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TRANSIENT KINETIC STUDY OF NICKEL-CATALYZED METHANATION: FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
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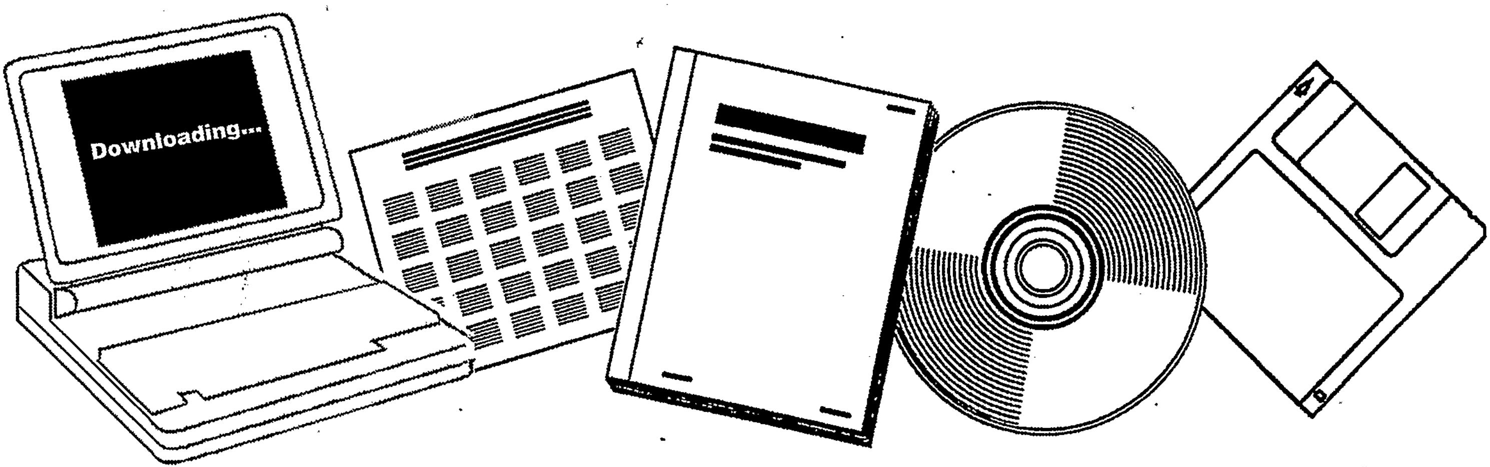

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Final Report

A TRANSIENT KINETIC STUDY OF NICKEL-CATALYZED METHANATION

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by

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ABSTRACT

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The results of this study are in two major parts. In the first part of the study the use of steady-state isotopic transients of multiple elements (C, H, and O) under actual methanation reaction conditions has permitted an assessment of the reactivity of water on a Ni powder catalyst. It was concluded based on the addition of isotopic water that oxygen, once reacted to form water, is able to readsorb even where the surface coverage of CO remains high. At the low relative partial pressures of water ($H_2O/CO < 12$, $P_{H_2O} < 0.7$ kPa) used, however, there was no effect of added water on the formation of methane. The surface residence time of water determined from isotopic transients contains the residence time on the surface during the primary formation reaction as well as the time spent during readsorption(s).

The second part of the study addressed how a catalyst modifier (in this case Cl) affects methanation in CO hydrogenation using steady-state isotopic transient kinetic analysis (SSITKA) of methanation. The results obtained using silica-supported Ru suggest that structural rearrangements induced by the presence of chlorine, rather than selective site blocking or electronic interactions, may be the primary mechanism of

chlorine modification of the catalytic properties of supported metals for CO hydrogenation. SSITKA indicated that the decrease in methanation activity with increasing initial Cl concentration was a function of a decrease in the number of reactive surface intermediates (or sites) and not of a change in site activity.

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PART I

GENERAL INTRODUCTION

The objective of this research was to determine how isotopic transient kinetic methods could be used to illuminate (i) the elementary pathways in methanation over metal catalysts and (ii) how reaction intermediates in methane synthesis can be manipulated. The first objective is the topic of Part II of this report. Carbon, hydrogen, and oxygen trajectories were traced during nickel-catalyzed methanation to obtain information about the nature of the controversial most abundant reaction intermediate (MARI). In the literature it has been offered that most likely the MARI may be governed by (i) the dissociation of CO, (ii) a hydrogen-assisted CO dissociation, or (iii) the formation of oxygenated-species. Primarily by the use of added water during reaction we were able to use SSITKA to shed additional light on this most important issue for a nickel-powder catalyst while preliminary work was also done for the cobalt and ruthenium systems. Specifically, questions addressed by the first major part of the report were:

- Is water, formed during the reaction, able to readsorb and participate in further reaction?
- Can water act to modify the active sites?
- Is CO dissociation assisted by hydrogen?
- Does CH_4 formation proceed via a CH_yO intermediate?

The second major part of the research, given in Part III of this report, addressed the modification of catalyzed methanation by chlorine doping. Thus, rather than pursuing a simple change-of-operating-conditions approach, the modification in selectivity was attempted by chemical modification of a methanation catalyst. Important questions have recently been raised about the role of trace amounts of chlorine during the hydrogenation of CO over dispersed ruthenium catalysts. A combined utilization of SSITKA of methanation and steady-state Fischer-Tropsch synthesis augmented by TEM allowed us to make major advances in elucidating chlorine's role during the ruthenium-catalyzed hydrogenation of CO.

The results given in Parts II and III have been presented/published as follows.

Presentations:

"*A Transient Kinetic Investigation of Methanation: Reaction Pathways for Oxygen,*" 6th DOE Meeting of Catalysis and Surface Chemistry, Gaithersburg, MD, Oct. 14-16, 1987 (presented by J.G. Goodwin Jr.).

"*Modification of the Catalytic Properties of Ru by Cl,*" 1987 AIChE Annual Meeting, New York, NY, Nov. 15-20, 1987 (presented by J.G. Goodwin Jr.).

"*Oxygen Reaction Trajectories During CO Hydrogenation: The Reactivity of Water on Ni,*" 9th International Congress on Catalysis, Calgary, Canada, June 26 - July 1, 1988, paper 112 (presented by J.G. Goodwin Jr.).

Publications:

"*Oxygen Reaction Trajectories During CO Hydrogenation: The Reactivity of Water on Ni,*" Proceedings 9th International Congress on Catalysis, Vol. 2 , 1988, pp. 875-882. (by Nwalor J.U., Hoost T.E., Godbole G.G., Goodwin Jr. J.G., and Biloen P.).

