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Conversion of Methylcyclopentane on Platinum-Tin Reforming Catalysts

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The conversion of methylcyclopentane was investigated over $PtSn/Al_2O_3$ catalysts containing 1% Pt and 0.06–4% Sn. Addition of tin increases the stability of catalytic activity and induces distinct selectivity changes. When the tin content is increased, hydrogenolysis of methylcyclopentane to hexanes and aromatization to benzene go through a maximum, while dehydrogenation to methylcyclopentenes remains roughly constant. Coke or sulfur deposition give an effect similar to tin addition for hydrogenolysis; the results for this reaction are therefore interpreted by the division of the platinum surface into small ensembles of platinum atoms which cannot hydrogenolyze. At high tin contents, the main reaction is dehydrogenation. Sulfur or coke do not reproduce the results obtained with tin on aromatization. Since this reaction has been proposed to proceed, like dehydrogenation, at a single platinum atom, the inhibition of aromatization by high tin contents is interpreted in terms of an electronic modification of platinum by tin.

INTRODUCTION

The application of $PtSn/Al_2O_3$ as reforming catalysts has given rise to many studies concerning the role of tin and its effect on the catalytic properties of platinum. The conclusions which find general agreement are that tin improves the stability of the catalyst by decreasing coke deposition and enhances the selectivity for aromatization. The origin of these beneficial effects remains controversial. In the view of Davis *et al.* (*1*) an electron transfer from tin to platinum is responsible for these effects. This interpretation has also been favored by Burch and Garla (*2*) who think that the electron enrichment of platinum weakens the Pt–C bond and increases the resistance to self-poisoning by coke. Bacaud *et al.* (*3*) provided evidence from Mössbauer spectroscopy for the formation of alloys at various Pt/Sn compositions. They attributed the catalytic behavior observed on diluted catalysts to the poisoning by tin of the stronger acidic sites of the alumina support responsible for cracking and coke deposition above 723 K. Nevertheless, these authors did not discard the possible dilution of the Pt surface into small ensembles which could prevent cracking. The interpretation of the catalytic properties in terms of the formation of small ensembles has been proposed by Dautzenberg *et al.* (*4*) and Gault *et al.* (*5*). In this interpretation Pt surface atoms are diluted by tin and the number of sites containing three or more adjacent platinum atoms decreases; this kind of site would be required for the formation of carbonaceous residues (*6*). However, this fact is not fully established; some authors have claimed that cracking reactions could be favored on very diluted alloys (*7, 8*). Such a behavior seems rather restricted to the alloys of Group VIII metals with Cu, and perhaps Au, and might be attributed to a peculiar site composed of Pt and Cu. This enhancement of cracking appears at very high Pt dilution (Pt/Cu < 0.01) and after a sharp decrease of the overall activity (*7, 9, 10*). Generally speaking, the experimental evidence shows a gradual disappearance of the C–C rupture reaction on alloying a Group VIII metal with a Group IB metal (for a review see Ref. (*11*)).

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It may be remarked that the conflicting experimental results on Pt–Sn catalysts were obtained with samples prepared in rather different ways. There is experimental evidence that the extent of reduction of tin varies with the platinum content of the catalyst (*12*), and with the occurrence of a calcination step of the PtSn catalyst in the preparation (*12, 13*). Water may also play an important role in the reduction (*3*) and therefore the degree of alloying may be controlled by such factors as the volume of sample used for the reduction.

For noncalcined catalysts, a good agreement exists in the literature (*3, 13, 14*) for an average degree of reduction of tin near 50% for a sample containing 0.3% Pt and 0.5% Sn. The degree of reduction decreases if a calcination of the sample is performed and part of the tin remains as Sn^{2+} ions which modify the acidic function of the support. Industrial reforming catalysts are usually calcined and used in temperature ranges ($\simeq$773 K) where the reaction follows a dual function mechanism. In that case, the catalytic properties depend on acidity and a modification of the acidic function explains reasonably the role of tin.

