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HOMOGENEOUS Rh-Sn ALKOXIDE COATINGS ON SILICA SURFACES: A NOVEL ROUTE FOR PREPARATION OF BIMETALLIC Rh-Sn CATALYSTS

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The reaction of [{(COD)Rh}$_2$Sn(OEt)$_6$], where COD = 1,5-cyclooctadiene and Et = ethyl, with silanol groups on silica surfaces is shown to lead to near-monolayer coverage of the silica by the Rh-Sn organometallic compound. Heating the supported compound at 498 K yields a catalyst that is active for benzene hydrogenation at room temperature. When the catalyst is reduced in H_2 at 823 K, the benzene hydrogenation activity increases with a simultaneous drop in the activity for n-butane hydrogenolysis. High temperature reduction leads to formation of Rh-Sn alloy particles with an average particle diameter of 2.5 nm. These particles are stable towards oxidation-reduction cycles involving oxidation at 773 K in 15% O_2. When normalized to the benzene hydrogenation activity, the n-butane hydrogenolysis activity of the bimetallic catalyst is suppressed by over 3 orders of magnitude when compared to a monometallic Rh catalyst.

Keywords: Rh-Sn catalyst, bimetallic catalysts, Rh-Sn alkoxide coatings, silica surfaces, hydrogenation activity

1. Introduction

Noble metal catalysts are often promoted by tin to improve or modify their catalytic properties [1–4]. For instance, incorporation of tin in alumina supported Pt-Sn catalysts results in suppressed hydrogenolysis activity and reduced coke formation compared to Pt alone [1]. Such supported, bimetallic catalysts are generally prepared via co-impregnation techniques using the appropriate metal precursors to yield small crystallites containing both metals. However, using this method, it is difficult to control the composition of the catalytically active metal species and the resulting catalyst often consists of metal particles of different size and composition [5]. An alternative method of bimetallic catalyst preparation

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involves first preparing monometallic catalyst, followed by reaction with a tin compound, such as $Sn(n\text{-}Bu)_4$, to yield the bimetallic species. Again, control over particle size and stoichiometry is difficult, but this method has been successfully used to prepare suppored Rh-Sn [2], Ru-Sn [3] and Pt-Sn [4] catalysts.

In this paper we describe an alternative method to prepare supported bimetallic tin catalysts, which utilizes the organometallic precursor, $[\{(COD)Rh\}_2Sn(OEt)_6]$ to prepare a Rh-Sn catalyst on a silica support. Similar methods have been used previously to support metal carbonyl clusters on metal oxides [6] and organometallic compounds on soluble, molecular metal oxide or polyoxoanion cluster models that resemble discrete fragments of metal oxide supports [7]. By reacting $[\{(COD)Rh\}_2Sn(OEt)_6]$ with the surface hydroxyl groups of metal oxides such as silica, we obtain homogeneous coatings of the Rh-Sn compound. After reduction at 823 K, we obtain Rh-Sn particles, 2.4 nm, that are stable to further thermal cycling. We have used nonporous, 270 nm diameter silica spheres as model supports to facilitate high resolution TEM examination and catalytic studies. We report here on the catalytic activity of these Rh-Sn catalysts towards ethylene and benzene hydrogenation and n-butane hydrogenolysis reactions. The results are compared with the behavior of a conventionally prepared Rh on silica catalyst in the same reactions.

2. Experimental

1. GENERAL PROCEDURES

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques as described previously [8]. All hydrocarbon and ether solvents were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves under a nitrogen atmosphere prior to use. The compound $[\{(COD)Rh\}_2Sn(OEt)_6]$ was prepared according to the literature procedure [9].

2. CATALYST PREPARATION

Silica spheres were prepared by hydrolysis of tetraethyl-orthosilicate according to the method of Stober et al. [10]. In a typical sample preparation, 300 mg of silica spheres were washed with water, then acetone and dried in vacuo in a Schlenk flask at room temperature. They were then suspended in 15 ml of tetrahydrofuran and a solution containing 100 mg of $[\{(COD)Rh\}_2Sn(OEt)_6]$ in 5 ml of THF was added with rapid stirring. The yellow suspension was stirred for 0. 5 hr, then filtered on a medium porosity sintered glass frit and dried in air to give a pale yellow powder. In some experiments, the silica spheres were dehydroxylated by heating in air at 383 K or at 773 K overnight before contacting with the Rh-Sn compound. For these preparations, the water and acetone wash was eliminated. The Rh catalyst used for comparison was nominally 0.1 wt% Rh supported on Cabosil HS-5 silica using $RhCl_3 \cdot xH_2O$ as precursor.