"The Effect of Chlorine Modification of Silica-Supported Ru on Its CO Hydrogenation Properties," accepted for publication in J. Catal. (by Iyagba E.T., Nwalor J.U., Hoost T.E., and Goodwin Jr. J.G.). [in part].

PART II

OXYGEN REACTION TRAJECTORIES DURING CO HYDROGENATION: THE REACTIVITY OF WATER ON NI

A study was made, for the first time, of the reaction trajectories of oxygen on the catalyst surface during methanation. In particular the formation of H_2O as well as its adsorption/readsorption on the catalyst surface during reaction was addressed.

INTRODUCTION

There is much controversy concerning the presence of oxygen in reaction intermediates during CO hydrogenation (1,2)*. This issue is very important to the understanding of the mechanism since oxygen may follow different trajectories depending on the catalyst and on the reaction conditions. Even if oxygen is not contained in the most abundant reaction intermediate (MARI) for methane, its history on the surface is important to fully understand since it must be removed in order to permit methanation to proceed.

One issue of great interest is the effect that water produced during CO hydrogenation may have on other surface reactions as a result of readsorption. Sughme and Bartholomew(3) studied the effect of water addition on methanation over a Ni/alumina/monolith catalyst. They found significant inhibition of methanation by water vapor for the reaction conditions of 498-573 K, P_{CO} = 7 kPa, P_{H_2} = 21 kPa, and P_{H_2O} = 4-69 kPa. At the highest reaction temperature there was as much as a 70 % decrease in the rate of methane formation. In addition, for a partial pressure of water of 69 kPa, there was an irreversible loss of catalyst activity at 498 K. In a later study, Erekson and Bartholomew(4) also found an increase in deactivation of Ni for methanation by H_2S as a result of added water vapor, confirming this combined effect on deactivation previously reported by Dalla Betta *et al.*(5,6). Since all the results to date are based on an analysis of only modifications in the rate of methane formation, how water acts to modify CO hydrogenation and under what conditions this occurs has not been previously

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*Parenthetical references placed superior to the line of text refer to the bibliography.

determined. These are all important issues since the partial pressure of water vapor in a methanation or Fischer-Tropsch reactor can go from zero at the entrance to as much as 50 % of the total partial pressure at the exit.

This study reports the results of an examination of CO hydrogenation over Ni powder which addressed the issue of water reactivity under methanation conditions using steady- state isotopic transient kinetic methods (7,8,9,10,11). This technique makes use of switches between isotopically labeled reactants or products during reaction without changing the partial pressures of reactants or disturbing steady-state reaction. This permits one to determine both the residence time (τ) and the abundance (N) of labeled reactant atoms on the catalyst surface under steady-state reaction conditions in addition to the standard measurements of overall rate of reaction and reaction selectivity. In this study, the transients for carbon and hydrogen as well as the ones for oxygen (in CO) were measured. To study the further reactivity of water once formed, isotopically labeled water was added to the reactant stream in amounts comparable to that produced under reaction, and steady-state isotopic transients were recorded.

EXPERIMENTAL

The nickel powder catalyst was reduced under flowing hydrogen for 12 hours at 673 K. Following such a pretreatment, the catalyst was found to have a surface area of 5.6 m^2/g as determined by hydrogen TPD and by H_2/D_2 transient adsorption at 623 K(12).

Steady-state isotopic kinetic transients were carried out during methanation over this Ni powder catalyst using a tubular copper reactor (6.35mm OD and 4.5 mm ID) operated at differential conversion conditions in order to minimize heat and mass transfer effects. The reaction conditions were 211 kPa total pressure, 473-573 K, P_{H_2} = 82-118 kPa, P_{CO} = 4.9-31 kPa, and P_{H_2O} = 0-0.7 kPa. A space velocity of approximately 20,000 hr^{-1} was used. In addition to the transients for carbon and hydrogen, that for oxygen was also employed. Isotopically labeled water in the form of both $H_2{}^{18}O$ and D_2O was added to the reactant stream using saturation of an inert stream.

The following isotopic switches were used in both directions:

$$[{}^{12}C^{16}O + Ar_{trace}] + H_2 + He \,//\, [90\%\ {}^{13}CO^{16}O + 10\%\ {}^{13}C^{18}O] + H_2 + He \tag{1}$$

$$^{12}CO + [H_2 + Ar] \,//\, {}^{12}CO + [D_2 + He] \tag{2}$$

$$H_2{}^{16}O + [{}^{12}CO + Ar_{trace}] + H_2 + He \,//\, H_2{}^{16}O + [{}^{13}CO] + H_2 + He \tag{3}$$

$$[H_2{}^{18}O + Ar] + {}^{12}CO + H_2 \,//\, [D_2{}^{16}O + He] + {}^{12}CO + H_2 \tag{4a}$$

$$[H_2{}^{18}O + Ar] + {}^{12}CO + H_2 \,//\, [H_2{}^{16}O + He] + {}^{12}CO + H_2 \tag{4b}$$

$$[H_2{}^{18}O + Ar] + H_2 \,//\, [H_2{}^{16}O + He] + H_2 \tag{5}$$

RESULTS

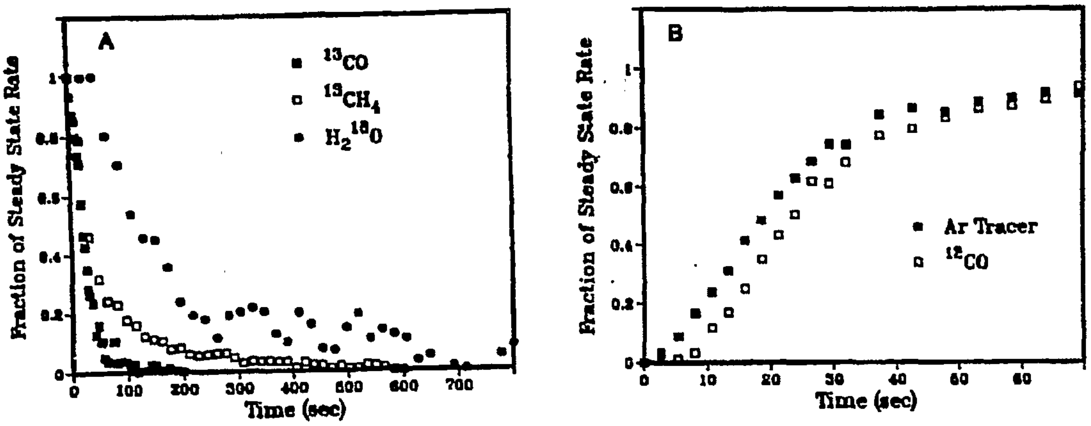

Figure 1. Steady-state isotopic transients taken under methanation conditions T = 493 K, P_T = 211 kPa, P_{CO} = 4.9 kPa, H_2/CO = 24, isotopic switch 1.

