An ESCA Study of Rhodium(III)-Exchanged Zeolite Catalysts

Rhodium(III)-exchanged molecular sieve zeolites have been noted to demonstrate a wide variety of catalytic properties (1–5) ranging from hydrogenation to induction of polymerization reactions. While X- and especially Y-type rhodium zeolites are frequently reported as demonstrating catalytic properties, zeolite A, with the highest ion-exchange capacity and thus the greatest support capacity for rhodium of any zeolite, has been infrequently cited as an effective catalyst. Although numerous ir studies have been conducted on the nature of rhodium complexes in zeolites (6–8) to date the only method employed for the direct study of the state of the rhodium atoms in the zeolite cages has been ESR (electron spin resonance) (9). This technique suffers from the extreme disadvantage of limiting the investigator to the observation of only the paramagnetic oxidation states of the atom in question. In the case of rhodium these are Rh^0 and Rh^{2+} notably omitting the Rh^{+3} cation presumably initially present after the exchange process and which therefore is the precursor to any catalytically active species or is the active species itself. ESCA (Electron Spectroscopy for Chemical Analysis) has proved (10–12) to be an effective tool in the analysis of zeolites. Additionally, ESCA has been demonstrated (13) to be an effective tool in characterizing supported rhodium catalysts. However, we have found no characterization of zeolite supported rhodium catalyst by ESCA in the literature. It has been postulated (9) on the basis of ESR data, that under certain conditions metallic rhodium clusters form in zeolites. This state of rhodium would be expected to be catalytically active. Additionally, ir data are supportive of a thermal reduction process (8). Knowing that ESCA could confirm the hypothesized formation of metallic rhodium, if correct, and also discern the presence of rhodium in other oxidation states inaccessible to ESR observation, we prepared samples of frequently cited rhodium(III) zeolite Y and seldom cited but high-support-capacity zeolite A and took ESCA spectra of these samples in both the original exchanged condition and after activation to the state wherein they would be employed in a catalytic capacity.

In the preparation of both rhodium(III) zeolite A and rhodium(III) zeolite Y, 1 g of Pfaltz & Bauer rhodium(III) bromide was dissolved in 25 ml of deionized water. An amount of the appropriate zeolite was added such that the total cationic content of the exchangeable zeolite was equal to the available cationic rhodium in solution. The exchanging mixtures, reddish brown in color, were allowed to stand for 72-h at room temperature; at the end of that time the supernatant liquid in both preparations was extensively decolorized. The zeolites employed were Matheson Coleman & Bell 1/16-in.- diameter 3A extrudate and Linde LZY-52 1/16-in. extrudate, respectively. The decolorization of the solutions constitutes visual evidence that the exchange of rhodium for the alkaline cations initially present in the zeolites was essentially complete, an unusual outcome in the case of a trivalent cation such as rhodium. Spectra obtained by means of a Hewlett–Packard 5950A ESCA spectrometer reveal that (at least in the approximately outer 50-Å layer of the exchanged extrudates) none of the original alkaline cations were found to be present, and the amount of rhodium ob-
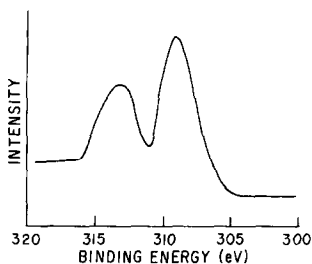
FIG. 1. ESCA spectrum of rhodium(III) 3d electrons obtained from rhodium(III)-exchanged zeolite A and Y samples.

served was equivalent (within the 10% error of a given measurement inherent in the instrument) to that needed to balance the negative charge of the framework if the rhodium cations were trivalent.

The ESCA recorded the $3d_{5/2}$ and $3d_{3/2}$ photoelectron lines for rhodium(III)-exchanged into the zeolites at 309.5 and 313.6 eV, respectively (Fig. 1) standardized to the C 1s line and utilizing an electron flood gun to ensure the absence of shifting due to differential charging. The illustrative figure represents raw data in which the $3d_{3/2}$ peak rose to a height of 20,042 counts from a background of approximately 9400 counts, while the $3d_{5/2}$ peak rose to 27,682. The peak areas were 137,488 and 266,666 counts, respectively. (While these are actual counting statistics, they cannot represent the true physical concentration to better than ±10% of the reading.) Maximum data displacement from the curve as drawn is approximately 200 counts. Considering the difference in environments of the rhodium(III) atoms, this corresponds very well with the published values (13) for Rh^{3+} in the form of Rh_2O_3 at 308.7 and 313.5 eV. This, and the stoichiometry of the cation charge considerations previously mentioned, firmly established that the exchanged rhodium exists initially as Rh^{3+} in the zeolite frameworks. The slight differences in splitting between our values and those previously reported in addition to the slight asymmetry of the Rh 3d peaks illustrated and the deviation of the ratio of these peak areas from the ratio of their

effective cross sections indicate that we are actually observing a mixture of oxidation states of rhodium where the Rh^{3+} species predominate.

