

The Chemical State of Tin in Platinum-Tin-Alumina Catalysts

SAYRA R. ADKINS AND BURTRON H. DAVIS

Institute for Mining and Minerals Research, University of Kentucky, P.O. Box 13015, Iron Works Pike, Lexington, Kentucky 40512

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Platinum-tin catalysts have been reduced in 1 atm of flowing hydrogen and then examined, without exposure to the atmosphere, by ESCA. The spectra indicate that the Group VIII metal is present in a metallic state in the reduced catalyst and that the majority of the tin is present in a valence state higher than Sn(0). Chemical reaction selectivities also show that the majority of the tin is not present as bulk tin oxide even in a 10% SnO₂ on alumina catalyst. The results are consistent with tin being present as an eggshell of "tin aluminate" surrounding the alumina support with the Pt(0) or Rh(0) supported on the "tin aluminate."

INTRODUCTION

The demand for high-octane gasoline in the 1940's resulted in naphtha reforming. Platinum supported on an acidic alumina became the preferred catalyst for commercial processes for years following the introduction of Platforming (1). In the late 1960's bimetallic, and even polymetallic, reforming catalysts with superior aging qualities were introduced and became widely accepted in commercial operations (2). The Pt-Re combination was the first bimetallic catalyst to gain widespread commercial acceptance. Following the initial introduction of the catalyst, probably the most popular view, at least for its greater stability, was that of alloy formation (3).

Another bimetallic combination that has been widely used for naphtha reforming and dehydrocyclization studies is Pt-Sn (4-12). The Pt-Sn catalyst has also been employed in commercial operations. There has been disagreement about the state of tin in these catalysts. Dautzenberg *et al.* (6) claimed that tin, in excess of 0.6 wt%, was fully reduced; the 0.6% not fully reduced tin was present as a complex with alumina. Mössbauer studies led to the identification of Pt-Sn alloys, Sn⁴⁺, Sn²⁺, and Pt not alloyed with tin (13-16). Studies with un-

ported catalysts showed clear evidence for Pt-Sn alloy formation in the reduced catalyst (17). The surface composition of this unsupported alloy was dependent on the nature of the gas in contact with the catalyst (18). Surface enrichment by the element with the lower heat of sublimation was observed for the reduced Pt-Sn alloy (19). Burch (20) concluded, on the basis of temperature-programmed reduction, that tin remained in the Sn(II) state. Bacaud *et al.* (21) reported that a Pt-Sn alloy was formed at high metal loadings but that their data was consistent with the presence of Sn(II) at low Pt loadings. Hoflund and co-workers (22) studied various Pt-Sn preparations, many of which had high metal loading, using a variety of characterization techniques.

Patterson *et al.* (23) designed an ESCA sample holder that permits the reduction, up to temperatures in the 500°C range, in 1 atm flowing hydrogen. The sample, in a H₂ atmosphere, is transferred into the evacuated insertion lock of ESCA instrument prior to exposure in the vacuum chamber. This probe was utilized to prepare Pt-Sn-Al₂O₃ catalysts that are reduced at 1 atm hydrogen pressure for ESCA examination to establish the state of Sn and Pt in a reduced catalyst.

EXPERIMENTAL

Catalysts

Various catalyst preparations were used in this study. Catalysts were prepared by impregnation using an acetone solution containing an amount of H_2PtCl_6 to produce a nominal 0.6 wt% Pt catalyst and sufficient SnCl_2 to produce a Pt : Sn = 1 : 4 molar ratio unless indicated otherwise. The acetone, used for impregnation, was allowed to evaporate in air prior to drying at 120°C. Unless noted otherwise, the catalyst, prior to reduction, contained the chloride present in the salts used for impregnation.

Catalyst 1. The alumina support was a high-area (230 m^2/g) nonacidic alumina (24).

Catalyst 2. Same as catalyst 1 except a high surface area (ca. 210 m^2/g) acidic alumina, prepared precipitation from aluminum chloride with ammonium hydroxide, was used as the support.

Catalyst 3. This impregnated catalyst was similar to catalyst 1. After the catalyst was air dried, it was calcined in air at 480°C for 16 h and then reduced in flowing H_2 at 480°C for 6 h. The reduced catalyst was washed with ca. 5% ammonium hydroxide to remove chloride. A second sequence of calcination, reduction, and ammonia washing was carried out.

