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METHANE SUPPRESSION IN THE FISCHER-TROPSCH SYNTHESIS: FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING

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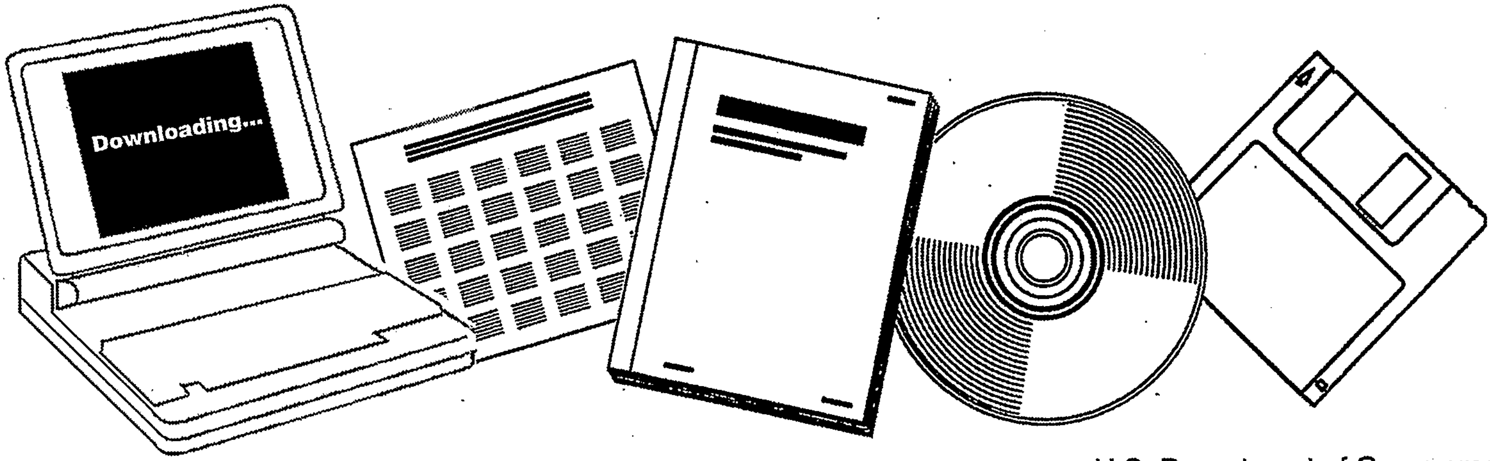

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FINAL REPORT

METHANE SUPPRESSION IN THE FISCHER-TROPSCH SYNTHESIS

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by

Elijah T. Iyagba
John U. Nwalor
Tjenga E. Hoost
James G. Goodwin, Jr.

Department of Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261

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ABSTRACT

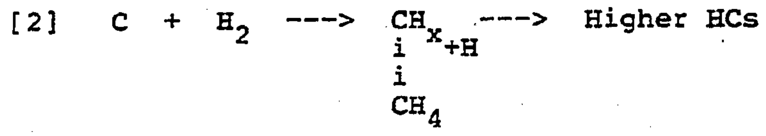
The objective of the project was to investigate the possibility of modifying methane formation during the F-T synthesis independent from other hydrocarbons by systematically changing catalyst characteristics. It would seem that the best way to decrease methane selectivity is still via the use of catalyst modifiers. In order to "tailor-make" catalyst surfaces which minimize "extraneous" methane synthesis without disrupting F-T synthesis, it is necessary for us to fully understand the mechanism(s) by which such modifiers operate. An investigation of Fischer-Tropsch synthesis on K- and Cl-modified Ru catalysts was carried out. The steady-state reaction results illustrate how chlorine enhances the selectivity of methane formation while potassium decreases it. In order to better understand methane selectivity changes, a detailed study of Cl-modification of Ru catalysts was made. Ammonia synthesis and methanation reaction results on the same series of catalysts (obtained by using the steady-state isotopic transient technique) in addition to the deactivation results for F-T 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 supported ruthenium catalysts. The results of this study indicate that catalyst modifiers may act to change the catalytic properties by inducing certain metal surface structures. This is a mechanism of modification which has, as yet, not been addressed in detail.

I. OBJECTIVES AND SCOPE OF WORK

For the Fischer-Tropsch process to be economically attractive, increased selectivities towards the formation of higher hydrocarbons at the expense of methane production is desired. It has been noted in the past that the amount of CH_4 production can vary significantly around that predicted by Anderson-Schulz-Flory kinetics [1] and a few studies aimed at selective CH_4 suppression have been carried out [2,3]. Other studies have focussed on the effect of promoters (alkali, vanadium, manganese, chromia, etc.), poisons, and supports on product distribution [4-9].

Recent results by Biloen and co-workers [10] suggest the existence of two pools of surface carbons leading to CH_4 via two distinct pathways:

$$[1]\quad C + H_2 \longrightarrow CH_4$$



$$[2]\quad C + H_2 \longrightarrow \begin{array}{l} CH_x \longrightarrow \text{Higher HCs} \\ \big\downarrow {\scriptstyle +H} \\ CH_4 \end{array}$$

The existence of two such reactive pools of CH_4 precursors, "extraneous" (eqn [1]) and "intrinsic" (eqn [2]), and consequently two reaction pathways to total methane production suggests possibilities for using catalyst modifiers, such as promoters, poisons, etc., to change the relative contributions from these two pools of intermediates.

The addition of alkali species are well known to diminish the selectivity in the F-T synthesis to methane while the addition of electronegative elements such as chlorine are known to have the reverse effect. Thorough understanding of the mode of action of catalyst modifiers could greatly facilitate the design and synthesis of new industrial heterogeneous catalysts for the purpose of tailoring catalyst activities and selectivities to particular needs, such as methane suppression in the Fischer-Tropsch synthesis. Such modification may take many forms, including site restructuring, selective poisoning, electronic promotion, direct adatom influencing, etc. The focus of the project was a study of how chlorine or potassium modification of supported Ru catalysts acts to change CH_4 selectivity in F-T synthesis.

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INTRODUCTION

The success of any indirect liquefaction scheme in being a viable alternative source of fuel depends, primarily, on the extent to which higher hydrocarbon production can be enhanced at the expense of methane formation. Several studies have shown that actual methane yields obtained in the Fischer-Tropsch synthesis are, in most cases, above the values predicted by Anderson-Schulz-Flory kinetics [11], however, cases in which the methane yields are below the predicted values have also been reported [12]. Measures aimed at methane suppression have included alloying two active metals (e.g., Co,Ru), adding a base (K_2CO_3), using of amphoteric (ThO_2) or acidic (MnO_2) "promoters", exploiting metal-support interactions (TiO_2), etc. These measures have all been shown to have some effect [13-17]. However, a question that has remained to be answered is whether there exists a fundamental limit to the extent that methane formation during the F-T synthesis can be suppressed.

Mechanistic studies carried out by Biloen and co-workers [10] suggest the existence of two reactive pools of CH_4 precursors, one of which, supposedly, produces methane exclusively (the extraneous pathway), the other producing methane and higher hydrocarbons as well (the intrinsic pathway). If these pools of intermediates are indeed confirmed to exist, then any methane suppression attempts would have to be directed at changing the distribution of the surface intermediates in favor of the intrinsic pathway precursors and at "steering" these precursors away from the pathway of methane formation. The key to the success of such an undertaking is the ability to establish how intrinsic and extraneous methane production vary with reaction conditions and catalyst formulation.

Catalyst modifiers, both poisons as well as chemical promoters, are known to greatly influence catalyst activity and selectivity [18-27]. Thus, particularly relevant and crucial to this study is the understanding of the mode of action of electopositive and electronegative ad-atoms on metal surfaces. In the Fischer-Tropsch synthesis, other important factors that can have dramatic effects on activity and selectivity include reaction conditions (H_2/CO ratios, temperature, pressure, etc.), catalyst particle size, and the nature of the support. With these many variables, it is vital that a well known catalyst system be studied.

The research plan entailed carrying out CO hydrogenation reactions on a well-characterized Ru/SiO_2 catalyst employing conventional steady-state reaction as well as steady-state isotopic transient methods and ascertaining how the methane yield was affected as the catalyst was modified with the addition of K or Cl. Steady-state reaction runs were used to show overall effects of these modifications, while steady-state isotopic transient experiments were used to determine coverages and residence times of the pool(s) of intermediates and so provide insights into the nature of the catalyst surface and the synthesis of CH_4. The results of the two techniques, carried out concurrently on the same series of catalysts acted to complement each other. Among the metals considered good F-T catalysts (Fe, Co, Ru), ruthenium was chosen for the study since there are less problems in its reduction and characterization than the base metals.

The essence of the research plan lay in the modification of a typical F-T catalyst using additives on opposite sides of the electronegativity scale in order to bring about changes in methane yield and in the relation of these changes to modification of CO hydrogenation.

2.0 EXPERIMENTAL

2.1 Catalyst Preparation and Characterization

The original catalyst for study was prepared by impregnating CAB-O-SIL silica (Grade L-90 with a surface area of about 100 m^2/g) to incipient wetness using an aqueous solution of $Ru(NO)(NO_3)_3$ obtained from Alfa products and then drying at 40° C for 24 hours. Reduction was carried out under a flow of H_2 (50 cc/min) by heating at 1° C per minute to 550° C and holding for 16 hours. After cooling down to room temperature, the catalysts were passivated by exposure to air.