If the Pt loading is increased to 1%, the volumetric and Mössbauer (NGR) experiments show that the degree of reduction of tin increases and total reduction to PtSn alloys may be obtained on a noncalcined sample (*3*). High dispersions of platinum are obtained in these systems (*13, 15*). High dispersions of tin are also indicated due to the presence, in the NGR spectrum of ^{119}Sn, of very asymmetric lines (Karyagin–Goldanski effect), shifted to a velocity corresponding to PtSn alloys. Since dispersions of 80% are obtained for platinum (*13, 15*), surface enrichment which occurs on PtSn films (*16*) loses any physical significance. These noncalcined catalysts therefore appear to be model systems useful for the investigation of the catalytic properties of dispersed PtSn alloys.

TABLE 1

Catalyst Composition

Catalyst	Nominal (wt%)		Measured (wt%)	
	Pt	Sn	Pt	Sn
I	1	0	ND[a]	
II	1	0.05	1.18	0.065
IIb	4	0.2	4.21	0.22
III	1	0.1	0.93	0.082
IV	1	0.2	1.09	0.23
V	1	0.5	0.95	0.55
VI	1	1	1.2	1.2
VII	1	2	ND	
VIII	1	4	ND	

[a] Not determined.

In this work we report the catalytic properties of $PtSn/Al_2O_3$ for the conversion of methylcyclopentane; a wide range of Pt/Sn composition was used, including those previously investigated by Mössbauer spectroscopy (*3*).

EXPERIMENTAL

1. Catalysts. Nonporous commercial alumina (Degussa 110 C, surface area 300 m^2 g^{-1}) was used as support. Tin was introduced first as $SnCl_2$, then platinum was added as H_2PtCl_6 according to the procedure described previously (*3*). The chemical analysis was performed as in this previous work. The compositions of the solids are reported in Table 1. The samples were reduced without any previous calcination step.

2. Conversion of methylcyclopentane (MCP). Catalytic activities were measured in a conventional flow reactor at atmospheric pressure. The reactant was MCP, pure grade from Fluka AG. The partial pressure of hydrogen and MCP were respectively 719 and 41.2 Torr. The temperature was fixed at 613, 633, and 673 K. At these temperatures bifunctional catalysis was found previously to be negligible. The sample weight was 0.3 g and the space velocity of the hydrocarbon equal to 1.25 g. h^{-1} (g cat.)$^{-1}$.

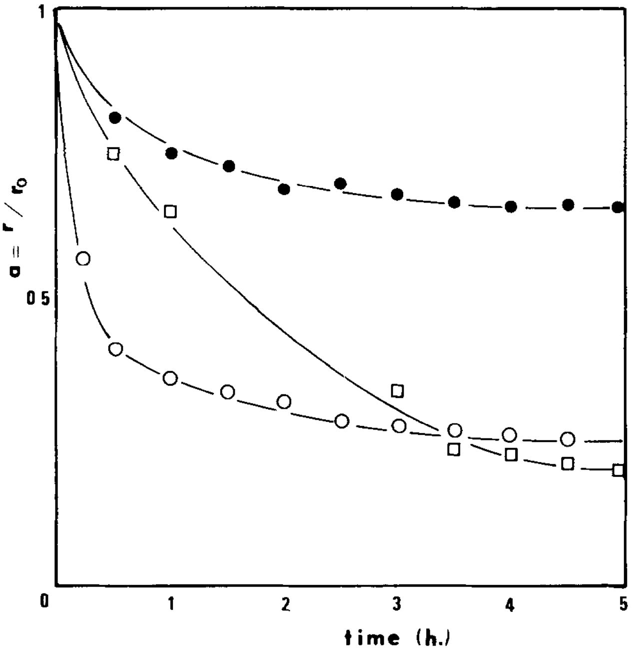

FIG. 1. Activity versus time for the conversion at 673 K of methylcyclopentane (MCP) over different catalysts: I (○), II (□), and IV (●).

