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Activated Chemisorption of Hydrogen on Supported Ruthenium

I. Influence of Adsorbed Chlorine on Accurate Surface Area Measurements

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Irreversible hydrogen adsorption onto Ru/Al_2O_3 catalysts prepared from $RuCl_3$ occurs with apparent activation energies as high as 16 kcal/mole at half-saturation coverage, whereas little or no apparent activation energy barriers are encountered over catalysts prepared in the absence of chlorine from $Ru_3(CO)_{12}$. Adsorption uptakes measured at 298 K on chlorine-containing specimens can be as little as one-half the value measured at 373 K even though 24-h equilibration times are used. Addition of low chlorine levels to chlorine-free precursors of 2.8-nm diameter indicates that the first chlorine adatoms to adsorb produce about six activated adsorption sites per chlorine adatom. Further chlorine addition to 2.8-nm crystallites poisons a maximum of 20% of the available hydrogen adsorption sites while ca. 38% of the remaining sites become so activated that they can be populated only after adsorption at ca. 373 K. Additional studies demonstrate that the above-noted effects cannot be attributed to (i) titration of surface oxygen, (ii) incomplete reduction of the catalyst, or (iii) hydrogen spillover. Rather, it appears that the presence of electronegative adatoms decreases electron density at nearby ruthenium atoms thereby inhibiting electron donation to, and dissociative chemisorption of, incoming hydrogen molecules. Observations from these studies suggest that hydrogen adsorption measurements may severely underestimate the number of surface ruthenium atoms. The magnitude of such errors increase at lower adsorption temperatures and at higher chlorine coverages.

INTRODUCTION

Selective chemisorption of hydrogen has been used extensively in the measurement of supported ruthenium surface areas (*1–8*). However, despite the wide acceptance of this characterization technique, some problems and inconsistencies still exist concerning the details of this procedure. For example, Dalla Betta (*1*) and Lam and Sinfelt (*2*) performed hydrogen chemisorption at room temperature, and obtained hydrogen uptakes by extrapolating the linear portion of the adsorption isotherm measured above 120 Torr to zero pressure. In contrast, other workers such as Taylor (*3*), King (*4*), and Bell *et al.* (*5*) chose an adsorption temperature at 373 K to perform similar measurements, while Yang and Goodwin (*7*) claim that it is not feasible to extrapolate the adsorption isotherm due to the contribution of weakly (i.e., reversibly) adsorbed hydrogen. The above-noted discrepancies manifest the necessity to examine the effects of adsorption parameters such as adsorption temperature, catalyst preparation methods, and the manner of data interpretation. These factors have significant effect on the accurate measurement of ruthenium dispersion and average crystallite size which form the basis for subsequent calculations of turnover frequency and/or oxygen–hydrogen titration studies (*9*).

Activated chemisorption of hydrogen on supported Group VIII transition metal catalysts has been reported by Paryjczak *et al.* (*10*) and also by Bartholomew *et al.* (*11–13*). Catalysts included alumina-supported iridium (*10*), alumina- and silica-supported cobalt (*11*), alumina-, silica-, and

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titania-supported nickel (*12*), as well as potassium-promoted–silica-supported iron (*13*). In all cases, hydrogen uptakes were observed to increase significantly with increasing adsorption temperatures. Based on TPD and volumetric adsorption data, Bartholomew *et al.* concluded that kinetically limited adsorption at lower temperatures (e.g., ambient) was due primarily to metal–support interactions, although other factors such as promoters and precalcination conditions may also have played a role.

In this study, the effects of adsorption temperature and catalyst preparation procedures have been examined. It was observed that hydrogen chemisorption on supported ruthenium catalysts, prepared from $RuCl_3$, was highly activated, whereas activated chemisorption was not significant on catalysts prepared in the absence of chlorine from $Ru_3(CO)_{12}$. These observations suggest that activated chemisorption of hydrogen may be related to the presence of electronegative chlorine adatoms. For this reason, an in-depth investigation was undertaken to study the effects of chlorine additives on the chemisorption properties of supported ruthenium catalysts. Adsorption kinetics have also been used where possible to provide insight into the nature of the activated chemisorption process. It is believed that these data may provide useful information leading to a more accurate characterization of ruthenium containing catalysts via hydrogen chemisorption.