In order to remove as much as possible of the residual chloride introduced as a contaminant in the support and in the metal precursor, the original catalyst was contacted with boiling water and centrifuged. This procedure was repeated three times, replacing the water after each centrifugation. Following the washing step the catalyst was dried in air at 110° C for 12 hours. The relatively Cl-free material obtained at this stage is refered to as the base catalyst. An alternative procedure of getting rid of residual Cl consisted of contacting the original catalyst with a dilute solution of ammonia overnight, stirring continuously. However, elemental analysis showed that some of the metal was removed as well, making hot water washing the better procedure. These procedures have been shown to be effective in removing Cl from supported Ru catalysts [28,29].

Chlorine doping to varying levels was achieved by impregnating the base catalyst to incipient wetness using pre-determined quantities/concentrations of dilute HCl, drying at 40° C for 24 hours, and re-reducing at 400° C for 16 hours in a flow of H_2. Potassium doping was carried out by the same procedure using an aqueous solution of KNO_3. Sequential addition of Cl and K to the reduced catalyst was carried out to minimize particle size variation as much as possible.

Atomic absorption was used to determine the actual metal loading of the catalysts, while the actual quantities of potassium and Cl retained on the modified catalysts were measured by Galbraith Laboratories. The Cl contents of the catalysts after reaction (CO hydrogenation and ammonia synthesis) were also measured.

Static gas volumetric chemisorption measurements for H_2 and CO were measured at 25° C on selected catalysts using the desorption isotherm method. Steady-state isotopic transient kinetic analysis (SSITKA) of H_2-D_2 exchange reactions, taking into account exchange occurring on the SiO_2 support, was utilized to obtain adsorption uptakes under reaction conditions.

Finally, average metal particle sizes were obtained from the chemisorption measurements. TEM of selected catalysts at various stages of preparation were taken in order to obtain the distribution of particle sizes. Specifically, TEM of the catalysts before and after Cl doping and after reaction were taken in order to ensure that particle size effects did not introduce an additional complication in the analysis of the results.

2.2 Reaction Studies

Fischer-Tropsch synthesis was carried out over a 235 - 255° C temperature range at atmospheric pressure on the original catalyst, the base catalyst, and the Cl and potassium modified catalysts. A space velocity of approximately 11,000 hr^{-1} and a H_2/CO ratio of 1 were maintained throughout (except during the experiments carried out to determine power rate exponents when H_2/CO ratios were varied between 0.25 and 2.25). Under these reaction conditions, CO conversions were able to be kept below 3%, ensuring differential operation. CO (99 % purity) was passed through molecular sieve and activated carbon traps for the removal of moisture, Fe carbonyls, and hydrocarbons before being fed into the reactor while H_2 (ultra-high purity) was used without further purification. The gas flow rates were controlled by Brooks mass flow controllers. Product analysis was obtained by on-line gas chromatography using an FID detector.

The catalysts which had been reduced in a separate reduction system were re-reduced in-situ at 400° C for a period of two hours prior to reaction. The catalyst was then cooled to the reaction temperature in flowing H_2. The product distribution from CO hydrogenation was obtained for initial conditions as well as being obtained as a function of time. Reactions were carried out for 10 minutes followed by 45 minutes in a H_2 flow. This procedure was repeated until consecutive injections produced essentially the same product distribution. This technique (usually referred to as "hydrogen bracketing") ensures maintaining a clean and stabilized catalytic surface for reaction. The reaction was then carried out continuously for a period of 9 hours with product analysis being done every hour.

SSITKA of methanation and ammonia synthesis were used for the catalysts with varying Cl levels in order to get an insight into the effects of Cl addition. Ammonia synthesis, being a structure sensitive reaction, was considered a good alternative choice for a catalytic probe on the surface of the catalysts. For methanation, a differential tubular reactor was used with a very high space velocity (around 126,000 hr^{-1}) to keep conversion low and, thereby, minimize heat and mass transfer effects. With the 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. A H_2/CO ratio of 10 was maintained in order to force ruthenium into 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 by using an Apple IIe computer with a Cyborg Isaac interface. In conjuction with MS analysis, gas chromatography was used to analyze the steady-state reactor effluent. Ammonia synthesis was carried out in a similar set-up, but a gradientless reactor was employed and the inlet gas was switched from $^{14}N_2/H_2$ to $^{15}N_2/H_2$, the H_2/N_2 ratio being 3. The reaction was carried out at 400° C, 204 kPa and a space velocity of 1125 hr^{-1}.

3.0 RESULTS

3.1 Effect of Cl-doping

The nomenclature used for catalyst identification is as follows: The original catalyst having been prepared using CAB-O-SIL silica is designated "3C", and becomes the base catalyst "3CWW" after hot water wash. The Cl doped catalysts are designated "3CWW x.xx", x.xx being the ratio of Cl atoms added to the total number of ruthenium atoms (nominal Cl/Ru ratios). A.A. analysis showed that the active metal loading of the base catalyst was 2.71 wt. % and remained the same after further treatments. A comparison of the actual and nominal Cl/Ru ratios is given in Table 1.

3.1.1 Chlorine Content

The amount of Cl retained on the catalyst increased sharply at low levels of dosage and leveled off around a nominal ratio of 0.3 (Figure 1). Beyond the saturation limit, the excess Cl was probably driven off as HCl during the re-reduction. In fact, loss of Cl at high temperatures of reduction [28,30] 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. The fact that hot water and ammonia wash can be used to get rid of residual Cl in the original catalyst suggests that Cl can be leached from the catalyst by the water and ammonia

Table 1: Characteristics of the Ru/SiO_2 catalysts

Catalyst	wt % Ru	wt % Cl	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	0.30	0.075
3CWW1.00	2.71	0.087	1	0.091

Table 2: Chlorine levels: Effect of CO hydrogenation and ammonia synthesis

Catalyst	Reaction	Time on stream (hr)	wt % Cl (before)	wt % Cl (after)
3CWW0.30	CO Hydrogenation	1	0.071	< 0.02
3CWW0.30	CO Hydrogenation	6	0.071	< 0.02
3CWW1.00	CO Hydrogenation	6	0.087	< 0.02
3CWW0.01	Ammonia Synthesis	24	0.028	0.019
3CWW0.30	Ammonia Synthesis	24	0.071	0.028

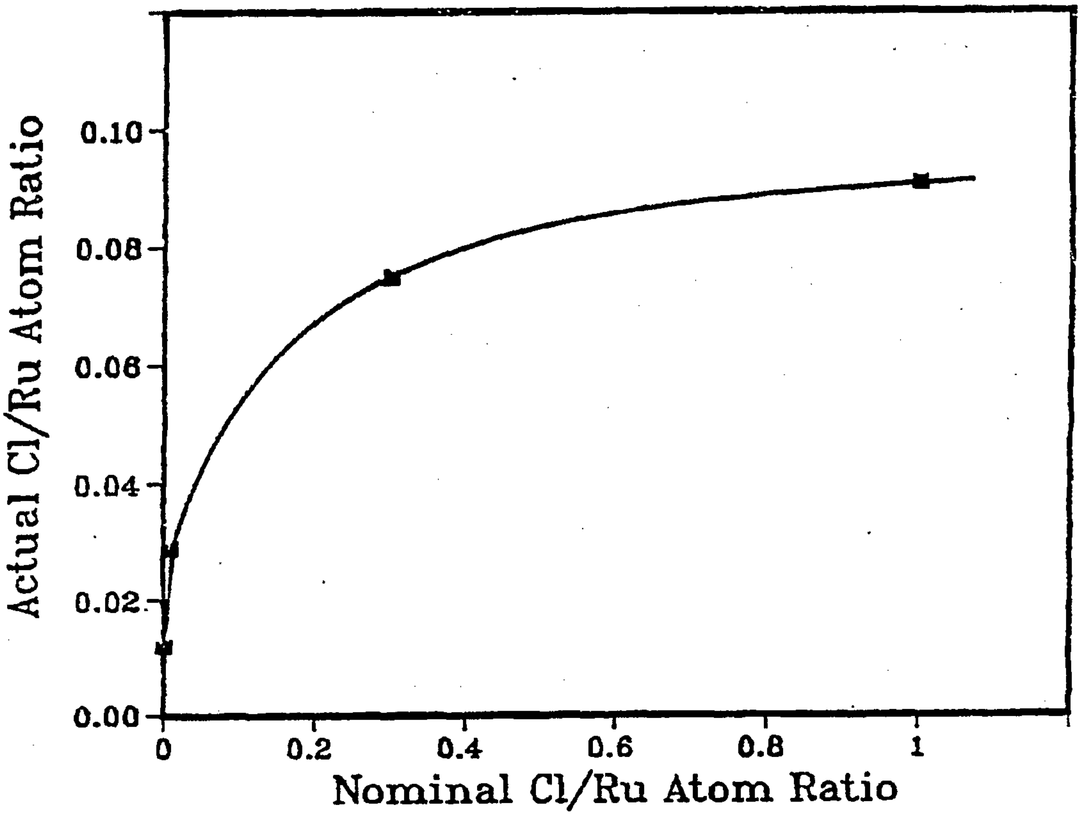


Figure 1: Actual Vs. Nominal Cl/Ru Ratio [Ru/SiO_2 - 3CWW]

produced during CO hydrogenation and ammonia synthesis reactions, respectively. This was indeed found to be the case from elemental analysis of the catalysts after both reactions. Table 2 shows a comparison of the Cl contents of several catalysts before and after reaction. CO hydrogenation had a drastic effect with Cl being removed to levels below detectability limits during the first hour of reaction at 240° C. Under ammonia synthesis at 400° C, smaller amounts of Cl were removed even after 24 hours on stream.