The samples were first reduced overnight under flowing hydrogen (GHSV = 6 liters h^{-1}.g cat^{-1}). The effluent gases were analyzed by on-line gas chromatography using a 6-m × $\frac{1}{8}$-in. column packed with squalane on Chromosorb W (10 wt%). The selectivities for cracking, ring opening to hexanes, dehydrogenation to methylcyclopentene (MCP^{2-}) and benzene (Bz) were determined, as well as the catalyst stability against self-deactivation.

RESULTS

The higher the temperature, the faster the deactivation rate.

Figure 1 shows for three samples that after an initial decrease in activity a stable conversion is readily reached, at 673 K. Compared to a Pt/Al_2O_3 catalyst, the sample containing the lowest amount of tin presents two distinct features: (i) it deactivates initially faster but stabilizes rapidly, and (ii) it is initially more active. This last result agrees with the finding by Gault *et al.* (*5*) of a maximum of the catalytic activity for the isomerization of 2-methylpentane at 250°C for a Pt/Sn atomic ratio of 7. For the samples of higher tin content (Pt/Sn below 5) the deactivation rate and the initial activity are lower. The changes in selectivity as a function of time are similar for all catalysts: ring-opening and cracking decrease while dehydrogenation and aromatization increase. This behavior becomes more and more pronounced when the temperature rises, as Fig. 2 shows at 673 K. Whatever the sample examined or the degree of surface poisoning, the ratio 3-methylpentane/n-hexane remains roughly constant and equal to 0.5–0.65 as shown in Table 2. Such a value indicates a nonselective hydrogen-

TABLE 2

Values of the 3-Methylpentane/n-Hexane Ratio for the Hydrogenolysis of Methylcyclopentane over Different Catalysts

	I	II	III	IV	V
3MP/nH	0.67	0.67	0.60	0.65	0.5

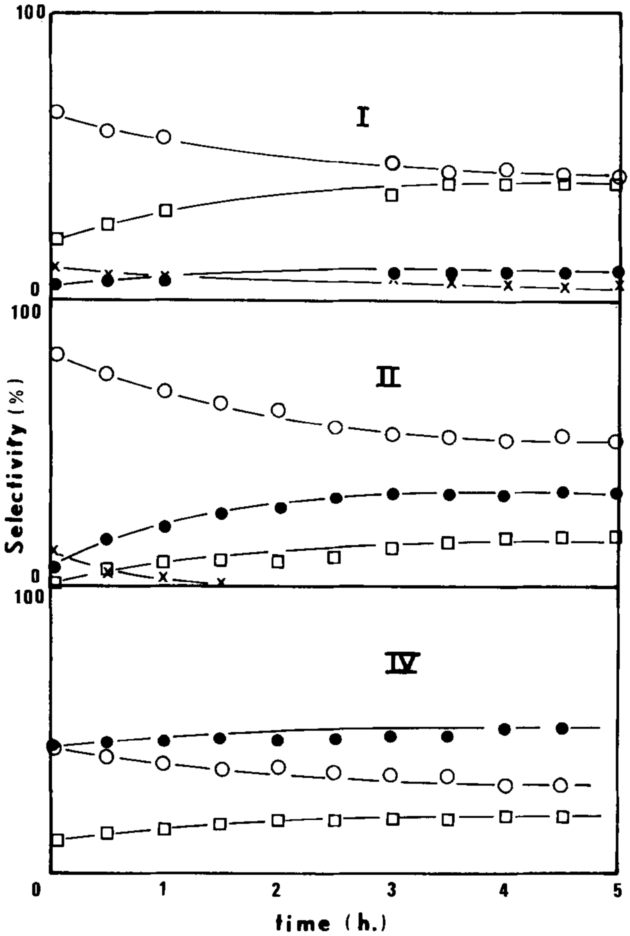

FIG. 2. Selectivity versus time for the conversion at 673 K of MCP over catalysts I, II, IV; cracking (×), ring opening (○), MCP^{2-} (□), and Bz (●).

olysis (*5*), which is characteristic of well-dispersed catalysts.