3. CATALYSTS CHARACTERIZATION

These catalysts were examined in a JEOL 2000-FX transmission electron microscope by suspending the powders on holey carbon films supported on 3 mm Cu grids. Elemental analysis was performed using a Tracor Northern energy dispersive X-ray analyzer. H_2 and CO uptakes were measured by static volumetric chemisorption in an all-glass apparatus pumped with a liquid nitrogen-baffled diffusion pump and a Baratron MKS pressure transducer. The sample was evacuated to a pressure of 2×10^{-7} Torr before the first chemisorption measurement. Uptakes of H_2 and CO were recorded on the fresh sample and after reduction overnight in 150 Torr H_2 at 498 K and at 823 K. Oxidation of the catalyst was performed at 773 K using 100 Torr O_2 overnight.

4. CATALYTIC REACTIVITY MEASUREMENTS

Reactivity measurements were performed using a 1/4 inch OD quartz U-tube flow reactor in which 50 mg of Rh/Sn on SiO_2 catalyst sample was supported using a quartz wool plug. Sample temperature was measured with an Omega 2010 temperature programmer controller using a type K thermocouple that was in direct contact with the catalyst powder. Gas flow rates were controlled using an Edwards mass flow controller. H_2, O_2 and He used for catalyst pretreatment were UHP grade from Big Three industries and were used without any additional purification. N-butane was research purity from Matheson, ethylene was obtained from Aldrich, 99.5% pure and the benzene used was 99.5% pure from Kodak chemicals. Before all reactivity measurements, the catalyst bed was flushed with helium for 30 min and then the catalyst was reduced in H_2 at temperatures ranging from 298 K–823 K. The catalyst was also subjected to oxidative treatments using 20 sccm He and 3 sccm O_2 at 773 K overnight. The activity of the catalyst for n-butane hydrogenolysis was measured with a 20/1 ratio of H_2/n-butane at a total pressure of 730 Torr. For ethylene hydrogenation, we used 20 sccm of H_2 and 2.3 sccm C_2H_4. Product analysis for n-butane hydrogenolysis as well as for ethylene hydrogenation was done using a HP 5890 GC using a 6 ft Porapak N column at 413 K and an FID detector. Benzene hydrogenation was performed by saturating 10 sccm H_2 with liquid benzene cooled in an ice water bath. The benzene hydrogenation products were analyzed using a 6 ft Carbowax-400/Chromosorb WHP column operated at 318 K.

3. Results

CHARACTERIZATION

Table 1 provides characterization data for the samples investigated in this work. Three samples of the Rh-Sn/SiO_2 catalyst were prepared using silica

Table 1
Characterization data

Catalyst code	Silica support	Treatment	Wt% Rh	Wt% Sn
A - $RhSn/SiO_2$	255 nm spheres	Water washed	0.31	0.5
B - $RhSn/SiO_2$	206 nm spheres	Preheated 383 K	0.39	0.33
C - $RhSn/SiO_2$	255 nm spheres	Preheated 773 K	0.13	0.25
D - Rh/SiO_2	Cabosil HS-5	untreated	nd	–

spheres that were dehydroxylated to differing extents: water-dashed, preheated 383 K and preheated 773 K. The metal loading was estimated using the Rh K_α, Sn L_α and the Si $K_{\alpha\text{-}\beta}$ peaks with the standardless thin film analysis program SMTF on the Tracor Northern energy dispersive spectroscopy (EDS) system. Without proper standards and in view of uncertainties in the cross sections for the Sn L_α, elemental analysis by EDS provides only qualitative indications of metal content. However, the EDS results clearly show that the loading of Rh-Sn varied with the amount of dehydroxylation of the support, with the 773 K treated silica having the lowest concentration of Rh-Sn. There was no difference, within experimental error, between the water-dashed silica and silica heated to 383 K both in the electron micrographs as well as the reactivity measurements. As a control, Rh/SiO_2 catalyst (sample D) was prepared by aqueous impregnation using $RhCl_3.xH_2O$ and was used for comparison purposes. This catalyst had a nominal weight loading of 0.1 wt% Rh, however the amount of Rh was below the detectability limits of the EDS technique.

Fig. 1 shows an electron micrograph of the uncoated silica spheres. The contrast seen in the sphere is typical of that from amorphous materials and electron diffraction confirms that these spheres are amorphous. Fig. 2a shows a micrograph of sample B (the 383 K-heat treated silica) coated with the Rh-Sn organometallic precursor without any subsequent thermal treatment. While the surface texture of the silica looks considerably different from that of the uncoated silica, it is difficult to quantify this difference. When the electron beam was focused on the silica spheres for EDS analysis, it was observed that small particles ≈ 20 Å in diameter appeared to form on the surface. Fig. 2b shows the same silica sphere seen in fig. 2a after such electron-beam irradiation. Diffuse spherical particles are seen uniformly dispersed over the surface of the silica sphere. Fig. 3 shows a micrograph of catalyst C (the 773 K-heated silica spheres) where the surface texture is seen to resemble that of the uncoated spheres. Focusing the electron beam did not cause any growth of particles as seen in fig. 2. After catalyst B had been subjected to several cycles involving oxidation at 773 K in 15% O_2 at 630 Torr and reduction in flowing H_2 at 630 Torr and 823 K and reactivity measurements, there was some particle growth due to the mobility of metallic species. Fig. 4 shows a micrograph of the used catalyst and the average particle diameter is seen to be ≈ 24 Å. The contrast from the amorphous silica,

Fig. 1. Micrograph of uncoated silica sphere.

as one moves inward from the edge of the sphere, makes it difficult to distinguish the particles as the silica support thickness increases. However, at the edges, spherical particles distributed uniformly over the surface of the silica are clearly revealed.

