Determination of Rhodium on Commercial Carbon- and Alumina-Supported Catalysts

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ABSTRACT

Methods are described to determine metallic rhodium on small samples of either carbon or alumina catalyst supports. After the catalysts were digested with hot mineral acids, the solutions were analyzed by an established colorimetric method and results were compared with those from an atomic absorption procedure. Statistical analysis showed that the two methods were equal in precision with a combined standard deviation of 0.08 for a 5.0% rhodium catalyst.

INTRODUCTION

Frankel (1,2) has reported a unique rhodium catalyst system for the selective hydroformylation of fatty esters and triglycerides. A simple method for determining rhodium on samples of alumina- or carbon-supported catalysts was needed for small scale process studies.

Classic methods for such determinations, reviewed by Walsh and Hausman (3), often involve elaborate fusion separations combined with gravimetric or colorimetric procedures. Fusion is not only time consuming and tedious, but also requires a comparatively large sample for analysis. This requirement is a distinct disadvantage when recycling small amounts of catalyst. We therefore developed procedures for dissolving rhodium in concentrated acids (3) and analyzed the resulting solutions by an established colorimetric method (4-7). Results were compared with those from an atomic absorption procedure. These procedures appear to be much simpler than those involving fusion.

EXPERIMENTAL PROCEDURES

Materials

Supported catalysts (5% rhodium on carbon or alumina) came from Engelhard Industries. Rhodium trichloride trihydrate was purchased from Alfa Inorganic. Stannous chloride, hydrochloric acid and sulfuric acid were reagent grade chemicals supplied by Allied Chemical Co.

Atomic Absorption Parameters

The spectrophotometer was a Perkin Elmer Model 303 equipped with recorder readout capable of expanding the scale 100x. Rhodium was determined at 343.5 nm with a spectral band width of 0.235 nm and a lamp current of 30 ma. A single slot, 5 cm nitrous oxide-acetylene burner head was used. Acetylene and nitrous oxide rotometer settings were 13.5 and 6.0 units, respectively.

Digestion of Alumina-Supported Catalysts

First, 200 mg ±0.1 mg of the catalyst was weighed into a 100 ml volumetric flask. Then concentrated sulfuric and hydrochloric acid, 2 and 5 ml, respectively, were added. The mixture was heated on a steam bath for 72 hr, after which the clear pink solution was cautiously made to volume with distilled water. A 200 mg sample of fine mesh alumina was digested in the same fashion to serve as a blank in atomic absorption determinations.

Digestion of Carbon-Supported Catalyst

Because of its hydroscopic nature, 200 mg ±0.1 mg of the catalyst was quickly weighed into a 30 ml Kjeldahl flask. Next 5 ml concentrated sulfuric acid and several glass boiling beads were added. The solution was heated at reflux temperature for 3-4 hr or until clear. The mixture was cooled to room temperature, quantitatively transferred (with caution) to a 100 ml volumetric flask and made to volume with distilled water.

Preparation of Standards

Rhodium trichloride trihydrate (0.1279 g) was weighed into a 100 ml volumetric flask and made to volume with distilled water to give a stock solution containing 500 μg Rh/ml. Convenient working standards for the colorimetric and atomic absorption methods are 200 and 50 μg/ml, respectively.

Colorimetric Determination of Rhodium with Stannous Chloride

Amounts (200-1000 μg Rh) of the working standard were transferred to 2 x 20 cm test tubes along with 5 ml 2 N HCl and 10 ml 10% stannous chloride solution in 2 N HCl. Samples were mixed thoroughly before heating for 1.5 hr in an oil bath maintained at 100 C. Samples were cooled

TABLE I

Comparison of Methods to Measure Rhodium on Supported Catalysts Prepared Commercially[a]

		Method									
		Colorimetric					Atomic absorption				
	Replicate	Determination, % rhodium on support									
Catalyst support	digestion	1	2	3	4	Mean[a]	1	2	3	4	Mean
Alumina[b]	A	5.03	5.14	5.07	5.11	5.05	4.96	5.05	5.13	5.05	4.99
	B	4.94	4.98	5.02	5.10		4.94	4.98	5.02	5.10	
Carbon	A	4.81	4.99	4.94	4.84	4.81	4.89	4.95	4.85	4.80	4.82
	B	4.98	4.76	4.63	4.71		4.88	4.82	4.82	4.74	
Spent alumina[c]	A	2.87	2.84	2.77	2.92	2.85	2.92	2.85	2.87	2.74	2.84
	B	2.99	3.08	2.86	2.97	2.97	---	---	---	---	---

[a] Standard deviation per observation = 0.08 for unused support.
[b] Fresh supports supplied as 5% rhodium metal on support.
[c] Spent hydroformylation catalyst.

