JOURNAL OF CATALYSIS 63, 119–128 (1980)

Conversion of *n*-Hexane over Monofunctional Supported and Unsupported PtSn Catalysts

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Received March 15, 1979; revised August 6, 1979

Distinct selectivity changes have been observed in the conversion of *n*-hexane over Pt upon its being alloyed with Sn. In systems consisting of PtSn on nonacidic supports, the presence of true alloys can be confirmed. Addition of Sn causes a drastic lowering of the rates of those reactions which produce catalyst poisons and hence gives an increase in stability. The change in selectivity can be interpreted in terms of a change in adsorption properties due to differences in the number of adjacent platinum atoms required for the various reaction pathways (ensemble effect). It is assumed that with these catalysts and at temperatures above 500°C, secondary reactions in the gas phase become important. Hexatrienes formed on the catalyst surface might then contribute to the benzene production and radicals might initiate hydrogenolysis. The present results allow some speculations on the role of the metal component in bimetallic dual-functional Pt catalyst systems.

INTRODUCTION

One of the factors which has renewed interest in catalysis by alloys was the finding that for various hydrocarbon-conversion processes, the conventional platinum catalysts could be substantially improved by the addition of certain metals, such as Re (*1*), Ge (*2*), and Sn (*3, 4*). An important observation, supported by numerous data (see, e.g., (*1–9*)), is the fact that the steady-state activity of these bimetallic catalysts is superior to that of monometallic catalysts, even if their initial activity is lower. This also holds for tin-modified supported platinum catalysts, but little fundamental work has been published on the exact role of tin (*10, 11*). According to one of the proposed hypotheses, the supported metals form "alloys" or bimetallic clusters (*12, 13*). In order to decide whether "alloy" formulation is indeed of importance, we have studied the conversion of *n*-hexane using well-defined, powdered PtSn alloys, and have compared their performance with that of supported PtSn catalysts. In addition, we have studied the catalytic behavior of pure platinum (supported and unsupported) to allow a comparison with that of the alloys.

Dual-functional catalysts of practical interest contain a metal and an acid function, but in the present work, which is directed toward elucidating variations of the metal function, it was decided to use essentially monofunctional Pt and PtSn catalysts, i.e., either unsupported powders or catalysts based on either silica or sodium-neutralized nonacidic alumina.

EXPERIMENTAL

A. Preparation of Specimens

The various supported Pt and PtSn catalysts tested in this study are listed in Table 1. Two different supports were used as carrier materials. Catalysts A through I were prepared with a commercial Universal Oil Products (UOP) alumina as the carrier and catalysts J and K with Davison silica (grade 70) as the carrier. Except for the carrier used for catalysts A and C, the UOP alumina was freed from chlorine by steaming at 500°C and then calcined for 3 h at 850°C, followed by neutralization with Na_2CO_3 (0.5 Na/100 g Al_2O_3) to render it

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0021-9517/80/050119-10$02.00/0

TABLE 1

Supported Pt and PtSn Catalysts used in this Study

Catalyst	Amount of metal impregnated (g metal/100 g support)		Support	Remarks
	Pt	Sn		
A	0.4	—	Alumina[a]	Pt impregnated as chloroplatinic acid
B	1.0	—	Alumina[b]	
C	0.4	0.4	Alumina[a]	Ptimpregnated as chloroplatinic acid; Sn as stannous chloride
D	1.0	0.25	Alumina[b]	Sn impregnated as tin stannate
E	1.0	1.0	Alumina[b]	
F	1.0	0.6	Alumina[b]	Separate impregnations, first Sn then Pt
G	1.0	0.6	Alumina[b]	Separate impregnations, first Pt then Sn
H	1.0	1.2	Alumina[b]	Separate impregnations, 0.6 Sn before and after Pt
I	2.0	1.2	Alumina[b]	
J	1.0	—	Silica[c]	
K	1.0	1.0	Silica[c]	

[a] Universal Oil Products (UOP).

[b] Cl- free, sodium-neutralized UOP alumina (0.5 g Na/100 g Al_2O_3).

