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# A Mössbauer Study of Automotive Emission Control Catalysts

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Mössbauer data have been obtained for a series of barium oxide stabilized ruthenium automotive emission control catalysts. The data indicate that the chemical form of the ruthenium in the stabilized catalysts is a mixture of $RuO_2$ and $BaRuO_3$. All of the ruthenium is reduced to the metallic state in the presence of a reducing gas atmosphere at high temperatures. The catalysts are destabilized as the oxidation–reduction cycle is repeated as indicated in the continually decreasing $BaRuO_3$ to $RuO_2$ ratio. Thus the destabilization appears to be caused by a physical separation of the ruthenium metal (metal atom clustering) from the stabilizing BaO phase.

## INTRODUCTION

Oxides of nitrogen are important components of photochemical smogs which exhibit significant adverse health effects. A major source of nitrogen oxides (primarily NO) is the exhaust gas from internal combustion engines; this situation was recognized by the Clean Air Act of 1970 which required the effective control of such emissions. Efforts to provide this control have centered on the development of catalysts that can selectively promote the reduction of nitrogen oxides to molecular nitrogen rather than to ammonia as has been observed for a majority of known catalysts (*1–3*). Ruthenium-containing catalysts have been found to exhibit a pronounced selectivity for reduction of nitrogen oxides to molecular nitrogen, and attention has recently been focused on the development of these materials as a means of controlling nitrogen oxide emissions (*4–8*).

The nitrogen oxide reduction catalysts are designed to operate in a reducing atmosphere. To provide appropriate conditions for the treatment of the total exhaust gases, current designs include a dual-bed system, where the internal combustion engine is operated net fuel rich and the first catalyst is used to promote the reduction of oxides of nitrogen to nitrogen gas. Air is then injected downstream of the reduction catalyst to make the stream net fuel lean, and the second bed catalyzes the oxidation of carbon monoxide and hydrocarbons. On warm-up, air is injected upstream of the reduction catalyst to control quickly the carbon monoxide and hydrocarbons by reaction in the manifold or over the reduction catalyst. The reduction catalysts, therefore, must be stable to repeated exposure to an oxidizing environment at high temperatures. In studies where ruthenium was used as the reduction catalyst, it soon became apparent that they exhibited very poor stability under oxidizing conditions. Analysis of spent catalysts revealed severe losses of the active component, which was readily explained by the formation and removal of the volatile ruthenium tetroxide (*7*).

Shelef and Gandhi (*7*) explored various ways to minimize the tendency of the ruthenium to volatilize under oxidizing conditions while still preserving the high activity and selectivity of the catalysts. One initially promising method was based on the stabilization of the ruthenium via the formation of nonvolatile ruthenates by the reaction with the basic oxides of barium and lanthanum. The ruthenates were incorporated into the support matrix by two different methods. In one method, the ruthenates were prepared *in situ* on the support material by impregnation, first with a solution of the nitrate of the stabilizing metal, followed by calcination to convert the nitrate to the oxide. The support was then impregnated with a solution of ruthenium trichloride. The catalyst was dried and reduced in hydrogen and then "fixed" by rapid heating in air at 900°C. This technique has been found to give a good dispersion of the resulting ruthenate, however, there is no direct evidence that every ruthenium atom has been deposited in the vicinity of the stabilizing oxide so as to assure the formation of the ruthenate. The second catalyst preparation technique involved the incorporation of a finely ground, presynthesized ruthenate into the support by using dilute suspensions of colloidal alumina as the binding agent. The disadvantage of this technique is a result of the limit on the particle size achievable by grinding. At best, the particle diameter is of the order of a few microns, which leaves most of the ruthenium atoms in the bulk and inaccessible to reacting molecules on the surface.

