

The Effect of Chlorine on Hydrogen Chemisorption by Silica-Supported Ru Catalysts: A Proton NMR Study

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Silica-supported ruthenium catalysts prepared from the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ precursor contain residual chlorine after reduction in flowing hydrogen. The amount of this chlorine was determined by X-ray fluorescence spectroscopy to be less than one monolayer on the ruthenium surfaces. Both volumetric hydrogen chemisorption and proton NMR show suppression of hydrogen chemisorption capacity associated with the presence of chlorine contamination, which can be removed effectively with hot water elution. The variations of the hydrogen chemisorption capacity with chlorine coverage suggests that chlorine would completely block and poison the Ru surfaces for hydrogen chemisorption at a Cl coverage of about 76%. The effect of residual chloride on the proton NMR resonance position and the spin–lattice relaxation time for the chemisorbed hydrogen indicates an electronic interaction between Cl adspecies and surface Ru, which results in the weakening of the H–Ru_s chemisorptive bond at the Ru surfaces. This reduced H–Ru_s interaction may be the cause for an increase in the ratio of the reversibly adsorbed hydrogen over the irreversibly adsorbed hydrogen with increasing Cl coverage. It is proposed that the mechanism for suppression of hydrogen chemisorption by chlorine involves both physical site blocking of surface Ru atoms and short-ranged electronic interactions between Cl adatoms and neighboring surface Ru atoms. © 1992 Academic Press, Inc.

INTRODUCTION

Selective hydrogen chemisorption is the most common technique used to measure the fraction of Ru atoms exposed at the surface (dispersion) in supported Ru catalysts. However, this method is not accurate when the ruthenium surfaces are contaminated with various adatoms. Chlorine is a common contaminant in supported Ru catalysts, since these catalysts are often prepared using the chlorine-containing precursor ruthenium trichloride.

The effect of residual chloride on the chemisorptive properties of Ru/SiO₂ catalysts has been studied by Gonzalez and co-workers (1). They found that catalysts prepared from the precursor $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

contained residual chloride after reduction at normal reduction temperatures (573–773 K). The residual chloride significantly suppressed the capacity for hydrogen chemisorption. Using a method of adding Cl₂ directly onto clean Ru/SiO₂ catalysts, Lu and Tatarchuk (2, 3) observed the same chlorine effect and attributed the attenuated hydrogen chemisorption at ambient temperatures to a short-ranged electronic modification of the surface Ru atoms by the pre-adsorbed chlorine. They also observed that hydrogen adsorption on chlorine-contaminated Ru catalysts is an activated process with activation energies in the range of 4 to 16 kcal/mole, depending on ruthenium particle size. Based on their observations of increased activation energy for hydrogen

adsorption with decrease in ruthenium particle size, they proposed that the electro-negative Cl atoms preferentially adsorb on defect-like Ru sites and inhibit electron donation from the basal plane Ru sites to hydrogen molecules.

The reducibility of ruthenium trichloride precursors incorporated on an alumina support has been studied by a number of researchers (4–6). It has been shown by Bossi *et al.* (6) that Cl^- ions have a much stronger tendency to remain in the $\text{Ru}/\text{Al}_2\text{O}_3$ than in the Ru/SiO_2 catalysts after hydrogen reduction under the same conditions. The presence of Cl^- ions may indicate an incomplete reduction of Ru^{3+} to Ru^0 .

Chen *et al.* (7) have studied the effect of chlorine on the chemisorption of carbon monoxide on Ru/SiO_2 catalysts using infrared spectroscopy. Their results indicate a significant change of the bonding of CO to surface Ru in the presence of coadsorbed chlorine. The Ru–CO bonding strength is suggested to be altered by withdrawal of *d*-electron density from Ru to the coadsorbed electronegative chlorine. This effect may enhance CO dissociation and consequently increase per-site methanation activity on Ru catalysts, as observed by Mieth and Schwarz on $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts (8). For the same reaction, Iyagba *et al.* (9) also found an initial increase in methane selectivity with increasing chlorine content on Ru/SiO_2 catalysts. However, the presence of chlorine on the Ru/SiO_2 catalysts strongly inhibits the hydrogenolysis of propane, as observed by Miura *et al.* (10). This opposite effect is possibly caused by one chlorine atom blocking and poisoning a group of ruthenium atoms necessary for the reaction.

Direct observations of the effect of residual chloride on hydrogen chemisorption by Ru catalysts are possible via proton NMR. A comparison of two separate studies on the chlorine-contaminated Ru/SiO_2 (11) and the clean Ru/SiO_2 (12) catalysts has indicated a significant difference in the NMR resonance position for the hydrogen chemi-

sorbed on ruthenium surfaces. A downfield shift of this resonance line in the presence of Cl was confirmed in a carefully conducted experiment (13).

To better understand the electronic and site blocking effects of chlorine on Ru/SiO_2 catalysts, a more detailed study was carried out and the results are presented here. ^1H NMR was used as a direct probe to observe the influence of residual chloride on the hydrogen chemisorbed on ruthenium. The techniques of volumetric hydrogen chemisorption and X-ray fluorescence were also employed to provide supplementary information to assist the interpretations of the proton NMR results.

