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# Mössbauer Effect Studies of Supported Ruthenium Catalysts

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The study of supported metal catalysts by Mössbauer spectroscopy has been extended to include ruthenium supported on alumina and silica. The Mössbauer spectral data show that $RuCl_3 \cdot 1\text{–}3H_2O$ undergoes a chemical change when impregnated on alumina but not when it is impregnated on a silica support. Catalyst samples impregnated with ruthenium trichloride upon calcination were found to contain small crystallites of $RuO_2$. Observations indicated that upon reduction, these samples contained small ruthenium particles in the metallic state. No compound formation from reaction of the ruthenium with the alumina or silica support was detected. The Mössbauer effect was found to be very sensitive to metal particle size. No Mössbauer effect could be observed for very small ruthenium particles supported on silica.

## INTRODUCTION

Heterogeneous catalysis is inherently a complex subject, and progress toward making it a science rather than an art has required knowledge and techniques in many fields. Consequently, in recent times such physical tools as electron microscopy and optical and magnetic resonance spectroscopy have seen increasing use in attempts to obtain detailed information on the surface structure of catalyst systems. A recent addition to this collection of physical tools is the spectroscopic technique based upon the Mössbauer effect.

Mössbauer spectroscopy has been used to study the oxidation and reduction processes in the pretreatment of supported iron catalysts (*1*), to measure the crystallite size of ferric oxide on high surface area supports (*2–5*) and to study the chemisorption of ammonia, water and hydrogen sulfide on supported iron catalysts (*6,7*). Unfortunately, most Mössbauer studies have been concerned almost exclusively with iron and tin catalyst systems, while only two studies have been reported on the much more important noble metal systems.

In the noble metal group, only supported gold and platinum catalysts have been studied by Mössbauer spectroscopy. Delgass and co-workers (*8*) performed a Mössbauer study of gold supported on MgO and $\eta$-$Al_2O_3$. The Mössbauer data taken after heat treatments showed that thermal decomposition began at temperatures greater than 140°C and that decomposition to metallic gold was not always complete. In addition, an unidentified gold species with an absorption peak at a more negative velocity than metallic gold was observed in the alumina sample. Similar studies on supported platinum (*9*) suggest that the strength of binding in the supported crystallites is similar to that of platinum in a foil. Unfortunately, the isomer shifts for platinum are very small, therefore direct chemical information about oxidation states of the platinum present in the catalyst has not been obtained. Results of these studies on platinum systems suggest that this element is not ideally suited for Mössbauer studies. The initial results for gold systems were promising although no follow-up work has been done. Consequently the total contribution that Mössbauer spectroscopy can make to studies of supported noble metal catalysts has not been completely determined. Thus, the search for a noble metal that is more ideally suited to Mössbauer studies of supported metal systems is of significant practical importance. A very promising candidate for such studies appears to be ruthenium. The Mössbauer effect in this metal has been successfully applied to the study of ruthenium coordination compounds as well as to mixed oxidation state compounds (*10–16*). These studies have made significant contributions to the characterization of complex multicentered ruthenium systems and in the generalization of structure and bonding effects in ruthenium compounds.

This paper reports an attempt to apply Mössbauer spectroscopy to the study of the structure and bonding of ruthenium, in both the oxidized and reduced states, supported on alumina and silica matrices.

## EXPERIMENTAL METHODS

*Mössbauer spectrometer.* The Mössbauer spectra were obtained with the apparatus previously described (*14*). The use of a germanium–lithium drifted detector (Elscint Ltd., Model GP/GC) resulted in improved resolution over that previously reported. All spectra were obtained at 4.2°K by use of a Kontes/Martin glass Dewar system where both the source and absorber were immersed directly in the liquid helium well (see Fig. 1). The source consisted of approximately 7 mCi of 16 day $^{99}$Rh contained in a host lattice of ruthenium metal prepared by New England Nuclear Corp., Boston, MA. Samples with absorber thicknesses in the range of 165–200 mg of natural Ru/cm$^2$ were used.