Catalyst 4. A $\text{Pt}_3\text{Sn}_8\text{Cl}_2^-$ cluster was prepared following a published procedure (25). An acetone solution of this complex was used to impregnate Degussa aluminum oxide C. The Pt/Sn ratio was that of the cluster.

Catalyst 5. A portion of the same acidic alumina support used for catalyst 2 was impregnated with an acetone solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to yield a nominal 10 wt% Sn on alumina catalyst.

Catalyst 6. Alumina from the same batch that was used to prepare catalyst 2 was impregnated using an ethanol solution of $(\text{NH}_4)_3\text{RhCl}_6$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Because of the limited solubility of the rhodium complex, two impregnations, with drying fol-

lowing the first impregnation, were used. The catalyst contained a nominal 0.6 wt% Rh and a Rh : Sn ratio of 1 : 4.

Catalyst 7. Cabot Corporation Monarch 1300 carbon was impregnated with an acetone solution of H_2PtCl_6 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Catalyst 8. This catalyst was the same as catalyst 6, except that Cabot Corporation Monarch 1300 carbon, rather than alumina, was used as the support.

SnO₂. Tin hydroxide was precipitated from a nitrate solution with ammonia; this precipitate was collected, dried at 120°C, and calcined at 570°C.

ESCA Measurements

Spectra were obtained using an AEI ES-200B spectrometer. The instrument was calibrated using the Cu $2p_{3/2}$ and $3p_{3/2}$ core level spacing of 857.6 eV. The spectrometer work function was set so that the Au $4f_{7/2}$ peak was 84.0 eV above the spectrometer Fermi level.

The spectra for unreduced catalysts 1 through 6 were obtained for samples mounted on copper-backed adhesive tape. The Sn spectra was obtained for a metal foil. Spectra for unreduced catalysts 7 and 8 were recorded for the pelleted form contained in the probe used for obtaining the *in situ*-reduced catalyst spectra.

To obtain spectra of reduced catalysts, a probe similar to that described by Hercules was used (23). This design permits a sample to be exposed to a pretreating atmosphere, isolated in a gas-tight compartment in the preheating gas, transported to the ESCA instrument, and inserted into the vacuum chamber. Catalyst powder was pressed (10 to 15 tons/inch²) into a pellet prior to reduction. The catalyst pellet was then cut to fit tightly into a rectangular cavity near the end of the sample probe. The sample thickness was adjusted so that the top of the pellet was approximately flush with the sample probe surface.

Catalyst reduction was carried out by placing the sample probe in a tube which

TABLE 1
Corrected ESCA Binding Energies for Tin-Containing Catalysts and Reference Materials

| Material | Sn ^a | | Rn ^b | | Pt ^c | | Cl | | Reference |
|------------------------|------------------|------------------|-------------------|------------------|-----------------|----------------|-------|-------------------|-----------|
| | Fresh | Reduced | Fresh | Reduced | Fresh | Reduced | Fresh | Reduced | |
| Catalyst 1 | 486.9 (495.5) | 487.0 (495.6) | — | — | — | — | — | — | Al 2p |
| Catalyst 2 | 487.0 (495.6) | 487.1 (495.7) | — | — | — | — | 199.2 | N.D. ^d | Al 2p |
| Catalyst 3 | 487.0 (495.7) | 487.0 (495.5) | — | — | — | — | — | — | Al 2p |
| Catalyst 4 | 487.1 (495.7) | 487.0 (495.7) | — | — | — | — | 199.6 | N.D. | Al 2p |
| Catalyst 5 | 487.1 (495.7) | — | — | — | — | — | — | — | Al 2p |
| Catalyst 6 | 487.2 (496.1) | 486.9 (495.5) | 309.3 (313.9) | 307.3 (311.6) | — | — | — | — | Al 2p |
| Catalyst 7 | 487.0 (495.5) | 486.6 (495.1) | — | — | 72.7 (75.4) | 71.9 (75.0) | — | — | Al 2p |
| Catalyst 8 | 487.0 (495.5) | 486.6 (495.1) | 308.7 (312.9) | 307.3 (312.0) | — | — | 199.3 | 200 | C 1s |
| Sn foil | 484.6 (493.0) | — | — | — | — | — | 199.1 | 199.5 | C 1s |
| SnO ₂ | 487.1 (495.7) | — | — | — | — | — | — | — | C 1s |
| Pt Metal (Literat.) | — | — | — | — | 70.9 | — | — | — | C 1s |
| Rh Metal (Literat.) | — | — | 307.0 (311.75) | — | — | — | — | — | C 1s |
| Pt-Sn-Cl Complex | 486.8 (495.3) | — | — | — | 72.3 (75.6) | — | 198.6 | — | C 1s |

^a Top number is B.E. for the Sn 3d_{5/2}; number in parenthesis is for Sn 3d_{3/2}.

