JOURNAL OF CATALYSIS **123**, 1–11 (1990)

The Effect of Chlorine Modification of Silica-Supported Ru on Its CO Hydrogenation Properties

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Received July 6, 1988; revised November 8, 1989

An investigation of CO hydrogenation on Cl-modified supported Ru catalysts has been carried out using both steady-state Fischer–Tropsch synthesis and steady-state isotopic transient kinetic analysis of methanation. The steady-state reaction results illustrate how the presence of chlorine acts to decrease catalytic activity and to enhance the selectivity of methane formation even though it is present on the catalyst only during the initial stages of the reaction. The deactivation results for F–T as well as the isotopic transient results 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 ruthenium for CO hydrogenation. Isotopic transients 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.

INTRODUCTION

Catalyst modifiers, poisons as well as chemical promoters, are known to greatly influence catalyst behavior (*1–11*). The use of all sorts of catalyst additives will help to promote advances in the design and synthesis of new industrial heterogenous catalysts as we strive to improve catalyst activities and selectivities. The mechanisms by which the poisons/promoters modify the catalytic properties of metals are far from being completely understood. Suggested mechanisms include geometric site blocking of active sites by the adatoms (*12–15*), metal-modifier electronic interactions leading to changes in the strength of metal-adsorbate bonds (*9, 15–21*), electrostatic field effects of the adatoms (*22–26*), and direct chemical interactions between the modifier and the adsorbed molecules (*26–31*).

Cl, S, and P are all well-known poisons for hydrogen and CO adsorption (*32*) and CO hydrogenation (*33*) 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 (*33*) 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 (*34–38*). While Narita *et al.* (*34, 35*) attributed the inhibition of CO and H_2 adsorption to the presence of Cl to site blockage only, Lu and Tatarchuk (*37, 38*) suggested that in addition to a blockage of sites there was an electronic activation of certain other sites. Thus, modifications in adsorptive and cata-

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0021-9517/90 $3.00

lytic properties by Cl have primarily been interpreted to be due to blockage/electronic effects of the adatom. However, most studies on 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 very commonly used in the preparation of supported Ru catalysts. In addition, this modifier is almost always present as an impurity in all 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. In addition to traditional steady-state reaction studies, steady-state isotopic transient kinetic analysis was utilized to provide greater insight into the mechanism of modification since it can differentiate between reaction site blockage and site modification.

EXPERIMENTAL

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 L-90 with a surface area of 90 m^2/g) to incipient wetness, drying at 110°C for 21 h, reducing at 550°C for 16 h, and washing the reduced catalyst with hot water to remove residual Cl present as a contaminant in the Ru precursor. Hot water washing has been shown to be effective in removing residual Cl from supported Ru catalysts (*36*). 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 h, and then re-reducing it at 400°C for 16 h. A portion of the base catalyst was impregnated with distilled water to incipient wetness, dried at 40°C, and re-reduced at 400°C, duplicating the Cl-doping procedure. Sequential addition of Cl to the reduced catalyst was carried out to minimize particle size variation as much as possible.

Atomic absorption (AA) was used to determine the actual metal loading of all the catalysts, while the actual quantities of Cl retained on the modified catalysts, before and after reaction, were measured by Galbraith Laboratories. Average metal particle sizes and particle size distributions for these catalysts were determined by TEM measurements. Ru particle sizes were also determined by H_2 chemisorption using conventional static gas volumetric (GV) implements with procedures similar to those used by Sayari *et al.* (*39*). Adsorption uptakes under reaction conditions were obtained from steady-state isotopic transient kinetic analysis of methanation. We emphasize that the transients in these experiments affected only the isotopic composition of the reaction mixture.

The nomenclature used for catalyst identification is as follows: The original catalyst prepared using CAB-O-SIL silica is designated "3C." Catalyst 3C after a hot water wash becomes the base catalyst and is designated "3CWW." The Cl-doped catalysts are designated "3CWWx.xx," x.xx being the ratio of Cl atoms added to the total number of ruthenium atoms (nominal Cl/Ru ratios). The distilled water-impregnated catalyst is designated 3CWW0.00. AA analysis showed that the active metal loading of the base catalyst was 2.71 wt% and remained the same after further treatments.