Figure 1 shows the results from a typical $^{13}CO//^{12}CO$ transient taken during methanation. Figure 1b shows the transient for the inert marker Ar which allows us to account for gas phase hold-up. The transient for ^{12}CO is seen to lag behind due to its absorption on the catalyst surface. Figure 1a shows the transient for ^{13}CO (the mirror image of that for ^{12}CO), CH_4, and H_2O due to the switch from ^{13}CO. The transient of H_2O is noisier than that of CH_4 due to the fact that only 10 % of the ^{13}CO was labeled with ^{18}O. From the transients of $^{13}CH_4$ and $H_2{}^{18}O$ produced during CO hydrogenation, it was observed that the residence time τ (and hence the size of the precursor adsorbed species reservoir) of H_2O was always greater than that of CH_4. The residence times and surface abundances of adsorbed CO and H_2O- and CH_4-intermediates are given in Table 1 for reaction at CO partial pressures of 27.2 kPa and of 4.9 kPa (the latter of whose transients are shown in Figure 1).

Table 1. Concentration and kinetic parameters for adsorbed species during methanation†.

Species	τ_i [sec]	N_i [μmol/$g_{cat.}$]
[A] $P_{CO} = 2.75$ kPa, $H_2/CO = 3$, $TOF = 0.029$ μmol/$g_{cat.}$		
CO	1.8	21
CH_4	89	2.6
H_2O	211	6.2
[B] $P_{CO} = 4.9$ kPa, $H_2/CO = 24$, $TOF = 0.031$ μmol/$g_{cat.}$		
CO	6.7	13.1
CH_4	39	1.2
H_2O	173	5.2

†$P_T = 211$ kPa, $T = 493$ K, switch 1.

As can be seen in Table 1, the effect of reducing the partial pressure of CO by a factor of 5.5 was to reduce by approximately half the surface abundance of adsorbed CO and of the precursors to CH_4. There was little effect on the amount of water precursors adsorbed on the surface.

An investigation of the effect of added water was made over a range of reaction conditions. Figure 2 shows the isotopic transient for ^{18}O in the form of HDO and D_2O following switches between the reaction mixture containing $C^{16}O$ and $H_2{}^{18}O$ and that containing $C^{16}O$ and $D_2{}^{16}O$ where the partial pressure of added water was held to 0.53 kPa. These results illustrate two phenomena: the adsorption of the oxygen of gas phase water in significant quantities and the rapid exchange of the hydrogen atoms of these water molecules with others on the catalyst surface. Little of the deuterium entering the reactor in water exited as HD and none as D_2. However, when the partial pressure of CO was reduced to zero while maintaining the flow of H_2 and D_2O, HD formation was substantial and the conversion to HDO decreased accordingly.

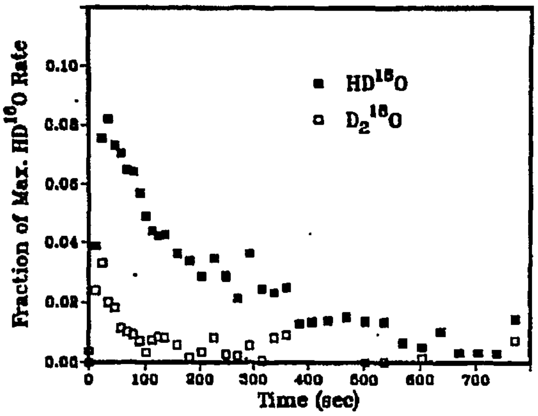

Figure 2. Transients of water containing ^{18}O and D following an isotopic switch 4a.

In order to magnify the effect of water, reaction studies were concentrated at the lower CO partial pressure of 4.9 kPa. There were two reasons for this. For one it was felt that, since CO is normally one of the most predominant surface species during reaction and competes strongly for adsorption sites, use of a low CO partial pressure would make observations of the water effects easier. Also, in the past the biggest effects of added water on reaction occurred for high H_2O/CO ratios. The second reason was an experimental one which prevented the use of high partial pressures of water due to plugging of the capillary line leading to the mass spectrometer.

Table 2 gives an indication of the trajectory of water in the reactor. In the absence of added water, the amount of water from reaction that was adsorbed was 5.2 $\mu mol/g_{cat}$. With the addition of 0.45 kPa of water vapor, however, there was a significant decrease in adsorbed water of reaction from 5.2 to 1.6 $\mu mol/g_{cat}$. The added water caused a 30 % decrease in the amount of adsorbed CO but no apparent decrease in the amount of adsorbed CH_4 precursor. It should be noted that, for stoichiometric reasons, the rate of water formation from CO is identical to the rate for CH_4 production. At the higher CO partial pressure of 27.2 kPa there was no significant effect either on the τ and coverage (N) of the CH_4 precursor or on those of adsorbed CO of adding small amounts (0.09-0.69 kPa) of water vapor in the temperature range 473-573 K.

Table 2. Effect of (re)adsorbed water on surface coverages.†

$P_{H_2O,added}$	N_{CO}	N_{CH_4}	$N_{H_2O,rxn}$	$N_{H_2O,added}$	N_{Total}	θ_{Total}
[kPa]	--------	--------	[μmol/$g_{cat.}$]	--------	--------	
0	13.1	1.2	5.2	0	19.5	0.21
0.45	9.2	1.3	1.6	12.9	25.0	0.27

† Reaction conditions: $P_T = 211$ kPa, $P_{CO} = 4.9$ kPa, $T = 493$ K.
Switch types: 1, 3, 4b.

DISCUSSION

The effect on reaction of decreasing the partial pressure of CO was an increase in the rate of methanation, as expected given the negative exponent for CO in the power law rate expression. There was also a decrease in the amount of adsorbed CO reflecting less than total saturation of the surface at the lower CO pressure.