The average Ru particle size/dispersion for 3CWW was estimated from coverages of CO and CH_x intermediates obtained during methanation utilizing SSITKA and are given in Table 3. TEM micrographs of selected catalysts are given in the apendix. There is no indication of a significant particle size variation between the base catalyst and the Cl-doped catalysts with particle diameters estimated to be mainly in the 20-40 A range for all the catalysts.

Table 3: Particle size from SSITKA CO + CH_x @ 200° C

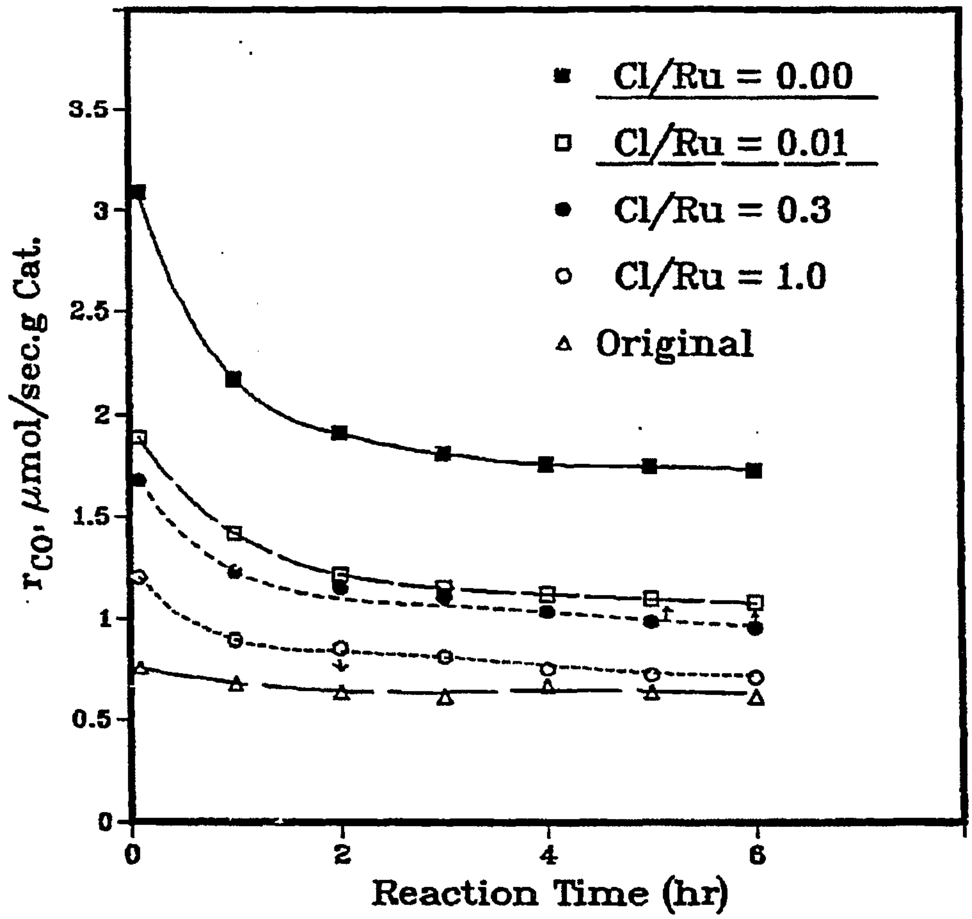
Catalyst	d_p	% D
3CWW	24.0	38.0

3.1.2 Fischer-Tropsch Reaction Results

A comparison of the catalytic activity (expressed as micromoles CO converted per second per gram catalyst) of the base catalyst and the Cl-doped catalysts over a six-hour period of continuous F-T reaction is shown in Figure 2. The base catalyst was the most active, followed by the Cl-modified catalysts in the order of increasing Cl content. It is significant to note that the relative rate of deactivation of all the catalysts was essentially the same so that the activities of all the catalysts upon reaching steady-state operation exhibited differences similar to those initially present.

With increasing Cl content, the methane selectivity increased slightly at the initial stages of the reacton, as shown in Figure 3. This initial selectivity comparison, obtained after 10 minutes of reaction, is considered to be a better indication of the effect of Cl since the complication of carbon build-up was minimal and all detectable Cl was removed after longer periods (>1 hour) of reaction. After four hours of reaction, the selectivities on all the catalysts were about the same (Figure 3).

The activity and selectivity comparisons were all carried out at the same reaction conditions of 240° C, H_2/CO ratio of 1, and total gas flow rate of 40 cc/min. Reactions were also carried out at 235, 245, 250 and 255° C. Apparent activation energies were calculated for the base catalyst as well as the Cl-doped catalysts from the rates of CO conversion and methane formation [Table 4] (the Arrhenius plots are given in the appendix). Also included in Table 4 are the exponents for the power rate law determined for the catalysts.



Reaction Temp. 240° C, H_2/CO Ratio 1

GHSV 9000 hr^{-1}, Total Pressure 1 atm.