EXPERIMENTAL

Materials. Hydrogen and helium used in this study were Linde prepurified grade (99.99% purity) and were further purified by passage through a Deoxo unit at 298 K, a copper turning trap at 500 K, and a 5X molecular sieve trap at 77 K. The catalyst support used was a Harshaw Al-3945 alumina powder with a BET surface area of 234 m^2/g. The chlorine content of this support was 45 ppm as determined by bulk analysis.

Catalysts. Supported ruthenium catalysts were prepared by the following methods:

(*a*) *Incipient wetness impregnation of $RuCl_3$.* Alumina support powders were air dried 4 h at 473 K and impregnated to incipient wetness (0.68 cm^3/g) using aqueous solutions of $RuCl_3 \cdot (1\text{–}3)H_2O$ (Alfa Products) at appropriate concentrations. Following impregnation, samples were calcined at 353 K for 12 h and stored for further use, Low calcination temperatures were employed to prevent catalyst sintering. Taylor (*3*) has shown that such effects can become appreciable at calcination temperatures as low as 373 K.

(*b*) *Vapor decomposition/deposition of $Ru_3(CO)_{12}$.* In this procedure, $Ru_3(CO)_{12}$ (Aesar) and powdered catalyst supports were placed in a stainless-steel tube, evacuated, and sealed under vacuum. The tube was heated in a sand bath to obtain a uniform temperature distribution while being agitated to aid mixing. The temperature was raised to 450 K for 3 h to sublime the ruthenium carbonyl compound, heated to 673 K for 2 h to decompose and deposit the carbonyl compound onto/into the catalyst support and then cooled to room temperature. It should be noted that catalysts prepared by this method are relatively free from chlorine contamination normally introduced during preparation procedures using chloride salts (*6, 14*), and are used as precursors for subsequent comparison studies involving the effects of chlorine additives.

Catalysts employed in this study have been denoted by a prefix in accordance with their preparation method. An "I" represents catalysts prepared by incipient wetness impregnation methods using $RuCl_3$; while the prefix "V" represents catalysts prepared by vapor decomposition of $Ru_3(CO)_{12}$.

Adsorption apparatus. The adsorption apparatus employed was a high-vacuum

Pyrex design with a base pressure of 10^{-4} Pa. High-vacuum greaseless stopcocks (Ace Glass) with Teflon plugs and Viton O-ring seals were used to manipulate gas storage/dosage and minimize hydrocarbon impurities. Adsorption pressures from 0 to 1.3×10^5 Pa were monitored to a precision of better than 1.3 Pa using a Texas Instruments precision manometer employing a fused-quartz Bourdon capsule. Adsorption temperatures were controlled to better than ±2 K by an Omega Engineering temperature controller. Water baths were also employed to minimize temperature variations during static adsorption or kinetic measurements.

Outputs from the manometer were connected to a strip-chart recorder to provide a continuous record of system pressure during kinetic studies. Pyrex and/or quartz adsorption cells of ca. 150-cm^3 volume were used. Catalyst samples were held in place between two coarse frits with average pore diameters of 150 ± 15 μm.

Catalyst reduction and adsorption. All catalysts received a common pretreatment and reduction procedure prior to adsorption studies which included (i) evacuation at 473 K for 8 h to remove traces of water, (ii) *in situ* reduction for 12 h at 673 K in 50-cm^3/min flowing hydrogen, and (iii) evacuation for 2 h at 673 K to remove surface hydrogen. When additional adsorption measurements were necessary, a 2-h re-reduction at 673 K followed by a 2-h evacuation was used to return the catalyst to an "initial state."