Figure 3 shows that aromatization is favored at high temperature, and also that the deactivation rate increases the higher the temperature.

The partial conversions measured at 673 K for different products are plotted on Fig. 4 as a function of tin content. Hydrogenolysis passes through a maximum at Pt/Sn = 20, aromatization at Pt/Sn = 5, expressed in weight ratios.

For tin contents larger than 1% the different activities fall to zero, except for MCP^{2-} formation which remains roughly unaltered.

Bacaud *et al.* (*12*) previously reported that the Pt/Sn ratio should not be the sole parameter governing the selectivity; it is necessary to take also into account the total amount of metallic phase. Table 3 shows the product distribution obtained on samples of similar Pt/Sn ratios with different loadings. It appears clearly that the selectivity for aromatization depends on the metal loading. Deactivation is also affected since catalyst IIb deactivates much more slowly than catalyst II.

A comparison of the respective effects of coke, sulfur, and tin on the catalytic behavior of platinum was undertaken. A feed of MCP poisoned by 10 ppm of thiophene was

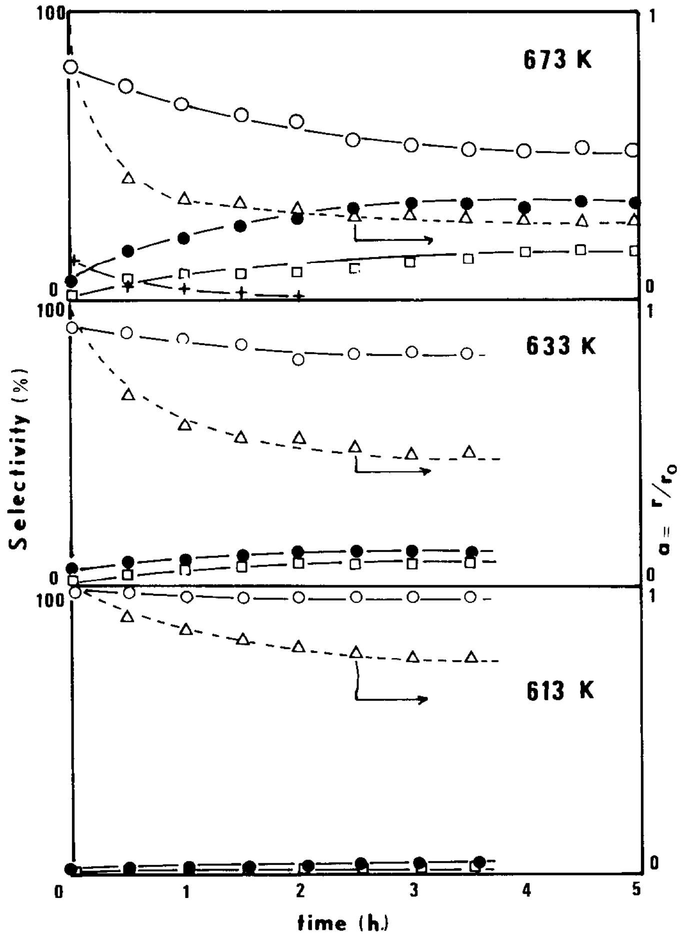

FIG. 3. Activity and selectivity versus time for the conversion of MCP on catalysts II; relative activity (△); selectivities for cracking (+), ring opening (○), MCP^{2-} (□), and Bz (●).