EXPERIMENTAL

Catalyst Preparation and Reduction

The Ru/SiO_2 catalysts were prepared by incipient wetness impregnation of an aqueous solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (AESAR) with a dried Cab-O-Sil HS5 silica support (300 m^2/g BET surface area). About 2.5 ml of impregnating solution per gram of SiO_2 was needed to achieve incipient wetness. The slurries obtained after impregnation were dried for 24 hr at room temperature and 6 hr in air at 383 K. Two Ru/SiO_2 catalysts were prepared with a Ru loading of 4 and 10 wt%, respectively.

Catalyst reduction was carried out using a volumetric chemisorption apparatus equipped with a high-vacuum system described elsewhere (12). Reduction by flowing hydrogen was performed directly inside a Pyrex cell connected to the chemisorption apparatus, which was loaded with approximately 1 g of a Ru catalyst sample. While flowing helium gas was introduced to the catalyst bed in the cell, temperature in the cell was raised to 423 K by a cylindrical furnace. The helium was then replaced by hydrogen at a flow rate of 50 cm^3/min . The cell temperature was further raised at a rate of 5 K/min to a final temperature of 723 K. Hydrogen reduction was carried out for 2

hr at this final temperature. Helium (99.999%) and hydrogen (99.8%) gases (Air Products) were used as received for the catalyst reduction process.

Water Elution Treatment

The technique of hot water washing to eliminate residual chloride from a Ru/SiO₂ catalyst was first used by Muira *et al.* (10) with no experimental details being reported. In the present study, the reduced Ru/SiO₂ catalyst samples were washed repeatedly in hot distilled water (363–368 K). Successive cycles of wash (one wash consisted of about 20 ml of water per gram sample) and reduction were performed for each sample. The washed samples were dried and reduced again in the flow-through cell at 673 K for 2 hr followed by a 2-hr evacuation period to an ultimate pressure of about 10⁻⁶ Torr to remove traces of water and surface hydrogen before hydrogen chemisorption measurements were taken. Hydrogen chemisorption was carried out at room temperature on the washed samples after every wash. The water after washing was measured for acidity by a digital ATC pH meter (Cole-Parmer) and also analyzed by atomic absorption spectroscopy for Ru content.

Volumetric Hydrogen Chemisorption

The volumetric hydrogen chemisorption was carried out in the above-mentioned chemisorption apparatus. Hydrogen gas for volumetric chemisorption was further purified by passing it through a catalytic hydrogen purifier (Engelhard Deoxo) in series with a gas purifier with Drierite and 5-Å molecular sieve (Alltech) to remove traces of oxygen and moisture. After reduction, the catalyst sample was evacuated at the reduction temperature to a final pressure of 10⁻⁶ Torr before it was cooled to ambient temperature (294 K) for hydrogen chemisorption experiments. The total hydrogen adsorption isotherm was measured in a

pressure range of 0–30 Torr. An equilibration time of 4 hr was used for the first dose and 1 hr for subsequent doses. The isotherm for reversible hydrogen adsorption was collected under the same conditions after a 10-min evacuation period to 10⁻⁶ Torr following the total adsorption. The irreversible hydrogen uptake was obtained by taking the difference between the values of the total and the reversible isotherms extrapolated to zero hydrogen pressure.

X-ray Fluorescence Analysis

The compositional analyses of Ru/SiO₂ catalyst samples for Cl were carried out using a Siemens SRS-200 sequential X-ray fluorescence spectrometer. A chromium X-ray tube operated at 50 kV and 50 mA was used as the excitation source.

A selected number of Ru/SiO₂ catalyst samples were analyzed quantitatively by the method of X-ray fluorescence (XRF) to determine the chlorine contents in these catalysts. The catalysts were reduced at least once prior to XRF analysis. Initially, about 0.1 g of a reduced catalyst sample was prepared for quantitative analysis by combining with 0.3 g of silica (Alfa) in a Spex grinding mill and the mixture was homogenized. The resulting sample was then poured into a Spex cup for XRF analysis. Polypropylene film with a thickness of 6.3 μm was used to seal the sample in the Spex cup.

Two different techniques were employed to quantify the amount of Cl present in the catalyst samples. The first method consisted of spiking the catalyst samples containing chlorine with sodium chloride and then extrapolating the observed Cl fluorescence intensities to obtain the initial concentration of Cl in the samples. The second method simply compared the intensity of a standard (NaCl) containing 1000 ppm Cl with those from the catalyst samples. The two methods yielded very close results on all the samples, with experimental errors of 1.5% or less. The average result of the two

measurements was reported in the present study.

NMR Sample Treatment

A needle-bellows device made of stainless steel was used for direct reduction of a catalyst sample in flowing hydrogen inside a 5-mm NMR tube (12). The 18-gauge syringe needle was capable of moving vertically by more than 6 cm through adjustable compression and extension of the bellows. Vacuum-tight connections were made between the NMR tube and the needle-bellows assembly and also between the assembly and the manifold mentioned above. In addition, a cylindrical furnace provided uniform heating around the NMR tube and the temperature of the furnace was monitored and controlled to ± 1 K.

With helium gas flowing through the needle, the needle was lowered to the bottom of the NMR tube, which contained approximately 60 mg of catalyst sample. The procedure for reduction in flowing hydrogen was the same as previously described for the volumetric chemisorption experiment, with a hydrogen flow rate of 15 cm³/min. After reduction, the needle was lifted out of the sample, and evacuation proceeded for 2 hr at the reduction temperature before the sample was allowed to cool to ambient temperature. Purified hydrogen was then dosed through the needle to the sample and the system was allowed to equilibrate for 4 hr. The NMR tube containing the sample was then immersed in a water bath and sealed off with a micro-torch. The exact sample weight was measured after the NMR tube was heat-sealed by subtracting the tare weight of the tube, which was measured prior to loading the sample.