^b Top number is B.E. for the Rh 3d_{5/2}; number in parenthesis is for Rh 3d_{3/2}.

^c Top number is B.E. for the Pt 4f_{7/2}; number in parenthesis is for Pt 4f_{5/2}.

^d N.D. = peak not detected above background noise.

could be heated. The catalyst was reduced in flowing hydrogen (1 atm) at 400°C for 17 h. After reduction the probe, with sample, was transported to the vacuum chamber of the ESCA in a hydrogen atmosphere. Once the probe was inserted into the instrument the sample may be exposed and oriented toward the X-ray beam.

Referencing catalyst ESCA binding energies to carbon is difficult since the lower energy C 1s peak may be merged with a larger, slightly higher binding energy peak (26). Thus, for alumina-supported catalysts the Al 2p peak was used as the reference peak for charge correction. Carbon was used as the reference for charge correction for carbon-supported catalysts and for the other samples described in this report that did not contain alumina.

RESULTS

The Sn 3d_{5/2} binding energy for tin and tin oxide were 484.6 and 487.1 eV, respectively (Table 1). These binding energy values are consistent with those reported in the literature (27). The 3d_{5/2} binding energy of tin in a sample of 10% tin on alumina was 487.1 eV. This binding energy of tin supported on alumina is the same as that of the unsupported tin oxide which prevents the use of ESCA binding energy alone to decide whether tin oxide particles that resemble bulk tin oxide exist on the catalyst surface. The conversion of an alcohol, can provide a chemical test for the presence of a significant amount of "bulk tin oxide."

Alumina is a very selective alcohol dehydration catalyst (28). The data in Table 2

TABLE 2
Selectivity of Tin Catalysts for the Conversion of 4-Methyl-2-pentanol

| Catalyst | Temp. (°C) | Conversion, mole% | | Dehydration selectivity (%) |
|---|------------|-------------------|-----------------|-----------------------------|
| | | Dehydration | Dehydrogenation | |
| Al ₂ O ₃ | 180 | 30 | Trace | ca. 100% |
| 10% SnO ₂ /Al ₂ O ₃ ^a | 220 | 11 | 0.5 | 96 |
| 10% SnO ₂ /Al ₂ O ₃ ^b | 210 | 5 | 0.6 | 89 |
| SnO ₂ | 225 | 0.6 | 30 | 2.0 |
| 10% Pt-Al ₂ O ₃ ^c | 190 | Trace | 28 | ca. 0 |

^a Pretreated with flowing oxygen at 525°C for 6 h.

^b Pretreated with flowing hydrogen at 525°C for 6 h.

^c Pretreated with hydrogen at 525°C; about 5–10% condensation products were also formed.

clearly show that the alumina used in this study has a high alcohol dehydration selectivity. Unsupported tin oxide, in contrast to alumina, is a very selective dehydrogenation catalyst. Platinum, a dehydrogenation catalyst, supported on alumina is a selective dehydrogenation catalyst. Alumina-supported tin oxide is a very selective dehydration catalyst following either hydrogen or oxygen pretreatment. Thus, alumina-supported tin, even for a 10 wt% loading, does not have the catalytic property expected for tin oxide. This indicates that a significant fraction of tin oxide is not present as bulk tin oxide particles on the alumina. X-Ray diffraction results support this conclusion. The diffraction pattern of the support was observed; however, none of the peaks expected for tin oxide were observed. The X-ray data would be consistent with the tin being present in a thin "eggshell" covering part or all of the alumina support. Both the alcohol conversion and X-ray diffraction studies indicate that tin oxide is not present even in a catalyst containing 10 wt% tin oxide. Similar results were obtained with 1, 3, and 5 wt% tin-alumina catalysts.

