, the larger the number of H atoms interacting in the slow step on the catalyst surface. This provides another example where the use of simple assumptions, such as surface uniformity, can provide a kinetic model as useful as one incorporating more complicated assumptions such as surface nonuniformity.

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