Catalyst samples prepared by either technique were found to exhibit considerable improvement in the prevention of ruthenium volatization while maintaining the desirable selective catalytic reduction of nitric oxide to molecular nitrogen (*7*). However, under vehicle operating conditions the loss of ruthenium from the stabilized catalysts was still found to be higher than acceptable. The reason for this gradual loss of ruthenium from the stabilized catalysts has been the subject of some research and speculation. It was suggested by Shelef and Gandhi (*7*) that the loss may result from a phase separation of the stabilizing agent and the ruthenium during repeated oxidation–reduction cycles. Other workers using a thermogravimetric technique to follow weight changes of similar stabilized ruthenium catalysts concluded that the loss of ruthenium was due to the migration of ruthenium metal and the subsequent gradual separation of ruthenium from the barium oxide phase (*9*). However, these latter authors were not successful in uniquely identifying the chemical composition of the supported catalyst formed by the high temperature calcination of alumina impregnated with a barium and ruthenium salt. Thus, it seemed appropriate to further probe the mechanisms for ruthenium loss from these stabilized ruthenate systems and to determine, if possible, the changes occurring in the chemical state of the ruthenium as the catalyst is cycled through different exhaust compositions. This paper reports our efforts to gain insight into these questions by the utilization of ruthenium-99 Mössbauer spectroscopy.

## EXPERIMENTAL METHODS

*Mössbauer spectrometer*. The Mössbauer spectra were obtained with the apparatus previously described (*10*, *11*). 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. The source consisted of approximately 7 mCi

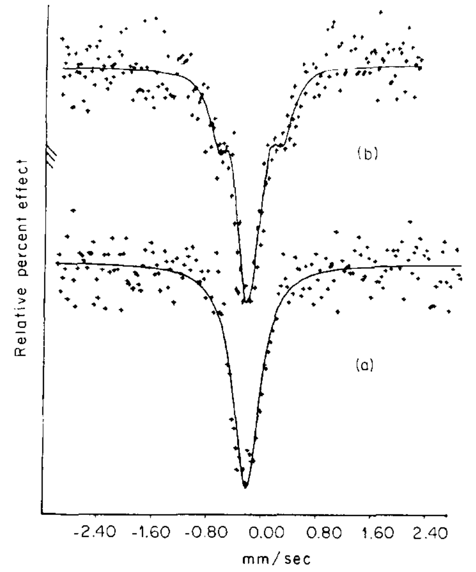

FIG. 1. Mössbauer spectra of: (a) barium ruthenate; (b) sample 4-A (12% barium and 4% ruthenium on an alumina support after initial "fixation" step).

of 16 day $^{99}$Rh contained in a host lattice of rhodium metal prepared by New England Nuclear Corp., Boston, Mass. This source gave slightly broader linewidths (0.45 mm/sec for a natural ruthenium metal absorber) than were obtained with previous sources (0.32 mm/sec) where the host lattice was ruthenium metal. Samples with absorber thickness in the range of 75–150 mg of natural Ru/cm$^2$ were used. In general, spectra were accumulated until the baseline contained between 1 and 2 million counts/channel. Spot checks on these samples with a second source in a natural ruthenium metal host lattice (which exhibited a linewidth of 0.31 mm/sec for a ruthenium metal absorber) gave reproducible values for isomer shift and quadrupole splitting values reported here.

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. Representative spectra are displayed in Fig. 1. 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 height

TABLE 1

Mössbauer Data for Stabilized Ruthenium Catalyst Samples after the Initial "Fixation" Step

| Sample No. | Content (wt%) | | Absorber thickness (mg Ru/cm$^2$) | No. of lines in spectrum | Isomer[a] shift (mm/sec) | Quadrupole splitting (mm/sec) | Peak area ratio[b] |
|---|---|---|---|---|---|---|---|
| | Ba | Ru | | | | | |
| 1-A | 4 | 2 | 75 | 3 | $-0.29 \pm 0.04$<br>$-0.21 \pm 0.04$ | 0<br>$0.52 \pm 0.05$ | 2.5:1.0 |
| 2-A | 8 | 2 | 79 | 3 | $-0.27 \pm 0.04$<br>$-0.23 \pm 0.04$ | 0<br>$0.49 \pm 0.05$ | 5.1:1.0 |
| 3-A | 8 | 4 | 150 | 3 | $-0.29 \pm 0.04$<br>$-0.22 \pm 0.04$ | 0<br>$0.50 \pm 0.05$ | 1.7:1.0 |
| 4-A | 12 | 4 | 147 | 3 | $-0.30 \pm 0.04$<br>$-0.24 \pm 0.04$ | 0<br>$0.53 \pm 0.05$ | 2.3:1.0 |
| Barium ruthenate | | | 345 | 1 | $-0.28 \pm 0.03$ | 0 | — |
| Ruthenium dioxide | | | 140 | 2 | $-0.23 \pm 0.03$ | $0.51 \pm 0.05$ | — |