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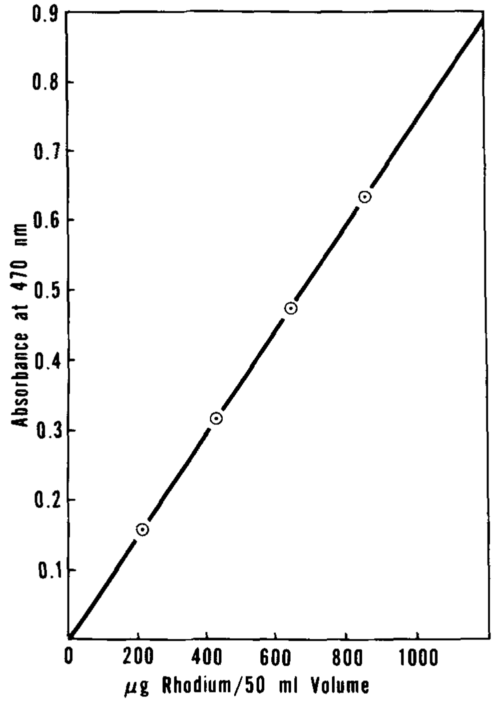

FIG. 1. Standard curve for colorimetric determination of rhodium with stannous chloride. Beckman DU spectrophotometer, 1 cm cells.

to room temperature and quantitatively transferred to 50 ml volumetric flasks with 2 N HCl. The absorbance was read at 470 nm in 1 cm cells against a blank carried through the procedure. To determine rhodium in digested catalysts, from 5 to 10 ml of the digest was substituted for the standard solution in this procedure.

Determination of Rhodium by Atomic Absorption

Digested catalysts were prepared for analysis by transferring either 2 or 3 ml of the digest to 10 ml volumetric flasks and making to volume with distilled water. Next 1, 2, 3 and 4 ml of the 50 µg Rh/ml standard were pipetted into 10 ml volumetric flasks along with digested alumina to serve as atomic absorption standards. The amount of digested alumina must equal the amount of digested catalyst, either 2 or 3 ml.

Similar standards were prepared for carbon catalyst (instead of the alumina blank); sulfuric acid was added to yield a final acid concentration equal to that of the diluted catalyst sample. Catalyst digest contains ca. 0.04 ml concentrated sulfuric acid per milliliter.

RESULTS AND DISCUSSION

Although both analytical methods require an aqueous solution, digestion procedures differ for each catalyst support. For carbon catalysts, boiling sulfuric acid alone is sufficient because during digestion the support is destroyed by oxidation. Digestion of carbon supports proceeds smoothly, provided heating is stopped as soon as digestion is complete. Prolonged heating may cause irreversible precipitation of rhodium salts. Digestion is considered complete when the solution is clear. Although digestion proceeds rather slowly, an arbitrary mixture (1-2.5) of sulfuric and hydrochloric acids at steam bath temperatures has proved satisfactory for alumina catalysts.

Attempts to speed digestion by heating at higher temperatures were unsuccessful, presumably because insoluble dehydrated salts are formed when alumina is present (3).

The stannous chloride method, as outlined by Sandell (4), was chosen for the colorimetric analysis. Although comparatively insensitive, it is simple, free from sulfate interferences, and the rhodium-tin complex is stable to light.

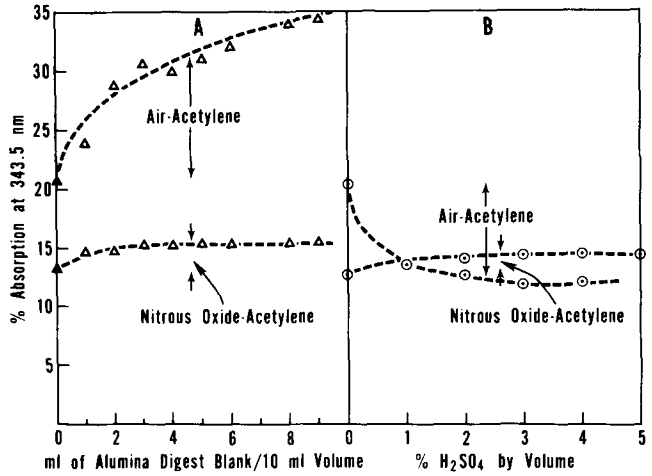

FIG. 2. Effect of sulfuric acid and aluminum salts on atomic absorption of a 10 µg/ml rhodium standard. (A) Aluminum salts; (B) sulfuric acid. See Experimental Procedures for preparation of blank. Arrows indicate magnitude of the interferences.