The chemisorptive uptake of H_2 and CO was also measured on these catalysts and is reported in table 2. The as-prepared RhSn compound on silica (A and B) showed no H_2 uptake at room temperature. We have previously demonstrated that $[\{(COD)Rh\}_2Sn(OEt)_6]$ quantitatively substitutes two carbon monoxide ligands for COD per Rh atom when the cluster is in solution [9]. In agreement

Table 2
Chemisorption uptakes

Catalyst	Hydrogen uptake (μmole/g)		CO uptake (μmole/g)		TEM size (Å)
	Reduced 498 K	Reduced 823	Reduced 498 K	Reduced 823	
A	13.7	6.6	7.7	4.3	–
B	19.4	10.0	–	–	24
C	–	–	–	–	–
D	7.5	–	6.1	–	nd

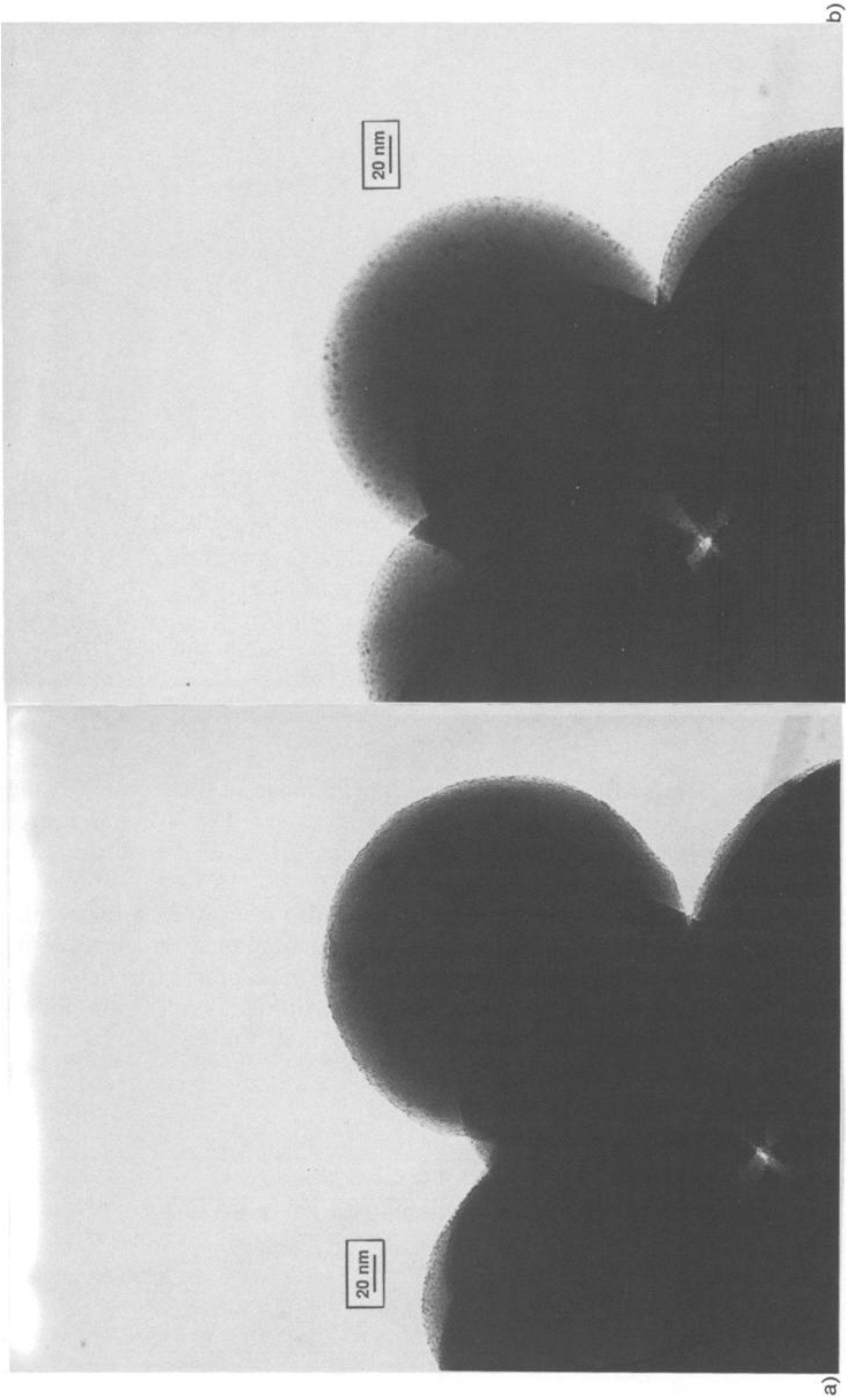


Fig. 2. Micrograph of Rh-Sn coated on silica spheres heat treated at 383 K overnight a) before electron beam irradiation b) after.