[a] Zero velocity is taken to be the center of the spectrum of a standard ruthenium metal sample.
[b] This is the ratio of the area of the single peak to the area of the pair of quadrupole split peaks.

TABLE 2

Mössbauer Data for Stabilized Ruthenium Catalysts after Treatment in a Simulated Auto Exhaust

| Sample No. | Treatment @700°C | No. of lines in spectrum | Isomer shift (mm/sec) | Quadrupole splitting (mm/sec) | Peak area[a] ratio |
|---|---|---|---|---|---|
| 4-B | Sample 4-A heated for 10 hr in a flowing SAE atmosphere | 1 | +0.02 ± 0.03 | 0 | — |
| 4-C | Sample 4-B heated for 30 min in a net oxidizing SAE atmosphere | 3 | −0.27 ± 0.04<br>−0.22 ± 0.03 | 0<br>0.53 ± 0.03 | 2.0:1.0 |
| 4-D | Sample 4-C cycled between net reducing SAE and net oxidizing SAE for 48 hr | 3 | −0.28 ± 0.04<br>−0.24 ± 0.03 | 0<br>0.50 ± 0.03 | 1.1:1.0 |
| 4-E | Sample 4-D cycled for 100 additional hours | 3 | −0.29 ± 0.05<br>−0.23 ± 0.03 | 0<br>0.52 ± 0.03 | 0.4:1.0 |
| 2-B | Sample 2-A cycled for 150 hr | 3 | −0.30 ± 0.04<br>−0.21 ± 0.03 | 0<br>0.49 ± 0.03 | 2.3:1.0 |

[a] Ratio of area of single peak to area of quadrupole pair.

values are given along with the data in Tables 1 and 2.

*Catalyst preparation.* The stabilized catalysts were prepared by the incipient wetness impregnation of a Davison $\eta$-alumina Grade 992-F (100–200 mesh) support, first by a solution of barium nitrate followed by calcination at 900°C for 8 hr to convert the nitrate to the oxide, and secondly by a solution of ruthenium trichloride ($RuCl_3 \cdot 3H_2O$, A. D. Mackay, Inc.). The sample was then dried for 24 hr at 100°C. The dried samples were reduced in flowing hydrogen for 2 hr at 150°C, 2 hr at 300°C and finally 2 hr at 400°C. The very small ruthenium metal particles were then "fixed" by rapid heating in flowing air at 900°C for 1 hr, according to the procedure of Shelef and Gandhi (*7*).

Table 1 shows the barium and ruthenium contents of the catalysts prepared by this procedure. The barium ruthenate sample was prepared by reacting a stoichiometric mixture of barium peroxide and powdered ruthenium metal at 1100°C according to the procedure of Donohue *et al.* (*12*).

*Catalyst treatment.* Catalyst samples were

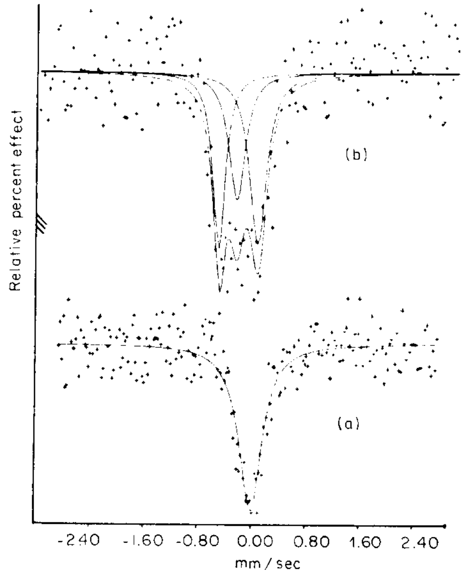

FIG. 2. Mössbauer spectra of: (a) sample 4-B (see Table 2); and (b) Sample 4-E (see Table 2).