Reaction Studies

Fischer–Tropsch synthesis was carried out in a differential reactor over the temperature range 235–255°C at atmospheric pressure. A space velocity of approximately 11,000 h^{-1} and a H_2/CO ratio of 1 were maintained throughout (except during the experiments carried out to determine power law rate exponents when H_2/CO ratios were varied between 0.25 and 2.25). A

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	2.7	0.07	0	0.074
3CWW	2.7	0.011	0	0.012
3CWW0.00	2.7	0.011	0	0.012
3CWW0.01	2.7	0.028	0.01	0.029
3CWW0.30	2.7	0.071	0.30	0.075
3CWW1.00	2.7	0.087	1	0.091

ratio of $H_2/CO = 1$ was used in order to compare deactivation characteristics of the catalysts. The ability of catalysts to perform at low H_2/CO ratios is considered desirable for the conversion of synthesis gas obtained by coal gasification. 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 (ultrahigh purity) was used without further purification. The catalysts were re-reduced *in situ* at 400°C for a period of 2 h prior to reaction. The activity and product distribution were obtained for initial conditions at reaction temperatures in the range 235–255°C (via "hydrogen bracketing") and then continuously for a period of 9 h at 240°C with product analysis being performed every hour by on-line gas chromatography using an FID detector.

Methanation was carried out in a differential tubular reactor utilizing a very high space velocity (around 126,000 h^{-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. He was used as a diluent such that the ratio of partial pressures of the gases was $He/H_2/CO = 78/20/2$. Ar was used as a marker in the ^{12}CO to determine gas-phase holdup. 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 by using an Apple IIe computer with a Cyborg Isaac interface. In conjunction with MS analysis, gas chromatography was used to analyze the steady-state reactor effluent.

RESULTS

Chlorine Content

A comparison of the actual and nominal Cl/Ru ratios is given in Table 1. The results for catalyst 3C as prepared indicate that the Cl level was close to that of saturation (see Fig. 1) even though the catalyst was prepared from research-grade $Ru(NO)(NO_3)_3$.

The amount of Cl retained on the Cl-modified catalysts increased sharply at low levels of dosage and started to level off around a nominal ratio of 0.3 (Fig. 1). This corresponds to a surface coverage of approximately 0.2 (see Fig. 5 and later discussions). 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 (*34, 35*) 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 washing can be used to decrease the amount of re-

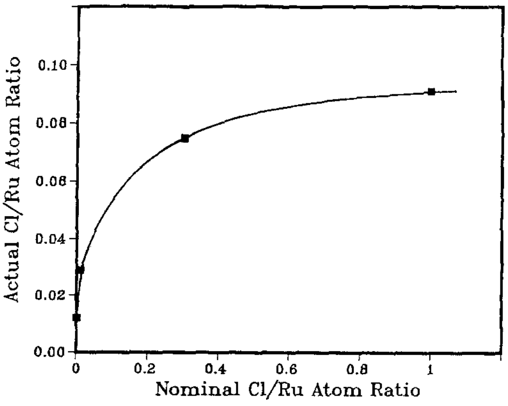

FIG. 1. Actual vs nominal Cl/Ru ratio.

TABLE 2

Chlorine Levels: Effect of CO Hydrogenation

Catalyst	Time on stream (h)	wt% Cl (before)	wt% Cl (after)
3CWW0.30	1	0.071	<0.02
3CWW0.30	6	0.071	<0.02
3CWW1.00	6	0.087	<0.02

sidual Cl in the original catalyst and the results of Kiskinova and Goodman (*33*) suggest that Cl may be leached from the catalyst by the steam produced during CO hydrogenation. Such a removal of Cl from these Ru catalysts during CO hydrogenation was found to be the case. Table 2 shows a comparison of the Cl contents of several catalysts before and after reaction. CO hydrogenation had such a drastic effect that Cl was removed to levels below detectability limits during the first hour of reaction at 240°C.