[c] Davison, grade 70.

nonacidic. After this treatment, the alumina showed no cyclization or isomerization activity for hexenes nor any ring-opening activity with methylcyclopentane when tested under the conditions specified in Section D and can thus be regarded as essentially nonacidic. To avoid the introduction of any acidity during impregnation of the carrier with metals, the platinum was deposited from an aqueous tetramine platinum(II) hydroxide solution and tin was coimpregnated as an aqueous tin tartrate solution, unless otherwise indicated in Table 1. After drying at 120°C the catalysts were calcined, first at 280°C for 1 h and then at 500°C for 3 hr (*14*).

A number of Sn/Al_2O_3 samples with the contents ranging from 0.8 to 2.3 g per 100 g Al_2O_3 were prepared in a similar way. The Sn was deposited on the carrier as an aqueous tin tartrate solution; as the carrier we used UOP alumina treated as indicated above.

The alloys Pt_3Sn, PtSn, Pt_2Sn_3, and $PtSn_2$ which are known to exist in the platinum–tin system (*15*), were prepared by melting weighed amounts of spectroscopically pure metals (Johnson and Matthey) in a tungsten electrode arc furnace in an atmosphere of pure argon. Homogeneous samples were obtained by melting and regrinding the alloy powders several times. Finally, the pellets were disintegrated in a boron carbide mortar, pulverized in ethanol in a tungsten carbide ball mill, and then vacuum dried at approximately 200°C. Powders of approximately 0.25 m^2/g were thus prepared. Platinum powder was made my reduction of the finely dispersed dioxide in flowing hydrogen at 500°C. The homogeneity of the compounds Pt_3Sn, PtSn, Pt_2Sn_3, and $PtSn_2$ was inspected by X-ray diffraction. Only minor deviations from the expected compositions were found.

B. Oxidation–Reduction Experiments

To determine the valence state of Sn in its active ("reduced") form in the supported catalysts, a number of Sn/Al_2O_3 samples were treated *in situ* for 16 h in an atmospheric once-through stream of hydrogen at approximately 500°C. Subsequently, the reactor system was flushed with nitrogen and a known amount of oxygen was circulated at room temperature until the pressure in the system remained constant. As the initial pressure was set at 1 bar, the amount of oxygen consumed followed from the pressure drop.

C. Temperature-Programmed Reduction (TPR) Experiments

For the characterization of the supported Pt and PtSn catalysts used in this study the common methods of physical characterization are ineffective because of the very high degree of metal(s) dispersion and low metal loadings. We therefore applied the TPR technique, the principles of which have been described elsewhere (*16, 17*). Using this sensitive technique, we measured the hydrogen consumption due to reduction of oxidized Pt, Sn, and PtSn metal surfaces while the samples were heated with linear temperature programming. The experimental arrangement was similar to the one reported recently by Wagstaff and Prins (*18*).

D. n-Hexane Conversion Experiments

The supported catalysts B and D through K were tested in the conversion of *n*-hexane (pure grade, from Phillips Petroleum Co.) in a conventional microflow reactor system using 2 ml of catalyst under the following conditions:

space velocity	$1\ g\ g^{-1}\ h^{-1}$
temperature	520°C
pressure	3 bar
H_2/*n*-hexane molar ratio	2

Before testing, the catalyst samples were reduced *in situ* for 16 h in atmospheric hydrogen at 500°C. An on-line glc with a column (4m × 4mm) filled with squalane on Chromosorb-P (20 : 100 pbw) at 50°C was used to analyze the reactor effluent samples. A precolumn hydrogenation section containing Pt/inert alumina (2 : 100 pbw) was kept at 85°C.

The Pt and PtSn alloy powders were tested by studying the differences in selectivity rather than the differences in activity in conversion of *n*-hexane. These tests were performed in a quartz down-flow reactor; the catalyst samples were heated with linear temperature programming from approximately 100 to about 550°C at atmospheric pressure and a molar ratio of hydrogen to *n*-hexane of 10 (temperature-programmed *n*-C_6 characterization). Supported Pt–Sn catalysts were also characterized in this way, except that the reactor contained 0.1 g of catalyst and a feed rate of $0.1\ g\ g^{-1}\ h^{-1}$ was applied. For the bulk alloys, the same rate of flow of *n*-hexane was used, but with several grams of metal powder, the BET surface area was kept constant at 0.35 m^2. Before testing the catalyst samples were activated by a short oxidation (0.5 h at 450°C in air) followed by a reduction (1 hr at 500°C in hydrogen).