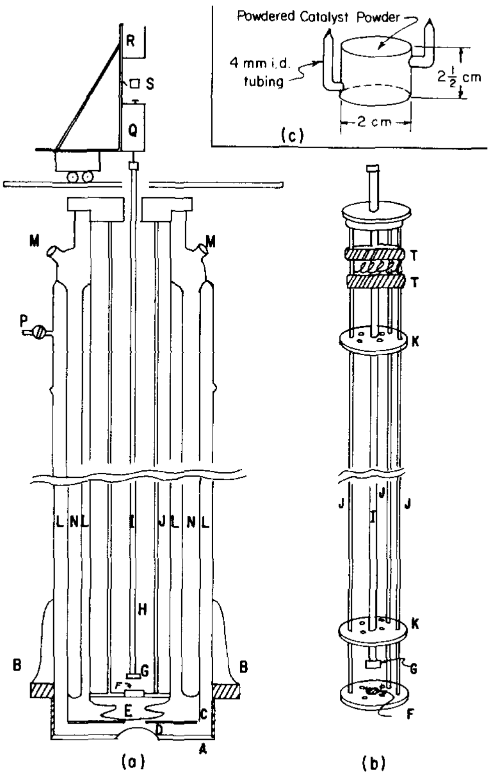

FIG. 1. Sketch of glass Dewar and quartz sample cell used for the Mössbauer measurements reported in this work. (a) Glass Dewar with drive assembly, linear motor and laser calibrator in position as during a spectral run; (b) drive assembly; (c) quartz sample cell: (A) aluminum base plate; (B) O-ring seal; (C) Kovar radiation sheield; (D) 0.001 in. Al foil; (E) Mylar windows (0.005 in. thick); (F) absorber [filled quartz sample cell (c)]; (G) source; (H) helium well; (I) drive rod (1/4 in tube: SS, 4 mil thick); (J) support rods (1/4 in. tubing: SS, 10 mil thick); (K) Teflon disks to strengthen drive assembly; (L) vacuum insulation space, silvered on both sides with a narrow unsilvered portion to read liquid level inside; (M) liquid nitrogen fill ports; (N) liquid nitrogen well; (P) evacuation port; (Q) motor; (R) laser generator (He–Ne); (S) interferometer; (T) Styrofoam insulation with glass wool in between.

In general, the base line for each spectrum contains between 1 and 2 million counts/channel.

Data reduction was carried out on a PDP-10 computer system. The spectra were subjected to a least-squares fit to a Lorentzian line shape with both the experimental points and the calculated least-squares curve plotted out directly by a Calcomp Model 563 plotter. Representative spectra are displayed in Figs. 2 and 3. The Mössbauer hyperfine parameters were calculated from the least-squares fit. Error analyses for the isomer shift, quadrupole splitting, and peak full width at half maximum values are given along with the data in Tables 2 and 3.

*Materials.* Davison silica gel Grade 923 (100–200 mesh, surface area approximately 285 m$^2$/g) and Davison $\eta$-alumina Grade 992-F (100–200 mesh, surface area approximately 210 m$^2$/g) were used as support materials. The support materials were impregnated with aqueous solutions of ruthenium trichloride ($RuCl_3 \cdot 1\text{–}3H_2O$, A. D. Mackay, Inc.). The incipient wetness method was used to impregnate the supports followed by oven drying at 110°C. Catalyst samples were made up to contain 10 wt% ruthenium. After drying, each sample was placed in a quartz cell and all further treatments were carried out on the sample in the cell.

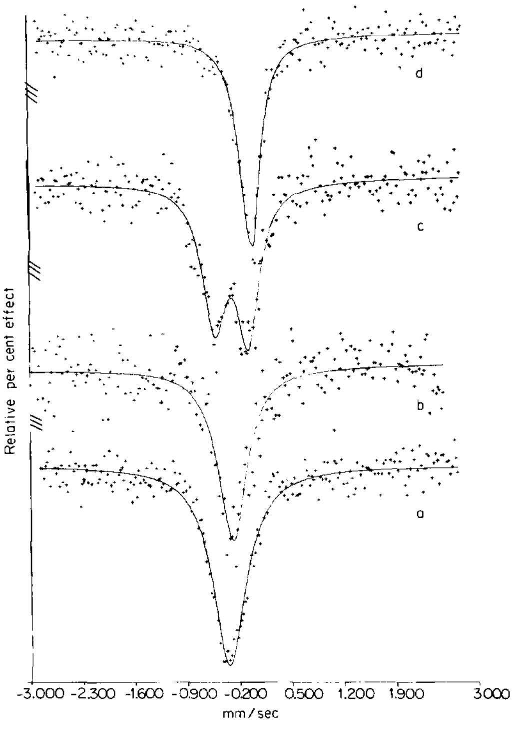

FIG. 2. Mössbauer spectra of: (a) $RuCl_3 \cdot 1\text{–}3H_2O$; (b) Sample 2-A ($RuCl_3 \cdot 1\text{–}3H_2O$ impregnated on a silica support); (c) Sample 2-B (ruthenium on a silica support after calcination); (d) Sample 2-C (ruthenium on a silica support after reduction).