At low surface coverage the Pt 4f ESCA peaks are so small, in comparison to the Al 2p peak of the support, that they cannot be measured. Thus, we are unable to measure

directly the binding energy of Pt on the alumina support.

Tin spectra showing the 3d_{5/2} and 3d_{3/2} peaks for the fresh, oxidized samples are shown in Fig. 1. The binding energies for these tin peaks are, within experimental error, essentially the same. The tin peaks in

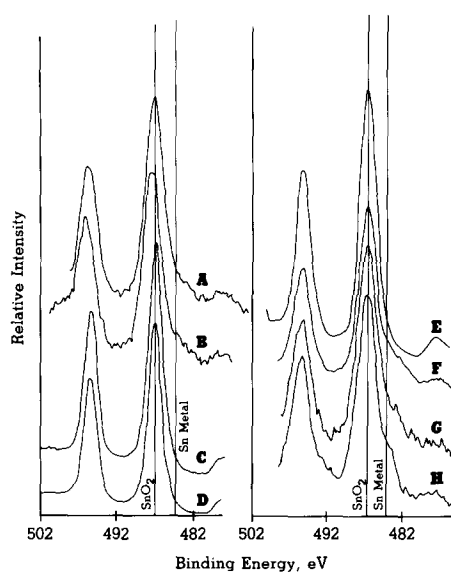


FIG. 1. The ESCA binding energy of the Sn 3d_{5/2} and 3d_{3/2} peaks for the fresh, oxidized catalysts: (A) SnO₂; (B) Rh-Sn-Al₂O₃ (6); (C) Pt-Sn-C (7); (D) Rh-Sn-C (8); (E) Pt-Sn-Al₂O₃ (1); (F) Pt-Sn-Al₂O₃ (2); (G) Pt-Sn-Al₂O₃ without chloride (3); (H) Pt₃Sn₈Cl₂₀-Al₂O₃ (4) (number in parentheses corresponds to the catalyst given in the Experimental Solution).

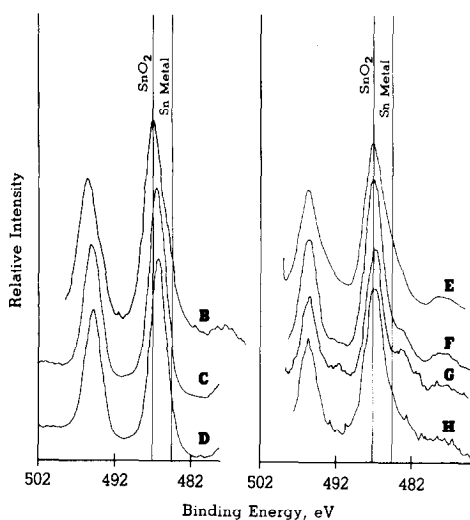


FIG. 2. The ESCA binding energy of the Sn $3d_{5/2}$ and $3d_{3/2}$ peaks for the reduced catalysts (letters correspond to same catalyst preparation as in Fig. 1).

Fig. 2 are for the hydrogen-reduced catalysts. With the possible exception of the carbon-supported catalysts, the binding energy of the tin peak of the reduced sample is identical to that of SnO₂ or 10% tin on alumina, and hence, to that of the oxidized catalyst. The binding energy of the reduced carbon-supported tin-containing bimetallic catalysts appears to be slightly lower than for the SnO₂. This may be due to the need to reference to carbon for this sample. However, even with the carbon-supported catalyst the tin was not present in a metallic form.

Since the Pt peak could not be utilized for ESCA measurements with the alumina-supported catalyst, a Rh-Sn-Al₂O₃ catalyst was prepared. Rhodium, unlike platinum, can be detected in the presence of the alumina support. In the oxidized catalyst the Rh binding energy is indicative of a high valence state. After reduction, the Rh in the Rh-Sn-Al₂O₃ catalyst appears to be present in the metallic state since the measured binding energy is the same as that reported for metallic rhodium (Fig. 3). The Rh in the oxidized Rh-Sn-C catalyst has a binding energy similar to that of the Rh-Sn-Al₂O₃ catalyst. After reduction, the

binding energy for Rh in the Rh-Sn-C catalyst corresponds to that of the metal. The Rh intensity is less with the carbon-supported catalyst than for the alumina-supported one, probably because of the higher surface area carbon which results in some of the Rh being present in the smaller pores in the interior of the support and, thus, not detected by ESCA measurements.