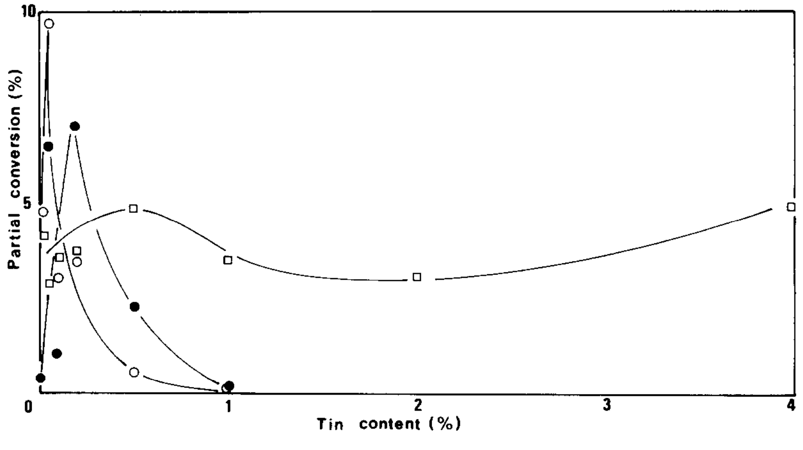

FIG. 4. Partial conversion of MCP as a function of the catalyst tin content: ring opening (○), MCP^{2-} (□), and Bz (●); Temp. 673 K.

TABLE 3

Product Distributions from MCP with Catalysts II and IIb

	II		IIb	
	Initial	Steady state	Initial	Steady state
$<C_6$	8.2	<1	<1	—
2MP	32.3	4.3	7.6	4.4
3MP	16.5	2.1	3.4	2.2
nH	20.3	3.1	5.7	3.6
MCP^{2-} (isomers)	0.6	2.8	3.6	3.5
Bz	7.4	6.4	0.9	0.5
MCP	14.8	81	78.5	85.5

processed on a Pt/Al_2O_3 sample which had been previously used for the conversion of pure MCP. Figure 5 shows the activity and the selectivity as a function of time, which may be considered here as a measure of the extent of contamination.

DISCUSSION

We assume here that the samples prepared according to the protocol used by Bacaud *et al.* (*3*), with the same materials, precursor and carrier, exhibit similar physical and chemical features, namely that, for a Pt content of 1 wt%, tin is completely reduced at low tin content (1 wt%) and that the metallic phase is well dispersed. The well-known stabilizing effect of tin in Pt–Sn catalysts appears clearly for Pt/Sn ratios below 5. At lower tin concentrations (Sn = 0.05%) the most significant phenomenon is an increase of activity.

In our view this effect is not related to a redispersion of the metallic phase in order to obtain smaller platinum aggregates. This interpretation was proposed by Gault *et al.* (*5*) to explain their increase in activity. In the present case the platinum dispersion is already high, as evidenced by the 3MP/nH ratio (Table 2). Thus a further division of the platinum particles should have little influence on the catalytic activity and is not likely to explain the behavior of sample II. We consider that a better interpretation may be found in an electron transfer from Sn to Pt. The initial sharp decrease of MCP