NMR Experiment

The home-built NMR spectrometer (14) used for the present study was operated at 220 MHz for proton resonance. A proton-free probe with a doubly wound coil (15) was used for all the NMR measurements. The probe quality factor Q was set at about

100 to obtain the optimal values of sensitivity and ring down time for a fixed pulse power. The spectrometer's receiving system has the characteristics of rapid recovery and acceptable linearity (16).

All proton NMR spectra were collected under a repetitive 90° single-pulse sequence. The recycle time between rf pulses was set at 0.2 sec to selectively suppress the intense signal associated with protons in the silanol group in the catalyst support, which has a relatively long spin-lattice relaxation time T_1 (on the order of seconds). The above repetition rate avoids T_1 saturation of the peak corresponding to hydrogen chemisorbed on ruthenium. The total number of scans for data acquisition on each catalyst sample was 10,000 for adequate signal-to-noise ratio. The inversion recovery pulse sequence (180°- τ -90°) was applied here to measure the spin-lattice relaxation times of the silanol protons (in the time domain) and of the hydrogen chemisorbed on ruthenium (in the frequency domain). TMS was used as the reference standard for the observed lineshifts.

For accuracy in spin counting, a water sample was doped with sufficient FeCl₃ such that the linewidths of the standard and unknown were comparable. The doped water was sealed in a capillary tube having the same length as the catalyst sample in the NMR tube to offset errors due to B_1 inhomogeneity of the coil. All proton NMR measurements were taken at ambient temperature (294 \pm 1 K).

RESULTS

The effectiveness of hot water washing in eliminating residual chloride on Ru/SiO₂ catalysts is demonstrated by the two proton NMR spectra shown in Fig. 1. The catalyst was 10% Ru/SiO₂ and the catalyst samples were under 30 Torr hydrogen pressure. Spectra A and B were taken on a washed (six washes) and an unwashed catalyst sample, respectively. An intense resonance at about 1 ppm (relative to TMS) was observed from both spectra, which corre-

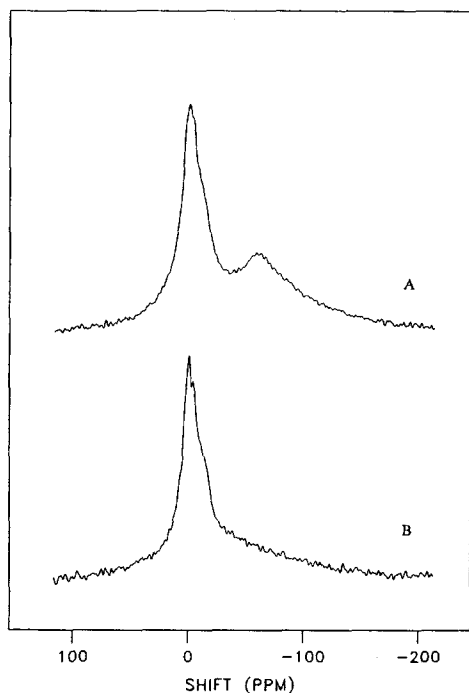


FIG. 1. NMR spectra of chemisorbed hydrogen on a (A) washed and (B) unwashed 10% Ru/SiO₂ catalyst under 30 Torr gaseous hydrogen. TMS was used as the reference for the lineshift.

sponds to the silanol proton in the silica support. A broad resonance upfield to the silanol peak at about -59 ppm was also observed in Spectrum A, and a broad shoulder having a first moment of -45 ppm was seen in Spectrum B. The lineshift results reported here are in agreement with the previous observations on chlorine-contaminated Ru/SiO₂ catalysts (11, 13, 15). The two spectra can be deconvoluted by fitting a Lorentzian line for the silanol peak and a Gaussian line for the hydrogen-on-ruthenium peak in the case of Spectrum B. Thus the intensity of the hydrogen-on-ruthenium peak can be obtained by integrating the area under the deconvoluted peak. Obviously, the intensity of the hydrogen-on-ruthenium peak on the washed catalyst is much higher (about 4 to 5 times) than that on the unwashed catalyst, indicating recovery of a large fraction of Ru adsorption sites after washing.

The effect of hot water washing on hydrogen chemisorption capacity for the 10% Ru/SiO₂ catalyst is illustrated in Fig. 2. Volumetric measurements from both the

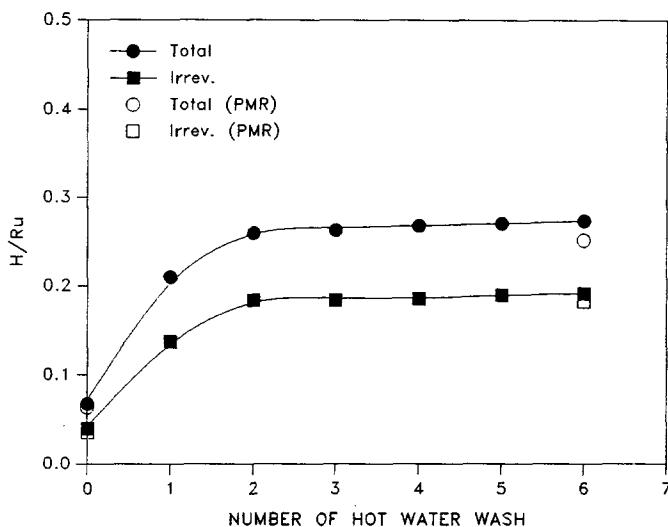


FIG. 2. Variations of the H/Ru ratios for both the total and the irreversible adsorption measured by the volumetric technique as functions of the number of hot water washes on a 10% Ru/SiO₂ catalyst. Values from the NMR measurements are also shown.