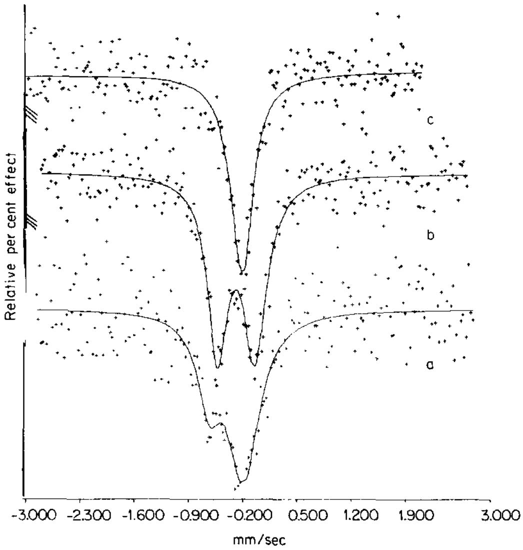

FIG. 3. Mössbauer Spectra of: (a) Sample 5-A ($RuCl_3 \cdot 1\text{–}3H_2O$ impregnated on alumina); (b) Sample 5-B (ruthenium on an alumina support after calcination); (c) Sample 5-C (ruthenium on an alumina support after reduction).

The sample compartment of each cell consisted of a quartz cylinder 25 mm in height by 20 mm in diameter with quartz windows on each end. Each cell was fitted with two arms made of 6 mm quartz tubing. These arms served as gas inlet–outlet and evacuation ports (see Fig. 1). The top of each arm was fitted with a quartz-to-Pyrex graded seal. The Pyrex tubing served both as a point of attachment of the cell to the vacuum line and as a means of closing the cell. The cell was closed by sealing the Pyrex tubing with a gas torch.

TABLE 1
PARTICLE SIZE OF SUPPORTED RUTHENIUM METAL

| Sample no. | Support | Treatment | Wt % Ru | Ru surface area ($m^2/g$)[a] | Av diam (Å) X-Ray | Av diam (Å) Ads |
|---|---|---|---|---|---|---|
| 1-B | $SiO_2$ | $H_2$ reduction | 10 | 57 | — | 85 |
| 2-C | $SiO_2$ | Calcined @ 400°C then reduced in $H_2$ | 10 | 22 | 240 | 230 |
| 3 | $\eta$-$Al_2O_3$ | $H_2$ reduction | 10 | 45 | 95 | 108 |
| 4 | $\eta$-$Al_2O_3$ | Calcined @ 300°C then reduced in $H_2$ | 10 | 33 | 160 | 151 |
| 5-C | $\eta$-$Al_2O_3$ | Calcined @ 400°C then reduced in $H_2$ | 10 | 18 | 295 | 275 |

[a] Calculated from hydrogen adsorption data.

Purified tank air was used to calcine and reoxidize the samples. Hydrogen for the reduction step was purified by passing it successively through a heated palladium catalyst, 13X molecular sieve, a liquid nitrogen trap and finally through the cell, which was lowered into a furnance. Anhydrous ammonia was purified by refluxing over sodium before distilling into storage bulbs. Matheson carbon monoxide, 99.5% pure, was passed through a trap at 195°K before use.

The average crystallite size of the supported ruthenium metal was determined both by X-ray line broadening using Warren's correction as described in Klug and Alexander (*17*) and by hydrogen absorption measurements. The hydrogen adsorption isotherms were obtained with a conventional Pyrex glass, constant volume adsorption system using the method of Dalla-Betta (*18*). Results of the calculation of ruthenium surface areas and particle size measurements are given in Table 1.