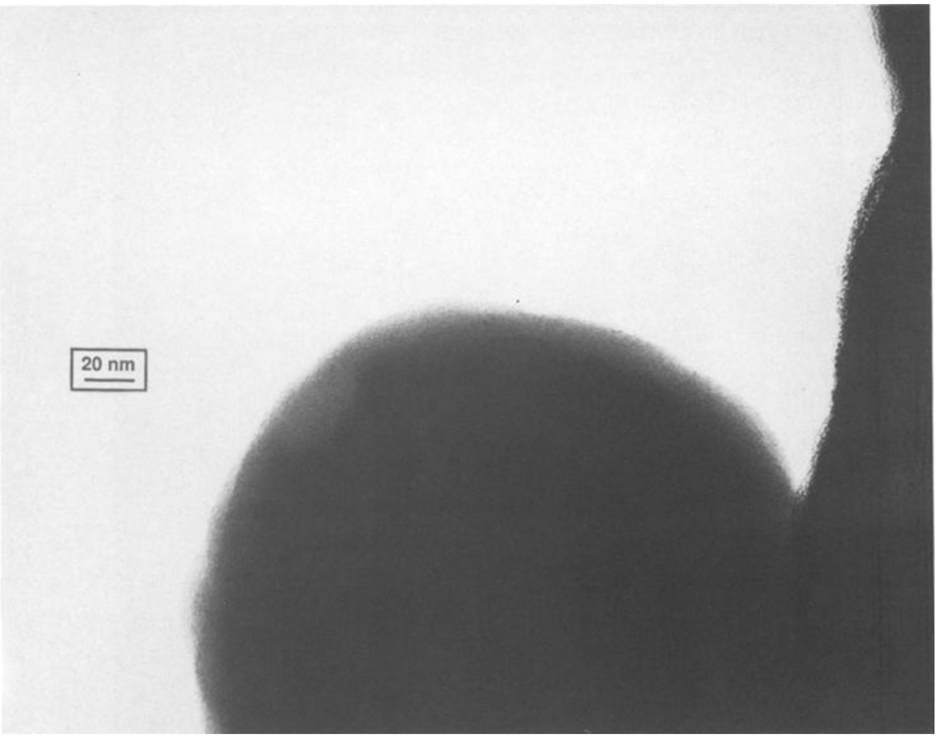


Fig. 3. Micrograph of Rh-Sn coated on silica spheres heat treated at 773 K overnight.

with this observation, a significant uptake of CO was observed by a supported Rh-Sn species. After reduction in 150 Torr H_2 at 498 K the sample was now able to chemisorb H_2 as seen in table 2 but the CO uptake dropped and became comparable to the H_2 uptake. Further reduction at 823 K decreased both the H_2 and CO uptakes. On the Rh/silica catalyst, no metallic particles could be seen by TEM which is understandable in view of the low metal loading on this catalyst. The H_2 chemisorption results are consistent with the dispersion of Rh being 100% on catalyst sample D.

REACTIVITY

The activity of the Rh-Sn/SiO_2 catalyst for benzene hydrogenation is shown in fig. 5. The activity was measured at 296 K using 10 sscm H_2 saturated with benzene at 273 K. The activity is reported per gram of catalyst since the H_2 uptake was not measured after each of these pretreatments. The as-prepared Rh-Sn compound on silica, was unreactive for benzene hydrogenation at room temperature. Exposure to flowing H_2 at 225 °C induced catalytic activity with a further increase in activity seen after H_2 reduction at 823 K. Oxidation of the catalyst using 3 sccm O_2 and 20 sccm He and subsequent reduction at 373 K increased the activity 2-fold over that of the 823 K-reduced catalyst. However, in