Pure hydrogen was dosed onto the catalyst after initial pretreatment and reduction procedures. Adsorption isotherms were typically collected at 273, 296, 338, and 373 K. After the first isotherm was recorded at each temperature the cell was evacuated for 10 min to desorb weakly bound hydrogen and a second isotherm collected under identical conditions. The difference between the extrapolated values of these two isotherms at zero pressure was taken as the net irreversible uptake at that temperature. Generally, 4–6 h was needed for equilibration of the first dose at a pressure near 30 Torr; however, 24 h was used in all studies. During this period the pressure was recorded continuously and the instantaneous adsorption rate determined by a differential method.

Irreversible hydrogen uptakes at 373 K were used to calculate ruthenium surface areas and average crystallite sizes assuming (i) a one-to-one adsorption stoichiometry between adsorbed hydrogen atoms and metallic ruthenium surface atoms, (ii) cubic crystallites with five sides exposed, and (iii) an average surface area of 0.0817 nm^2 per surface ruthenium atom (*1*, *7*).

RESULTS AND DISCUSSION

Temperature Dependence of Hydrogen Chemisorption on Catalysts Prepared from $RuCl_3$ and $Ru_3(CO)_{12}$

Hydrogen adsorption isotherms collected at 273, 296, 338, and 373 K over catalyst specimens prepared from $RuCl_3$ are shown in Fig. 1. Both reversible and irreversible adsorption are evident. The upper traces (solid points) represent the total isotherms which include both reversible and irreversible uptakes, while the lower traces (open points) represent the reversible uptakes, defined as that part of adsorbed hydrogen

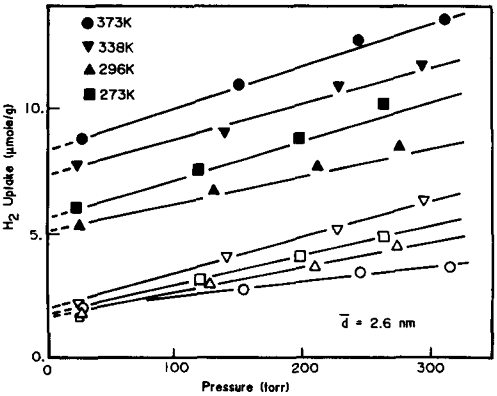

FIG. 1. Hydrogen adsorption isotherms on an I-0.43% Ru/Al_2O_3 catalyst. Solid points represent reversible plus irreversible hydrogen uptakes, open points represent reversible hydrogen uptakes only.

which could be removed by evacuation for 10) min at the adsorption temperature. According to Yang and Goodwin (*7*), this reversibly adsorbed hydrogen is associated with the metal and may exist in either a precursor state or a state of low adsorption energy. Observations made during this study support the above arguments and demonstrate that the amount of reversibly adsorbed hydrogen decreased as a given catalyst was sintered, which also indicates that some reversible adsorption was associated with the metal. It was also noticed that reversible uptakes had a general tendency to increase initially with increasing adsorption temperature, then decrease as the temperature exceeded 338 K possibly due to a mild activation and subsequent desorption/depopulation of weakly bound states.

Another trend presented in Fig. 1 is the increase in irreversible hydrogen uptake with increasing adsorption temperature despite the fact that the first adsorption dose was allowed to equilibrate for 24 h. This temperature dependence was further demonstrated by a "temperature jump" experiment in which pure hydrogen was dosed at room temperature following the standard pretreatment-reduction procedure, while the catalyst was allowed to equilibrate in ca. 30 Torr of hydrogen for 24 h. The adsorption uptake was then measured before the adsorption temperature was raised ("jumped") from 296 to 373 K (or some other specified temperatures) for 5.5 h. This "jump" in adsorption temperature enabled adsorption which normally required higher activation energy to proceed. Finally the adsorption temperature was slowly lowered to 296 K (cooling rate of ca. 5 K/min) and a new uptake measured. The reversible uptake was also measured to account for the contribution from weakly bound states. The parameter recorded in these experiments corresponded to the percentage increase in irreversible hydrogen adsorption resulting from the 5.5-h "jump" in adsorption temperature compared to the amount of irreversible hydrogen adsorption which occurred in the previous 24 h at 296 K. The increase in uptake did not result simply from conversion of reversibly bound hydrogen to irreversibly bound hydrogen, since comparable reversible uptakes were measured both before and after the temperature jump.