TABLE I
XRF and Proton NMR Results for the
10% Ru/SiO₂ Catalyst

Number of hot water washes ^a	Cl wt% ^b	30 Torr H ₂		Irreversible H	
		Shift (ppm)	width (kHz)	Shift (ppm)	width (kHz)
0	0.43	-45	17.9	-42	18.8
6	0.00	-59	13.1	-57	14.7

^a Approximately 20 ml of distilled water per gram of catalyst was counted as one wash.

^b The data were obtained from XRF measurements.

total and the irreversible hydrogen adsorption are given as the filled circles and squares. The results indicate a significant increase in hydrogen chemisorption capacity after the first two washes and only small improvements for further washes. Note that the amounts of both the reversible and the irreversible hydrogen chemisorption increase after washing. The results from the NMR measurements for the unwashed and the washed (six times) catalysts are also shown as the open circles and squares in the figure. The values measured from NMR are consistently about 10% lower than the values obtained from the volumetric hydrogen chemisorption. The dispersion of the chlorine-free Ru catalyst is about 0.19 (corresponding to an average Ru particle size of about 5.3 nm), as measured by the irreversibly bound hydrogen assuming a 1:1 stoichiometry between this adsorbed state of hydrogen and the surface ruthenium.

Table I shows the effect of residual chloride, as measured by XRF, on the proton NMR full linewidth and line position (as inferred from the first moment of the broadened lines) for the washed and the unwashed 10% Ru/SiO₂ catalyst. The XRF results are reported in weight percentage of chlorine over the total weight of the catalyst. The XRF data clearly show that considerable amount of residual chloride remains in the unwashed catalyst while the washed catalyst is chlorine-free. The pro-

ton NMR data indicated that a noticeable upfield shift of the upfield peak corresponding to hydrogen-on-ruthenium was present under the two hydrogen adsorption conditions (30 Torr and evacuation to 10⁻⁶ Torr for 10 min after adsorption) after the chlorine-contaminated catalyst was washed. Also, the full linewidth for the upfield peak became narrower by about 4–5 kHz after washing.

The techniques of volumetric chemisorption of hydrogen and ¹H NMR were also applied to measure the chemisorptive properties of the 4% Ru/SiO₂ catalysts. Three NMR spectra collected under 30 Torr hydrogen pressure for: (A) 4% Ru/SiO₂ with five washes; (B) 4% Ru/SiO₂ with only one wash; and (C) unwashed 4% Ru/SiO₂ samples are shown in Fig. 3. Again, two resonances representing the silanol proton (downfield peak) and the hydrogen adsorbed on ruthenium (upfield peak) are observed. The first moment of the upfield peak in Spectra A, B, and C is located at about -61 ppm, -53 ppm, and -43 ppm, respectively. Hot water washing not only moves the upfield peak further toward upfield but also increases the upfield peak intensities by a factor of about 6.

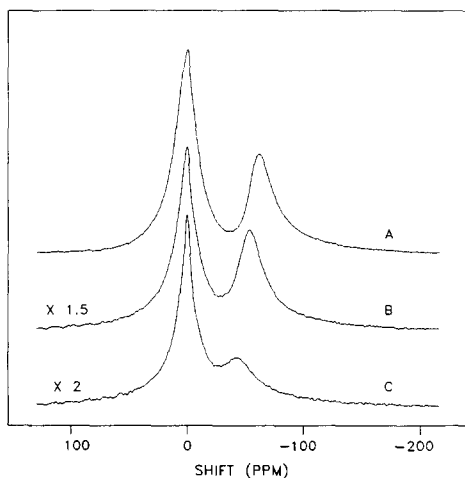


FIG. 3. NMR spectra of adsorbed hydrogen on a 4% Ru/SiO₂ catalyst under 30 Torr hydrogen gas after (A) five washes, (B) one wash, and (C) no wash by hot water. TMS was used as the reference for the lineshift.

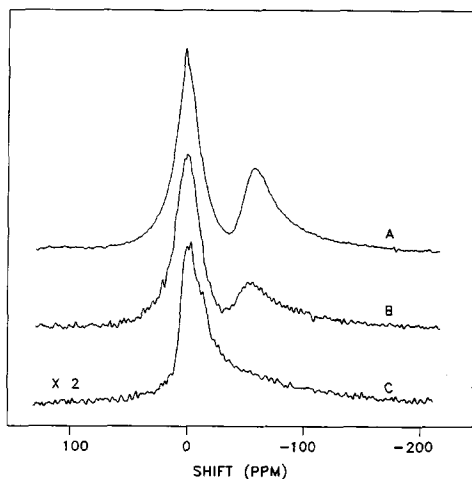


Fig. 4. NMR spectra of adsorbed hydrogen on a 4% Ru/SiO₂ catalyst under evacuation condition (10^{-6} Torr for 10 min) after exposure to 30 Torr hydrogen for a catalyst sample with (A) five washes, (B) one wash, and (C) no wash by hot water. TMS was used as the reference for the lineshift.