## RESULTS AND DISCUSSION

The samples listed in Table 1 may be classified into two categories according to treatment following impregnation. Samples 1-B and 3 after impregnation and drying at 110°C for 24 hr, were reduced in flowing hydrogen for 2 hr at 150°C, 2 hr at 300°C and finally 2 hr at 400°C. Samples 2-C and 5-C, after impregnation and drying at 110°C for 24 hr, were calcined in flowing air for 2 hr at 150°C, 2 hr at 300°C and finally 3 hr at 400°C. These samples were then reduced in flowing hydrogen for 2 hr at 150°C, 2 hr at 300°C and 3 hr at 400°C. Sample 4, after impregnation and drying, was calcined for 2 hr at 150°C and 2 hr at 300°C. This sample was then reduced in flowing hydrogen for 2 hr at 150°C, 2 hr at 300°C and 2 hr at 400°C.

The data in Table 1 show that the average particle size increases for those samples that are calcined before being reduced. The average particle size also increases as the temperature and length of the calcination step increases. Similar results have been observed by Dalla-Betta (*18*).

X-Ray diffraction patterns were obtained for each of the samples in Table 1. In no case, either before or after calcining or reduction treatments, were there any lines observed in the X-ray diffraction patterns that could be identified with compound formation between the ruthenium species and the support.

*Silica support.* Mössbauer spectral data obtained for ruthenium on a silica support during various stages of treatment are given in Table 2 and Fig. 2.

The Mössbauer spectrum for sample 1-A ($RuCl_3 \cdot 3H_2O$ impregnated on silica and then dried for 24 hr at 110°C shows that the impregnated ruthenium complex is absorbed on the surface of the silica support without undergoing a chemical

TABLE 2

MÖSSBAUER PARAMETERS FOR RUTHENIUM SUPPORTED ON SILICA

| Sample no. | Treatment | Absorber thickness (mg Ru/cm$^2$) | Isomer[a] shift (mm/sec) | Quadrupole splitting (mm/sec) | Peak width (Γ) @ half-height (mm/sec) |
|---|---|---|---|---|---|
| 1-A | Before reduction | 175 | −0.34 ± 0.02 | 0 | 0.53 ± 0.04 |
| 1-B | After reduction | 175 | (No spectrum observed) | | |
| 2-A | Before reduction | 165 | −0.35 ± 0.02 | 0 | 0.54 ± 0.04 |
| 2-B | After calcination | 165 | −0.27 ± 0.02 | 0.46 ± 0.02 | $\Gamma_1$ = 0.37 ± 0.04<br>$\Gamma_2$ = 0.36 ± 0.04 |
| 2-C | After reduction | 165 | +0.02 ± 0.02 | 0 | 0.34 ± 0.03 |
| Ruthenium species[b] | | | | | |
| $RuCl_3 \cdot 1\text{-}3H_2O$ | — | 525 | −0.34 ± 0.02 | 0 | 0.52 ± 0.04 |
| Ru Metal powder | — | 185 | 0.00 ± 0.02 | 0 | 0.32 ± 0.03 |
| $RuO_2$ | — | 380 | −0.23 ± 0.03 | 0.51 ± 0.05 | 0.57 ± 0.03 |
| $RuO_4$ | — | 340 | +1.06 ± 0.01 | 0 | 0.28 ± 0.02 |
| $KRuO_4$ | — | 520 | +0.82 ± 0.02 | 0.37 ± 0.02 | 0.40 ± 0.04 |
| $BaRuO_4 \cdot H_2O$ | — | 320 | +0.38 ± 0.01 | 0.44 ± 0.02 | 0.30 ± 0.02 |
| $[Ru(NH_3)_6]Cl_2$ | — | 367 | −0.72 ± 0.02 | 0 | 0.33 ± 0.05 |
| $[Ru(NH_3)_5CO]Br$ | — | 151 | −0.54 ± 0.02 | 0 | 0.39 ± 0.05 |
| $[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$ | — | 142 | −0.16 ± 0.02 | 0.34 ± 0.02 | 0.31 ± 0.05 |
| $[Ru(CO)_3Cl_2]_2$ | — | 181 | −0.31 ± 0.02 | 0 | 0.42 ± 0.04 |
| $Ru_3(CO)_{12}$ | — | 735 | −0.24 ± 0.02 | 0 | 0.51 ± 0.05 |

[a] Zero velocity is taken to be the center of the spectrum of a standard ruthenium metal sample.