Dispersion

The average Ru particle size (d_p) and dispersion for the catalysts were estimated from coverages of CO and CH_x intermediates obtained during methanation utilizing isotopic transients as well as from TEM and static gas volumetric measurements and are given in Table 3. The Ru particle size distributions obtained by analysis of the TEM results are presented in Table 3. Clearly, there is no indication of a significant particle size variation between the base catalysts and the Cl-doped catalysts after rereduction.

The d_p's measured by static H_2 chemisorption were larger than the d_p's determined by TEM. Apparently, this was due to chlorine's effect on the surface metal atoms. The actual amount of chlorine in the catalysts is known (Table 1). If it is assumed that the Cl affected only hydrogen chemisorption on surface Ru atoms on a one-to-one atom basis, the corrected d_p^{GV}'s of both catalysts 3CWW and 3CWW0.30 would be 30 Å, which would bring them very close to the d_p^{TEM} range. Given that Cl atoms can affect hydrogen chemisorption on more than one surface Ru atom and the difference in experimental methodology, the agreement between the TEM and the H_2 GV results is quite satisfactory.

Mean particle sizes based on isotopic transients during methanation (d_p^{it}) were calculated from the CO_{ads} and CH_x intermediate abundancies (from Table 6) with the additional assumption that the interaction of these surface species with surface Ru is one-to-one. As was noted before, water produced under methanation conditions effectively removed the Cl from the catalysts. Thus, these estimates accord quite well

TABLE 3

Average Particle Size and Distribution of Ru Crystallites

Catalyst	Percentage of total number of particles (by TEM) in diameter range							d_p^{TEM} (Å)	d_p^{it} (Å)	d_p^{GV} (Å)
	15–25 Å	25–35 Å	35–45 Å	45–55 Å	55–65 Å	65–75 Å	75–85 Å			
3C	72	22	3	1	1	1	0	24	—	—
3CWW	71	16	11	0	0	1	0	25	22	32
3CWW0.00	55	23	15	2	2	1	2	29	—	—
3CWW0.01	60	27	7	4	2	1	1	27	24	—
3CWW0.30	62	24	7	3	2	1	1	27	—	41
3CWW1.00	57	16	16	3	4	1	3	29	26	—

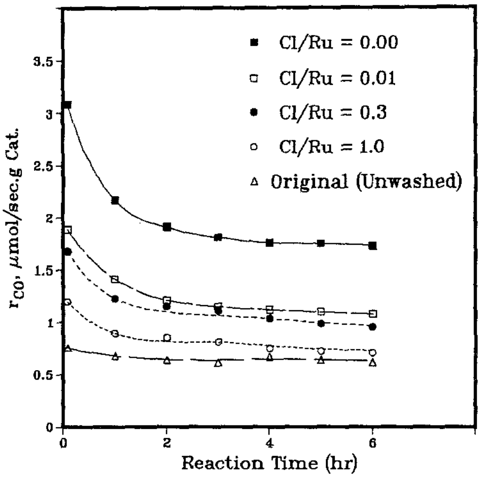

FIG. 2. Catalytic activity of Ru/SiO$_2$.

TABLE 4

Methane Selectivities on the Various Catalysts at 240°C

Catalyst	Initial reaction		After 4 h of reaction	
	% CH$_4$ sel.	% CO conv.	% CH$_4$ sel.	% CO conv.
3C	73.0	0.62	69.9	0.45
3CWW	54.2	1.78	66.6	1.15
3CWW0.00	55.3	1.74	67.9	1.09
3CWW0.01	60.3	1.16	66.3	0.73
3CWW0.30	60.7	1.03	68.6	0.69
3CWW1.00	61.3	0.71	64.8	0.48

with the TEM results and the corrected d_p^{GV}'s discussed previously.