treated at 700°C with several different gas compositions flowing at a gas space velocity (GSV) of approximately 75,000/hr. The specific samples that resulted from these treatments are listed in Table 2. During treatment, the catalyst samples were held in a quartz boat positioned in the center of a tube furnace. The treatment gases were metered into the tube furnace by means of rotameters. Gas mixtures were prepared by mixing appropriate reagent grade gases from cylinders. The simulated auto exhaust (SAE) used to treat several of the catalyst samples had the following composition:

| Component | Content (mole%) |
|---|---|
| $H_2$ | 0.33 |
| $O_2$ | 0.35 |
| $H_2O$ | 10.00 |
| CO | 2.00 |
| $CO_2$ | 13.00 |
| $C_3H_8$ | 0.10 |
| NO | 0.10 |
| $N_2$ | 74.12 |

When the SAE was made up to simulate a net oxidizing condition, 2.0% $O_2$ was substituted for the 2.0% CO.

## RESULTS AND DISCUSSION

The data in Table 1 correspond to studies of catalysts containing 2 and 4 wt% ruthenium. The 2% sample corresponds to the minimum concentration of ruthenium on alumina for which we were able to obtain a resolved Mössbauer spectra. These ruthenium concentrations are about 10 times higher than would ordinarily be used in an automotive catalyst. However, the relative concentrations of ruthenium and barium are comparable to those used in actual catalyst systems and the observed results should be relevant to these systems.

The Mössbauer spectra for the catalyst samples were obtained immediately after the "fixation" step, which corresponded to a rapid heating at 900°C in flowing air. As the data in Table 1 indicate, the spectral data points for each stabilized catalyst were fitted to a three line spectrum which represented the two-line $RuO_2$ spectrum and the singlet attributable to $BaRuO_3$. Figure 2b represents the case where the ruthenate content is smallest (see sample 4-E of Table 2) and thus would be susceptible to the greatest error since the singlet is essentially "buried" in the more intense doublet. However, in all cases reported, the three line computer fit to the stabilized catalyst spectra gave the lowest chi-square values among the several attempts to fit alternate spectral patterns such as a broad singlet or a doublet. The three line spectral pattern also produced the only meaningful set of Mössbauer spectral parameters for known compounds of Ba, Ru, and $O_2$. If we assume that the recoil-free fraction for barium ruthenate and ruthenium dioxide are similar, then a comparison of the areas under the respective peaks should provide a measure of the relative concentrations of the two species in the catalyst. In fact, when this assumption was tested by making up a physical mixture of ruthenium metal and ruthenium dioxide (1:1 on a Ru atom ratio) the area ratio was within 5% agreement with the expected value. In comparing the peak areas we observe that as the barium content increases so does the fraction of ruthenium in the barium ruthenate phase. However, the data show that a total "fixation" of all ruthenium in the form of barium ruthenate is never achieved, even when the weight ratio of barium to ruthenium is 4:1. This indicates that it is impossible to deposit each ruthenium atom next to a stabilizing BaO group on the catalyst surface.

In comparing the peak area ratio for samples 1-A and 3-A we can see how the ruthenium concentration affects the degree of stabilization. In both of these samples the weight ratio of barium to ruthenium is 2:1 but the 2% ruthenium sample shows a higher degree of stabilization (2.5 $BaRuO_3$:1.0 $RuO_2$) than the 4% sample (1.7 $BaRuO_3$:1.0 $RuO_2$). This suggests that in those automotive catalysts where the nominal ruthenium content is 0.2% a higher degree of stabilization than was found for the samples in Table 1 should be obtained. However, even with a low concentration of ruthenium, the data indicate that it would not be possible to stabilize all of the ruthenium atoms when using barium concentrations in the 3–12% range.