Figure 2: Catalytic Activity of Ru/SiO_2

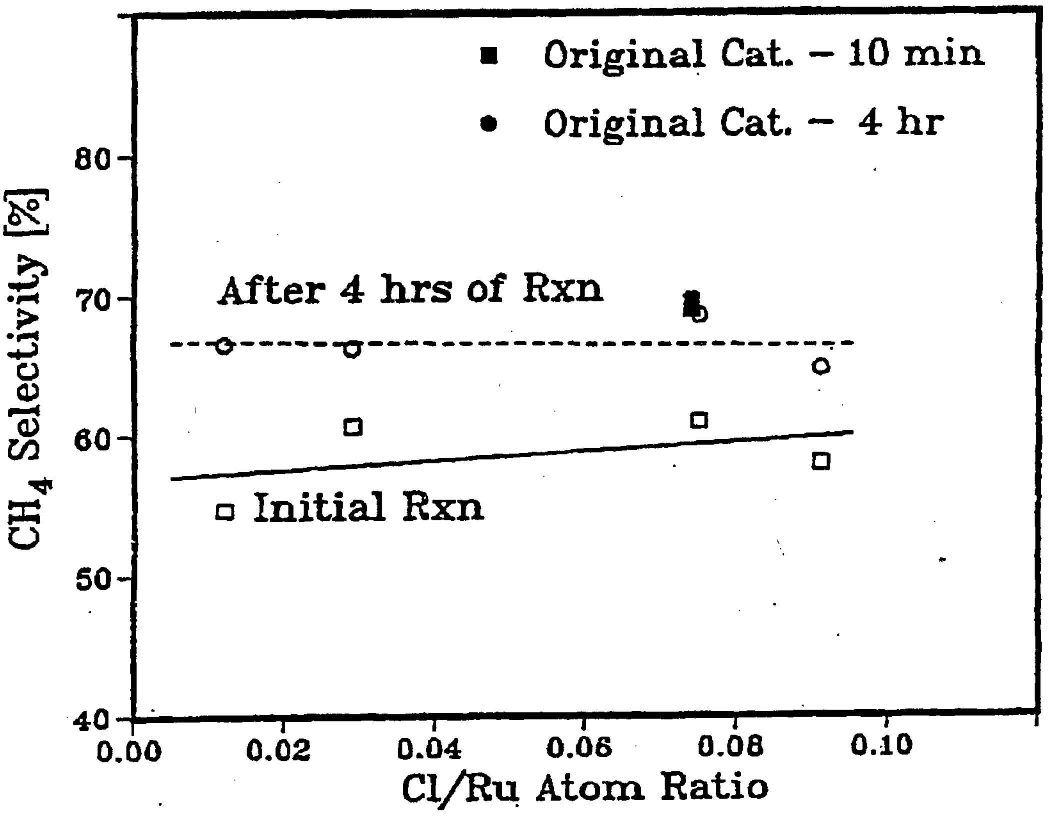


Figure 3: CH_4 Selectivity Vs. Cl/Ru on Ru/SiO_2

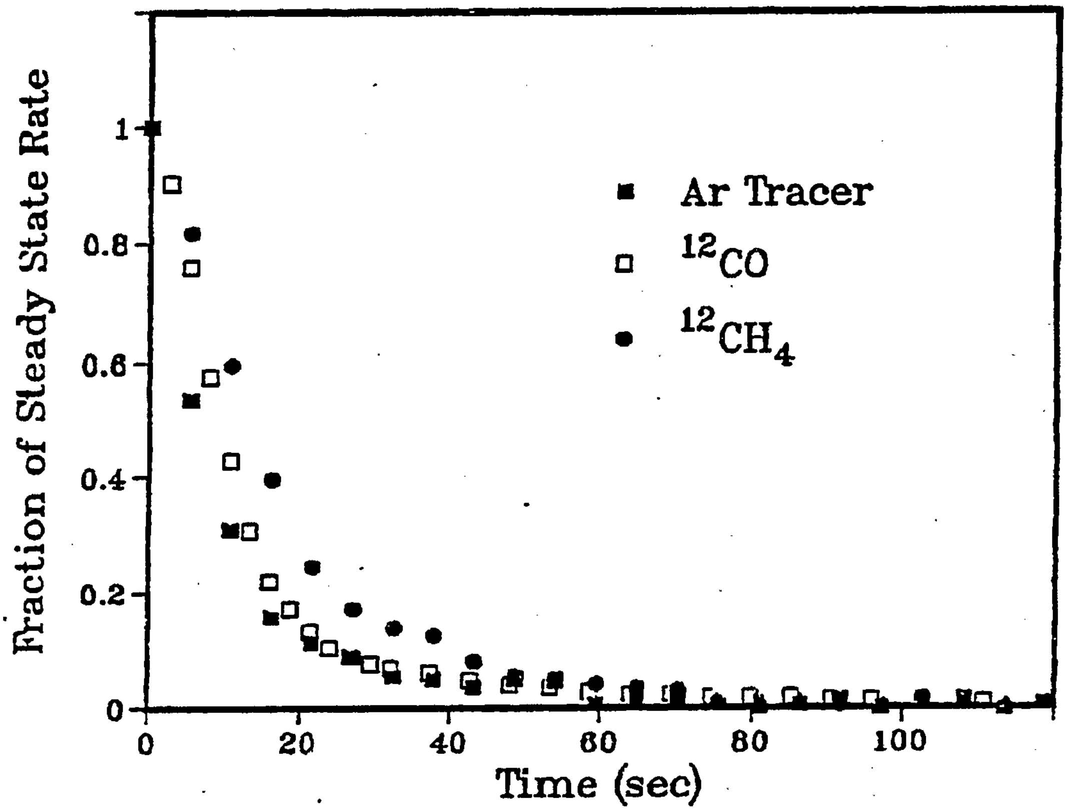
Table 4: Rate Expression Parameters for F-T

$$-r_{CO} = k\, P_{H2}^{x}\, P_{CO}^{y}$$

Catalyst	E_{CO} (kcal/mol)	E_{CH4} (kcal/mol)	x	y
3CWW	18	28	1.51	-0.68
3CWW0.01	22	32	1.71	-0.86
3CWW0.30	21	29	1.61	-0.72
3CWW1.00	20	28	1.47	-0.62
1% Ru/SiO_2	-	-	1.60	-0.6 [31]
5% Ru/SiO_2	-	-	1.5	-0.6 [32]

3.1.3 Methanation (SSITKA)

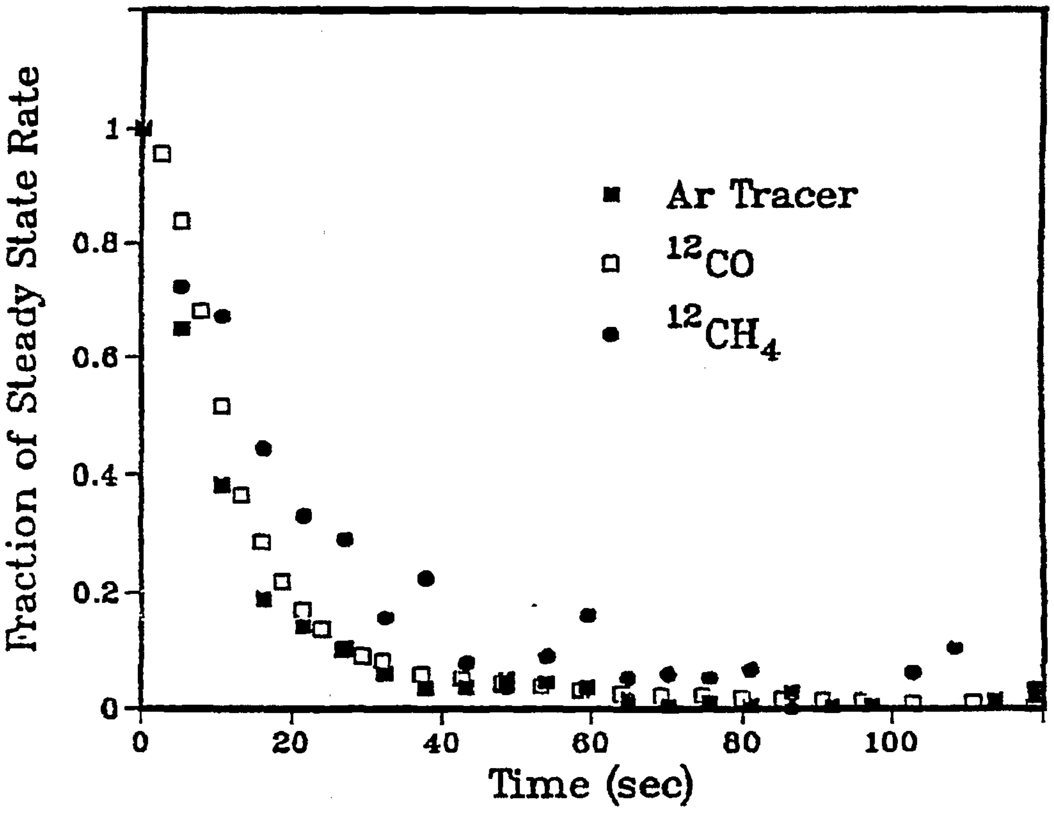
Steady-state isotopic transients obtained by switching from ^{12}CO to ^{13}CO over the base catalyst and the Cl/Ru = 1 doped catalyst during methanation are shown in Figures 4 and 5, respectively. The product of the area between the Ar and the ^{12}CO decay curves and the CO flow rate gives the amount of adsorbed CO under reaction conditions. Also, integration to get the area under the $^{12}CH_4$ decay curve yields the relaxation time constant of the decay curve (tau), a measure of the average lifetime of the intermediates on the surface. The reciprocal of tau, k is the reactivity constant or intrinsic TOF over the sites taking part in the reaction. The product of tau and the steady-state rate of



T_{rxn} = 200 C; P_T = 190 kPa;

P_{CO} = 3.8 kPa; H_2/CO = 10.

Figure 4: SSIT during Methanation over Ru/SiO_2 [3CWW].



T_{rxn} = 200 C; P_T = 190 kPa;

P_{CO} = 3.8 kPa; H_2/CO = 10.

Figure 5: SSIT during Methanation over Cl-doped Ru/SiO_2 [3CWW1.0].

formation of CH_4 yields the abundancy (N) of the surface intermediates leading to the formation of methane. The parameters calculated for the Cl-doped and Cl-free catalysts are summarized in Table 5.

3.1.4 Ammonia Synthesis (SSITKA)

A similar analysis of the isotopic transients obtained after a $^{14}N_2/^{15}N_2$ switch over the base catalyst and Cl-doped catalysts during ammonia synthesis provided the parameters given in Table 6. The reaction rates were measured independently from a combined GC and MS analysis. Ammonia synthesis being a structure-sensitive reaction, additional precautions were taken to ensure that the Cl-doped and Cl-free catalysts had identical pretreatments. Thus, a portion of the base catalyst (3CWW) was re-impregnated with distilled water and re-reduced at 400° C (designated 3CWW0.00), duplicating the Cl-doping procedure. The activity of 3CWW0.00 (in terms of the rate of ammonia synthesis) decreased slightly after 20 hours of reaction while that of 3CWW0.01 remained the same. On 3CWW0.30, the activity increased slightly with time on stream. Overall, the catalysts became increasingly less active with increasing Cl content even though there were no significant changes in tau (reactivity of the intermediates) as the Cl level increased.

Table 5: Reaction Parameters from SSITKA - Methanation

Catalyst	tau{CO} (sec)	N{CO} (umole/g)	tau{CH_x} (sec)	N{CH_x} (umole/g)	Reaction Rate (mol/s/g) x 10^9
3CWW	3.8	109	8.2	3.4	15.9
3CWW0.01	3.2	93	11.9	3.1	12.9
3CWW0.30	4.8	118	13.5	2.9	10.9
3CWW1.00	3.0	79	10.2	1.6	7.9

$T_{rxn} = 200^\circ$ C, P_{rxn} = 190 kPa, H_2/CO/He = 20/2/78 ml/min

Table 6: Reaction Parameters from SSITKA - Ammonia Synthesis

Catalyst	T ° C	t_{rxn} (hrs)	tau{NH_x} (sec)	N{NH_x} (umole/g)	Reaction Rate (mol/s/g) x 10^9
3CWW	400	3	*	2.8	3.4
"	400	22	1269	4.4	3.4
"	400	24	1178	4.0	3.4
3CWW0.00	400	3	985	5.0	5.02
"	400	18.5	1344	6.3	4.65
"	400	20.5	1081	5.0	4.65
3CWW0.01	405	3	1218	3.1	2.60
"	400	5	1131	2.9	2.60
"	400	15	1461	3.9	2.60
3CWW0.30	400	5	1486	1.3	0.88
"	400	21.3	1455	2.0	1.37

3.2 Effect of K-doping

Two potassium-doped catalysts were prepared (K/Ru nominal ratios of 0.1 and 0.3) by impregnating a different batch of pre-reduced catalyst (1C). This catalyst was not washed with hot water and so had a Cl content of 0.091 wt % as well. The metal loading was 2.69 wt %, and the actual potassium content of the 0.1 K/Ru doped catalyst was 0.02 wt %. Steady-state F-T reactions only were carried out on the potassium modified catalysts, designated 1CK-0.1 and 1CK-0.3.