Fischer–Tropsch Reaction

A comparison of the specific catalytic activities of the base catalyst and the Cl-doped catalysts over a 6-h period of continuous F-T reaction is shown in Fig. 2. The catalysts decreased in activity with increasing Cl content. The relative rate of deactivation (on a percentage loss of activity basis) 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.

For higher initial Cl content, the methane selectivity was slightly higher at the initial stages of the reaction, as shown in Table 4. The methane selectivity was greatest for the original, unwashed catalyst, probably because it had one of the highest Cl contents and this Cl—having been present during catalyst preparation—was most likely in the most intimate contact with the metal. Addition of catalyst modifiers such as promoters are well known to be more effective when co-impregnated with the metal salt than when added after reduction of the metal. The initial selectivity comparison, obtained after 10 min of reaction, is considered a better indication of the effect of Cl since the complication of carbon buildup was minimal and since all detectable Cl was removed after longer periods (>1 h) of reaction. The selectivity difference observed was a real function of the catalyst and not of the CO conversion which was held approximately constant at 1%. After 4 h of reaction, the selectivities on all the catalysts were about the same. Apparent activation energies (see Table 5) were calculated for the base catalyst as well as for the Cl-doped catalysts from the rates of methane formation and CO conversion (the Arrhenius plots are shown in Figs. 3 and 4). Also included in Table 5 are the exponents for the power rate law determined for the catalysts.

Isotopic Transients during Methanation

For further insight into the effects of Cl modification, steady-state isotopic tran-

TABLE 5

Rate Expression Parameters for F–T
$-R_{CO} = kP_{H2}^{x} P_{CO}^{y}$

Catalyst	E_{CO} (kcal/mol)	E_{CH4} (kcal/mol)	x	y	Ref.
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	(44)
5% Ru/SiO$_2$	—	—	1.5	−0.6	(45)

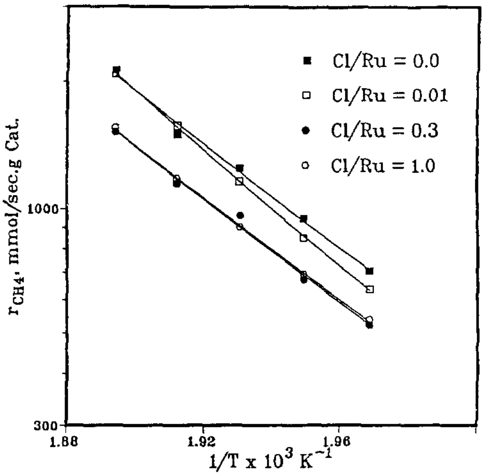

FIG. 3. Arrhenius plots: Effect of chlorine doping (based on rate of CH_4 formation).

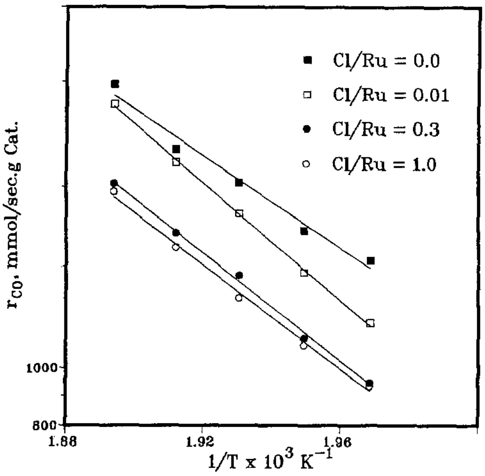

FIG. 4. Arrhenius plots: Effect of chlorine doping (based on rate of CO conversion).