[b] Parameters for various ruthenium species for comparison.

change. The Mössbauer parameters for this sample are the same within experimental error as those observed for unsupported $RuCl_3 \cdot 3H_2O$. The appearance of a single, slightly broadened peak in the Mössbauer spectrum for both of these samples is somewhat surprising, for it has been proposed (*19*) that commercial ruthenium trichloride is a water-soluble mixture of aquochloro complexes of polynuclear ruthenium. Such a polynuclear mixture would be expected to exhibit a quadrupole split spectrum as has been observed for other polynuclear ruthenium complexes (*20*). The appearance of a single peak indicates that only one ruthenium oxidation state exists. The corresponding isomer shift for this peak of −0.34 mm/sec suggests that the ruthenium is equivalent to the +4 oxidation state (*16*).

After obtaining the Mössbauer spectrum for sample 1-A, it was reduced according to the previously described procedure. This reduced sample is called 1-B. After the accumulation of approximately 2 million counts in each channel, no absorption peaks could be detected in the Mössbauer spectrum for this sample. This was somewhat surprising since this sample gave a well-resolved spectrum prior to the reduction step. Chemical analysis showed that there was no loss of ruthenium from the catalyst sample during the reduction procedure. The absence of an observable spectrum for this sample must be the result of a decrease in the nuclear recoil-free fraction following the reduction of the complex to the metallic state.

It has been observed by Suzdalev *et al.* (*21*) that in highly dispersed tin the probability of the Mössbauer effect diminishes as the particle diameter decreases. It has also been shown by Van Wilringen (*22*) that in metal powders the particles may be so small that a single particle is unable to give a "recoilless" Mössbauer transition. Van Wilringen defined the critical size of a particle as being that mass which is just sufficiently large to absorb the recoil of the gamma quantum without observable exchange of energy. The critical size can be calculated if it is assumed that the recoil energy is unobservable if it gives rise to a line displacement less than the natural line width.

Using a value for the ruthenium-99 gamma recoil energy given by Stevens and Stevens (*23*) it follows that the mass absorbing the recoil energy should be at least $19.4 \times 10^5$ times the mass of a single $^{99}$Ru nucleus. For spherical particles of ruthenium (density 12.3 g/cm$^3$) this leads to a critical particle diameter of 368 Å. Data in Table 1 show that the small ruthenium particles (85 Å) in sample 1-B are much smaller than the critical size. Since no Mössbauer spectrum was observed for this sample, it must follow that either no recoil energy or possibily only an insignificant amount of the recoil energy is transferred to the support. This suggests that the strength of the binding of the ruthenium to the silica support is very weak and that the binding forces between the atoms in the small catalyst particles are similar to those between ruthenium atoms in the powdered metal.

In order to increase the particle size of the supported metal we decided to calcine the sample before the reduction step. The new impregnated sample (2-A) before treatment exhibited a Mössbauer spectrum identical to that observed for sample 1-A. After the calcination step, a Mössbauer spectrum was obtained (sample 2-B). The data as given in Fig. 2 and Table 2 show a well-resolved doublet corresponding to an isomer shift of −0.27 mm/sec and a quadrupole splitting of 0.46 mm/sec. These parameters agree very well with the isomer shift (−0.22 mm/sec) and quadrupole splitting (0.51 mm/sec) which have been observed for RuO$_2$ (*11*). The absence of any unidentified peaks in the spectrum indicates that essentially all of the ruthenium is present as small crystallites of RuO$_2$.

Sample 2-B was reduced according to the previously described procedure. The reduced sample (2-C) was evacuated to a pressure of $10^{-6}$ Torr (1 Torr = 133.3 N m$^{-2}$) at a temperature of 400°C before the cell was sealed. Therefore, the Mössbauer spectrum for this sample corresponds to a metal surface that is free of chemisorbed hydrogen. Even though the average particle size of the metal (240 Å) in this sample is still less than the critical particle size, a Mössbauer spectrum was observed. This spectrum exhibited a single absorption peak with an isomer shift that agrees exactly within experimental error to that observed for powdered ruthenium metal. The absence of any other lines in the spectrum indicates that all of the ruthenium has been reduced to the zero valence, metal state. This observation is somewhat surprising when compared to the results of Mössbauer studies obtained for other metal catalyst systems in the reduced state. For example, studies (*4*) of supported iron catalysts have shown that small supported iron particles cannot be reduced completely to the metallic state. This observation has been explained as being the result of a small fraction of the iron nuclei remaining in higher oxidation states because of surface interaction with the support material. It is apparent that such surface interactions do not occur with ruthenium.