3.2.1 Characterization Results

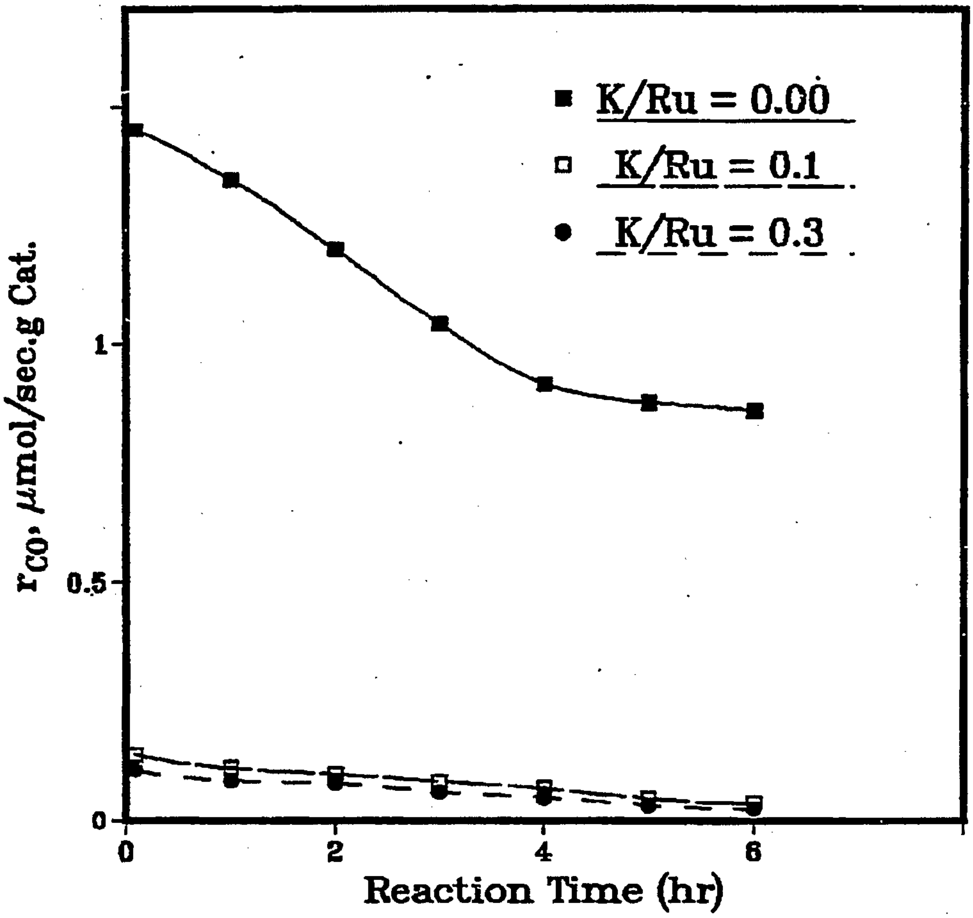
Average metal particle sizes obtained from H_2 chemisorption measurements can be in error as a result of underestimation of the surface metal atoms due to blockage and/or activation by modifiers/impurities. CO chemisorption is not typically an accurate method for characterization either, since the stoichiometry may change as the Ru particles become smaller [33]. Despite these difficulties, H_2 chemisorption is considered to be the best overall method for the determination of Ru metal surface areas in highly-dispersed Ru catalysts. Thus, an estimation of average Ru particle size was calculated for the "1C" series of catalysts from hydrogen adsorption measurements at 25° C. Assuming a stoichiometry of $H_{irr}/Ru = 1$ and cubic Ru particles with five sides exposed to the gas phase, the average Ru crystallite diameter was calculated using the relationship d = 5/s.p, s and p being the surface area of Ru per gram of Ru and the density of the metal, respectively. CO irreversible adsorption uptakes were measured at 25° C as well. The results are given in Table 7.

Table 7: Average Ru particle size/Dispersion of the catalysts

STATIC CHEMISORPTION AT 25° C					
Catalyst	H_{irr}	d_p	% D	CO_{irr}	CO/H
1C	40.2	29.8	30.7	173.7	4.3
1C-K0.1	27.4	-	-	104.10	3.8
1C-K0.3	15.9	-	-	53.52	3.5

3.2.2 Fischer-Tropsch Reaction Results

The activity comparison between "1C" and K-doped 1C on the basis of the rate of overall CO conversion to hydrocarbons over a six hour period is shown in Figure 6. The reaction conditions were exactly the same as those for the Cl-doped series of catalysts. It is again observed that the activity of the catalyst decreased with increasing modifier (in this case potassium) content. The activity loss is more severe with K-doping as an order of magnitude decrease in activity was observed even on the catalyst with the lower K content.



Reaction Temp. 240° C, H_2/CO Ratio 1

GHSV 9000 hr^{-1}, Total Pressure 1 atm.

Figure 6: Activity of Ru/SiO_2: Effect of K

Methane selectivity also decreased with increasing potassium content as shown in Table 8. With potassium doping, the differences in selectivity remained even after 6 hours of reaction, though not as much as the initial differences. This maintenance of selectivity is due in large part to a lack of mechanism for removal of K during reaction. The chain growth probabilities (alpha) determined from A-S-F plots of the product distributions obtained are also included in Table 8.

Table 8: F-T Reaction Parameters: Effect of K-doping

	K/Ru = 0.0	K/Ru = 0.1	K/Ru = 0.3
Selectivity (wt %) (initial)			
C_1	72.6	42.1	35.0
Selectivity (wt %) (after 6 hr of rxn)			
C_1	59.7	40.7	27.4
C_2	12.6	23.5	42.7
C_3	12.9	15.5	12.0
C_{4+}	14.8	20.3	17.9
alpha	0.72	0.72	0.85
r_{CO}, umole/sec g Cat (initial)	1.40	0.20	0.08
r_{CO}, umole/sec g Cat (after 6 hours of rxn)	0.90	0.12	0.05

4.0 DISCUSSION OF RESULTS

4.1 Methane Selectivity

A comparison of methane selectivity on the base catalyst and the Cl-doped catalysts revealed that, at the initial stages of reaction, the selectivity was higher on the Cl-doped catalysts, more so with increasing Cl content. As the reaction progressed, the methane selectivity increased on all the catalysts, but at a faster rate on the base catalyst. After 2 hours of reaction, the methane selectivity on the base catalyst and the Cl-doped catalysts were essentially the same. This trend is not surprising since Cl was being removed during the course of reaction while carbon, a highly electronegative element also, was being deposited. It is the effect of carbon on the surface, apparently, that ultimately sets the methane selectivity for the whole series of catalysts, regardless of the initial Cl content and even though relative differences in activity are maintained. Although, CO conversions can have relatively large effects on hydrocarbon product distributions [34], the selectivity differences are real based on making comparisons at comparable conversions.

It is well known that alkali-doping of transition metals increases the selectivity towards higher hydrocarbons during CO hydrogenation [23,35]. As stipulated by the electron backdonation model [36], electropositive ad-atoms, by their electron donating abilities, strengthen the metal-carbon bond in addition to weakening the carbon-oxygen bond. This action facillitates CO bond dissociation, increases the residence time of CH_x species on the surface, and increases the chances for chain growth. CO hydrogenation results obtained in this study on the potassium modified catalysts are in agreement with other findings with regard to activity and selectivity changes. Figure 7 shows modified Schultz-Flory plots of the product distribution over "1C", "1C-K0.1" and "1C-K0.3", yielding chain growth probabilities (alpha) of 0.72, 0.72 and 0.85, respectively. Thus, a higher tendency for chain growth is indicated on 1C-K0.3. The catalyst with the lower quantity of potassium doping (1C-K0.1) appears to have had an identical chain growth probability as "1C". However, there is a much higher "overshoot" in C_1 production for "1C". As indicated earlier, the "1C" series of catalysts had significant quantities of Cl as well so that some of the effects of potassium may have been masked, particularly at the lower loading.