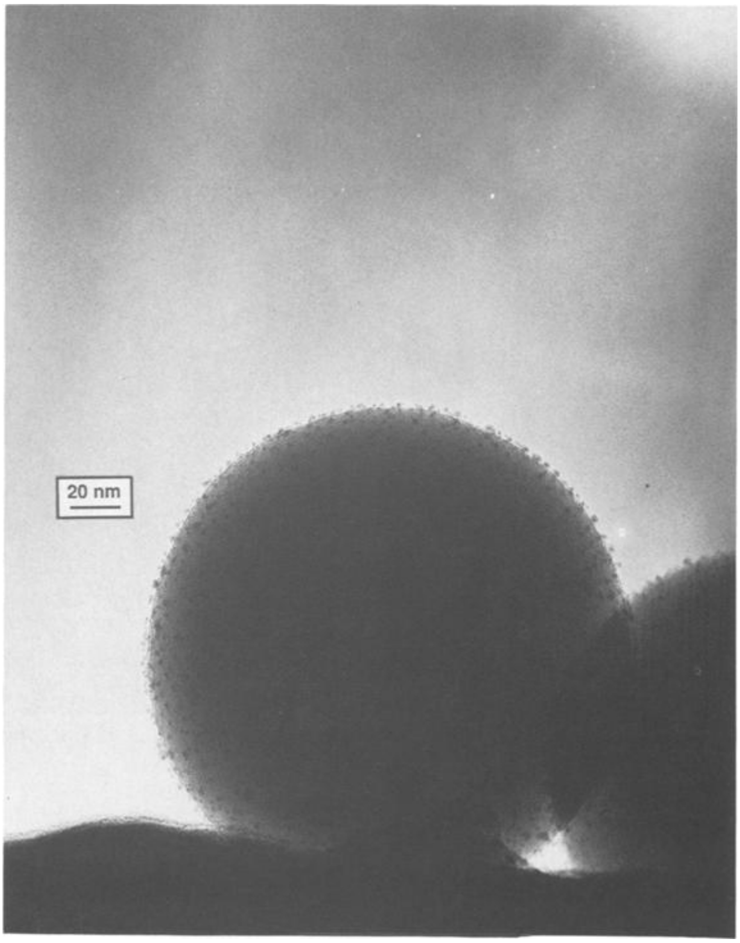


Fig. 4. Micrograph of catalyst B after oxidation at 773 K and reduction at 823 K and reactivity measurements.

the next cycle, reduction at 823 K in H_2 led to a drop in activity as seen in fig. 5. The last data point in fig. 5 was obtained after oxidizing the catalyst and directly performing the reaction at 296 K. It shows that the oxidized catalyst reduces even at room temperature and, after approximately a 45 min. induction period, the catalyst activity reaches that of the 773 K oxidized and 373 K reduced surface. The specific activity of these catalysts for benzene hydrogenation normalized to their H_2 uptake is shown in fig. 6. The turnover frequency for benzene hydrogenation on dispersed Rh after 823 K reduction was one order of magnitude lower than that on RhSn reduced 823 K. There was no influence of reduction temperature on the activity of the Rh catalyst. The activity of these catalysts for ethylene hydrogenation was also measured using 20 sccm H_2 and 2.3 sccm C_2H_4.

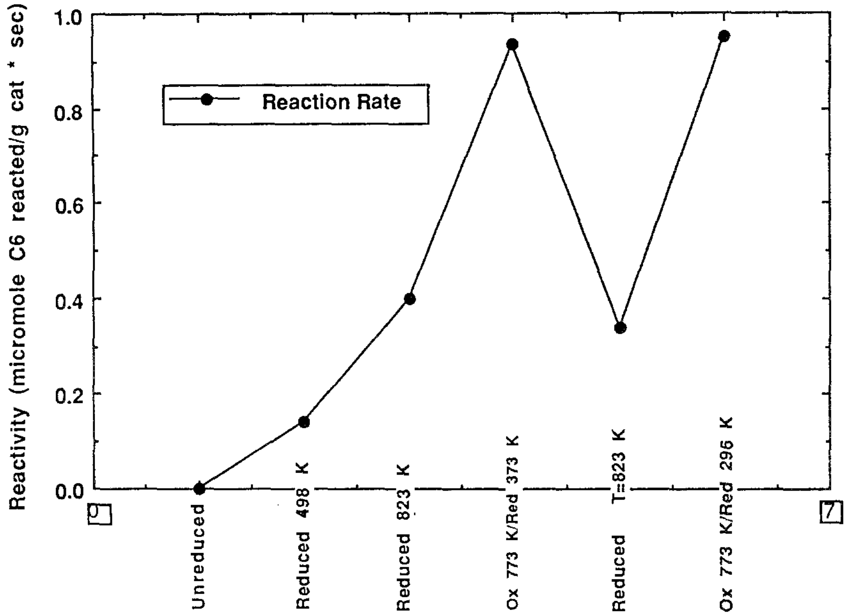


Fig. 5. Influence of pretreatment on benzene hydrogenation activity using 10 sccm H_2 saturated with benzene at 273 K.

All of the catalysts investigated here were reactive even at 195 K. However, the catalysts deactivated very quickly making it extremely difficult to obtain reproducible data.