sient kinetic analysis 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 Cl-doped catalysts during methanation. These isotopic transients enable the deconvolution of the reaction rate into contributions due to coverage of the intermediates versus contributions due to the reactivity of the reaction intermediates. The essential features of the technique have been described elsewhere (*40–42*). Important kinetic parameters that can be monitored after switching between the isotopes include the amount of adsorbed CO under reaction conditions and the relaxation time constant of the decay curve (τ), a measure of the average lifetime of the intermediates on the surface. The reciprocal of τ, k, is the pseudo-first-order reactivity constant (*43*) and a measure of the intrinsic TOF over the sites taking part in the reaction. The product of τ and the steady-state rate of formation of CH_4 yields the abundancy (N) of the surface intermediates leading to the formation of methane. For each catalyst, the surface concentrations of unreacted CO and reactive intermediates as well as their residence times on the surface were determined during methanation utilizing isotopic transients. The parameters calculated for these Cl-containing catalysts are summarized in Table 6. These results show that

TABLE 6

Reaction Parameters from Isotopic Transients during Methanation[a]

Catalyst	τ_{CO} (s)	N_{CO} (μmol/g)	τ_{CHx} (s)	N_{CHx} (μmol/g)	R_{CH4} (μmol/s g)	TOF[b] (s^{-1})	TOF[c] (s^{-1})
3CWW	3.5 ± 0.6	99 ± 17.3	8.4 ± 0.6	3.4 ± 0.25	0.41	0.12	0.0040
3CWW0.01	3.2	91	11.1	2.9	0.26	0.09	0.0028
3CWW1.00	3.2	84	8.9	1.4	0.16	0.11	0.0018

[a] T_{rxn} = 200°C, P_{rxn} = 190 kPa, $H_2/CO/He$ = 20/2/78 ml/min.
[b] True TOF = $1/\tau_{CHx}$.
[c] TOF based on R_{CH4} and CO + CH_x intermediate coverage during reaction.

the τ_{CO} did not change, indicating that the strength of the sites for CO adsorption were not influenced by the addition of Cl; however, the decrease in N_{CO} indicates such that it appears that sites which had previously been in intimate contact with Cl did not recover after the chlorine was removed from the catalyst. Similarly, the mean reactivity of sites producing methane was not appreciably affected by the concentration of initial Cl. However, the surface coverage in CH_4 intermediates was greatly affected. Turnover frequencies on the catalyst are also compared. The TOF derived from τ_{CH_x} is, of course, a much better measure of the strength of the reaction sites since it addresses the activity of these sites more directly, unlike the TOF based on the available-surface-metal approach (using the CO plus CH_x abundancies) which lumps in the CO adsorption sites which do not directly contribute toward the production of methane. This latter TOF is more like that traditionally used.

DISCUSSION

CO Hydrogenation

A comparison of methane selectivity on the base catalyst with that on the Cl-doped catalysts reveals that at the initial stages of reaction the selectivity was higher on the Cl-doped catalysts, and 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 h of reaction, the methane selectivities for 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, even though relative differences in activity are maintained. Although CO conversions can have relatively large effects on hydrocarbon product distributions (*12*), the selectivity differences are real based on making comparisons at comparable conversions.

The loss in activity for F–T synthesis of the catalysts with the addition of Cl as well as the decreased surface concentration of methane intermediates during methanation could be due to site blockage or electronic modification of the catalysts, the most prevalent mechanisms employed to explain catalyst additive effects. Much of the experimental evidence to date for sulfur poisoning of metals during CO hydrogenation, for example, has been interpreted to indicate that poisoning is predominantly due to blockage of active sites by adsorbed sulfur (*13, 14*).

As mentioned earlier, elemental analysis of the Cl-doped catalysts after reaction showed that even high loadings of Cl in a Ru/SiO_2 catalyst were completely removed (below the detectability level) in less than one hour of reaction. It would appear that the rapid removal of Cl under CO hydrogenation at 250°C is due to the generation of water vapor in a reducing atmosphere ($99^{+}\%$ H_2 + CO, and $<1\%$ H_2O), apparently without a significant alteration in metal particle size distribution. If catalyst deactivation was due to site blockage and/or additive-metal surface interactions, the F–T activities on the Cl-doped catalysts, irrespective of the initial Cl loading, might be expected to approach the base catalyst activity with time-on-stream due to the compensating effects of increasing site availability with Cl removal and site blockage from coke deposition. On the contrary, it was found that the relative activities of these highly dispersed metal catalysts were maintained according to their initial Cl loading throughout the 6-h F–T reaction runs (Fig. 2). The differences which remained could not be attributed to some very small amount of residual Cl. In addition, there was no evidence to indicate that the Cl-modified catalysts deactivated at a faster rate than the base catalyst. The