Several unanswered questions remain. If alkali doping enhances CO dissociation, why are the methanation and F-T reaction rates strongly depressed by the addition of an alkali metal? If Cl addition suppresses H_2 chemisorption [28-30,37,38], why is the relative rate of CH_4 formation increased on the Cl-doped catalysts, indicating an enhanced relative hydrogenation ability? Contrary to our observation of loss of activity with Cl addition, phosphorus is reported to have enhanced the activity of Ru catalysts [6]. Obviously, several mechanisms of modification by the additives are at play. If catalyst properties are to be tailored to particular needs through the

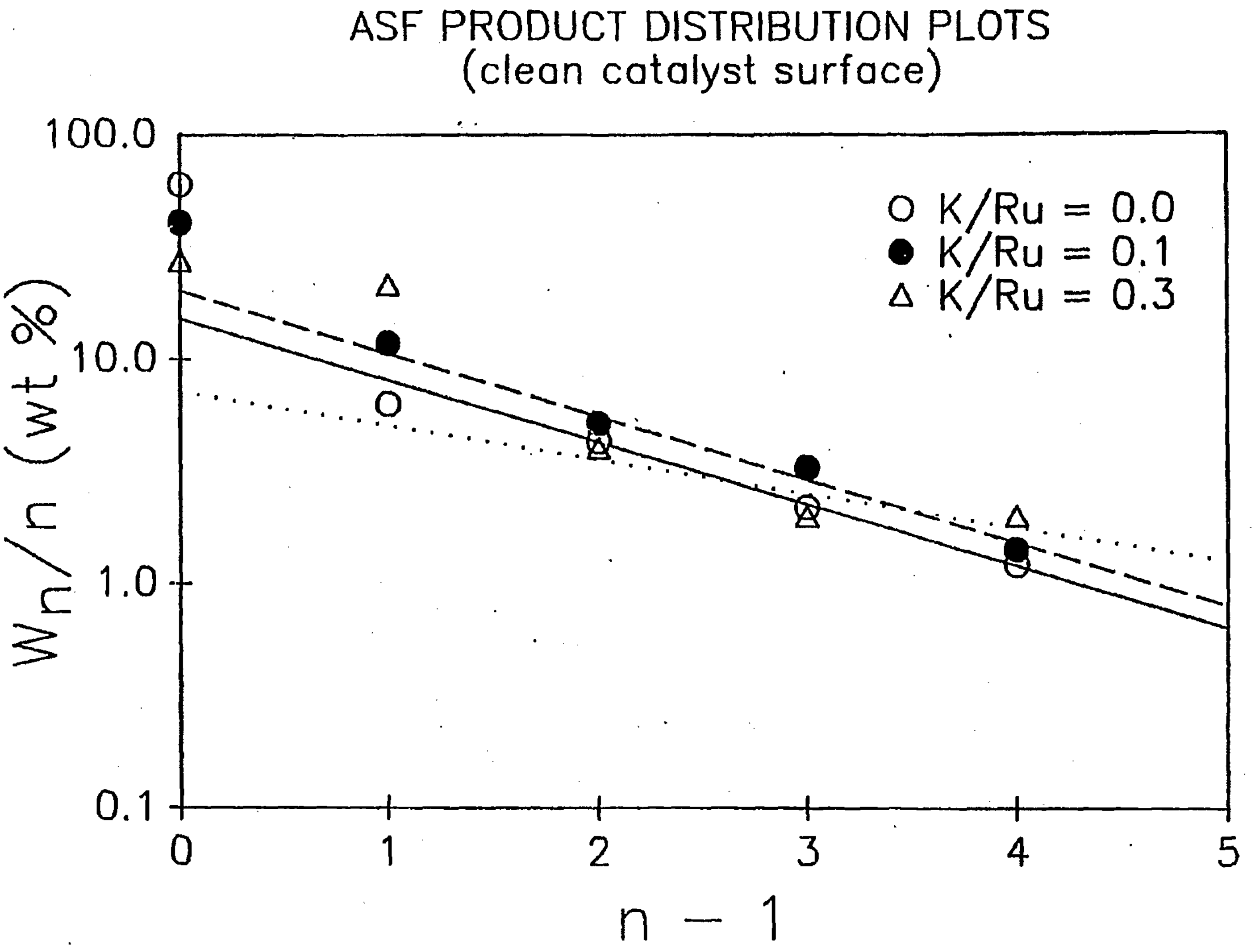


Figure 7: Product Distribution on Ru/SiO_2 and K-Ru/SiO_2

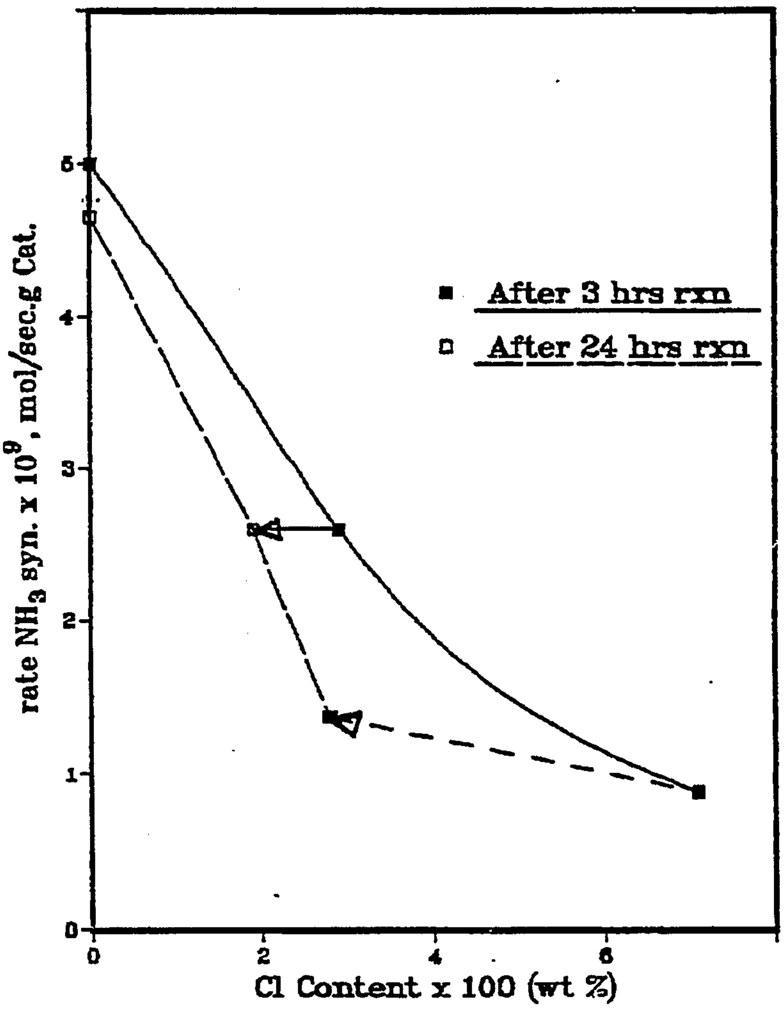
addition of modifiers, a thorough understanding of the mechanisms that may be operating in the particular system is crucial. A closer look at the mechanism of Cl modification was undertaken.

4.2 Mechanisms of Modification

The loss in activity of the catalysts with the addition of Cl or potassium during F-T synthesis as well as the decreased reactivity of intermediates during methanation and ammonia synthesis with Cl addition could be due to site blockage or electronic modification of the catalysts, the most prevalent mechanisms often employed to explain additive effects. Sulfur poisoning of metals during CO hydrogenation and ammonia synthesis, for example, has been extensively studied [39,40]. Much of the experimental evidence to date has been interpreted to indicate that poisoning is predominantly due to site blockage of active sites by adsorbed sulfur. McClory and Gonzalez [34] have speculated that site blockage by potassium may be the primary effect of that promoter rather than an electronic modification of the metal. In addition, catalytic effects which refers to direct interaction (bonding, electrostatic field, etc.) between the modifier and the reactant(s) [41-43] and structural effects arising from surface rearrangements induced by the modifier presence [44-48] have been proposed. Yates and co-workers [49] addressed the issue of the spatial extent of the K-CO interaction on Ni(111) and found both long range delocalized and short range localized interactions depending on the coverage of K. At low K coverages, the existence of CO islands centered on K adatoms was suggested with the K having an observable radius of influence of 8 - 9 A. At higher K coverages, short range K-CO interactions due to the formation of a K-CO complex were suggested.

As discussed in section 2.1, however, Cl was removed in the course of the reaction during ammonia synthesis and CO hydrogenation, more so during the latter. If catalyst deactivation was due to site blockage and/or additive-metal surface interactions, the F-T activities on the Cl-doped catalysts might be expected to go through an initial decline and then increase with Cl removal, approaching the base catalyst activity. On the contrary, the catalysts maintained the initial differences in activity throughout the 6-hour F-T reaction runs in a differential reactor. Under ammonia synthesis, the situation was no different. Figure 8 shows the variation of the rate of reaction on the catalysts with Cl content after 3 hours and after 24 hours of reaction. The rates remained about the same after 24 hours of reaction. The modest increases in activity for the Cl-doped samples fell way short of that expected considering the reduction in the quantity of Cl on the catalyst. Thus, the modifier-induced changes in activity remained long after the Cl was gone, an indication that factors other than site blockage and electronic effects are at play.

It could be speculated in the case of CO hydrogenation that, perhaps, the presence of Cl brings about a rapid catalyst deactivation at the initial stages of the reaction by increasing the rate of carbon build-up, so that the catalyst is unable to



Reaction Temp. 400° C, Total Pressure 2 atm.

Figure 8: Catalytic Activity of Ru/SiO$_2$ as a function of Cl Content

recover its activity even after the Cl is removed. If this was the case, however, the activity would have been recovered during ammonia synthesis since nitrogen does not poison the surface. There was no evidence that the metal particle size distribution changed.