RESULTS

A. Oxidation–Reduction Experiments

To investigate whether upon reduction tin will be present in the zero-valent state a series of oxidation–reduction experiments were carried out on air-calcined Sn/Al_2O_3 samples in which the tin content was varied from 0.8 to 2.3 wt%. After careful reduction in hydrogen the amount of metallic Sn present in these samples was determined by means of titration with oxygen.

From Fig. 1, it can be seen that the slope of the theoretical curve for $Sn + O_2 \rightarrow SnO_2$ is about the same as the slope drawn through the experimental data. This indicates that after reduction Sn will be present in the zero-valent state. The difference between theory and experiment shows that complete reduction is difficult to achieve with alumina as the support. From the intercept with the *x*-axis, we calculated that with each sample 0.6 ± 0.2 wt% Sn (based on support) is chemically complexed by the alumina in such a way that this amount cannot be reduced to metallic tin.

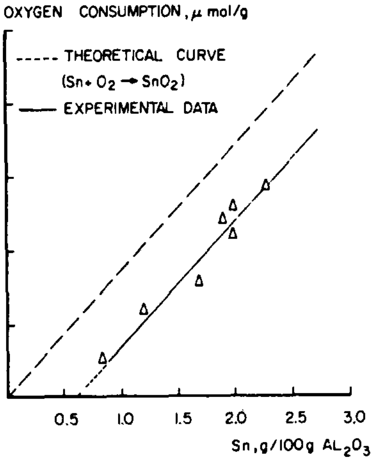

FIG. 1. Reducibility of supported tin oxide.

B. Temperature-Programmed Reduction Profiles

To determine whether zero-valent Pt and Sn atoms are in intimate contact with each other after reduction of the catalyst we characterized some of the samples, viz., Pt/Al_2O_3 (catalyst A), 0.5 g Sn/100 g Al_2O_3, and PtSn/Al_2O_3 (catalyst C), through temperature-programmed reduction profiles.[2] As the reduced systems cannot be studied as such by TPR, we used the approach recently reported by Wagstaff and Prins (*18*): the TPR profiles were measured after careful reduction at 500°C, followed by oxidation at 180°C; this treatment proved to disturb the system to a very slight extent only. Figure 2 shows the TPR profiles of the three samples investigated. It is clear that the profile obtained for the PtSn/Al_2O_3 sample differs considerably from what one would expect from superimposing the separate profiles for Pt/Al_2O_3 and Sn/Al_2O_3. A common major reduction process now occurs under the broad peak with a maximum at about 100°C. This finding is specific to TPR measured after *mild* oxidation; severe oxidation produces a separate SnO_2 phase and leads to a TPR profile which is close to the superimposition of the separate profiles for Pt/Al_2O_3 and Sn/Al_2O_3. A comparison with the reduction profile for Sn/Al_2-O_3 strongly suggests that in the PtSn/Al_2O_3 sample only a small amount of free Sn is present. The rather low reduction temperature of the Pt/Al_2O_3 sample indicates that after mild oxidation at 180°C much of the adsorbed oxygen is bound weakly to the platinum. For the PtSn/Al_2O_3 sample we observe an increase in reduction temperature, which apparently is associated with the presence of Sn. We therefore conclude that these profiles provide evidence of an interaction between Pt and Sn atoms upon reduction. In the reduced supported PtSn catalysts bimetallic clusters or "alloyed" particles are present in which Pt and Sn atoms are in intimate contact with each other.

C. X-Ray Diffraction Data

The literature (*15*) describes five phases in the PtSn system: Pt_3Sn, PtSn, Pt_2Sn_3, $PtSn_2$, and $PtSn_4$. To find out whether any of these are present in our supported PtSn catalysts, we subjected the following samples to X-ray diffraction analysis:

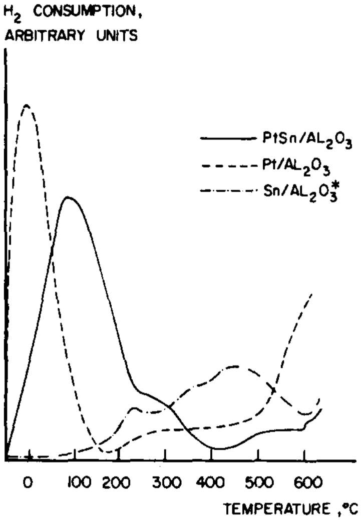

FIG. 2. TPR profiles after oxidation at 180°C. *We estimate that about 30–40 wt% of the metal is reduced to zero-valent Sn, assuming SnO_2 to be present upon oxidation.