Similar trends in the upfield lineshifts and intensities were observed for the same set of 4% Ru/SiO₂ catalysts after evacuation at 10^{-6} Torr for 10 min following adsorption under 30 Torr hydrogen, as shown in Fig. 4. The maxima in the upfield peaks in spectra A, B, and C are centered at about -58 ppm, -52 ppm, and -42 ppm, respectively. The upfield resonance line for the unwashed 4% Ru/SiO₂ catalyst (Fig. 4) has a rather weak intensity and appears as a shoulder on the righthand side of the intense silanol peak.

Hot water washing of the chlorine-contaminated 4% Ru/SiO₂ catalyst has a similar effect on the hydrogen chemisorption capacity as on the 10% Ru/SiO₂ catalyst. As shown in Fig. 5, the amount of hydrogen chemisorbed on ruthenium increases with increasing number of hot water washing. It is noted that the increasing trend is more gradual for the 4% Ru/SiO₂ than for the 10% Ru/SiO₂ catalyst and it levels off after about five washes. The intensity measurements on the upfield peaks from the corresponding proton NMR spectra shown earlier in Figs. 3 and 4 were also plotted in Fig.

5 for direct comparison with the volumetric hydrogen chemisorption. The results obtained from the two methods are in good agreement with the NMR measurements giving slightly lower values (about 8% lower at 6 washes) than those from volumetric measurements. Hot water washing increases the total hydrogen chemisorption capacity by a factor of about 6 for the 4% Ru/SiO₂ catalyst. The dispersion of the chlorine-free Ru catalyst is about 0.36 (corresponding to an average Ru particle size of 2.8 nm), as measured by strong hydrogen chemisorption.

The analysis of residual chloride by XRF and the proton NMR results for three washed and one unwashed 4% Ru/SiO₂ catalysts are shown in Table 2. The XRF results are given in weight percentage of chlorine over the total weight of the catalyst. The XRF data indicated that some amount of chloride still remained in the unwashed catalyst after reduction and the chlorine content in the catalyst decreased rapidly with increasing number of washes. The proton NMR measurements also indicated that a considerable upfield shift of the upfield peak associated with hydrogen chemisorbed on ruthenium was present under the two hydrogen adsorption conditions (30 Torr and evacuation to 10^{-6} Torr after adsorption) after every hot water wash on

TABLE 2
XRF and Proton NMR Results for the
4% Ru/SiO₂ Catalyst

Number of hot water washes ^a	Cl wt% ^b	30 Torr H ₂		Irreversible H	
		Shift (ppm)	width (kHz)	Shift (ppm)	width (kHz)
0	0.33	-43	11.1	-42	16.0
1	0.12	-53	6.8	-52	9.2
5	0.01	-61	6.0	-58	8.1
6	0.00	-62	5.8	-59	7.8

^a Approximately 20 ml of distilled water per gram of catalyst was counted as one wash.

^b The data were obtained from XRF measurements.

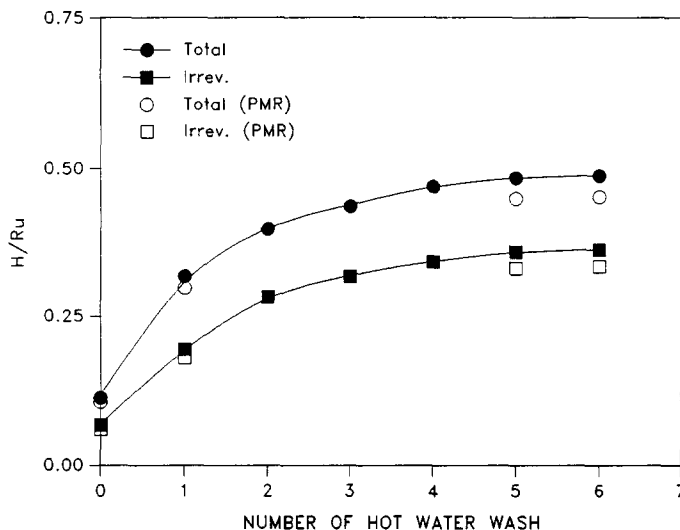


FIG. 5. Variations of the H/Ru ratios for both the total and the irreversible adsorption measured by the volumetric technique as functions of the number of hot water washes on a 4% Ru/SiO₂ catalysts. Values from the NMR measurements are also shown.

the chlorine-contaminated catalyst. In addition, the full linewidth for the upfield peak decreases as the number of washes was increased.