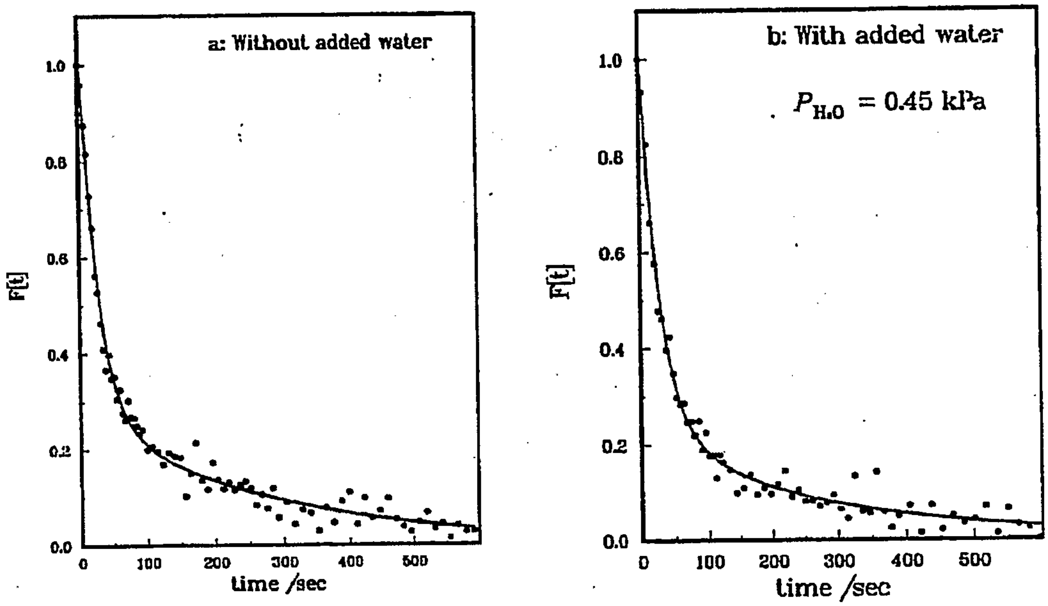

Figure 3. Methane transient profiles: effect of added water. $T = 493$ K, $P_{H_2,CO,He} = 117.6, 4.9, 88.5$ kPa.

Based on the results of the experiments with added water vapor, it can be concluded that water of reaction or added water is able to (re)adsorb at methanation conditions. This is true for even relatively high partial pressures of CO and relatively

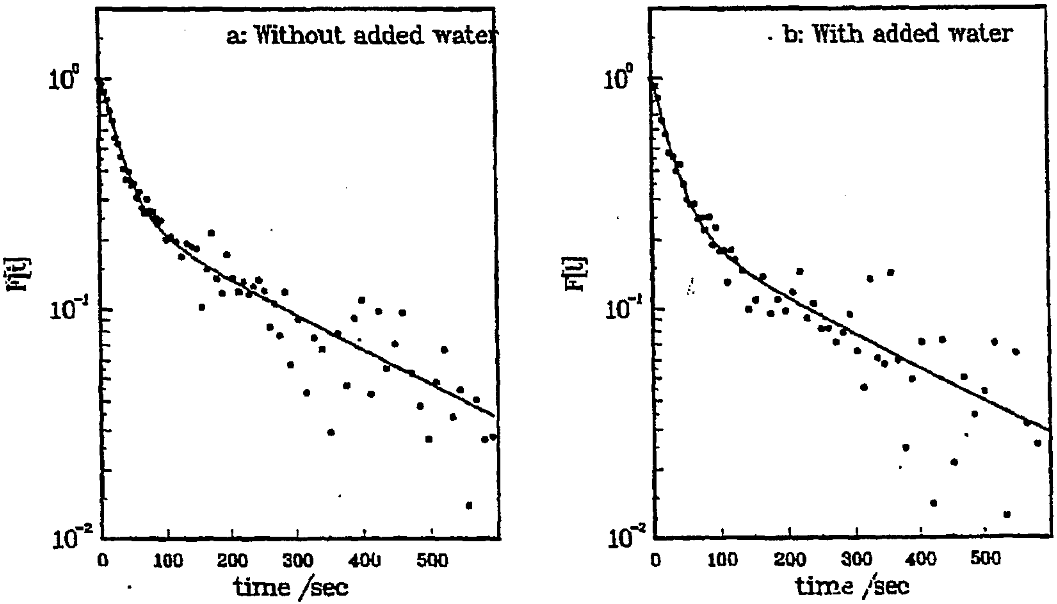

Figure 4. Semilog curves of the CH_4 transients.

low ones of water vapor. While water in the gas phase at the level $H_2O/CO = 0.03 - 0.75$ appears to have some effect on the adsorption of CO at low partial pressures, it has no effect on the residence time and surface concentration of CH_4 precursor. There was, consequently, no effect of water on the rate of CO conversion for these conditions. A subsequent analysis of the methane transients looked into the possibility that water might influence the heterogeneity of the methane reaction sites, even though it did not affect the average reactivity to methane. In the analysis Figures 3a and 3b are first redrawn as a semilogarithmic plots (Figures 4a and 4b) which by their convexity to the origin reveal the heterogeneous nature of the methanation sites for reaction without and with added water, respectively. Using the method of de Pontes *et al.* the isotopic transients are transformed into *a priori* reactivity distributions for active methanation sites (Figures 5a

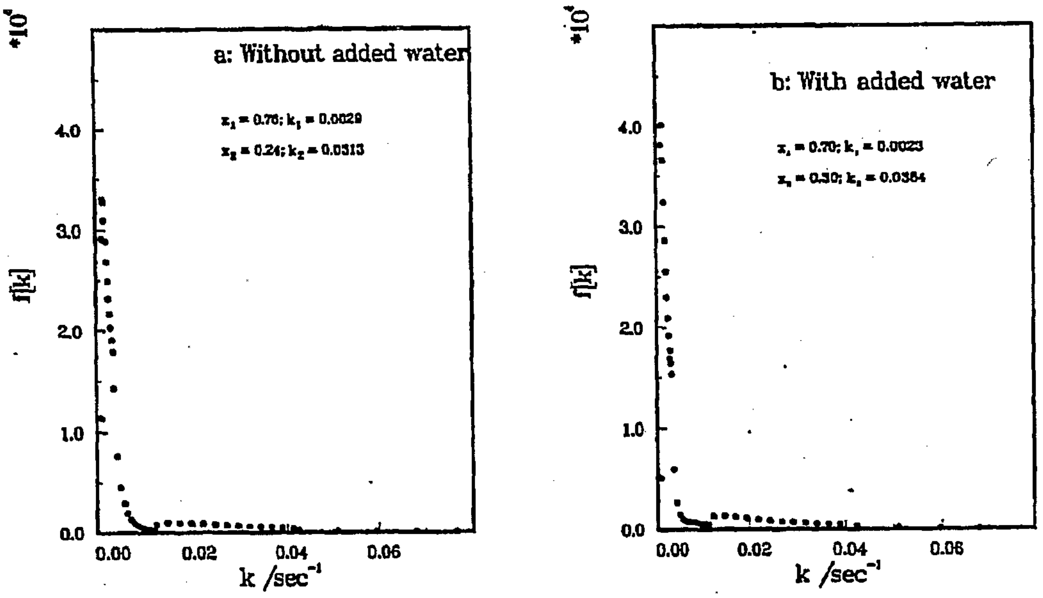

Figure 5. Reactivity distribution functions for the active sites.

and 5b). From these the relative contributions of the reaction sites to the reaction rate have been determined (Figures 6a and 6b). The distributions confirm that there is no significant effect of water on the CH_x intermediates because of changes in the heterogeneity of active sites. Comparing these results to those in the literature(3), it can be concluded that, in order to affect methanation either reversibly or irreversibly, it is necessary for the relative concentration of H_2O to be much greater than that used here.