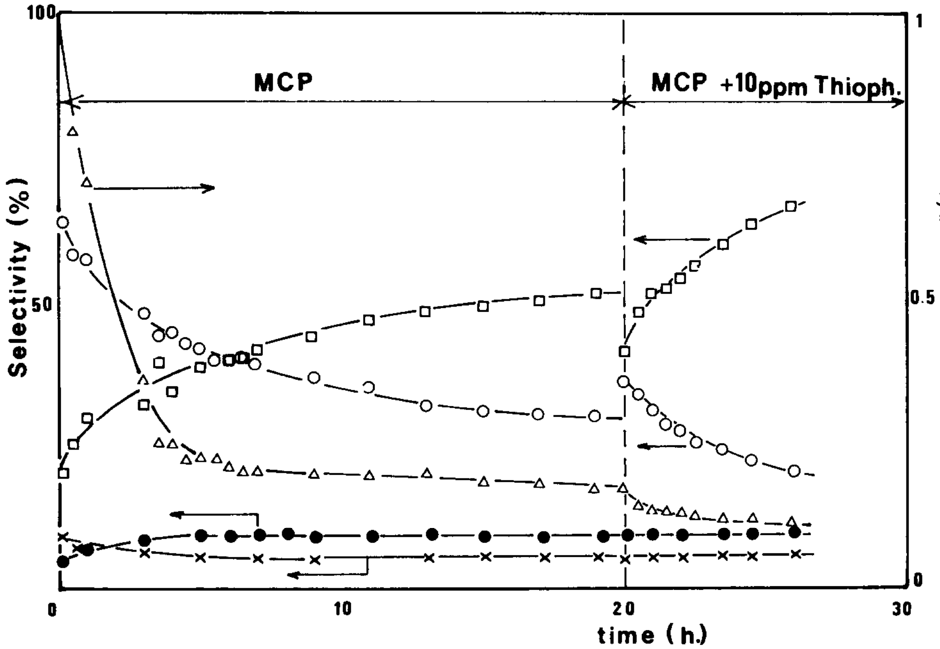

FIG. 5. Activity and selectivity versus time for the conversion at 673 K of MCP on catalyst I; relative activity (△), and selectivities for cracking (×), ring opening (○), MCP^{2-} (□), and Bz (●).

conversion on sample II at 673 K may be related to the enhancement of hydrogenolysis leading to coke formation.

Dautzenberg *et al.* (*4*) and Burch (*13*) by temperature-programmed desorption and Bacaud *et al.* (*3*) by Mössbauer spectroscopy have found that the Pt–Sn supported catalysts are inhomogeneous. Karpinski and Clarke (*17*) reached the same conclusion for films in which different phases coexist. It seems likely that in these catalysts many species may be present, such as free Pt particles, Pt–Sn particles of different compositions, and tin ions the relative abundance of which depends on the total metal loading. The difference in the product distribution of sample II and IIb can be accounted for by this phenomenon. This fact can also provide some explanation for the discrepancies observed in the literature on the catalytic behavior of catalysts characterized by the same Pt/Sn ratio but with different loadings. The selectivity pattern of sample IIb reproduces that of Pt/Al_2O_3; nevertheless, this sample has a distinct behavior toward coking since it deactivates more slowly than Pt/Al_2O_3 and reaches a stable value. A possible interpretation could be found in the ensemble theory (*4–6*) assuming that the size of the ensemble necessary for coke formation is much larger than the size of the site active for ring opening. In that case the introduction of a small amount of tin could dramatically decrease coke formation leaving the other reactions unaffected.

When more than 0.1% Sn is added to a 1% Pt catalyst, hydrogenolysis (cracking and ring-opening to hexanes) decreases whereas dehydrogenation remains constant and aromatization goes through a maximum. At this point we must specify the reaction path leading from MCP to benzene. Around 500°C, the scheme commonly accepted goes through the isomerization of MCP^{2-} on acidic sites followed by dehydrogenation on platinum (*2, 18*). At 250°C the reaction is restricted to platinum and different pathways were proposed first by Isagulyants *et al.* (*19*) and recently by Amir-Ebrahimi *et al.* (*20*) to describe aromatization catalyzed by the metallic phase. In the case of alloys, it has been proposed that Pt atoms, which are unable to hydrogenolyze because of surface dilution, become available for less demanding reactions such as dehydrogenation which would proceed at a single Pt atom (*21*).

Bacaud *et al.* (*3*) have shown previously that on a noncalcined sample containing 1% Pt and 0.5% Sn, tin is totally reduced to the metal and alloyed to platinum: the acidic function of the carrier must remain substantially unaltered and free for olefin isomerisation. However, Fig. 4 shows that benzene formation decreases steeply in a range of tin concentrations where no tin ions could be detected by Mössbauer spectroscopy. Since MCP^{2-} remains constant it is likely that benzene mainly comes from a reaction catalyzed by platinum, as proposed by many authors (*19, 20*). According to the reaction mechanism proposed, a single metal atom would be sufficient to catalyze cyclization (*20*). Further tin addition does not affect the dehydrogenation function, whereas ring enlargement (aromatization) disappears. Since these two reactions have been stated to proceed at a single platinum atom, dilution of the platinum surface by tin cannot explain the experimental result. The disappearance of aromatization is most likely to be due to the weakening of the Pt–C bond induced by a modification of the electronic properties of Pt by Sn.