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[2] The Sn/Al_2O_3 sample was prepared by impregnating the alumina with $SnCl_4$ instead of Sn tartrate, followed by calcination at 450°C. The alumina support was the same as that used for catalysts A and C.

(a) 1 wt% Pt + 1 wt% Sn on SiO_2 (catalyst K),
(b) 1 wt% Pt + 1 wt% Sn on Al_2O_3 (catalyst E),
(c) 2 wt% Pt + 1.2 wt% Sn on Al_2O_3 (catalyst I).

Diffraction analysis showed that after calcination in air (3 h at 350°C) finely dispersed SnO_2 was present in all the samples. The silica-supported sample also contained some coarse Pt particles of approximately 10 nm. After reduction of the silica sample (H_2, 350°C, 3 h), the PtSn alloy was present. In sample (E) this compound could not be detected, probably due to the low metal content and/or a high degree of dispersion. In the case of the $PtSn/Al_2O_3$ preparation (I) (higher metal load) the "PtSn" alloy was detected, but only after the sample had been subjected to a treatment at 650°C in hydrogen for 100 h.

The above results show that alloy formation readily takes place on silica and that the dispersion of the metals is higher on alumina than on silica.

D. n-Hexane Conversion Experiments

(1) The role of Sn in supported catalysts. To study the influence of tin on the performance of supported platinum catalysts we did some *n*-hexane conversion experiments in microflow operation. In these experiments we tested tin-modified as well as tin-free platinum catalysts based either on silica or on nonacidic alumina. As can be seen from Fig. 3, addition of tin to alumina-supported and to silica-supported platinum markedly reduces the deactivation of the dehydrocyclization activity for benzene. From the effluent compositions given in Table 2 for catalysts G and B it furthermore follows that not only the stability but also the selectivity of the platinum function are modified by addition of tin. Particularly the formation of methycyclopentane is suppressed. In line with the increased stability of the tin-containing catalysts, we found coke deposition to be reduced considerably. After approximately 7 h of operation the carbon content of the tin-containing catalysts was only about 10% of that found for the tin-free samples. We therefore conclude that the formation of coke deposits on the metal function is reduced by changing the intrinsic catalytic properties of platinum by the addition of tin.

TABLE 2

Effect of Sequence of Metal Impregnation on the Performance of PtSn/Alumina Catalysts

First impregnation	Pt	Sn	Pt	Sn
Second impregnation	—	Pt	Sn	Pt
Third impregnation	—	—	—	Sn
Product distribution[a]				
Methane through butane	21.0	20.4	20.8	19.3
Isopentane	0.7	0.5	0.0	0.0
n-Pentane	6.6	4.3	3.5	3.4
2-Methylpentane	5.5	7.5	4.8	4.0
3-Methylpentane	3.0	4.8	2.6	2.0
Methylcyclopentane	18.0	17.9	4.8	4.1
Benzene	45.3	44.9	63.6	67.2

[a] Weight percentage of converted *n*-hexane at catalyst ages where the benzene contents of the effluents are equal.

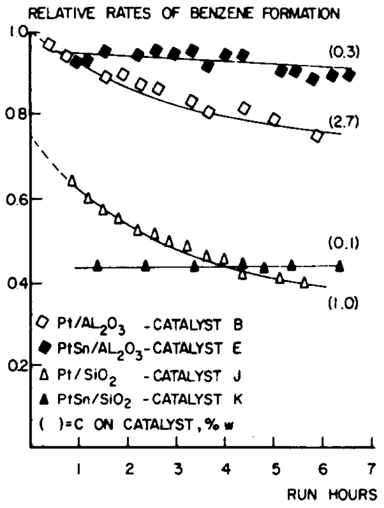

FIG. 3. Modification of the Pt function by addition of Sn.

To investigate the role of tin in more detail, we tested two catalyst systems consisting of 1/1 physical mixtures of Pt and

PtSn with nonacidic alumina, mixed with acidic alumina (both in the form of 40- to 150-μm particles).