Results from the various measurements listed above indicate that the residence time on the surface for the water product is always greater than that for methane (as determined also in a preliminary study of Ni/SiO_2, Ru/SiO_2, and Co powder). Consequently, the reservoir of surface intermediates for water formation exceeds that for methane formation. The question can be raised as to whether this is reflective of the

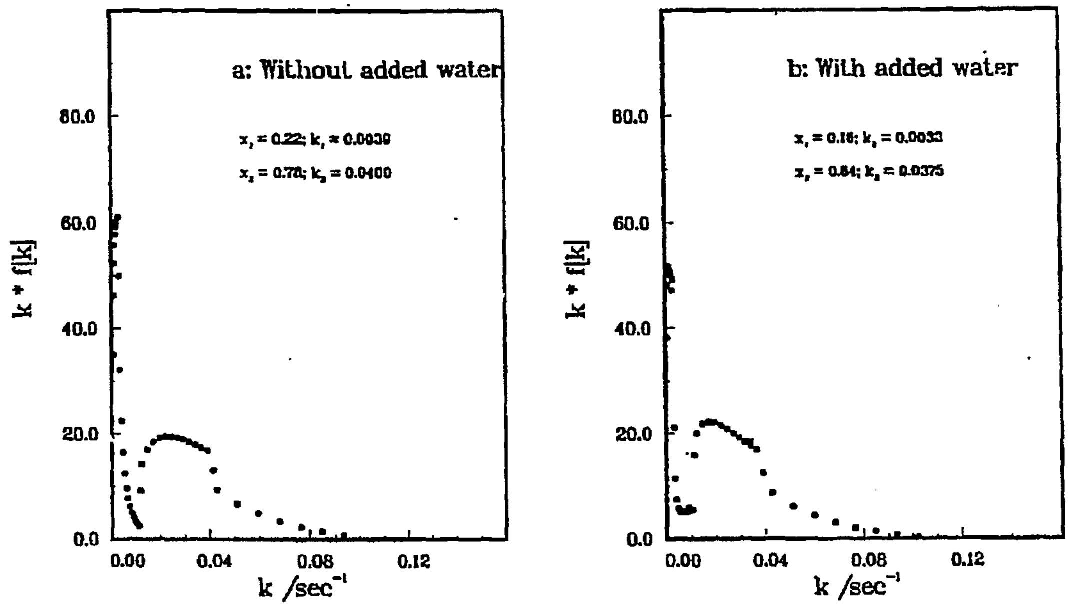

Figure 6. Relative contributions of the active sites to the reaction rate.

slowest step in the formation reaction. Part of the answer to this question is apparent from Figure 7. This figure shows that the surface residence time for added water decreases as the concentration of water vapor in the gas phase increases. This result can be easily explained. The probability for readsorption of a molecule which adsorbs and desorbs is determined by the competition for available sites. Thus, as the concentration of water in the gas phase increases, the probability for one or more readsorptions of a given water molecule (and more specifically for the labeled oxygen atom of that molecule) decreases. Hence, the average surface residence time measured for the adsorbing water molecules decreases. This same effect of the partial pressure of water is also seen for the surface residence time of the water from reaction. Thus, for the experiments whose surface concentrations are given in Table 2, $\tau_{H_2O,rxn}$ decreases from

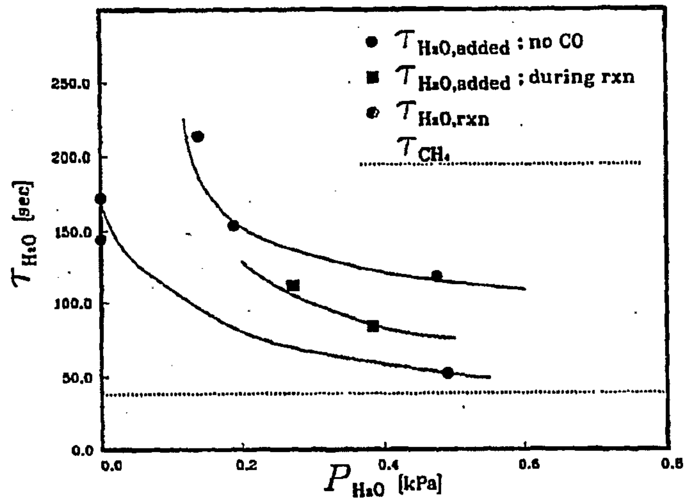

Figure 7. Effect of the P_{H_2O} on the residence time of water at 493 K and P_{CO} = 0-4.9 kPa.

173 to 52 sec as the partial pressure of added water vapor increased from 0 to 0.45 kPa. The larger reservoir of water intermediates (*cf.* N_{CH_x}) on the catalyst surface seen during normal methanation without added water seems to be tied up primarily to readsorption of water on the support and a chromatographic effect. The surface residence time and reservoir size of the water and methane intermediates appear to be catalyst specific with the silica-supported Ru and Co exhibiting the largest of these differences between these properties of methane and those of water. All of this difference is not just due to the presence of the silica support since silica-supported Ni exhibits properties similar to those of Ni powder.