A rhodium standard curve by the stannous chloride method is plotted in Figure 1. Maynes and McBryde (5) reported that 498 µg Rh/50 ml volume gave an average optical density reading of 0.378 at 470 nm. Because our value of 0.370 agrees with the literature, our rhodium salt must approach 100% purity. Also, standard curves determined with granular rhodium metal, solubilized in boiling sulfuric acid, gave extinction coefficients identical to those prepared from the chloride salt. Our standard curve is reproducible, i.e., curves prepared a month apart differed little in their slopes. Therefore, once established, a standard curve need not be run for each set of analyses.

Attempts to analyze digested catalyst solutions by atomic absorption in an air-acetylene flame were unsuccessful because of the interferences from sulfuric acid and aluminum salts. The effects and magnitudes of these interferences on the atomic absorption of a 10 µg/ml rhodium standard are seen in Figure 2. Figure 2A shows the effect of aluminum salts in air-acetylene and nitrous oxide-acetylene flames and typical problems encountered in analysis of alumina-supported rhodium. In the air-acetylene flame, aluminum salts in the sample matrix markedly enhance rhodium absorption and the effect is influenced by the relative concentration. Results in the nitrous oxide-acetylene flame show that this effect is significantly reduced because rhodium absorption is only slightly enhanced and depends less on matrix composition. Figure 2B shows the effect of sulfuric acid alone on rhodium absorption in the two flames and pertains to analysis of carbon-supported rhodium. Sulfuric acid exerts a strong depressing effect on rhodium absorption in the air-acetylene flame, whereas a slight enhancing effect is evident in the nitrous oxide-acetylene flame. Similar interferences have been observed by other workers (7).

Although interferences are significantly reduced in the nitrous oxide-acetylene flame, they cannot be ignored. Results were best when standards were matched with matrix components. For alumina supports, matching can be accomplished by digestion of a blank sample of alumina and adding portions to the atomic absorption standards. Similarly for carbon catalyst, a blank solution (4-5%) of sulfuric acid can be prepared and fractions added to the standards. Figure 2 shows that in the nitrous oxide-acetylene flame, the matrix matches do not have to be perfect because the magnitude of the interference is largely independent of sulfuric acid or aluminum salt concentration.

Supported rhodium (5% metal) on carbon and alumina, commercially prepared, were chosen to develop the determination needed. Duplicate portions of carbon and alumina supports were digested and analyzed by colorimetric and atomic absorption methods. Comparative analytical data are given in Table I. Samples A and B represent replicate digestions of the same lot of catalyst. Both colorimetric and atomic absorption data indicate that the particular lot of alumina catalyst contained ca. 5% rhodium as specified by the manufacturer.

Comparison of the colorimetric and atomic absorption data for the carbon-supported catalyst shows excellent agreement between the two methods. Such catalysts assayed less than 5% rhodium. Supported catalysts in general and, in our experience, carbon catalysts in particular are somewhat hydroscopic; thus any moisture absorbed during weighing or from the time the catalyst was packaged would account for the low rhodium content of carbon-supported catalysts. Analytical data from the two methods were treated statistically by analysis of variance with the following conclusions: (a) There were no significant differences associated between the two methods; (b) there was no significant interaction of method with digestion or support; (c) variance for the colorimetric method was larger than for the atomic absorption method ($S^2 = 0.0091$ vs. 0.0037) but not significantly larger. Therefore both variances were combined for a value of $s = \sqrt{0.0064}$ or 0.08. Statistically, there was a significant difference between two digests of the same support, but from a practical standpoint the data are in satisfactory agreement. We are unaware of any published error estimates for standard fusion procedures, so that a comparison of methods themselves is not possible.

All our experience in analysis of spent supports has been with alumina. Analytical data for a spent alumina hydroformylation catalyst are given in Table I, where replicate digestions (A and B) are compared by methods. The data for digestion A indicate good agreement between methods, and error estimates are of the same order as for unused supports. When colorimetric data are compared, digestions A and B vary ca. 4%.

Our spent supports contain small quantities of strongly adsorbed organic material that does not digest. This condition may account for the variable data. Attempts to remove the organic material by calcination at 500 C in air produced an acid-insoluble support. Heating rhodium in air or oxygen produces a film of rhodium oxide, which is insoluble in all acids (8). Furthermore the solubility of alumina in acids reportedly decreases by calcination (9).

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