The Pt $4f_{7/2}$ peak can be observed for a carbon-supported catalyst (Fig. 4). Both the oxidized and reduced Pt-Sn-C catalysts have Pt at a higher binding energy than reported in the literature for metallic Pt; however, the reduced catalyst clearly has Pt at a lower binding energy than the oxidized form does. Thus, platinum is in a reduced state on the carbon-supported catalyst.

Alumina, by retaining the chloride added with the impregnating salts, differs from silica and carbon. This is shown by the data in Table 3 for alumina- and carbon-supported

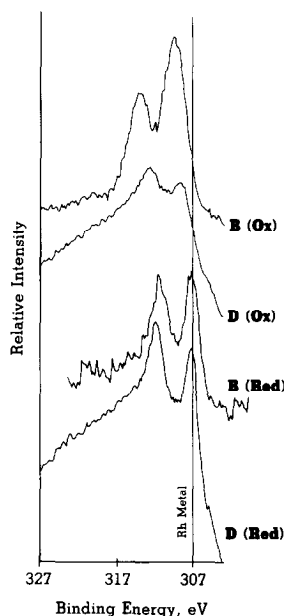


FIG. 3. The ESCA binding energy of the Rh $3d_{5/2}$ for oxidized and reduced catalysts: B(Ox), oxidized Rh-Sn-Al₂O₃ (6); D (Ox), oxidized Rh-Sn-C (8); B (Red), reduced Rh-Sn-Al₂O₃ (6); and D (Red), reduced Rh-Sn-C (8).

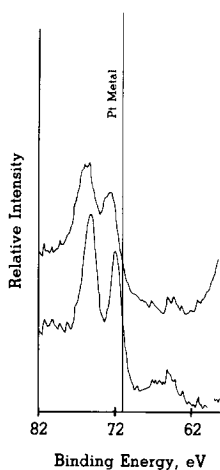


FIG. 4. The ESCA binding energy of the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks for C (Ox), oxidized Pt-Sn-C (7); C (Red), reduced Pt-Sn-C (7).

catalysts. The alumina-supported catalysts had all been used, after reduction at 550°C in flowing hydrogen, for dehydrocyclization of alkanes at 482°C for several hours (5, 29, 30). More than 50%, and in most cases nearly 90%, of the initial chloride was retained by these alumina-supported catalysts. This was clearly not the case with the carbon-supported catalysts since these retained less than 10% of the original chloride following hydrogen reduction.

The surface chloride level of the reduced alumina catalyst was too low to be detected

TABLE 3

Chemical Analysis Data for Pt and Pt-Sn Catalysts After Reduction at 550°C and Use as a Dehydrocyclization Catalyst at 482°C^a

| Catalyst | % Pt(Rh) | % Sn | % Cl | Cl Retained % of added |
|--------------------------------------|----------|------|-------------------|------------------------|
| Pt-Al ₂ O ₃ | 0.6 | — | 0.53 ^b | 81 |
| Rh-Al ₂ O ₃ | 0.4 | — | 0.71 | 86 |
| Pt-Sn-Al ₂ O ₃ | 0.48 | 1.0 | 0.67 | 60 |
| Pt-Sn-Al ₂ O ₃ | 0.37 | 0.2 | 0.55 | 105 |
| Pt-Sn-Al ₂ O ₃ | 0.61 | 2.0 | 1.10 | 59 |
| Pt-C | 1.0 | — | 0.1 | 9.2 |
| Pt-C | 2.2 | — | 0.19 | 7.8 |

^a Chloride was not added during the activation of dehydrocyclization run.

^b Average of 10 portions of catalyst after reduction and use as dehydrocyclization catalyst.

by ESCA measurements. Surface chloride could be detected in the catalyst prior to reduction. Based on the chemical analysis in Table 3 for similar catalysts and catalyst pretreatments and the ESCA data, we conclude that the chloride should be present in the alumina-supported catalyst used for the ESCA studies; however, it must not be present in the first few atomic layers of the sample because it is not detectable by ESCA. The spectra in Fig. 5 clearly show that the chloride in the reduced carbon-supported catalyst is within the portion of the sample that ESCA can detect even though the chloride ESCA peak intensity of both of the reduced carbon-supported catalysts is much less than for the just-dried catalysts. The chemical analysis data in Table 3 indicates that chloride should be present in low concentrations; if this is the case the chloride in the carbon-supported catalyst must be located near the surface for the reduced as well as for the just-dried catalysts.