Figure 2 shows the results obtained from such temperature jump experiments at 338, 373, 423, and 473 K on I-2.0% Ru/Al_2O_3 (3.0 nm) specimens. As noted in Fig. 2, 54 and 81% increases in irreversible hydrogen uptake result from temperature jumps to 338 and 373 K, respectively. Further increases in adsorption temperature beyond 373 K did not result in additional uptakes probably due to saturation of the ruthenium surface by hydrogen.

Hydrogen chemisorption on catalyst samples prepared in the absence of chlorine using $Ru_3(CO)_{12}$ did not exhibit the above noted trend. Only a 6% increase in irreversible uptake was observed following similar jumps in adsorption temperature. This distinctive difference in adsorption behavior apparently arose from differences in the catalyst preparation methods. Indeed, it has been reported by Don *et al.* (*14*) that significant amounts of chlorine are retained on the surfaces of ruthenium powders prepared by reduction of $RuCl_3$ in flowing H_2 at 673 K, whereas relatively clean ruthenium

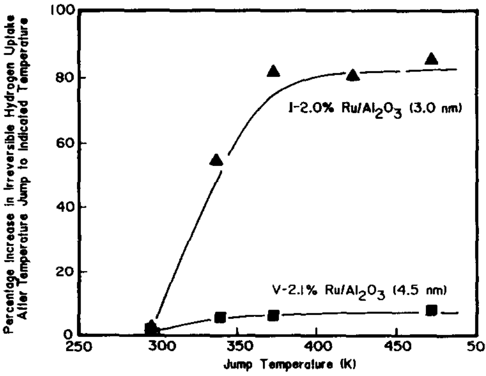

FIG. 2. Percentage increase in irreversible hydrogen uptake after a 5.5-h temperature jump to the indicated temperature.

surfaces can be prepared by reduction of $Ru_3(CO)_{12}$. Tightly bound chlorine impurities, produced during reduction of $RuCl_3$, were only removed after hydrogen reduction at temperatures of ca. 1200 K (*14*). Similar treatments are not feasible for supported catalysts as significant decreases in ruthenium dispersion would result.

Potential Effects of Surface Oxygen Titration and/or Hydrogen Spillover

Since hydrogen is known to react readily with surface oxygen at 373 K (*3, 6, 9*), it is possible that the increases in hydrogen uptake observed at higher adsorption temperatures could result from hydrogen consumption during titration of surface oxygen. To determine whether catalysts examined in this study were adequately reduced, I-0.43% Ru/Al_2O_3 (2.6 nm) catalysts were reduced and evacuated following the standard pretreatment procedure described previously. Specimens were then dosed with excess oxygen at 720 K for 8 h and the consumption of O_2 recorded. By knowing the ruthenium loading and assuming the formation of RuO_2, the percentage of ruthenium that had been initially reduced was calculated to be between 95 and 105%, in good agreement with the general findings of Gay (*8*) and Clausen *et al.* (*15*).

Considerations of this type were also extended to evaluate the possibility of reoxidation of surface ruthenium atoms by background impurities such as O_2 and H_2O during evacuation. This possibility was examined in detail by the following experiment. First, a 373 K temperature jump procedure was applied to an I-5% Ru/Al_2O_3 (3.8 nm) catalyst specimen. This specimen was subsequently heated *in situ* under ca. 30 Torr of hydrogen at 573 K for 2 h to desorb water which may have resulted from hydrogen titration of surface and/or residual oxygen. A liquid nitrogen trap, which served as a cryogenic pump, was placed in close proximity to the adsorption cell to collect desorbed water. Trapped water was then expanded into a known volume and the pressure monitored. Results of these experiments revealed that no measurable amounts of water or other condensibles could be detected, suggesting that complications introduced by titration of surface impurities could be discounted.