Type	Metal function	Acidic function
I	Pt[a]	Cl-γ-Al_2O_3[c]
II	PtSn[b]	Cl-γ-Al_2O_3

[a] Pt/Al_2O_3 (cat. B).
[b] PtSn/Al_2O_3 (cat. D).
[c] 0.5 g Cl/100 g Al_2O_3.

After accelerated aging the conversion of *n*-hexane to isohexane was followed as a function of time. The aging was effected by heating the physical mixtures in an H_2/n-hexane (10/1 molar ratio) stream from 100 to 515°C at atmospheric pressure through linear temperature programming (25°C/5 min). The results are compared in Fig. 4, which shows that with PtSn as the metal function, a more stable catalyst combination is obtained than with tin-free platinum. The figure further shows that the two physical-mixture catalysts give considerably higher isomerization yields than does catalyst D (PtSn on Al_2O_3), tested without addition of acidic alumina. This demonstrates that with the physical mixture the major part of the isohexane conversion follows the bifunctional route

$$n - C_6 \underset{M}{\rightleftarrows} n - C_6^{2-} \underset{A}{\rightleftarrows} i - C_6^{2-} \underset{M}{\rightleftarrows} i - C_6,$$

in which M stands for Pt or PtSn and A for acidic alumina. Since after aging a much higher activity has been retained, it is evident that the PtSn-containing physical mixture is considerably more stable for isomerization than the type I catalyst mixture. We therefore again conclude that Sn is directly involved in changing the deactivation characteristics of platinum. As a result, the deactivation of the metal function in the type II mixture is drastically inhibited. The results make it clear that the longer duration of the platinum activity also prolongs the acidic isomerization activity.

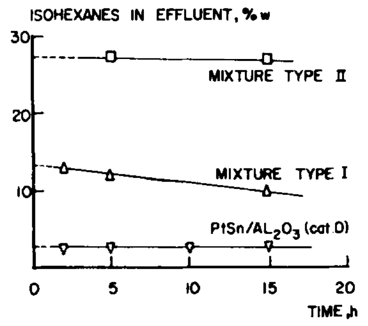

FIG. 4. Isomerization activity of various "aged" physical-mixture catalysts. Space velocity, 1 g g^{-1} h^{-1}; temp., 515°C; atm pressure; H_2/n-hexane molar ratio, 10/1.

(2) *Effect of Sequence of Metal Deposition*

The effect of adding tin to a supported Pt catalyst might, in principle, also be due to an interaction of tin (oxide) with the support, which might indirectly change the catalytic properties of platinum. Therefore, keeping in mind the observations described in Section A, we tested various modifications of the impregnation procedure. Four catalysts were prepared, all containing 1 wt% Pt but differing as follows:

(a) no Sn added (catalyst B);
(b) Sn added after deposition of platinum (catalyst G);
(c) Sn added prior to platinum deposition (catalyst F);
(d) 0.6 wt% Sn applied both before and after Pt deposition (catalyst H).

Each impregnation was followed by calcination in air at 500°C for 3 h.

The *n*-hexane conversion results obtained with these four catalysts are listed in Table 2. The data show that impregnation of tin prior to Pt does not lead to a modified catalyst performance. The products obtained with catalyst F and that formed with the catalyst containing Pt only are very similar; it is worth noting that these products have a high methylcyclopentane content (ca. 18%), which is typical of a non-tin-modified platinum catalyst. The lack of effect of tin in this case is in line with the statement that tin oxide reacts with the alumina (cf. Section A). The SnPtSn catalyst H shows the typical performance of a tin-modified catalyst (only 4.1% methylcyclopentane). The results clearly indicate that at low tin content the sequence of metal impregnation is an important factor. From this observation, we conclude that the interaction of platinum with a tin (oxide)-modified support is not important but that the modification of the Pt function through "alloying" with Sn is essential.