A second type of approach to this problem is to compare the dilution of platinum surface by tin, coke, and sulfur, as proposed by Biloen *et al.* (*4b*). If surface dilution is the main parameter, similar behavior must be observed in these three cases. The experimental results obtained on a well-dispersed Pt/Al_2O_3 catalyst are reported in Figs. 2, 3, and 5. It appears that MCP^{2-} remains at the same level with tin addition, carbon or sulfur deposition; in these three cases hydrogenolysis decreases. However, the formation of benzene is kept roughly constant on coke and sulfur addition but goes through a maximum as a function of tin content. It is generally agreed that in the interaction between Pt and tin (*13, 22*) or carbon (*2, 23*) the electron donation occurs from the modifier to Pt. On the parent Pt–Pb system (*24*), the infrared band of linearly adsorbed CO is significantly shifted (60 cm^{-1}) to lower frequencies, thus showing the occurrence of an electron donation from Pb to Pt. On the other hand, Pt donates electrons to sulfur in the Pt–S interaction (*25, 26*). Thus the electronic state of platinum must be different when this metal is modified by tin, coke, or sulfur. However, the behavior remains the same for hydrogenolysis of MCP; the conclusion is that dilution of the platinum surface in small ensembles can explain the experimental results. The electronic properties are probably not implied in the slow step of the ring-opening reaction.

A useful comparison may be made between our results on Pt–Sn catalysts and those obtained on Pt–Au by Clarke *et al.* (*27, 28*) and van Schaik *et al.* (*29*). In these two studies the conversion of MCP or cyclopentane to dehydrogenated species, Bz, $\mathrm{MCP_S}^{2-}$, and cP^{2-}, increases with the amount of Au in Pt. However, in contrast with the present study the Bz formation, obtained also by a pure metallic mechanism, is the main reaction even at very high gold content. Note that Au is electron-withdrawing for Pt, which as evidenced by Mössbauer spectroscopy (*30*) is the opposite of Sn. Thus it appears that coke, sulfur, or gold do not affect markedly the rate of aromatization, whereas tin has a large effect; indeed, small quantities of tin greatly enhance the rate of aromatization. A dilution effect cannot explain the specific effect of tin. Nor can enrichment of the outermost layer with tin (*16*) explain the experimental results, because the formation of methylcyclopentene clearly shows that the catalyst surface contains platinum atoms. These surface platinum atoms, which can catalyze dehydrogenation, are unable to carry out hydrogenolysis or aromatization and it may therefore be concluded that their electronic structure has been modified by tin, as Mössbauer spectroscopy shows. The conclusion that aromatization is sensitive to a modification of the electronic properties of the platinum atom is consistent with the well-known observation that Pt is the best catalyst for aromatization among the metals of Group VIII which have similar crystalline structures. The nature of the intermediate species, postulated as a carbene–alkene complex coordinated to platinum (*20*), suggests a reactivity depending on the electron density at the metal atom.

In conclusion, the addition of tin to platinum has several effects which may be summarized:

1. A stabilizing effect on the catalytic activity and a decrease of hydrogenolysis. Coke and sulfur have similar effects. It is therefore assumed that the main role of tin here is to dilute the platinum surface.
2. An enhancement of aromatization, which passes through a maximum and then falls to zero as a function of the tin content. Dehydrogenation of methylcyclopentane to methylcyclopentene remains unchanged. This type of behavior is not reproduced by the deposition of carbonaceous residues or sulfur poisoning. Since it is widely assumed that these two reactions proceed at ensembles of very small size, the changes of selectivity are attributed to the modification of the Pt–C bond strength induced by the changes of electronic density at platinum atoms. Such changes of electronic densities find experimental support in the physical examination of the catalyst by Mössbauer spectroscopy.

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