The effect of residual chloride on the spin-lattice relaxation of adsorbed hydrogen is reported in Table 3, which lists the proton spin-lattice relaxation times for

TABLE 3

Effects of Hot Water Washing on Spin-Lattice Relaxation Times for the 4% Ru/SiO₂ Catalyst under 30 Torr Hydrogen

Number of hot water washes ^a (Chlorine coverage)	Spin-lattice relaxation time (sec)	
	Upfield peak (H/Ru _s)	Downfield peak (silanol)
0 (0.65)	0.025	7.4
1 (0.24)	0.015	5.1
5 (0.02)	0.011	2.4
6 (0.00)	0.011	2.2

^a Approximately 20 ml of distilled water per gram of catalyst was counted as one wash.

both the upfield (hydrogen on ruthenium) and the downfield (silanol) peaks measured from the 4% Ru/SiO₂ catalyst under a hydrogen pressure of 30 Torr. It is interesting to note that the spin-lattice relaxation times for both the hydrogen-on-ruthenium (upfield) peak and the silanol (downfield) peak decreased as the chlorine content was lowered. This result clearly indicates that dipolar coupling of ¹H to the quadrupolar nucleus ³⁵Cl is not a dominant factor in proton spin-lattice relaxation.

Also shown in Table 3 are the corresponding values of Cl coverage for each number of wash. The correlation between the number of washes and the chlorine content in the 4% Ru/SiO₂ catalyst was established by experimental data obtained from XRF. Using the weight percentage of chlorine in the catalyst measured from XRF, the chlorine coverage Cl/Ru_(s) were calculated based on the dispersion of the chlorine-free 4% Ru/SiO₂ catalyst, which was measured by the H/Ru ratio of the irreversibly adsorbed hydrogen (12). The results shown in Table 3 indicate a considerable

amount of Cl was retained in the unwashed catalyst but the amount of Cl remaining after six washes was below the limits of detection by XRF. The Cl/Ru_(s) ratios indicate submonolayer coverage of chlorine in all catalyst samples, and that about 65% of the Ru surfaces was contaminated by Cl in the unwashed catalyst.

The above calculations are based on the assumptions that no detectable chlorine was retained in the silica support after reduction in hydrogen and that chlorine was only associated with the surface ruthenium. The first assumption seems to be valid since no chlorine was detected by XRF on a pure SiO₂ sample treated with 6N HCl solution and reduced under the same conditions as the catalyst samples. Also, the results of the calculated chlorine coverage are reasonable, since chlorine is not expected to remain inside the bulk Ru particles at the reduction temperature (723 K) because of its volatility.

The solution after hot water washing was found to be acidic, especially for the first few washes. The acidity of the washed solution decreased as the number of water washes increased and eventually became nearly neutral. For example, the pH of the solution after one wash for the 4% Ru/SiO₂ catalyst was 2.9, and that after five washes 7.1, approaching the value of pH = 7.5 for the distilled water. Also, the solution after one wash was found to contain Cl⁻ ions as indicated qualitatively by observing the formation of a white precipitation when silver nitrate was added. In a separate experiment, the RuCl₃ · 3H₂O precursor was first dissolved in distilled water and then heated to about 90°C. The resulting solution became a black suspension with the formation of Ru(OH)₃ precipitation in an acidic solution with a pH value as low as 1.5 (measured at room temperature).

The hot water washing procedure was first reported by Miura *et al.* (10) as an effective means of removing residual chloride from a Ru/SiO₂ catalyst prepared from the

RuCl₃ · 3H₂O precursor. This procedure has the advantage over the ammonia cold washing procedure in that it does not wash out Ru from the catalyst. This finding was verified in the present study by atomic absorption spectroscopy on the solution after wash showing only trace quantities of ruthenium (<0.5 ppm). Our attempts using cold water washing (results not shown) indicated that it was much less effective than hot water washing for removal of Cl from Ru/SiO₂ catalysts.

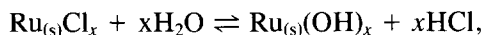
DISCUSSION

Chemistry of Water Elution

The effectiveness of hot water washing in eliminating residual chloride from hydrogen-reduced Ru/SiO₂ catalysts has been confirmed in the present study. However, the chemistry involved in the water washing process is not well understood and has not been discussed in the literature. Sufficient experimental evidence has been gathered from the present study to enable us to propose a simple mechanism for this process.

The experimental results have shown that chlorine does not remain in the silica support after reduction in flowing hydrogen at 450°C, as indicated by the XRF result on a silica support treated with hydrochloric acid. Since the ruthenium particles are likely to remain intact under the very mild condition of hot water washing and since all the residual chloride in the catalysts can be washed out as indicated by XRF, the residual chloride must be interacting with the Ru surfaces rather than remaining inside the bulk Ru particles.

The fact that the washed solution is acidic and contains Cl⁻ ions indicates that the process is analogous to a complete hydrolysis of RuCl₃ compound with formation of Ru(OH)₃ and HCl. Therefore, the water washing process on the Ru/SiO₂ catalysts is essentially a surface hydrolysis process, i.e.,



with Cl being replaced by the OH group at the Ru surfaces and entering the solution as HCl. The stoichiometric coefficient x in the above equation should be less than one because only submonolayer Cl coverages were found in the Ru/SiO₂ catalysts (see Table 3). Since the hydroxyl group stays on the Ru surfaces after water washing, virtually no ruthenium is washed out, as verified by atomic absorption spectroscopy on the solution from washing.

Furthermore, since the hydrolysis of RuCl₃ is known to be an endothermic process, increased temperature of water should favor the removal of Cl from the Ru surfaces. Indeed, we have observed that hot water washing is much more effective than cold water washing for removal of Cl from Ru/SiO₂ catalysts.