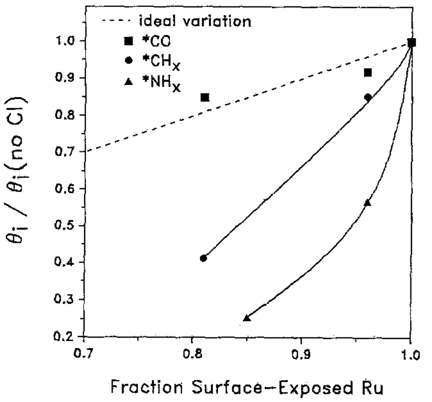

FIG. 5. Cl-induced fractional variation in intermediate coverages with surface-exposed ruthenium.

results show that the effect of the Cl presence lingered long after it was removed, an indication that factors other than site blockage and electronic effects are at play.

The apparent activation energies for CO reaction and methane formation remained essentially unchanged with Cl doping. This suggests that there was no change in the reaction pathway over the Cl-doped catalysts. Also, the exponents of the power rate law did not vary significantly upon Cl doping and compare favorably with the results of Vannice (*44*) and Ekerdt and Bell (*45*).

Isotopic Transients during Methanation

In methanation, Cl also played the role of inhibitor and acted to decrease greatly the concentration of the CH$_x$ surface intermediates without affecting the coverage in CO more than what would be expected from simple site blockage (Table 6 and Fig. 5). The decrease in reaction rate can be attributed to the decrease in N_{CHx}, while the reactivity of the sites did not appear to be affected by the addition of Cl, as the τ's for both CH$_x$ and CO remained essentially constant. From our observations regarding Cl retention during the F–T reaction and the results reported for methanation (*33*), it is safe to assume that Cl was no longer present in significant amounts on the Cl-doped catalysts at the time the transients were obtained, which was 20 min after initiation of the reaction. While this would explain the lack of an effect on the intrinsic activity of the catalysts, the reduction in the coverage of the intermediates, and hence the reaction rate, must have been due to a Cl-induced transformation of active planes into inactive surface structures.

In Fig. 5 the percentage surface-exposed Ru was calculated on the basis of (i) the Ru dispersion determined from TEM results, (ii) the original amount of Cl present after reduction but with the Cl content of SiO$_2$ subtracted off, and (iii) an assumption of one Ru surface atom blocked per Cl atom. Figure 5 shows that the fractional coverage of the CH$_x$ surface intermediates deviated from a purely geometric surface blockage, implying ensemble effects from the sites modified by the departed Cl. Fractional CO coverage, however, varied as simple site blockage, possibly due to the fact that CO requires a single atom for adsorption. However, the results clearly show that the differences observed depend on the initial Cl loading on the catalysts, as was the case during the steady-state F–T reaction runs. Therefore, for these structurally impaired sites, a situation like that seen by Goodman and Kiskinova (*33*) may be possible. For sulfur poisoning of a nickel catalyst these researchers reported a similar nonlinear dependence of the methanation rate on the poison's coverage, and it was postulated that this might be due to the interference of the poison with sites used for the formation and subsequent hydrogenation of the methane intermediates. In our case the sites impaired by the departed Cl may have hampered the production of methane in a similar fashion.

Possible Mechanism(s) of Modification

The steady state Fischer–Tropsch and methanation results clearly show that the added Cl modified the catalysts. In a consideration of the possible mechanisms of modification, simple site blockage and electronic effects are 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 ($1/\tau_{CHx}$) of the catalysts did not change with Cl doping. In addition, the apparent activation energies and the exponents of the power rate expression were not significantly altered by Cl.