The data in Table 2 and Fig. 2 show the effect of a simulated automobile exhaust (SAE) on the chemical state of ruthenium when the catalyst is operating at 700°C. Sample 4-B corresponds to a portion of sample 4-A after 10 hr of treatment at 700°C in a flowing stream of SAE. The Mössbauer spectrum for this sample displayed a single peak with an isomer shift corresponding to that found for ruthenium metal. This indicates that all of the $BaRuO_3$ and $RuO_2$ in the initial sample has been reduced to ruthenium metal. Sample 4-B was then heated for 30 min at 700°C in a modified SAE stream. The SAE was modified by substituting 2% $O_2$ for the 2% CO. This converted the SAE stream from a net reducing mixture to a net oxidizing mixture. The Mössbauer spectrum for this sample shows that all of the ruthenium metal has been converted back to $BaRuO_3$ and $RuO_2$. It is also interesting to note that some of the ruthenium stabilization was lost in cycling sample 4-A to sample 4-C as indicated by a reduction in the $BaRuO_3$:$RuO_2$ ratio from 2.3:1.0 to 2.0:1.0. This observation indicates that phase separation between the stabilizing agent and the ruthenium begins to occur after one oxidation–reduction cycle.

For the purpose of determining whether additional cycling would produce a continuation in phase separation, sample 4-C was cycled for 48 hr to produce sample 4-D. The cycling corresponded to 50 min operation in a net reducing SAE atmosphere and 10 min in a net oxidizing atmosphere. This cycle was repeated 48 times. The sample was analyzed after the last 10 min in the oxidizing atmosphere. The Mössbauer spectrum again indicates that all of the ruthenium is present in the form of either $BaRuO_3$ or $RuO_2$. The peak area ratio has also dropped to 1.1:1.0 which indicates that a significant amount of phase separation has occurred between ruthenium and the stabilizing agent.

The cycling of sample 4-D was continued for an additional 100 hr to produce sample 4-E. The data again show the presence only of $BaRuO_3$ and $RuO_2$. The drop in the peak ratio to 0.4:1.0 indicates significant phase separation. This sample also displayed a slight reduction ($\sim$5%) in the total peak area. This indicates a small loss in total ruthenium content from the catalyst. Loss in ruthenium metal from these catalysts has generally been attributed to the formation of higher volatile oxides. However, the Mössbauer spectra of sample 4-E does not indicate the presence of any higher oxides of ruthenium. Although, it is possible that their concentration in this sample may be below the minimum Mössbauer detection level since at 700°C one would not expect a significant concentration of the higher oxides to form.

Sample 2-B in Table 2 corresponds to an oxidation–reduction cycle treatment of sample 2-A for 150 hr. The Mössbauer spectrum for this sample was again obtained after the net oxidation treatment. Again, the data show that the 2% ruthenium sample behaves like the 4% sample in that repeated cycling between an oxidizing and reducing atmosphere causes significant phase separation between ruthenium and the stabilizing agent.

## CONCLUSION

This study has shown that Mössbauer spectroscopy can provide chemically significant data about the state of ruthenium in automobile emission control catalysts. The data obtained by this technique indicate that it is probably not possible to stabilize every ruthenium atom by the "in place" impregnation of an alumina support with a barium stabilizing agent. The Mössbauer data also show that a significant loss in ruthenium stabilization occurs when the catalyst is cycled between a net reducing exhaust mixture and a net oxidizing exhaust mixture. This loss in stabilization is apparently due to the separation of ruthenium metal from the stabilizing barium oxide phase. These preliminary results are encouraging in that another tool is now available to elucidate the chemical changes which take place in these complex, heterogeneous catalyst systems. Further work is planned on other stabilized ruthenium systems and the combination of Mössbauer and ESCA spectroscopy as simultaneous "bulk" and "surface" probes is being investigated for a variety of supported ruthenium catalyst models.

## ACKNOWLEDGMENTS

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