Interaction between Surface Ru and Cl

For Cl adsorbed on small Ru particles, we propose that the surface Ru and Cl are partially charged while interacting with each other, i.e., Ru_(s)^{σ+}Cl_x^{σ-} ($0 < \sigma < 1$). This is reasonable considering the difference in electronegativity between the two elements. In addition, the partially charged surface Ru also interacts with, and is stabilized electronically by the inner-layer atoms of the Ru particles, as evidenced by the fact that Ru is not washed out with hot water. It is very likely that electronegative Cl adatoms tend to attract electron density from those surface Ru atoms in direct contact with the Cl adatoms, which may further influence the electronic state of the neighboring vacant surface Ru atoms and the second-layer Ru atoms beneath the occupied surface Ru atoms. This electrostatic effect is possibly short-ranged and does not propagate further into the Ru core, as noted by two theoretical calculations (20, 21). The same electrostatic poisoning effect was also noted by Kishinova and Goodman (17) studying the effect of Cl on adsorption of CO and H₂ on Ni(100) and by Norskov *et*

al. (18) and Lang *et al.* (19) studying various adsorbates. The results of the present study have also suggested a variation of Ru_s-Cl interaction with the Ru particle size. The different trends shown in Figs. 2 and 5 indicate that under identical conditions surface Cl adsorbed on a larger Ru particle undergoes surface hydrolysis more readily than that adsorbed on a smaller Ru particle. This observation is consistent with the results reported by Lu and Tatarchuk (3) showing an increase in activation energy for hydrogen adsorption with decreasing Ru particle size.

It has been suggested from a previous study (13) that adsorbed chlorine tends to draw the 4*d* electrons from the surface Ru atoms, decreasing the density of 4*d* electrons of surface Ru, which is essential for dissociative hydrogen chemisorption. This interpretation is consistent with the observations from the present study, which shows a striking change in the lineshift for the hydrogen-on-ruthenium peak in the presence of chlorine (see Figs. 1 and 3 and also Tables 1 and 2). Since the valence *d* electrons are responsible for the upfield Knight shift of the hydrogen chemisorbed on all noble transition metals (11), the downfield movement of this peak with increasing Cl coverage (see Fig. 6) correlates with a decrease in the 4*d* electron density at the Fermi level on Ru surfaces. The entire ruthenium surface could be affected electronically at sufficiently high Cl coverage.

Effect of Cl on Hydrogen Chemisorption

The increasing trend of the spin-lattice relaxation time for the hydrogen adsorbed on Ru with increasing Cl coverage (see Table 3) could be an indication of weakening of the H-Ru_s interaction in the presence of Cl adatoms. A possible interpretation of these results is that Cl adatoms bonded to the Ru particle's surface reduce the mobility and the concentration of adsorbed hydrogen, thus reducing proton relaxation via time dependent homonuclear dipolar coupling. In addition, withdrawal of surface

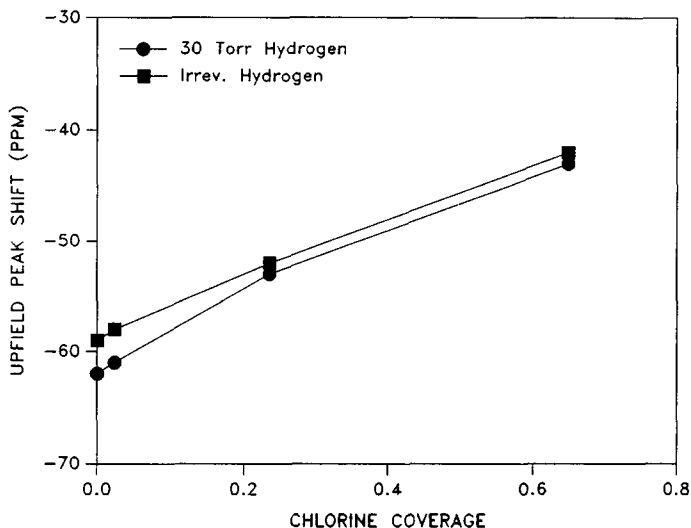


FIG. 6. Variations of the upfield peak shift on a 4% Ru/SiO₂ catalyst under 30 Torr hydrogen and evacuation after adsorption in 30 Torr hydrogen as a function of chlorine coverage.

conduction electron density by the presence of bound Cl^{σ-} could reduce proton relaxation via coupling to conduction electrons. This result is consistent with the observed downfield movement of the upfield peak associated with the Knight shift interaction between chemisorbed hydrogen and surface Ru with increasing Cl coverage. The electronic influence of coadsorbed Cl on hydrogen chemisorbed on surfaces of Ru particles may proceed by one of the following two mechanisms. First, the coadsorbed Cl adatoms attract 4*d* valence electron density from neighboring surface Ru atoms, decreasing its availability for the H-Ru_s bond. This "through-the-Ru_s" electronic interaction between coadsorbed Cl and H is consistent with the observed variation of the Knight shift, which is an indication of a modified Ru conduction band. Second, the partially charged Cl adatoms may exert an electrostatic field that will affect directly the neighboring H-Ru_s chemisorptive bond. However, this "through-the-space" electronic interaction is expected to be short-ranged and does not significantly affect the 4*d* conduction electrons of the surface Ru atoms. Judging from the magni-

tude of the variation in the observed proton Knight shift, the indirect electronic interaction between Cl and H through the surface Ru is likely to prevail over the direct H-Cl interaction.