Numerous recent reports have indicated (8, 14) that some cations may be thermally reduced in a zeolite framework. Exchanged zeolites in general have been extensively noted in an enormous variety of catalytic processes (15). Additionally, the catalytic properties of zeolites are strongly dependent upon dehydration of the lattice before exposure to the reactants to be catalyzed (16). Being extremely hygroscopic, zeolites are "activated" by a combination of vacuum and thermal treatments. While the thermal treatment (approx. 300°C would be typical) is generally milder than the 500–600°C reported to reduce some cations such as copper (8) to metallic form within a zeolite, the reduction of Rh^{3+} to rhodium metal by inadvertent changes in the system due to typical activation conditions might serve as an explanation of the catalytic behavior of rhodium(III)-exchanged zeolites. For conditions more dramatic than typical activation (oxygen roasting at 500°C) Atanasova et al. (9) have postulated that rhodium is reduced to metallic form in zeolite Y on the basis of an ESR signal which they attribute to paramagnetic Rh^0. Brinen and Melera have clearly demonstrated (13) that the catalytic activity of rhodium supported on charcoal is dependent upon the amount of Rh^0 present in proportion to Rh^{3+} (in the form of Rh_2O_3 in the case they studied). Considering these facts, reduction of Rh^{3+} to Rh^0 would be a viable explanation for the observations of many rhodium catalytic activities.

Activation of rhodium(III)-exchanged zeolite A and rhodium(III)-exchanged zeolite Y at 300°C and 2×10^{-3} Torr for 2 h leads to markedly different reactions. Visually, while the zeolite A sample retains its original light brown color, the Y-type zeolite turns distinctly black. The ESCA spectrum of the rhodium-exchanged A-type zeolite after activation revealed that the rhodium
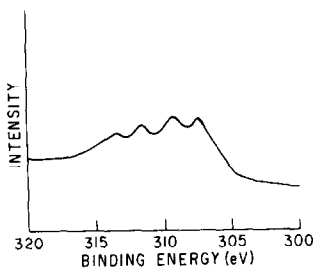
FIG. 2. ESCA spectrum of rhodium 3d electrons obtained from an activated rhodium(III)-exchanged zeolite Y sample.

was still predominantly (within the instrument's limits of error) in the 3+ oxidation state. However, the now black Y-type sample demonstrated a marked change in its ESCA spectrum (Fig. 2). In addition to the Rh^{3+} peaks at 309.5 and 313.6 eV two additional peaks appear at 307.7 and 311.8 eV. The peaks rise to heights varying from 6992 counts at 313.6 eV to 8030 counts at 309.5 eV from a background of approximately 5000 counts. Again, the maximum data displacement is approximately 200 counts from the curve as portrayed. These compare very well with the literature values of 307.1 and 311.9 eV (*13*) for the 3d lines of rhodium metal foil. We note a shift of 1.8 eV from the initial Rh^{3+} to the new rhodium species, comparing favorably with the reported (*13*) shift of 1.6 eV between rhodium metal foil and Rh^{3+} in the form of Rh_2O_3. We must conclude from these findings that Rh^{3+} is reduced by the conditions of activation of Rh^0 in the zeolite Y framework. Noting the lack of a similar reduction effect in zeolite A and the lack of catalytic activity demonstrated by this type in comparison to the widely cited Y-type rhodium zeolites, and nothing that Rh^0 is the catalytic agent (in contrast to inactive Rh^{3+}) of charcoal supported rhodium, it is reasonable to assume that metallic rhodium is the true catalytic agent in what heretofore have been referred to as rhodium(III) zeolite catalysts.

A slight deviation from the 3 to 1 aluminum-to-rhodium ratio, as indicated by ESCA, is found in the heat-treated zeolite Y sample. Considering that the peak area of the Al 2s was found to be 15,398 counts, the expected total peak area of the rhodium 3d lines would be expected to be approximately 103,000 counts. However, the experimental value of 118,730 is seen to be slightly above our 10% error limits. This slightly increased reading for rhodium indicates migration of the metal to some position in the zeolite lattice; however, the commonly observed phenomenon of migration and agglomeration of metals to the exterior of a crystalline particle upon reduction is clearly not present.

In conclusion, in support of previously reported ESR data (*9*) ESCA indicates that rhodium(III) may be thermally reduced to rhodium metal in the zeolite Y lattice. Additionally, it has been demonstrated that this reduction occurs under markedly milder conditions than the comparable reduction of any other metal previously reported in the literature. It is noted that in addition to its lack of catalytic properties, zeolite A lacks the ability to reduce rhodium(III) in a similar manner. While the smaller pore geometry of zeolite A (in comparison to zeolite Y) would inhibit many reactions by the exclusion of large reactant molecules, the lack of catalysis of smaller molecules by zeolite A can only be attributed to differences in the state of exchanged cations. It is strongly suggested that the metallic rhodium produced by the activation of rhodium(III)-exchanged zeolite Y, and not the Rh(III) cations, are the probable catalytic species in so-called rhodium(III) zeolite catalysts.

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