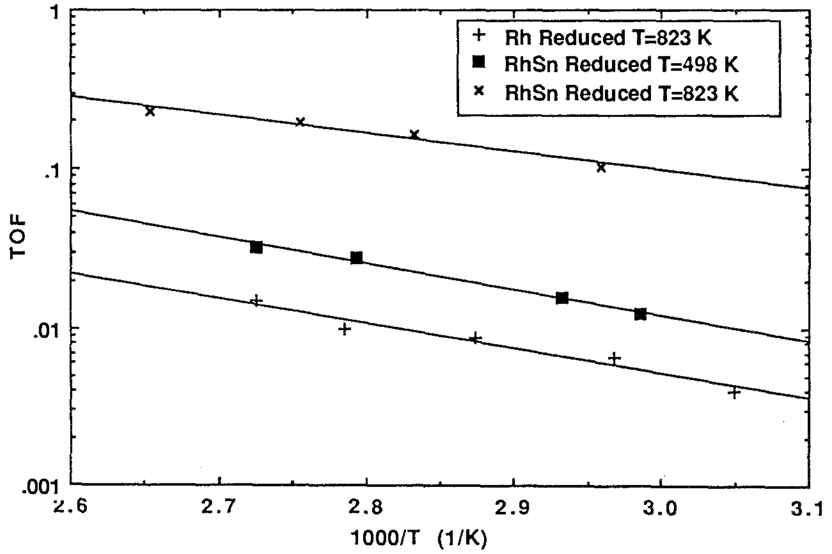


Fig. 6. Arrhenius plot for benzene hydrogenation using 10 sccm H_2 saturated with benzene at 273 K.

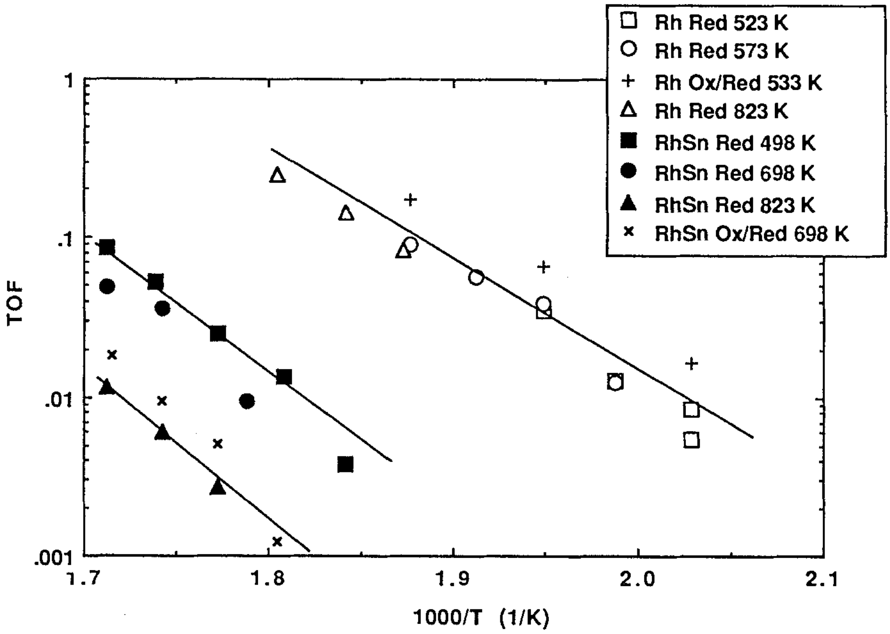
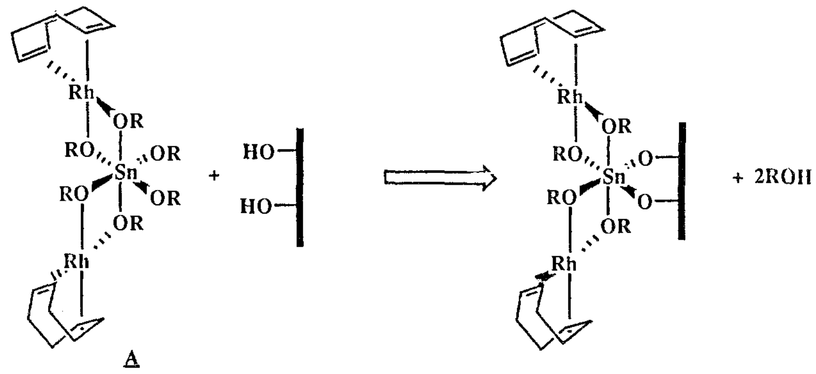


Fig. 7. Arrhenius plot for n-butane hydrogenolysis. H_2/n-butane = 20; $P = 730$ Torr.