Another potential explanation for the observed increases in hydrogen uptake at elevated temperatures is hydrogen spillover. Indeed, hydrogen is known to migrate from metal adsorption sites onto the support in a number of adsorption systems (*16, 17*). The rate of spillover generally increases with increasing adsorption temperature, hydrogen pressure, and metal dispersion (*16*). In the context of this study, however, spillover was not believed to provide a plausible explanation for the observed behavior since values of metal dispersion calculated from hydrogen uptakes at 373 K were always less than or equal to 0.35 and hydrogen uptakes did not increase with increasing adsorption temperatures beyond 373 K or adsorption times beyond 5.5 h (Fig. 2).

Effects of Chlorine Additives

A chlorine-free catalyst precursor, namely, V-2.3% Ru/Al_2O_3 (2.8 nm), was employed to study the effects of chlorine additives. Samples from this precursor batch were slowly passivated, removed from the adsorption system, and dosed to incipient wetness with an aqueous solution of HCl of appropriate concentration. Ratios of the number of dosed chlorine atoms to the number of surface ruthenium atoms, $Cl_{(d)}/Ru_{(s)}$, ranged from 0.1 to 50.0. After chlorine dosage, samples were dried at 353 K for 12 h and stored for further use. The ratio of chlorine atoms retained by the catalyst after reduction to the number of surface ruthenium atoms before addition of chlorine (viz., $Cl_{(r)}/Ru_{(s)}$) has been defined as the monolayers equivalent of chlorine retained. This quantity was determined by means of bulk chlorine analyses using Coulometric titration methods (Galbraith).

Two effects on hydrogen chemisorption

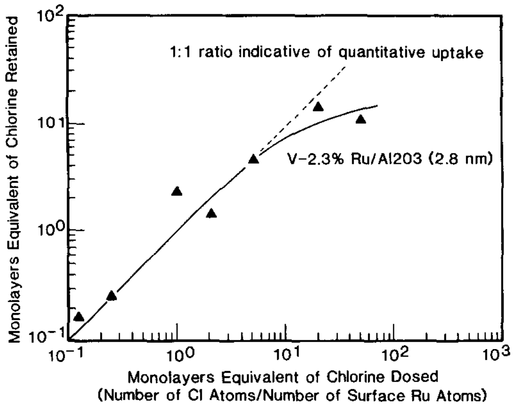

FIG. 3. Monolayers equivalent of chlorine retained vs monolayers equivalent of chlorine dosed.

were observed to result from chlorine addition: (i) activated chemisorption and (ii) site poisoning. Since activated adsorption was not observed over chlorine-free specimens, the difference in hydrogen uptake between a 24-h adsorption at 298 K and after a 373-K temperature jump, was taken, by definition, to represent the number of sites which became activated by chlorine. Differences in the irreversible hydrogen uptake at 373 K, between chlorinated catalysts and unchlorinated precursors, were used to indicate the number of hydrogen adsorption sites which became lost/poisoned by chlorine adatoms.

Figures 3 and 4 present results obtained from the above-noted chlorine studies. In Fig. 3, the monolayers equivalent of chlorine retained are compared vs the monolayers equivalent of chlorine dosed. As shown, the first portion of chlorine dosed (viz., $Cl_{(d)}/Ru_{(s)} \leq 10.0$) is totally retained by the catalyst. While direct differentiation between chlorine adatoms retained by ruthenium vs chlorine adatoms retained by alumina support is not possible in this experiment, as demonstrated in Fig. 4, changes in the number of (i) activated chemisorption sites and (ii) chlorine blocked sites, all occur at chlorine dosage levels below one monolayer. These data suggest that low dosage levels of chlorine have higher affinities for surface ruthenium sites compared to the much larger surface areas provided by the alumina support. This argument is further supported by the findings of Gudde and Lambert (*18*) who reported, based on AES and LEED data, that chlorine adsorbed on Ru(100) surface planes with high efficiency.