The observed oxygen trajectories during methanation over the catalyst have been

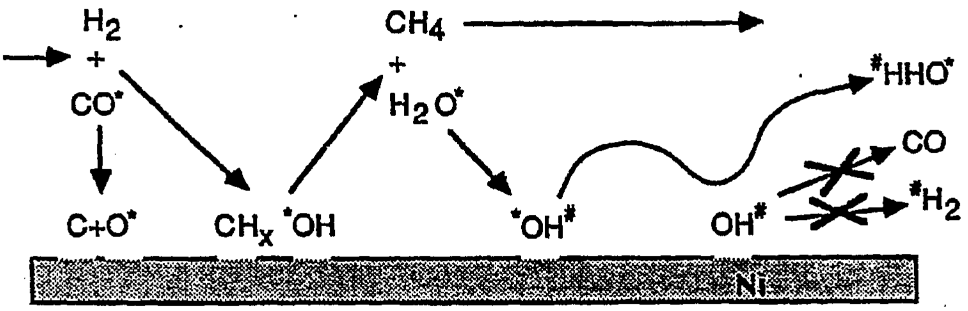

Figure 8. Oxygen trajectories during methanation over Ni powder.

summarized in Figure 8. Based on the results of the experiments carried out by adding water to the gas phase and switching between various isotopes ($H_2{}^{16}O$, $H_2{}^{18}O$, and $D_2{}^{16}O$) it was concluded that the hydrogen atoms of the water molecules can readily exchange with hydrogen atoms on the Ni surface. These atoms then re-enter the effluent stream primarily as hydrogen atoms in water molecules but hardly as recombined hydrogen molecules except in the absence of CO. Based on the results from the experiments using $C^{16}O$ and added $H_2{}^{18}O$, there was no evidence to indicate that the oxygen of water could recombine with carbon. Thus, for these reaction conditions, the formation of water from CO and hydrogen was an irreversible reaction --at least for oxygen.

As the above discussion has indicated, when discussing the reaction parameters for a readsorbing product like water, it is necessary to consider the τ measured to be a combination of a τ due to primary reaction and a τ due to readsorption, *i.e.*,

$$\tau_{\text{meas.}} = \tau_{\text{rxn}} + \tau_{\text{reads.}}$$

The results of this study suggest that, as well as decreasing the catalyst bed length, the addition of these product molecules to the reactants in various amounts may permit the absolute τ_{rxn} to be approached asymptotically using labeling of the reaction product, provided the addition of the molecules do not affect the primary reaction. For the investigation of the formation of water during methanation at these conditions this appears to be possible.

CONCLUSIONS

The steady-state isotopic transient technique has been used to investigate the adsorptive and reactive properties of water during methanation over a Ni powder catalyst. It can be concluded that water molecules readily adsorb/desorb on Ni surfaces under methanation conditions. This adsorption or readsorption phenomenon does not appear to be strongly dependent upon the partial pressure of CO in the range 4.9-31 kPa. The hydrogen atoms of the water molecules were able to rapidly exchange with hydrogen atoms on the catalyst surface. There was no evidence however, for reaction of the oxygen in the adsorbed water with carbon or for any effect of adsorbed water on methane formation for low relative partial pressures of water vapor ($P_{H_2O} < 0.75$ kPa) and in the temperature range 473-573 K. Any mechanistic evaluation of oxygen trajectories during methanation must account for the readsorption process of product water.

PART III

EFFECT OF CHLORINE MODIFICATION ON RU-CATALYZED METHANATION

An investigation of the issue of chemical modification of reaction intermediates during methanation over well-dispersed catalysts has been carried out for chlorine-doped Ru/SiO_2 catalysts(13) to address the still unclear role of chlorine and chlorine precursors in these catalytic systems. What follows will answer some important questions about the role of Cl, as a modifier, on catalysts under reaction conditions.

INTRODUCTION

Catalyst modifiers, both poisons as well as chemical promoters, are known to greatly influence catalyst activity and selectivity(14,15). The mechanisms by which the poisons/promoters modify the catalytic properties of metals are far from completely understood. Suggested mechanisms include geometric site blocking of active sites by the adatoms (16,17,18), metal-modifier electronic interactions leading to changes in the strength of metal-adsorbate bonds (19,20,21), and direct chemical interactions between the modifier and adsorbed molecules (22). The use of all sorts of catalyst additives will greatly increase in the design and synthesis of new industrial heterogeneous catalysts as we strive to improve catalyst activities and selectivities.

Cl, S, and P are all well-known poisons for hydrogen and CO adsorption(23) and CO hydrogenation(24) on group VIII transition metals. The magnitude of their effect appears to be correlated to their electronegativity (Cl > S > P). Among these three modifiers, Cl was found to be somewhat unique in that Kiskinova and Goodman(23) did not observe an effect of Cl on methanation on a Ni(100) surface, supposedly due to its removal as HCl in the initial stages of the reaction. However preliminary results in our laboratory on CO hydrogenation over Cl-doped supported Ru indicated significant effects of Cl on the catalytic properties.

Recently, CO and H_2 chemisorption studies have been carried out on Cl-predosed supported ruthenium catalysts(25,26,27,28,29). While Narita *et al.*(25,26) attributed the inhibition of CO and H_2 adsorption in the presence of Cl to site blockage only, Lu and Taterchuk(28,29) suggested that, in addition to a blockage of sites, there was an electronic activation of certain other sites. Thus modifications in adsorptive and catalytic properties by Cl have primarily been interpreted to be due to blockage/electronic effects of the adatom. However, most studies of the effect of modifiers on supported metal catalysts have been concerned with overall effects on the catalytic properties.

The objective of this study was to investigate Cl modification of the CO hydrogenation properties of supported Ru and to delineate the mechanism of modification. This is especially important to understand since $RuCl_3$ is one of the common salts used in the preparation of supported Ru catalysts. In addition, this modifier is almost always present as an impurity in many other Ru salts due to their method of preparation. In particular, it is important to fully appreciate any effects that trace levels may have on the ultimate catalytic properties. Steady-state isotopic transient kinetic analysis (SSITKA) was utilized to provide greater insight into the mechanism of modification since it can differentiate between reaction site blockage and site modification.

EXPERIMENTAL

1 Catalyst Preparation and Characterization

The base catalyst was prepared by adding a solution of $Ru(NO)(NO_3)_3$ obtained from Alfa products to Cab-O-Sil silica (Grade L90, 90 m^2/g) to incipient wetness, drying at 110 °C for 12 hours, reducing at 550 °C for 16 hours, and washing the reduced catalyst with hot water to remove residual Cl from Ru catalysts(27). Several levels of Cl-doped catalysts were obtained by impregnating portions of the base catalyst with appropriate concentrations of dilute HCl to incipient wetness, drying it at 40 °C for 24 hours, and then reducing it at 400 °C for 16 hours. Sequential addition of Cl to the reduced catalyst was carried out to minimize particle size variations as much as possible.

Atomic absorption was used to determine the actual metal loading of all catalysts while the actual quantities of Cl retained on the modified catalysts, before and after reaction, were measured at Galbraith Laboratories. Average metal particle sizes and particle size distributions for these catalysts were determined by H_2 chemisorption and TEM measurements, respectively. Adsorption uptakes under reaction conditions were obtained from steady-state isotopic transient kinetic analysis (SSITKA) of methanation.