The activity of these catalysts for hydrogenolysis of n-butane is shown in fig. 7. The Rh-Sn compound on silica after activation at 225 °C in H_2 exhibited hydrogenolysis activity approximately one order of magnitude lower than the 0.1 wt% Rh/silica catalyst. After activation in H_2 at 550 °C, the hydrogenolysis activity of the Rh-Sn catalyst dropped over an order of magnitude. We believe that a Rh-Sn alloy is formed during the activation at 550 °C as has been reported earlier [2], which causes the suppression in hydrogenolysis activity. The behavior of the Rh-Sn catalyst was found to be unaffected by oxidation-reduction cycles involving oxidation at 500 °C in 15% O_2 in helium and subsequent reduction at 550 °C in flowing H_2. Likewise, the hydrogenolysis activity of the Rh/silica catalyst was unaffected by the oxidation reduction cycles as seen from fig. 7.

4. Discussion

The electron micrographs in fig. 2–4 confirm that the reaction of the silica surface with [{COD)Rh}$_2$Sn(OEt)$_6$] leads to a homogeneous coating. We have recently structurally characterized [{(COD)Rh}$_2$Sn(OEt)$_6$] both in the solid state and in solution, and have shown that it exhibits the structure, A, depicted in Scheme 1. below. It consists of a distorted octahedral tin(IV) moiety surrounded by six ethoxide ligands in which two cis-edges are coordinated to [(COD)Rh]$^+$ cations to produce a molecule with approximate C_2 molecular symmetry. We



Scheme 1.

expect that the two terminal ethoxide ligands react with hydroxide groups on the surface of the silica spheres to liberate ethanol as shown in scheme 1.

Reflectance IR experiments are in progress on the carbonyl derivative supported catalyst precursor to test this hypothesis. The reaction of scheme 1 is consistent with the observation that when the silica surface was dehydroxylated by heating to 773 K, the loading of the Rh-Sn compound decreased. This is consistent with the data in table 1 and the electron micrographs of catalyst C in fig. 4. We conclude that the reaction of $[\{(COD)Rh\}_2Sn(OEt)_6]$ with the silica surface is limited by the number of surface hydroxyl groups. Had traces of moisture been present in the THF used to mediate the reaction of scheme 1, or excess coordinated water present on the silica spheres, we would have expected to observe large aggregates of a hydrolyzed rhodium-tin oxide on the surface. No large aggregates were detected on any sample prepared by this method.

After heat treatment during the activity measurements, the catalyst precursor decomposed to give particles with an average diameter of 24 Å. The areal density of these particles can be estimated since the spherical morphology of the silica support ensures a simple relationship between projected area on the electron micrograph and the actual surface area. From the micrograph in fig. 4, we estimate the areal density to be 6×10^{11} particles per cm^2. The 24 Å particle size is consistent with approximately 250 atoms per particle. If isolated Rh_2Sn clusters were present on the silica surface, they would be difficult to detect due to the strong contrast from amorphous silica. The agglomeration of these clusters due to electron beam induced heating improves their visibility as seen from a comparison of figs. 2a and 2b. Based on the areal concentration of the metallic particles, and assuming that the particle density is a weighted average of the bulk densities of Rh and Sn, we can estimate a metal loading of 0.86 wt% for sample B. This corresponds to 53 μmoles Rh per gm catalyst. If the dispersion of Rh was 40% (corresponding to a particle size of 24 Å) we would expect a chemisorptive uptake of 10.6 μmoles H_2/gm assuming a H/Rh ratio $= 1$. The chemisorptive uptake reported in table 2 for catalyst B after reduction at 823 K is consistent with this number and in turn implies that the density of the Rh-Sn cluster on the silica sphere must be 1.25 per nm^2. This number is smaller than the expected number of surface hydroxyl groups on the silica surface, ≈ 4.6 per nm^2 [11]. Hence, steric effects may limit the number of $[\{(COD)Rh\}_2Sn(OEt)_6]$ molecules that can be deposited on the silica surface. In fact, based on the unit cell parameters derived from the single crystals of the Rh-Sn cluster, we would expect a monolayer of this cluster to contain between 0.3–0.5 clusters per nm^2.

The reactivity data suggest that the Rh-Sn alkoxide compound is intact when supported on silica. After heating the supported cluster at 498 K, we believe that the ligands are cleaved and leave behind dispersed Rh and Sn in a form that is now reactive for hydrogenation as well as hydrogenolysis reactions. We have previously demonstrated from TGA data that pure $[\{(COD)Rh\}_2Sn(OEt)_6]$ shows an onset of weight loss at approximately 160 ° C, which is complete by 200 ° C. The weight loss is 55%, corresponding to loss of all the organic fragments [9]. When the silica supported material is further heated to 823 K in H_2, formation of a Rh-Sn alloy and aggregation into particles having an average diameter of 24 Å is observed. The formation of the alloy can be inferred from the enhanced hydrogenation activity along with a suppressed hydrogenolysis activity. In this state, the relative activities for n-butane hydrogenolysis at 555 K and for benzene hydrogenation at 357 K are respectively 0.01 and 25 for the Rh-Sn (catalyst B) and the Rh (catalyst D). The suppression in hydrogenolysis with respect to hydrogenation activity is ≈ 2500 times due to the formation of a Rh-Sn alloy.