(*3*) *Temperature-programmed n-Hexane Conversion Profiles*

Using Pt powder as a catalyst we measured the *n*-hexane conversion pattern at temperatures increasing from about 100 to 550°C. The main reaction products observed are methylpentane isomers, benzene, and cracked products (methane through pentane), together with a minor amount of methylcyclopentane. For clarity only the sum of the isomeric 2- and 3-methylpentanes and the sum of the cracking products are shown in Fig. 5, in addition to the amount of benzene. For Pt one can discern two distinct temperature regions, namely, 275–450 and 480–550°C. In the lower-temperature-range isomerization benzene formation and cracking reactions all exhibit distinct maxima. In the higher-temperature region benzene production and cracking also show an increase in rate.

Using the same test procedure we also determined the hexane conversion patterns over various well-defined powdered platinum–tin alloys, viz., Pt_3Sn, PtSn, Pt_2Sn_3, and $PtSn_2$. The latter two were found to be inactive; the results obtained with Pt_3Sn and PtSn are shown in Figs. 5B and C.

These results show that upon alloying platinum with tin, a characteristic change in the conversion-versus-temperature pattern takes place: the low-temperature reactions typical for platinum (cyclization, isomerization, and hydrogenolysis) vanish, whereas in the high-temperature region ($T > 480°C$) benzene formation and hydrogenolysis are hardly affected. The results with these bulk alloys therefore demonstrate that the catalytically inert metal Sn basically modifies the catalytic properties of the Pt-containing particles.

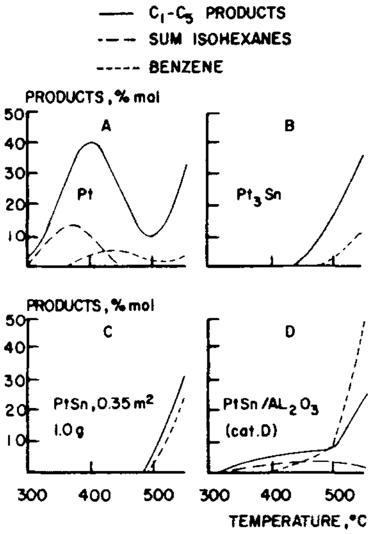

FIG. 5. The catalytic selectivities of pure Pt, various unsupported PtSn bulk alloys, and a supported $PtSn/Al_2O_3$ catalyst.

In agreement with the data shown for the bulk alloys PtSn and Pt_3Sn we found that with the bimetallic supported catalyst D (1 wt% Pt–0.25 wt% Sn/Al_2O_3) benzene formation without extensive cracking starts to proceed at a high rate at temperatures above 500°C (see Fig. 5D). Furthermore the conversion pattern observed over the supported PtSn catalyst also differs notably from the pattern found for Pt powder in that hardly any of the low-temperature reactions occurring over the latter are evident. The close resemblance of the conversion patterns of the bulk alloys to that of the supported catalyst suggests that a true PtSn alloy is (or, various true alloys are) present in the supported catalyst. With both systems selective benzene formation without extensive cracking occurs in the high-temperature region.

DISCUSSION

The oxidation–reduction experiments with the Sn/Al_2O_3 samples and the TPR profiles of Pt/Al_2O_3, Sn/Al_2O_3, and $PtSn/Al_2O_3$ provide strong evidence that the zero-valent Pt and Sn atoms formed upon catalyst reduction are in intimate contact with each other. A comparison of the catalytic specificities of well-defined, powdered platinum–tin alloy catalysts (Pt_3Sn and PtSn) with those of the corresponding supported catalysts points to the presence of true platinum–tin alloys, or bimetallic clusters, in the supported catalysts.

The results obtained with the supported catalysts, however, do not allow us to conclude unambiguously whether for the supported catalysts, special compounds or metal combinations are responsible for the activity and/or selectivity. Only a small fraction of the available surface area of the carrier is covered by metal species. It seems unrealistic to assume that after impregnation with platinum and tin in a certain ratio, the metals will interact in such a way that the overall Pt/Sn ratio also holds for the resulting individual PtSn particles. Close inspection of the performance of the $PtSn/Al_2O_3$ catalyst in the low-temperature range even indicates the presence of some unalloyed platinum; with the Pt_3Sn and PtSn alloys the low-temperature reactions were absent. Thus, the supprted PtSn catalyst is not homogeneously alloyed; it also contains free Pt and Pt-rich alloys, possibly together with particles of PtSn alloys with a relatively high tin content.