Figure 4 also demonstrates that the percentage of sites which become activated by the addition of chlorine increases with the $Cl_{(r)}/Ru_{(s)}$ ratio until 20% of the available adsorption sites are lost over these 2.8-nm crystallites. These data indicate that only a fraction of the available ruthenium surface atoms (i.e., specific sites) are responsible for the strong adsorption of chlorine and also that activated chemisorption is caused by chlorine adatoms.

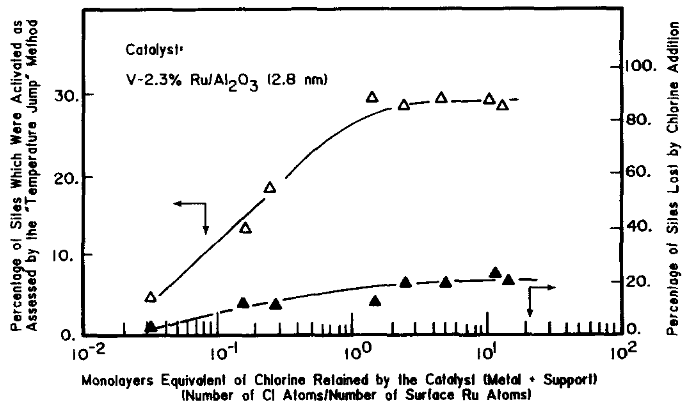

FIG. 4. Percentage of sites activated and percentage of sites lost vs the amount of chlorine retained.

Adsorption Activation Energies

As described by other workers (*1, 3, 8, 19, 20*), hydrogen adsorption onto supported ruthenium can often be a slow process with complex kinetics. In general it may begin with a period of fast adsorption followed by a regime which can be adequately fit to an Elovich equation (*8*). Beyond this regime, at relatively high coverages, a slow form of adsorption may occur at an almost constant rate throughout the rest of the adsorption process. The time required for equilibration may never be clearly defined, since pressure changes caused by slow adsorption near saturation coverage may be too small to be measured and/or masked by thermal variations in the laboratory during the experiment.

To examine the effects of chlorine on the apparent activation energy, a V-2.1% Ru/Al_2O_3 (4.5 nm) catalyst precursor was used to prepare three samples with different chlorine dosages. The level of chlorine dosed onto these specimens (i.e., $Cl_{(d)}$/$Ru_{(s)}$) was equal to 0.0, 0.50, and 18.93, respectively. The adsorption rate, in the form of the pressure change vs time, was monitored for ca. 2 h after hydrogen dosage. The surface coverage of hydrogen, θ_H, was defined/calculated based on the assumptions that (i) only monolayer adsorption occurred, (ii) reversible adsorption occurred rapidly and was not reflected in measured adsorption rates greater than 3 min after dosing, and (iii) surface saturation by hydrogen occurred in all cases at 373 K. Activation energies at various coverages were calculated from Arrhenius plots of measured adsorption rates determined at different adsorption temperatures and at constant coverages (see Fig. 5).

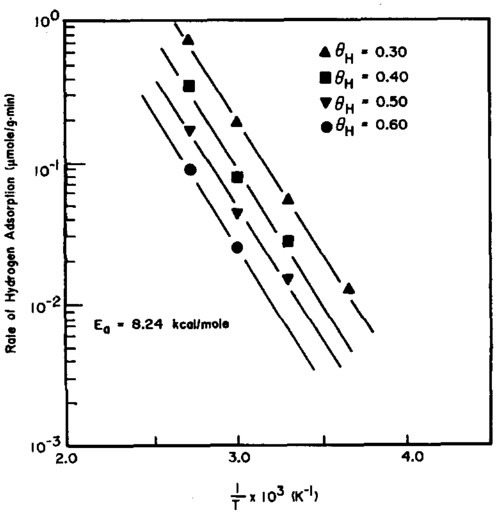

FIG. 5. Arrhenius plot for hydrogen chemisorption on a chlorinated V-2.1% Ru/Al_2O_3 (4.5 nm) catalyst. θ_H is the hydrogen surface coverage, and E_a is the apparent activation energy for hydrogen chemisorption.