Several recent papers in the literature have shown that certain elements (Cl, S) can bring about significant rearrangement of Ag, Cu [44-46], and Pt [47] surfaces. How this may occur has been discussed by Marks and Heine [48]. Supported metal clusters 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. Thus, it is quite plausible that structural modifications of the surfaces of the metal crystallites induced by the Cl presence is the predominant mechanism by which Cl modifies the catalytic properties of Ru.

Certainly, site blockage is not being ruled out completely, particularly during ammonia synthesis as the Cl was removed very slowly. The question then arises as to whether there is site specificity in the Cl adsorption (selective poisoning)? Figure 9 reveals that the base catalyst had a heterogeneous surface at the start of the reaction (related to the non-linearity of the semi-

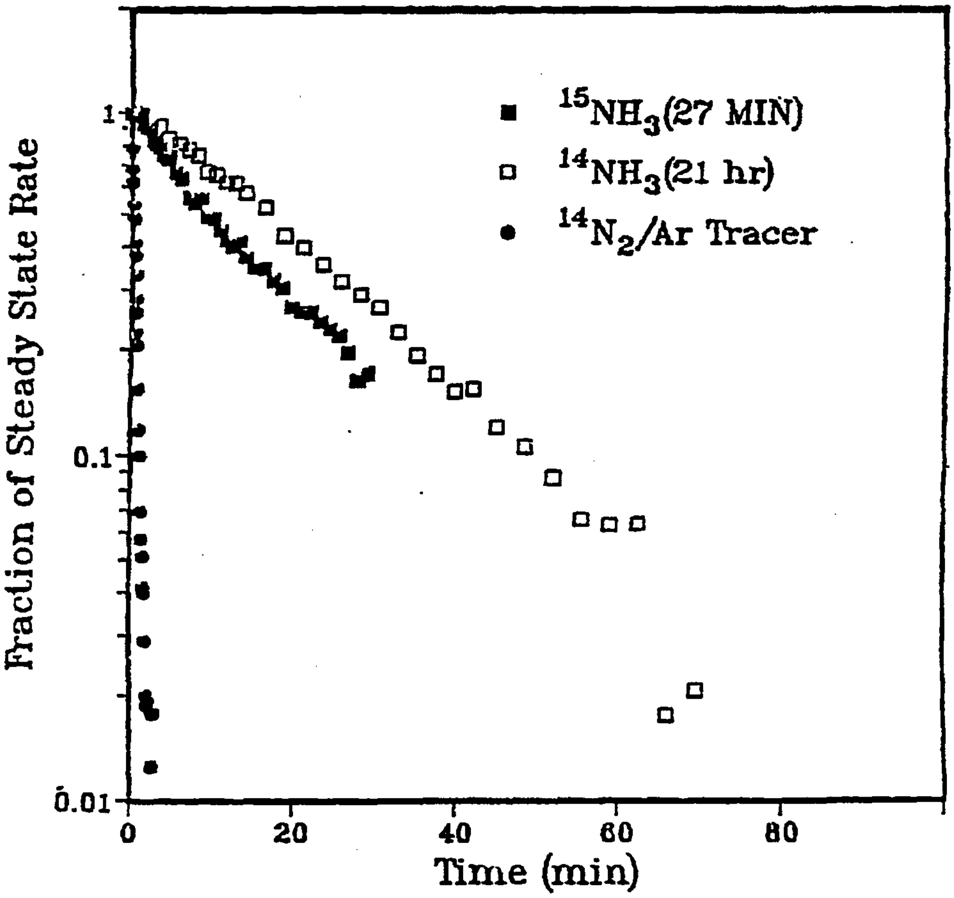


Figure 9: SSITKA - NH_3 Transients [3CWW]

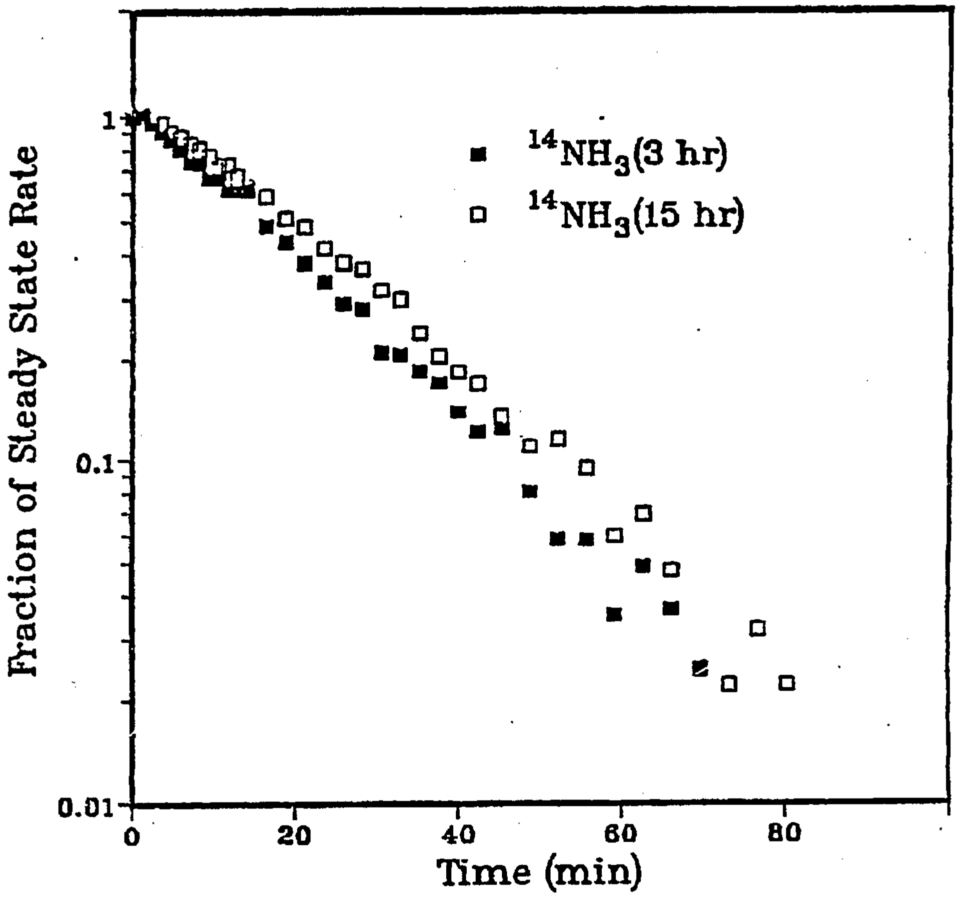


Figure 10: SSITKA - NH_3 Transients [3CWW0.01]