In several pertinent papers [see, e.g., Refs. (8–13, 19)] much attention has been paid to the class of binary alloys consisting of a group VIII element and a metal of negligible catalytic activity. From this work, it follows that alloying an active metal with an inert one can alter the ratio of products in two ways: either because the adsorption bound with the atoms of the active metal is modified by the "ligand effect" of the alloy partner, or because the "ensembles" with one, two, or three contiguous atoms of the active metal exhibit selectivities different from that of the active metal in the undiluted state. Usually the latter "ensemble effect" may cause rather drastic changes in selectivity (*9*). In line with this it has been proposed (*20*) that at least three contiguous sites are required for the formation of carbonaceous residues. Such a self-poisoning process can be regarded as a polymerization reaction of extensively dehydrogenated surface species (*21*). It should be remarked that a detailed analysis of the products obtained at high temperature (≥525°C) showed that with the Pt powder catalyst methane was the major hydrogenolysis product. With the two PtSn powders, however, methane formation was relatively insignificant. This indicates that secondary reactions take place to a larger extent with Pt than with PtSn powders. Accordingly, the formation of carbonaceous products through polymerization of dehydrogenated surface species is expected to take place to a lesser extent when Pt is alloyed with Sn. Inhibition of this self-poisoning process might be particularly effective in the case of PtSn catalyst because PtSn alloys form ordered structures in which the Pt and Sn atoms preferentially surround each other. Furthermore theory (*22*) predicts for platinum–tin alloys a strong enrichment of the Pt surface with Sn, which has been confirmed by Auger and XPS work (*23*) and TPD data (*24*) on platinum–tin alloys. Consequently, the degree of isolation of Pt atoms can be expected to be appreciable; the concentration of sites containing at least three Pt atoms will be rather low. Similarly, one can easily understand that Pt_2Sn_3 and $PtSn_2$ are totally inactive if the concentration of Pt in the surface is nearly zero.

During the temperature-programmed *n*-hexane conversion tests we observed that upon alloying of Pt with Sn all the reactions at low temperatures (around 300°C) were suppressed, and that at high temperatures (≥500°C) isomerization and methylcyclopentane formation were suppressed to a varying extent, whereas hydrogenolysis and benzene formation were hardly affected. As described above, the catalyzed reactions which are expected to be suppressed are the ones requiring ensembles with relatively large numbers of adjacent platinum atoms on the surface. There is general agreement (*8–13*), however, that at about 300°C, larger ensembles are required for metal-catalyzed hydrogenolysis than for isomerization or cyclization. To explain this apparent inconsistency we assume that alloying Pt with Sn suppresses all the reactions, except (de)hydrogenation of chemisorbed reactants, which can be catalyzed by a monoatomic Pt ensemble (*25*). Because of the endothermicity of dehydrogenation reactions, no catalytic conversion is observed in our temperature-programmed *n*-hexane conversion tests at low temperatures (around 300°C). At high temperatures ($\geq$500°C) gas-phase reactions become important in addition to reactions on the catalyst surface. Since the formation of radicals only requires the abstraction of one hydrogen atom, we suppose that Pt and its Sn alloys both catalyze the formation of radicals and that these will further react in the gas phase at high temperatures ($\geq$500°C) with similar effectiveness. This appears to be a reasonable assumption because Greensfelder, Voge, and Good (*26*) have shown that even active carbon is capable of catalyzing the formation of radicals, notably resulting in 20 wt% cracking of *n*-hexane at 500°C. The radical reactions will then lead to hydrogenolysis.

For the catalytic dehydrogenation of propane to propene over highly diluted Pt in gold alloys it has recently been shown (*25*) that only one Pt atom is involved in the rate-determining step. With respect to benzene formation it might be conceivable that at about 500°C hexatrienes are formed over the PtSn alloys via a rate-determining stepwise dehydrogenation process, in each step again only one platinum atom being required. As derived from the data of Paál and Tétényi (*27*), who fed *cis*-1,3,4-hexatriene into an empty reactor, gas-phase ring closure appears to be fast enough to account for the rates of benzene formation observed in our studies. It therefore seems conceivable that with Pt and PtSn catalysts hydrogenolysis and benzene formation at about 500°C occur via catalytic dehydrogenation followed by reactions in the gas phase. In hydrogenolysis it is probably the gas-phase reactions that are rate determining, whereas in benzene formation the catalytic stepwise formation of hexatrienes might be the slowest step.