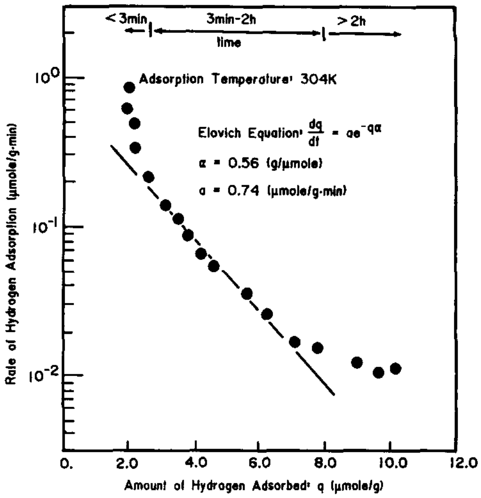

FIG. 6. Elovich fit of hydrogen adsorption rate vs coverage. Catalyst: V-2.1% Ru/Al_2O_3 (4.5 nm), $Cl_{(d)}$/$Ru_{(s)}$ = 91.65, $Cl_{(r)}$/$Ru_{(s)}$ = 18.93.

An alternate method for collecting kinetic data is to obtain activation energies based on adsorption rates measured at zero coverage, since the above-noted assumptions are not required. With this in mind, the rate of adsorption was fit to the Elovich equation shown in Fig. 6. Unfortunately, the Elovich equation could fit only adsorption data collected between ca. 3 min and 2 h after dosage, negating the potential applicability of this procedure.

The apparent activation energies measured over V-2.1% Ru/Al_2O_3 catalysts (4.5 nm) at approximately half-coverage increased from 0–1 kcal/mole over chlorine-free specimens to values of 7–8 and 8–9 kcal/mole as these catalysts were dosed with 0.5 and 18.93 monolayers equivalent of chlorine, respectively (see Fig. 5). Similar studies performed in our laboratory using catalysts prepared from $RuCl_3$, yielded activation energies as high as 16 kcal/mole over 2.6-nm crystallites (*21*). The observed increases in activation energy caused by low levels of chlorine addition parallel similar observations presented in the previous section which noted that low levels of chlorine have higher affinities for ruthenium surfaces compared to those provided by the support. These results provide direct evidence for the enhancement of activated chemisorption by adsorbed chlorine which may result from combinations of various electronic and geometric factors.

Electronic Considerations

Numerous theoretical and experimental studies have shown that the electronic structure of transition metals can be significantly modified by electronegative adatoms such as Cl, S, and P (*22–27*). UPS studies by Kelemen and Fisher (*22*) have shown that the work function of Ru(001) surfaces increases linearly with the sulfur coverage. Kiskinova and Goodman (*24*) reported reductions in the adsorption rate, the activation energies for desorption, and the hydrogen and carbon monoxide uptakes over Ni(100) surfaces in the presence of Cl, S, and P adatoms. It was claimed that the magnitude of these perturbations could be correlated with the electronegativities of the adatoms. These results suggested that a reduction in local electron density at a metal surface may be induced by electronegative adatoms.

The above rationale may be extended to the present observations of activated hydrogen chemisorption on chlorinated ruthenium catalysts. Since the formation of Ru–H chemisorption bonds requires donation of electrons from surface ruthenium atoms to incoming hydrogen molecules, the presence of electronegative species may cause a decrease in local electron density thereby creating a higher activation energy barrier for dissociative hydrogen chemisorption. A converse rationale has been employed by Ertl *et al.* (*26*) to explain the diminution of activated nitrogen adsorption over Fe(100) surfaces in the presence of potassium promoters. Although their work involved a different adsorption system, the effects of surface additives on the activation energy for adsorption were clearly demonstrated.