The chemisorption capacities of both the irreversible and the reversible hydrogen are markedly suppressed in the presence of chlorine (see Figs. 2 and 5). Figure 7 shows the relationship between the chemisorption capacities for these two adsorbed states of hydrogen and the chlorine coverage on the 4% Ru/SiO₂ catalysts. The hydrogen chemisorption capacities are expressed in the H/Ru ratio for both the irreversibly and the reversibly adsorbed hydrogen measured by proton NMR. As can be seen in Fig. 7, surface Cl atoms suppress the surface concentration of the irreversibly adsorbed hydrogen to a greater extent than that of the reversibly adsorbed hydrogen. The surface concentration of the irreversibly adsorbed hydrogen exhibits a nearly linear decreasing trend with increasing Cl coverage while that of the reversibly adsorbed hydrogen shows only a gradual decreasing trend. Both trends are under the diagonal dashed line, which would represent one-to-one

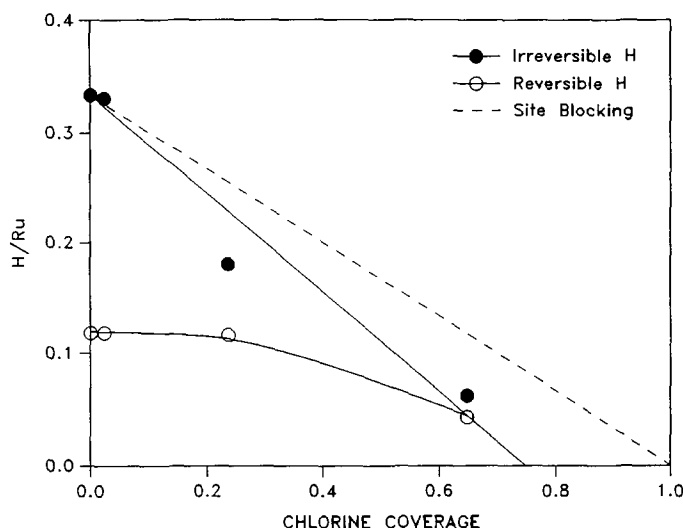


FIG. 7. Plot of the H/Ru ratios for both the irreversible and the reversible hydrogen as a function of the chlorine coverage on a 4% Ru/SiO₂ catalyst. The diagonal dashed line represents simple site blocking on Ru by the chlorine.

physical site blocking of surface Ru by the adsorbed chlorine. At a Cl coverage of about 0.76, the hydrogen coverage for the two adsorbed states extrapolates to zero. This implies that the adsorbed Cl not only physically blocks the Ru sites but also poisons or deactivates adjacent Ru sites for hydrogen chemisorption. On the average, about three coadsorbed Cl atoms will block and deactivate four surface Ru atoms for hydrogen chemisorption, i.e., three Cl adatoms poison only one vacant surface Ru atom. This result confirms the above-mentioned postulate that the electronic influence of chlorine adatoms on the Ru surfaces is rather short ranged.

Effect of Cl on Hydrogen Spillover

It has been reported in a previous proton NMR study (12) on a number of clean Ru/SiO₂ catalysts that the reversibly bound hydrogen is responsible for spillover of hydrogen from Ru onto the silica support. A longer spin-lattice relaxation time for the silanol proton is associated with less hydrogen spillover. The results of the spin-lattice relaxation time (T_1) for the silanol proton on

the 4% Ru/SiO₂ catalysts under 30 Torr hydrogen (Table 3) clearly indicate an increasing trend in T_1 as the chlorine coverage increases. This means that there is less hydrogen spillover to the silica support when the extent of Cl contamination on Ru particles is increased. This observation is in agreement with the fact that chlorine suppresses the adsorption of the reversibly bound hydrogen (Figs. 5 and 7), which is essential for hydrogen spillover.

CONCLUSIONS

Silica-supported ruthenium catalysts prepared from the ruthenium trichloride precursor contain sufficient residual chloride after reduction in flowing hydrogen at normal reduction temperatures to markedly suppress the chemisorption capacities of both the irreversibly and the reversibly bound hydrogen on the Ru surfaces. The residual chloride remains in the Ru catalysts in the form of partially charged adatoms adsorbed on surfaces of Ru particles, which can be removed effectively with hot water elution via a surface hydrolysis process. Complete suppression of hydrogen

chemisorption by surface chlorine on the Ru surfaces occurs at a Cl coverage of about 76%, indicating that three chlorine atoms can block and deactivate four surface Ru sites for hydrogen chemisorption. The observed increase in the ratio of the reversibly adsorbed hydrogen over the irreversibly adsorbed hydrogen with increasing Cl coverage is caused by the reduced H-Ru_s interaction due to the presence of chlorine. Surface chlorine also results in a decrease of hydrogen spillover from Ru surfaces to the silica support.

The residual chloride has significant effects on the proton NMR resonance position and the spin-lattice relaxation time for the chemisorbed hydrogen indicating an electronic interaction between Cl adatoms and surface Ru atoms, which results in the weakening of the H-Ru_s chemisorptive bond at the Ru surfaces. The mechanism for suppression of hydrogen chemisorption by chlorine is proposed to involve both physical site blocking of surface Ru atoms and short-ranged electronic interactions between Cl adatoms, surface Ru atoms interacting with the chlorine, and neighboring surface Ru atoms.

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