The fact that a Mössbauer spectrum was observed for this sample in spite of the subcritical particle size, indicates that the "effective" Mössbauer mass of the particles must be greater than the critical mass. This suggests that weak binding forces exist between the small metal particles and the silica support. Another possible explanation is that the observed Mössbauer effect may be due to a small fraction of metal particles that are larger than 368 Å. In either case, additional work is necessary in order to establish the absolute minimum ruthenium particle size on silica for which a Mössbauer effect can be observed.

Attempts were made to obtain Mössbauer spectra of chemisorbed CO, $NH_3$ and $H_2S$ on the reduced ruthenium catalyst. In each case, the chemisorbed species were introduced to a total pressure of 50 Torr at 25°C in the sample cell. The Mössbauer spectra obtained for each of these samples exhibited a single line that was identical within experimental error to that observed for the reduced catalyst. This suggests that either the ratio of surface ruthenium atoms to bulk ruthenium atoms is not great enough to observe surface effects, or that the chemisorption of these molecules on a ruthenium atom does not perturb its electronic structure enough to bring about an observable change in the Mössbauer spectrum.

It is possible that the application of Mössbauer spectroscopy to the study of chemisorption in ruthenium catalyst systems may be more effectively exploited by using zeolite catalysts such as has been done for supported iron systems (*24,25*). Such studies are in our future plans.

*Alumina support.* To investigate the nature of ruthenium supported on alumina, several samples of $\eta$-alumina were impregnated with ruthenium trichloride and treated in a manner as previously described. Mössbauer spectral data obtained for these samples are given in Table 3 and Fig. 3.

A single narrow absorption peak was observed in the Mössbauer spectra of catalyst samples 3 and 4. It should be noted that each of these samples was evacuated to a pressure of $10^{-6}$ Torr at 400°C, therefore their spectra represent a surface free of chemisorbed hydrogen. Within experimental error their Mössbauer parameters correspond exactly to those observed for ruthenium metal. As was observed in the case of the reduced silica catalysts, there is no evidence for the existence of any ruthenium species other than the reduced metal. Even though sample 3 was reduced directly, whereas sample 4 was calcined before reduction, the Mössbauer data show that other than for average particle size the state of the ruthenium is the same in both samples.

Both catalyst sample 3 with an average particle size of 95 Å and sample 4 with a particle size of 160 Å contain supported ruthenium crystallites that are much smaller than the critical partical size. The occurrence of a Mössbauer effect in these samples indicates that fairly strong binding forces exist between the metal particles and the alumina support. The data also show that the Mössbauer effect increases as the average particle size increases.

A Mössbauer spectrum was obtained for untreated impregnated ruthenium tri-

TABLE 3
MÖSSBAUER PARAMETERS FOR RUTHENIUM SUPPORTED ON ALUMINA

| Sample no. | Treatment | Absorber thickness (mg Ru/cm$^2$) | Isomer shift (mm/sec) | Quadrupole splitting (mm/sec) | Peak width (Γ) @ Half-height (mm/sec) | % Abs |
|---|---|---|---|---|---|---|
| 3 | After reduction | 185 | +0.01 ± 0.02 | 0 | 0.41 ± 0.04 | 0.2 |
| 4 | Reduced after low temp calcination | 180 | +0.01 ± 0.02 | 0 | 0.43 ± 0.04 | 0.3 |
| 5-A | Before reduction | 190 | −0.41 ± 0.03 | 0.45 ± 0.02 | $\Gamma_1$ = 0.35 ± 0.04<br>$\Gamma_2$ = 0.49 ± 0.04 | — |
| 5-B | After calcination | 190 | −0.27 ± 0.03 | 0.49 ± 0.02 | $\Gamma_1$ = 0.33 ± 0.04<br>$\Gamma_2$ = 0.35 ± 0.04 | — |
| 5-C | After reduction | 190 | −0.02 ± 0.02 | 0 | 0.38 ± 0.04 | 0.6 |