DISCUSSION

The activity of aluminum and tin oxides for 2-octanol conversion, under similar

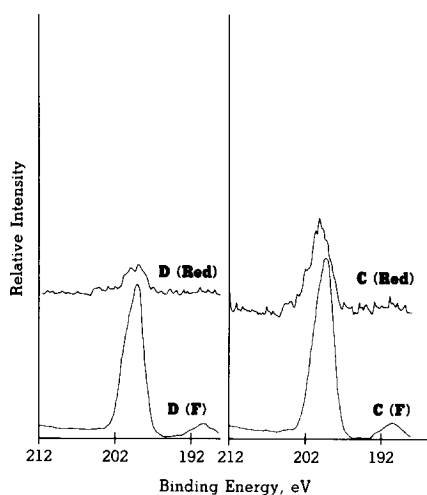


FIG. 5. The ESCA binding energy for chloride in the dried and reduced catalysts: D (F), Rh-Sn-C (8) catalyst after drying at 120°C; D (Red), Rh-Sn-C after reduction at 450°C; C (F) Pt-Sn-C (7) catalyst after drying at 120°C; C (Red) Pt-Sn-C (7) after reduction at 450°C.

conditions, does not vary as much as do alumina and a 1% Na-alumina catalyst (31). If the added tin poisoned alumina as sodium does then the catalytic activity should be primarily due to tin oxide. The Sn-Al₂O₃ catalyst should resemble the Pt-Al₂O₃ catalyst, where dehydrogenation was the predominate conversion, if the supported tin resembled tin oxide. However, even the 10% Sn on alumina was a very selective dehydration catalyst. Thus, the alcohol conversion results clearly show that, even with 10% Sn supported on an alumina with a surface area in excess of 200 m²/g, there is no evidence for a supported tin oxide phase. This was the case whether the catalyst pretreatment was reduction by hydrogen or oxidation by oxygen at 525°C.

Chemical analysis of a number of Pt and Pt-Sn-Al₂O₃ catalysts that were prepared by impregnation with the chloride salts showed that most of the chloride was retained after hydrogen reduction and even after use for dehydrocyclization studies for 4 to 8 h at 482°C. An intense chloride peak was observed in the ESCA spectra for unreduced samples of Pt-Sn-alumina catalysts. After reduction a chloride peak was not observed in the ESCA spectra. The carbon catalyst behaved differently. Chemical analysis showed Pt-C, after reduction and use as a dehydrocyclization catalyst, contained less than 10% of the chloride added by impregnation. In the unreduced Pt-Sn-C and Rh-Sn-C catalysts, a chloride peak was observed in the ESCA spectra. There was not a major difference in the relative intensity of the Sn and the Cl peak areas for the unreduced alumina- or carbon-supported metal catalysts. After reduction, a small chloride peak was observable in the ESCA spectra for both the Pt-Sn-C and Rh-Sn-C catalysts. Thus, the carbon-supported metals contained more surface chloride after reduction than the alumina-supported catalyst did. Chemical analysis of similar samples show that the reduced alumina-supported catalyst contains, for equivalent metal loadings, much more total

chloride than the reduced carbon-supported catalysts. This is taken to indicate that nearly all of the chloride added during the metals impregnation diffused into the alumina support during the hydrogen reduction so as not to be detected by ESCA.

ESCA, like all spectral techniques, has a lower detection limit that is not an absolute value but depends upon the sample. The inability to detect a 0.6% Pt on our catalysts was due to the location of the Pt peak within the very intense peak due to the large surface concentration aluminum and not due to inability of the ESCA instrument to detect Pt at the 0.6 wt% level. In fact, the Pt peak was readily observed in the ESCA spectra when carbon was the support. We are faced with a similar problem in determining low levels of metallic tin (Sn(0)) in the Pt:Sn catalysts. If half of the total tin was present as Sn(0) two peaks should be observed or, in the worst case, the half-width of the Sn peak should be much broader than for the Sn(4) oxide and the position of the peak maximum should shift to lower binding energy. There is no evidence for either two peaks, wider peaks or peak shift to lower binding energy. While a lower limit for Sn(0) detection cannot be set it seems reasonable to expect to see a peak that represents $\frac{1}{2}$ of the larger peak or about 15% of the larger peak.