Geometric Considerations

The presence of electropositive adatoms (e.g., potassium, sodium) does not necessitate a decrease in the activation barrier for dissociative adsorption on transition metal surfaces. In the work of Bartholomew *et al.* (*11, 13*), it was observed that hydrogen chemisorption became more activated as boron and potassium were added to cobalt and iron catalysts. Shyu *et al.* (*28*) also reported that hydrogen chemisorption on silica-supported ruthenium catalysts was suppressed (possibly due to activated chemisorption) after doping with alkali ion promoters. These results may be attributed to the blockage of surface diffusion pathways by promoters. Indeed, it is possible that surface diffusion and rearrangement of the adlayer may become the rate-limiting steps for adsorption at high coverages. If this is the case, then it is conceivable that geometric blocking by adatoms/promoters can inhibit surface movement of adsorbed states and impose a kinetic barrier on the adsorption process.

Relative Importance of Electronic Effects vs Geometric Effects

Indirect evidence favoring the influence of electronic effects can be found in Fig. 7. In this figure, the percentage of sites activated is plotted vs the percentage of sites lost due to chlorine addition. As noted from the slope of the curve at low chlorine dosage levels, six adsorption sites become activated for every adsorption site which is

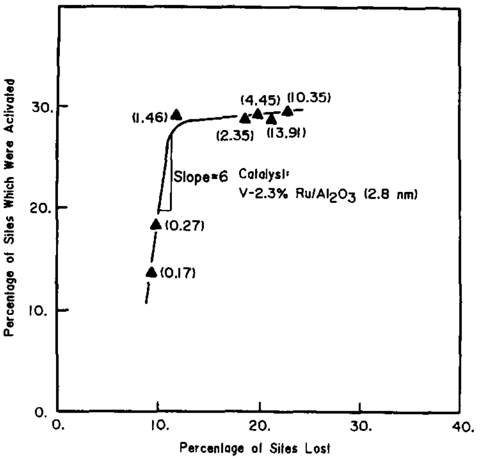

FIG. 7. Percentage of sites activated by chlorine addition vs percentage of sites lost by chlorine addition. The number in parentheses indicates the $Cl_{(r)}/Ru_{(s)}$ ratio of the specimen.

lost. Furthermore, this ratio decreases significantly at higher chlorine coverages. This trend contrasts that which would be expected if a geometric effect prevailed, since kinetic limitations imposed by site blockage are expected to become more severe as the coverage of chlorine is increased. Therefore, it can be suggested that the activated adsorption behavior observed in this study is due primarily to electronic modification of ruthenium by adsorbed chlorine.

A more detailed discussion concerning this behavior will be presented in part II of this study (*29*).

CONCLUSIONS

The effect of pre-adsorbed chlorine adatoms on the chemisorptive properties of alumina-supported ruthenium crystallites has been investigated. Electronegative chlorine adatoms appear to decrease the local electron density at nearby surface ruthenium atoms and create a higher activation energy for hydrogen chemisorption approaching 16 kcal/mole (*21*). As a consequence, attenuated hydrogen chemisorption at ambient adsorption temperatures is observed. This activated chemisorption behavior has been observed exclusively on catalyst samples prepared from $RuCl_3$, indicating that significant amounts of surface chlorine are retained on these samples after drying, calcination, and H_2 reduction at 673 K. Catalysts prepared by vapor decomposition/deposition of $Ru_3(CO)_{12}$ in the absence of chlorine do not exhibit the above-noted behavior.

Addition of chlorine to uncontaminated ruthenium catalysts causes an increase in the adsorption activation energy as well as site poisoning. The increased activation barrier can be overcome by adsorption at 373 K; while site poisoning appears irreversible over the temperature range examined in this study (ca. <673 K).

Observations from this study suggest that hydrogen chemisorption measurements at room temperature significantly underestimate the surface areas of supported ruthenium catalysts. Alternatively, the 373-K temperature jump procedure described in this work can provide more reliable and accurate assessments of the true surface area. It appears that hydrogen chemisorption can be used as a sensitive probe for monitoring the electronic and geometric modification of supported ruthenium surfaces by adsorbed chlorine as discussed in detail in the next paper (*29*).

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