chloride on an alumina support (5-A). The spectrum as shown in Fig. 3 exhibits an asymmetric doublet with an isomer shift of −0.41 mm/sec and a quadrupole splitting of 0.45 mm/sec. This spectrum is significantly different from the spectrum obtained for unsupported $RuCl_3 \cdot 1\text{–}3H_2O$ and $RuCl_3 \cdot 1\text{–}3H_2O$ supported on silica. The isomer shift is slightly more negative than that observed for the unsupported ruthenium trichloride and falls in a region that borders on the upper end of isomer shifts observed for Ru(III) complexes and the lower end of isomer shifts for Ru(IV) complexes. Therefore, it is difficult to determine whether the ruthenium has undergone a change in oxidation state or has been coordinated to the support. The appearance of the quadrupole splitting does indicate that either the symmetry and/or the composition of the ruthenium complex undergoes a significant change upon adsorption on the alumina support. The asymmetry in the quadrupole splitting has been observed in other ruthenium complexes (*14,15*) and may arise from the Goldanskii effect. The Goldanskii effect is the result of anisotropy in the recoil-free fraction in the gamma ray absorption. It would be expected to be present in a compound adsorbed on a surface since the vibrational amplitude of the ruthenium nucleus normal and parallel to the surface would not be expected to be the same.

Sample 5-A was calcined to form catalyst sample 5-B. The Mössbauer spectrum for this sample shows that all of the ruthenium was converted to $RuO_2$. This sample was then reduced and evacuated to a pressure of $10^{-6}$ Torr at a temperature of 400°C. The spectrum for this sample (5-C) exhibited a single line with spectral parameters that agree with those observed for the other reduced alumina samples. The Mössbauer effect (0.6%) was greater than that observed for the other reduced alumina samples. This is expected, since the average particle size of sample 5-C (295 Å) is twice the average particle size of the other samples.

Again, attempts were made to obtain Mössbauer spectra for CO, $NH_3$ and $H_2S$ chemisorbed (at 25°C) on the reduced catalyst samples. The Mössbauer spectra obtained for each of these samples exhibited a single line that was identical within experimental error to that observed for reduced ruthenium on an alumina support. It is somewhat surprising that no chemisorption effects were observed with catalyst sample 3. The average metal particle size in this sample is only 95 Å, which should give a favorable surface to bulk metal atom ratio.

## CONCLUSIONS

This study has shown that it is possible to obtain Mössbauer spectral data for unenriched ruthenium supported on an alumina or silica matrix. The data show that $RuCl_3 \cdot 1\text{–}3H_2O$ is adsorbed on a silica support without undergoing a chemical change, whereas when this complex is adsorbed on an alumina support a change in the chemical environment of the ruthenium nucleus occurs. This study has also shown that when a supported ruthenium catalyst is calcined all of the ruthenium is quantitatively converted to $RuO_2$. It has also been established that the reduction of a supported ruthenium catalyst converts all of the ruthenium to the metallic state.

This study has also shown that there are several limiting factors in applying Mössbauer spectroscopy to studies of supported ruthenium catalyst systems. One severe limitation in applying this technique to studies of ruthenium supported on silica is the inability to observe a Mössbauer effect for very small metal particles. It is possible that the limit on the metal particle size for this system may be lowered by using ruthenium metal that is enriched in ruthenium-99. Future studies in this laboratory are being directed toward this goal.

While it was not possible to observe a

Mössbauer effect for small ruthenium particles on a silica support, it was possible to obtain Mössbauer data for such particles on an alumina support. Therefore, Mössbauer spectroscopy could prove to be a very valuable tool in future studies on such systems. One particular area where Mössbauer spectroscopy could be most useful is in studies of alkali metal promoted ruthenium–alumina catalysts. It has been proposed that the promotion is caused by an electron donation from the alkali metal to the ruthenium metal (*26*). Since our study shows that changes in the oxidation state of supported ruthenium can be observed by Mössbauer spectroscopy, this technique should be able to establish whether this promotional mechanism is correct.

This study has also demonstrated the inability of Mossbauer spectroscopy to observe chemisorption phenomena on alumina and silica supported ruthenium. This inability may be due to a poor surface metal to bulk metal ratio in the catalyst samples studied. This limitation could possibly be circumvented by the use of ruthenium-atom-exchanged zeolite absorber samples. Such samples should have a high fraction of crystallographically well-defined, surface ruthenium atoms. Because of the favorable structure of the zeolites and the great interest in the catalytic properties of supported ruthenium (*27*), we feel that these systems are prime candidates for Mössbauer studies.

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