With reference to the observations made with the physical-mixture catalyst systems, a speculative deactivation mechanism can be proposed for dual-functional catalysts. This mechanism is based on the ideas developed for the inhibition of self-poisoning of the metal function occurring with PtSn catalysts and on the assumption that (partial) alloying also takes place with relevant dual-functional catalysts. For dual-functional catalysts it is assumed that the initial intermediate (e.g., a dehydrogenated species such as an olefin) involved in the formation of carbonaceous deposits is catalytically created by the metal function. Via diffusion this intermediate is transported to the acidic function where it is converted into a carbon precursor (e.g., a dimerized olefin). This carbon precursor may migrate to the metal function or stay on the acidic function. Finally, it is converted into a carbonaceous deposit. However, as explained above, several contiguous Pt sites are required for the formation of carbon residues on the metal function. Since upon alloying the concentration of "large" ensembles will be reduced the rate of deposit formation on the metal function will be lower. Besides, tin may also inhibit the formation of initial intermediates, leading to reduced carbon deposition both on the acidic and on the metal function. Apart from PtSn, other bimetallic dual-functional platinum catalyst systems (*1*, *2*) might also exhibit the observed higher stabilities for these reasons. More experiments are needed to elucidate this deactivation mechanism further.

REFERENCES

1. Kluksdahl, H. E., U. S. Patent 3,415,737 (1968).
2. McCallister, T. P., and O'Neal, K. R., German Offenlegungsschrift 2.104.429 (1971).
3. Dautzenberg, F. M., German Offenlegungsschrift 2.121.765 (1971).
4. Dautzenberg, F. M., and Kouwenkoven, H. W., German Offenlegungsschrift 2.153.891 (1972).
5. Cecil, R. R., Kmak, W. S., Sinfelt, J. H., and Chambers, L. W., *Oil Gas J.* **70,** 50 (1972).
6. Sinfelt, J. H., *AIChE J.* **19,** 678 (1973).
7. Robinson, R. C., Frederickson, L. A., and Jacobsen, R. L., *Proc. Div. Refin. Amer. Petrol. Inst.* **52,** 163 (1972).
8. Roberti, A., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **28,** 381 (1973).
9. Sachtler, W. M. H., and van Santen, R. A., *Advan. Catal.* **26,** 69 (1977).
10. Karpinski, Z., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **71,** 893 (1975).
11. Davis, B. H., *J. Catal.* **46,** 348 (1977).
12. Sinfelt, J. H., Carter, J. H., and Yates, D. J. C., *J. Catal.* **24,** 283 (1972).
13. Sinfelt, J. H., *J. Catal.* **29,** 308 (1973).
14. Dautzenberg, F. M., and Wolters, H. B. M., *J. Catal.* **51,** 26 (1978).
15. Hansen, M., "Constitution of Binary Alloys, p. 1142. McGraw-Hill, New York, 1958.
16. Robertson, S. D., McNicol, B. D., de Baas, J. H., Kloet, S. C., and Jenkins, J. W., *J. Catal.* **37,** 424 (1975).
17. Jenkins, J. W., McNicol, B. D., and Robertson, S. D., *Chem. Technol.* 316, (1977).
18. Wagstaff, N., and Prins, R., *J. Catal.* **59,** 434 (1979).
19. Ponec, V., and Sachtler, W. M. H., *J. Catal.* **24,** 250 (1972).
20. Clarke, J. K. A., *Chem. Rev.* **75** (3), 391 (1975).
21. Moyes, R. B., and Wells, P. B., *Advan. Catal.* **23,** 121 (1973).
22. Van Santen, R. A., and Sachtler, W. M. H., *J. Catal.* **33,** 202 (1974).
23. Bouwman, R., and Biloen, P., *Surface Sci.* **41,** 348 (1974).
24. Verbeek, H., and Sachtler, W. M. H., *J. Catal.* **42,** 257 (1976).
25. Biloen, P., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **50,** 77 (1977).
26. Greensfelder, B. S., Voge, H. H., and Good, J. M., *Ind. Eng. Chem.* **41,** 2573 (1949).
27. Paál, Z., and Tétényi, P., *J. Catal.* **30,** 350 (1973).