The nomenclature used for catalyst identification is as follows. The original catalyst having been prepared using Cab-O-Sil silica is designated "3C." Catalyst "3C" after a hot water wash becomes the base catalyst which is designated "3CWW." The Cl-doped catalysts are named "3CWWx.xx," x.xx being the nominal ratio of Cl atoms added to the total number of ruthenium atoms. AA analysis showed that the active metal loading of the base catalyst was 2.71 wt % and remained the same after further treatments.

2 Reaction Studies

Methanation was carried out in a differential tubular reactor utilizing a very high space velocity (*circa* 126,000 hr^{-1}) to keep conversion low and, thereby minimize heat and mass transfer effects. With the surface reaction maintained at steady state, isotopic transients were generated by switching the inlet gas from $^{12}CO/H_2$ to $^{13}CO/H_2$ at 190 kPa total pressure and 200 °C. Argon was used as a marker in the ^{12}CO to determine gas phase hold-up. A H_2/CO ratio of 10 was maintained, thereby forcing the reaction to methanation in order to simplify product analysis. On-line mass spectrometry was used with continuous sampling at the reactor outlet and data acquisition was accomplished using an Apple microcomputer equipped with a Cyborg Isaac interface. In conjunction with MS analysis, gas chromatography was used to analyze the steady-state reactor effluent.

RESULTS AND DISCUSSION

1 Chlorine content

Table 3. Characteristics of the Ru/SiO_2 catalysts.

Catalyst	Ru wt %	Cl wt %	Cl/Ru nominal	Cl/Ru actual
SiO_2	0	0.0093	--	--
3C	2.71	0.07	0	0.074
3CWW	2.71	0.011	0	0.012
3CWW0.01	2.71	0.028	0.01	0.029
3CWW0.30	2.71	0.071	0.3	0.075
3CWW1.00	2.71	0.087	1.0	0.091

A comparison of the actual and nominal Cl/Ru ratios is given in Table 3. The results for catalyst 3C as prepared indicate that the chlorine level was close to that of saturation (see Figure 9) even though the catalyst was prepared from research grade ruthenium nitrosyl nitrate. The amount of Cl retained on the modified catalysts increased sharply at low levels of dosage and leveled off around a nominal ratio of 0.3 (Figure 9). Beyond the saturation limit, the excess Cl was probably driven off as HCl during the rereduction. In fact, loss of Cl at high temperatures of reduction(25,26) was a major concern, which is why the catalysts after Cl doping were reduced at 400 °C, instead of at the initial reduction temperature of 550 °C.

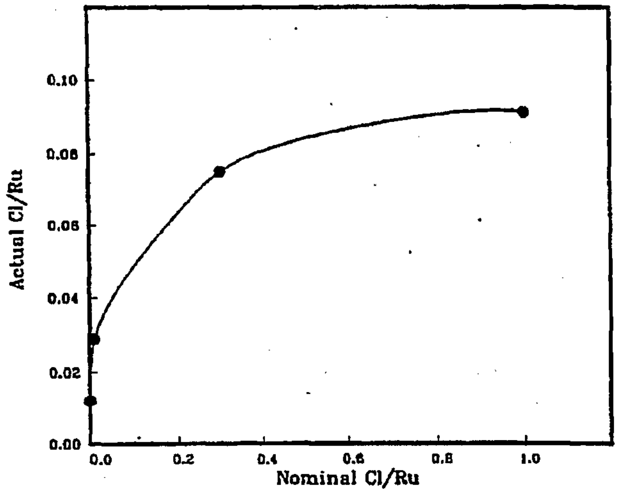

Figure 9. Chlorine retention by 3 wt % Ru/SiO_2.

2 Dispersion

The average Ru particle size and dispersion for the catalysts were estimated from coverages of CO and CH_x intermediates obtained during methanation utilizing SSITKA as well as from TEM and are given in Table 4. The particle size distributions are presented in Table 4. Clearly there is no indication of a significant particle size variation between the base catalyst and the Cl-doped catalysts after rereduction.

Table 4. Average particle size and distribution of Ru crystallites.

Catalyst	Percent of total number of particles (by TEM) in diameter range [in Å]							$\hat{d}_p^{TEM}$	$\hat{d}_p^{SSITKA}$
	15-25	25-35	35-45	45-55	55-65	65-75	75-85 Å	[Å]	[Å]
3CWW	71	16	11	0	0	1	0	25	24
3CWW0.01	60	27	7	4	2	1	1	27	--
3CWW0.30	62	24	7	3	2	1	1	27	--
3CWW1.00	57	16	16	3	4	1	3	29	--

3 SSITKA of Methanation

To get an insight into the effects of Cl modification, SSITKA of methanation was used for the catalysts with varying Cl levels. Steady-state isotopic transients were obtained by switching between ^{12}CO and ^{13}CO over the base catalyst and the chlorine-doped catalysts during methanation. SSITKA enabled the deconvolution of the reaction rate into contributions due to coverage of the reaction intermediates *versus* contributions due to the reactivity of those intermediates. The essential features of the technique have been described elsewhere(30,9,12).

Table 5. Effect of chlorine modification during methanation†.

Cl/Ru	τ_{CO} [sec]	N_{CO} [μmol/$g_{cat.}$].	τ_{CH_x} [sec]	N_{CH_x} [μmol/$g_{cat.}$]	*TOF* [μmol/s $g_{cat.}$]
0	3.5±0.6	101±17.3	8.4±0.6	3.4±0.25	0.41
0.01	3.2	91	11.1	2.9	0.26
1.00	3.2	85	8.9	1.4	0.16

† $T_{rxn} = 200$ °C, $P_{rxn} = 190$ kPa, $H_2 / CO / He = 20/2/78$ ml/min.

In methanation chlorine plays the role of inhibitor and acts to decrease the concentration of CH_x surface intermediates without significantly influencing the CO coverage 5. Figure 10 shows how the fractional coverage of the CH_4 precursors deviates from pure geometric surface blockage, implying preferential site blockage or ensemble effects of chlorine. Percent surface exposed Ru was calculated based on the original amount of Cl present and an assumption of one Ru surface atom blocked per Cl atom. Deviation of the fractional CO coverage from simple site blockage was less than for the CH_x intermediates possibly due to the fact that CO may form a more stable surface species (Figure 10). A *post-mortem* elemental analysis of these chlorinated catalysts used in a concurrent Fischer-Tropsch reaction study$^{(13)}$ showed that most of the chlorine had been removed, possibly by reaction products. Even so, the chlorine's effect could still be observed long after its removal, suggesting that the modification must have been structural (*nota bene*, TEM evidence excluded sintering).