TEM analysis of the catalyst after oxidation-reduction cycling of the Rh-Sn catalyst shows that the bimetallic does not phase segregate upon oxidation. The catalyst is reduced slowly at room temperature by H_2 and after about 45 min., achieves the hydrogenation activity of a catalyst that is oxidized and reduced at 373 K. The increase in hydrogenation activity is caused by surface roughening due to the volume increase upon oxidation and the inability of the particle to anneal upon reduction under mild conditions [12]. A similar phenomenon was not detected during the hydrogenolysis runs because higher temperatures were required to detect hydrogenolysis activity on the Rh-Sn catalyst, and at these temperatures the metal particles have a better chance to anneal. In summary, we have shown that use of the Rh-Sn alkoxide precursors leads to formation of bimetallic particles whose reactivity behavior is completely different from that of supported Rh. A similar catalyst preparation was also used with a Degussa P25 TiO_2 support and found to yield small metallic particles similar to those seen in fig. 4.

5. Conclusions

A novel route has been developed for the preparation of Rh-Sn bimetallic catalysts which involves the homogeneous coating of a silica support with

$[\{(COD)Rh\}_2Sn(OEt)_6]$ molecules. Activation of the coated silica appears to yield a bimetallic Rh-Sn catalyst that exhibits enhanced hydrogenation activity compared to monometallic Rh while suppressing its hydrogenolysis activity. The resulting catalyst is stable to oxidation at 500 ° C.

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References

[1] J.H. Sinfelt, *Bimetallic Catalysts* (Wiley, NY, 1978).

[2] J.P. Candy, O.A. Ferretti, G. Mabilon, J. P. Bournonville, A. El Mansour, J.M. Basset and G. Martino, J. Catal. 112 (1988) 210.

[3] B. Coq, A. Bittar, T. Tazi and F. Figueras, J. Mol. Catal. 55 (1989) 34.

[4] J. Margitfalvi, S. Szabo and F. Nagy, Stud. Surf. Sci. Catal. 27 (1986) 373.

[5] A.K. Datye, L.F. Allard and J. Schwank, *Analytical Electron Microscopy* (San Francisco Press, 1984) p. 205.

[6] a: C. Dossi, R. Psaro, D. Roberto, R. Ugo and G. Zanderighi, Inorg. Chem. 29 (1990) 4368;
b: T. Schwartz, Acc. Chem. Res. 18 (1985) 302;
c: B.C. Gates, in: *Organometallic Chemistry: Basis for the Design of Supported Catalysts; Catalyst Design, Progress and Perspectives*, ed. L.L. Hegedus (John Wiley and Sons, New York, 1987).

[7] a: V.W. Day and W.G. Klemperer, Science (Washington D.C.) 228 (1985) 533;
b: H.K. Chae, W.G. Klemperer and V.W. Day, Inorg. Chem. 28 (1989) 1423;
c: Y. Hayashi, T. Toriumi and K. Isobe, J. Am. Chem. Soc. 110 (1988) 3666;
d: R.G. Finke, B. Rapko and P.J. Domaille, Organometallics 5 (1984) 174;
e: R.G. Finke, D.K. Lyon, K. Nomiya, S. Sur and N. Mizuno, Inorg. Chem. 29 (1990) 1784;
f: D.K. Lyon and R.G. Finke, ibid 29 (1990) 1789;
g: M.T. Pope, *Heteropoly and Isopoly Oxometallates*, Inorganic Chemistry Concepts No. 8 (Springer-Verlag, New York, 1983; p. 118;
h: V.W. Day, W.G. Klemperer and D.J. Main, Inorg. Chem. 29 (1990) 2345;
i: W.G. Klemperer and D.J. Main, Inorg. Chem. 29 (1990) 2355.

[8] See e.g. M.J. Hampden-Smith, D.S. Williams and A.L. Rheingold, Inorg. Chem. 29 (1990) 4076.

[9] a: T.A. Wark, E.A. Gulliver, L.C. Jones, M.J. Hampden-Smith, A.L. Rheingold and J.C. Huffman, *Better Ceramics Through Chemistry IV* (Mat. Res. Soc. Symp.) in Press:

b: T.A. Wark, E.A. Gulliver, M.J. Hampden-Smith and A.L. Rheingold, Inorg. Chem. 29 (1990) 4360.
[10] W. Stober and A. Fink, J. Coll. Interface Sci. 26 (1968) 62.
[11] B.G. Linsen, *Physical and Chemical Aspects of Adsorbents and Catalysts* (Academic Press, New York, 1970) p. 260.
[12] A.D. Logan and A.K. Datye, J. Phys. Chem., submitted.