The 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 responsible. In addition, there was no change in Ru content after Cl addition and re-reduction probably because the Cl content was too low to form any significant amounts of volatile ruthenium chloride. This lack of volatility would undoubtedly also help to prevent sintering.

It is possible that the presence of Cl caused a rapid initial deactivation of the catalysts during the first few seconds of reaction as a result of a transformation of active surface carbon to an inactive form. However, this would not explain the results found for these catalysts under ammonia synthesis (*46, 47*) where a parallel difference in activity was also seen. In particular, when Nwalor (*46*) used the same catalyst series to catalyze ammonia synthesis (at 400°C, 204 kPa, $H_2/N_2 = 3$) the effect of chlorine on the coverage of the reaction intermediates was much greater (Fig. 5) than what had been observed during CO hydrogenation due to the strong structure sensitivity of the former reaction. This dependence on initial Cl content was observed despite the possibility of N-induced restructuring after much of the Cl had been leached from the catalysts. In the case of the Fischer–Tropsch results (Fig. 2), it is difficult to imagine that initial differences in rapid deactivation for the catalysts would be followed by identical percentage losses of activity over a 6-h reaction period. In addition, the isotopic transient study was performed at $H_2/CO = 10$, where any significant coke deposition should be minimal.

It is doubtful that there is any contribution to the deactivation by the silica support. It is known that silica can be partially dissolved in very basic solutions, giving rise to supported metal catalysts with silica-decorated metal particles (*48*); however, SiO_2 is very stable in slightly acidic solutions. CO adsorption measured by isotopic transients during reaction does not indicate any great loss of metal surface area. Due to the low Cl concentrations in evidence and the relatively low temperatures used, it is doubtful that any Si chlorides would be formed.

Recently, there have been indications that certain elements (Cl, S) can bring about significant rearrangement of Ag, Cu (*49–51*), and Pt (*52*) surfaces. How this may occur has been discussed by Marks and Heine (*52*). Although perhaps electronic in origin, such as is the case when an adatom is chemisorbed on the surface, 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 the low-coordinated metal surface atoms. For example, results showing that even hydrogen chemisorption can cause an expansion of metal–metal distances in the bulk of Pt crystallites in Y zeolite have been reported (*53*), while chemisorption of CO induced disintegration of Rh particles in Y zeolite (*54*).

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 (*55*). 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 re-reduction of the catalysts, oxygen would be released with an attendant structural transformation to the more symmetrical HCP structure of Ru. It is possible that a modifier, such as Cl, may be able to induce new inactive metal surface structures during the oxidation–reduction cycles, possibly by stabilizing them, without modifying the underlying bulk metal particles. Thus, metal surface 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 distribution did not change significantly.

Since all of the Cl-modified catalysts were prepared from the same batch of reduced Ru/silica and were re-reduced under the same conditions (thereby minimizing particle size variation as evidenced by TEM), structural modification of the metal crystallite surfaces induced by the Cl presence is suggested to be a possible mechanism by which Cl modifies the catalytic properties of Ru for CO hydrogenation. Similar explanations concerning the fate and the structural effect of Cl during Rh-catalyzed CO hydrogenation have been communicated by Kip *et al.* (*56*), even though the CO hydrogenation properties of their catalysts were modified differently. Why Cl doping affected CO hydrogenation on supported catalysts but did not affect it on single crystal Ni (*33*) 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 (*36*).

CONCLUSIONS

Chlorine addition to silica-supported Ru catalysts was found initially to increase slightly the methane selectivity 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 active sites, as the average 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 by the authors to be the most plausible 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.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support for this work by the Department of Energy (Grants DE-AC22-84PC70020 and DE-FG02-86ER13624) and the National Science Foundation (Grant CBT-8715541). One of us (J.U.N.) also thanks the United States Information Agency for a Fullbright Junior Fellowship. The authors thank John Shott of the University of Pittsburgh Applied Research Center for the TEM work.

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