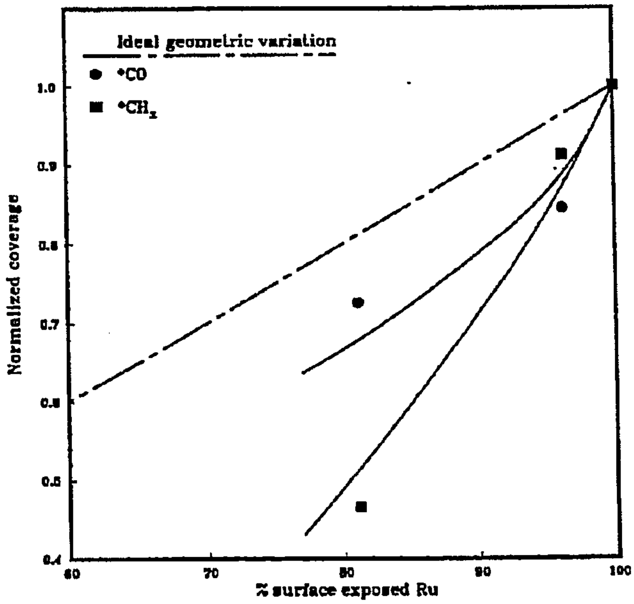

Figure 10. Deviations from ideal coverage for CO and CH_x during methanation.

4 Structural Modifications

Recently, there have been indications that certain elements (Cl, S) can bring about significant rearrangement of Ag, Cu(31,32,33) and Pt(34) surfaces. How this may occur has been discussed by Marks and Heine(34). Though electronic in origin, the resultant geometric changes can have dramatic influences on the catalytic properties of these metals, particularly for structure-sensitive reactions such as alkane hydrogenolysis and ammonia synthesis. Supported metal crystallites should be even more susceptible to structural rearrangement due to their high surface free energy, their innate surface heterogeneity when highly dispersed, and the possible greater ease of interaction between the modifier and low coordinated metal surface atoms. Although site blockage is believed to be the primary mechanism of sulfur poisoning, some investigators have speculated that at high coverages, surface reconstruction induced by the presence of sulfur becomes an increasingly important factor in effecting changes in catalytic activity on metal catalysts(35). Considering how the catalysts were prepared, it is most likely that some bulk oxidation of the reduced metal occurred in the base catalyst during the washing and drying steps before Cl doping. Ru metal has a hexagonal close-packed structure, with a nearest-neighbor metal atom distance of 2.7 Å, whereas RuO_2 is tetragonal. During rereduction of the catalysts, oxygen would be released with an attendant structural transformation to the more symmetric HCP structure of Ru. It is possible that modifiers such as Cl, may be able to induce new metal structures during the oxidation-reduction cycles, possibly by stabilizing them. Thus, metal structures may have varied somewhat for these catalysts compared to the base Ru catalysts due to preparation effects induced by the presence of Cl even though the particle size did not change significantly. The methanation results in conjunction with the concurrent Fischer-Tropsch study(13) clearly show that the added Cl modified the catalysts. In considering the possible mechanisms of modification, site blockage and electronic effects were ruled out as the primary mechanisms, the main evidence being the rapid removal of the added Cl and the fact that the intrinsic *TOF* for methanation ($1/\tau$) of the catalysts did not change with Cl-doping. In addition, an effect due to rapid carbon deposition during the initial stages of reaction --while Cl was present-- was also ruled out based on CO adsorption as well as on similar results seen in NH_3 synthesis(35). TEM results show that the average particle size of the Ru crystallites did not change with Cl-doping, ruling out loss of the active surface area due to sintering as being responsible. Since all of the Cl-modified catalysts were prepared from the same batch of reduced Ru/silica and were rereduced under the same conditions (thereby minimizing particle size variation as evidenced by TEM), structural modification of the metal crystallites induced by the presence of Cl is suggested to be the predominant mechanism by which Cl modifies the catalytic properties of Ru for CO hydrogenation. Why Cl doping affected CO hydrogenation on supported Ru but did not affect it on single crystal Ni(24) may be due either to the fact that the surfaces of small crystallites are more susceptible to rearrangement because of their high surface free energy or to the fact that the strength of Cl modification of group VIII metals may be metal specific(27).

CONCLUSIONS

Chlorine addition to silica-supported Ru catalysts was found to increase initially the methane selectivity slightly but to reduce significantly the activity of the catalyst for CO hydrogenation for all reaction periods. For methanation, the major effect of Cl on the rate of reaction seemed to be a decrease in the active sites, as the rate per site (true *TOF*) did not seem to be greatly affected. A unique property of Cl appears to be that it brings about "permanent" changes in the catalyst even though it is present on the catalyst surface only for a short period of time after the reaction is initiated.

Structural rearrangements induced by the presence of Cl, rather than selective site blocking or electronic interactions, are suggested to be the primary mechanism of Ru modification by Cl. The results imply that stabilization of certain metal surface structures may be an important element in how modifier species change catalyst properties.

PART IV

SUMMARY

In the first major part of the study, a combination of C, H, and O tracings using SSITKA during nickel-catalyzed methanation has permitted an assessment of the reactivity of water. We were able to conclude that

- water molecules readily adsorb/desorb on Ni during methanation; *i.e.*, $\tau_{meas.} = \tau_{formation} + \tau_{re\text{-}ads.}$.
- At low P_{H_2O} (< 0.5 kPa), added H_2O has little/no effect on the active methanation sites but competes for H_2O adsorption sites.
- Hydrogens of adsorbed H_2O readily exchange but do not recombine to form H_2 except in the absence of CO.
- Oxygen of H_2O does not react with *C.
- At very high P_{H_2O}, H_2O probably can
    - compete with CO for adsorption on the active sites,
    - cause restructuring of the metal surface.

Furthermore, based on addition of small amounts of oxygen during methanation, it was concluded that on Ni powder CO_2 is not formed from CO + H_2 but is readily formed from the reaction of added oxygen with *C and/or *CO. This suggests that either "free" *O may not exist as a result of *CO dissociation implying either hydrogen-assisted CO or the formation of CH_yO; or CO_2 is formed from *CO + *O but on Ni under methanation conditions active sites for CO dissociation are mainly covered by *CH_x.

The second major part of the study focused on the ramifications of chlorine addition to a supported ruthenium catalyst as a means of modulating methanation. One of the most important observations was that while chlorine is effectively leached out of the catalyst during the initial reaction period --possibly by water formed during the hydrogenation of CO-- its effect in modifying activity remained. From SSITKA parameters it was established that chlorine did effect changes in the catalyst before its departure. These modifications are suggested to be structural; however, the possibility of sintering has been excluded. Such structural rearrangements by chlorine did not influence the reactivity of the active sites, rather they reduced the abundancy of active surface intermediates of methane.

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