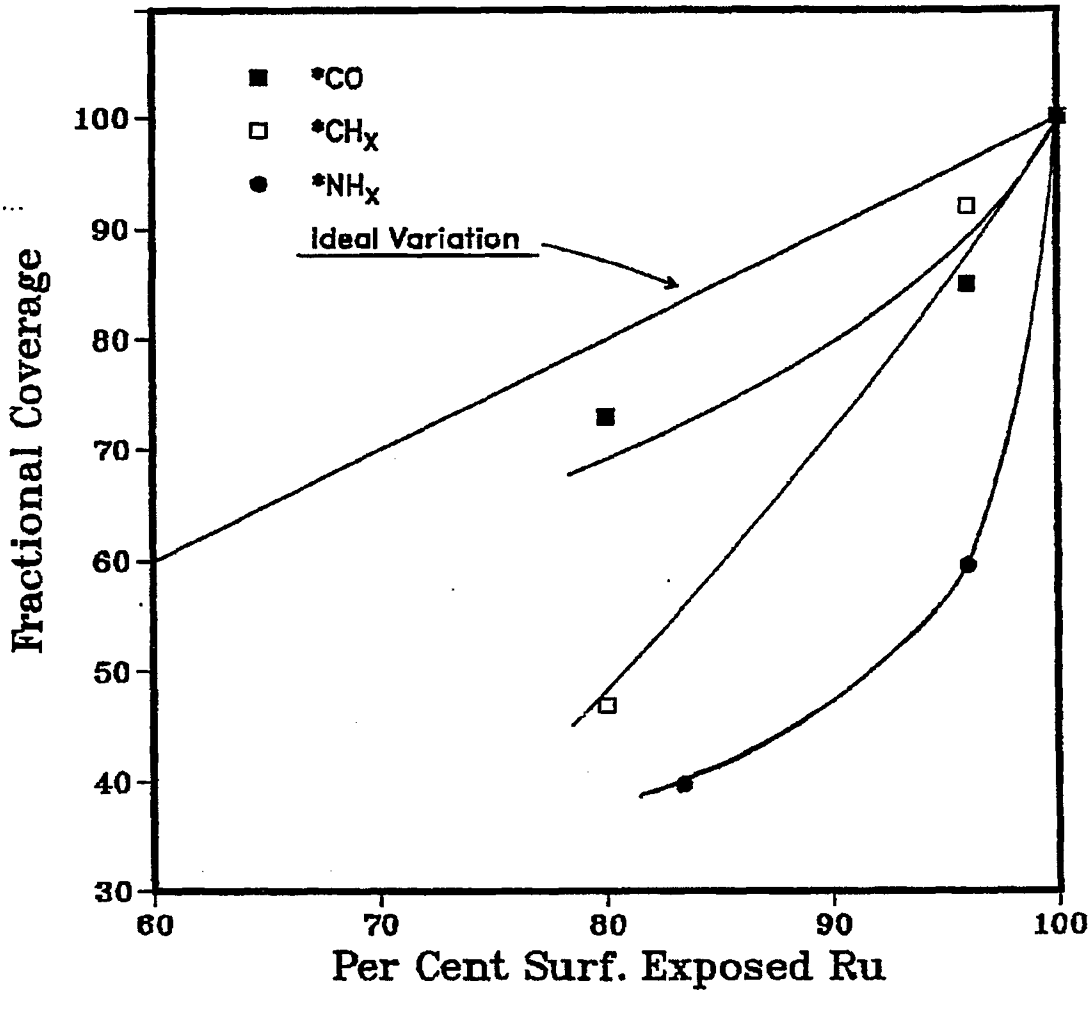


Figure 11: CO, CH$_x$ and NH$_x$ Coverage Vs. % Surf. Exposed Ru

log plot) but exhibited a homogeneous one after 21 hours of reaction. The Cl-doped catalyst (3CWW0.01) did not exhibit this initial heterogeneity [Figure 10], an indication, perhaps that Cl preferentially sits on the most active sites resulting in a more homogeneous surface from the onset. In methanation, Cl also played the role of inhibitor and acted to decrease the concentration of both CO and CH_x surface intermediates. Figure 11 shows that the fractional coverage of the CH_x surface intermediates deviated from a purely geometric surface blockage implying preferential site blockage or ensemble effects from the Cl. In fact, on a normalized basis the deviation from simple surface blockage was the same for both ammonia synthesis and CO hydrogenation.

5.0 CONCLUSIONS

For CO hydrogenation, addition of potassium to Ru/SiO_2 causes a reduction of the rate of methane formation and an increase in chain growth probability. The drawback, however, is an attendant loss in activity with increasing potassium content. Chlorine addition has the opposite effect with regard to the methane selectivity but also reduces the activity of the catalyst. A unique property of Cl is 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. For methanation, the major effect of Cl on the rate of reaction seems to be a decrease in active sites, as the rate per site (true TOF) did not seem to be greatly affected. For ammonia synthesis, Cl also causes a decrease in the concentration of NH_x surface intermediates and appears to remove initial surface heterogeneities by preferential blockage of certain active sites and, possibly, by inducing surface reconstruction as well.

The results of this study illustrate the use of catalyst modifiers in bringing about changes in methane yield in F-T synthesis. While Cl enhances the selectivity of methane formation, K has the opposite effect. Structural rearrangements induced by the presence of Cl, rather than selective site blocking or electronic interactions, is suggested by the authors to be the primary mechanism of Ru modification by Cl. The results suggest that stabilization of certain metal surface structures may be an important element in how modifier species change catalyst properties.

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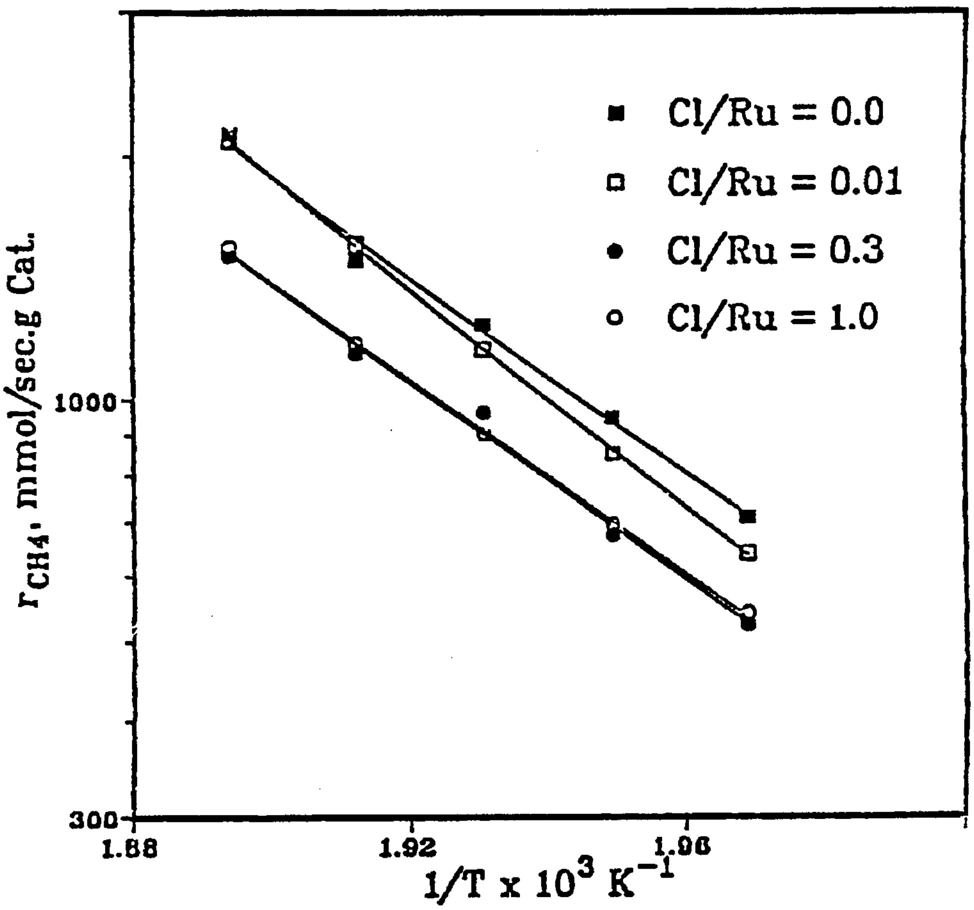
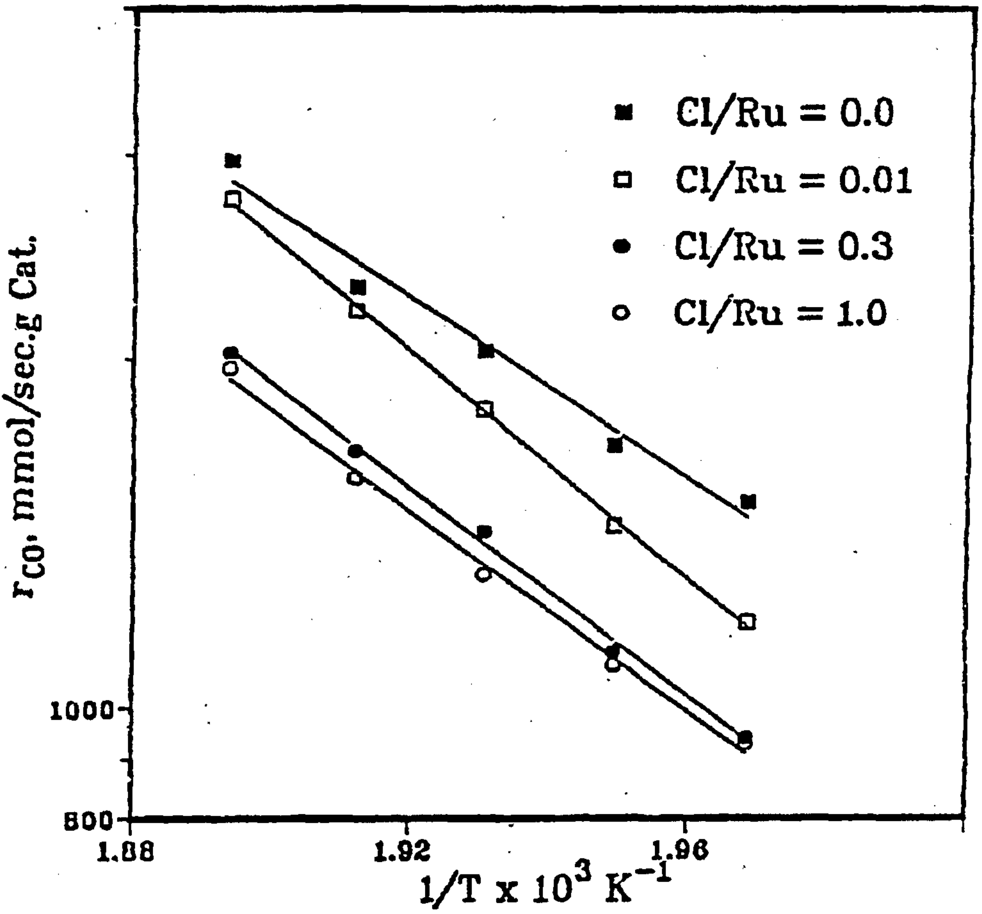
APPENDIX



GHSV 1100 hr^{-1}, Total Pressure 1 atm.

Figure A1: Arrhenius Plots: Effect of Chlorine Doping
(Based on Rate of CH_4 Formation)



GHSV 9000 hr^{-1}, Total Pressure 1 atm.

Figure A2: Arrhenius Plots: Effect of Chlorine Doping
(Based on Rate of CO Conversion)

Figure A3: TEM Micrograph of 3CWW0.00

Figure A4: TEM Micrograph of 3CWW0.30

Figure A5: TEM Micrograph of 3CWW1.00

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