There is essentially no difference for the tin ESCA peak shape or position for the reduced and oxidized alumina-supported sample. This was the case for the chloride-containing impregnated materials, the samples treated to remove chloride, and the sample where Pt-Sn was added as a bimetallic cluster compound. The tin peaks in the reduced Rh-Sn-C and Pt-Sn-C were shifted to about 0.4 eV lower binding energy than in the oxidized catalyst. However, the tin peak position in the oxidized catalyst was at the same position as for the alumina-supported catalyst. This supports the view that tin is present in a lower valence state in the reduced catalyst than in the fresh material when carbon is the sup-

port. None of the tin ESCA peaks for the reduced catalysts showed evidence of metallic tin. Clearly, if a significant fraction of the tin (e.g., $\frac{1}{2}$ as much as the Group VIII metal content) was reduced to the metal it should have been apparent in the ESCA spectra.

Because of the interference of the alumina peak with the Pt 4f peaks, the state of Pt in the alumina-supported catalysts could not be determined. In the reduced catalyst rhodium had, when present with tin on an alumina support, a binding energy that was identical to that of rhodium metal. Thus, the Rh was reduced to the metal state under conditions where there was no apparent shift to a lower binding energy for the supported tin.

Carbon-supported catalysts were prepared to learn more about the state of platinum. The tin peak was shifted to lower binding energies after reduction for both the Rh- and Pt-containing samples. Rhodium had a binding energy corresponding to that of the bulk metal. Platinum, on the other hand had a higher binding energy than that reported for the metal. The carbon reference charge shift was the same for both Rh and Pt catalysts and should therefore not be responsible for the higher binding of Pt. Thus, it is not certain that Pt was completely reduced to the metal in the Pt-Sn-C catalyst.

The ESCA probe permitted exposure of the catalyst pellet to flowing hydrogen at 400°C for 17–18 h. However, the probe design did not require hydrogen to flow through the pellet. Thus, one cannot completely eliminate the possibility that hydrogen had equal access to the total catalyst pellet in the same manner as if the pellet was present in a catalyst bed in flowing hydrogen. Likewise, the catalyst was reduced at 1 atm in flowing hydrogen rather than in an atmosphere simulating commercial start-up where gases such as H₂O, HCl, H₂S, etc. may be present. However, Davis (30) found that Sn altered the activity and aromatic product selectivity when the catalyst

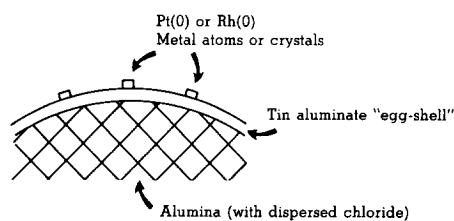


FIG. 6. Schematic representation of a reduced Pt-Sn-Al₂O₃ catalyst.

was reduced and used at 1 atm pressure. Also, the aromatic selectivity of a Pt-Sn catalyst was the same whether the *n*-octane dehydrocyclization was carried out at 1 or 14 atm with a H₂:hydrocarbon ratio of 10:1 (29). The results for the state of tin in the Pt-Sn catalysts used in the ESCA studies should be comparable to the Pt-Sn catalysts used by Davis in earlier dehydrocyclization studies (29).

The ESCA results make it clear that Pt-Sn-Al₂O₃ and Pt-Sn-C catalysts do not have a major fraction of the tin presence in a metallic form. Judging from the relative area of the Pt and Sn peaks, it seems likely that even if an alloy with a composition as Pt₄Sn was formed, sufficient metallic Sn would be present to be detected. By inference from the Rh-Sn-Al₂O₃ catalyst one would conclude that the Pt was present in the metallic state on alumina-supported catalysts. However, the results for the Rh-Sn-C and Pt-Sn-C catalysts cause us to be somewhat uncertain of the valence state of the Pt when present with tin on a carbon support. The ESCA results and the alcohol conversion data support a model for the alumina catalyst as schematically shown in Fig. 6. The added tin is present in the oxidized or reduced catalyst as a thin film and strongly interacts with the alumina so that it does not resemble tin oxide. Presumably, this form of tin resembles, or is, a tin aluminate. Platinum, in order to show altered activity, selectivity, and aging stability, should be associated with this tin aluminate portion of the surface.

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