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Adsorption and Hydrogenation of Ethylene, 1-Hexene, and Benzene and CO Adsorption on Pt/Al_2O_3 and Pt–Sn/Al_2O_3 Catalysts

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Adsorption and hydrogenation of ethylene, 1-hexene, and benzene, and carbon monoxide adsorption on alumina-supported Pt and Pt–Sn catalysts were studied. Gravimetric experiments and infrared (IR) absorption spectroscopy combined with chemisorption measurements were used for this purpose. Additionally fresh and coked catalysts were characterized by the IR spectra of CO and chemisorption data. Added tin causes a slight increase in benzene adsorption and a distinct decrease in ethylene and 1-hexene uptakes, whereas the hydrogenation activity is inhibited. Adsorption and catalytic data with benzene can be explained by a model of flat adsorption on Pt/Al_2O_3 and tilted adsorption on Pt–Sn/Al_2O_3 and are consistent with electronic modification of platinum by tin. Electronic interaction between platinum and tin is also indicated by the IR data. The most active sites for hydrocarbon decomposition on the platinum surface are the same as those on which carbon monoxide is multiply bonded. Deposited coke and tin block the same active sites on the platinum surface.

INTRODUCTION

During the last decade bimetallic catalysts have found a very wide application in the reforming process. These catalysts demonstrate principal advantages over catalysts containing one metal only. The effects of a second metallic component are very specific and depend on the nature of the two metals, their ratio, and the type of reaction. For example, it has been reported that the activity for benzene hydrogenation of tin-containing Pd and Ni catalysts is much lower than that of the tin-free catalysts (*1*), whereas Yermakov *et al.* (*2*) found an increased activity for the same reaction of silica-supported Pt–Mo and Pd–Mo catalysts. Various reasons can be invoked to explain these findings, e.g., (i) variation of the bond strength between chemisorbed hydrocarbons and the surface atoms because of the interaction between the two metals (electronic effect), and (ii) dilution of the active phase by the second metal (geometric effect). A systematic study of the nature and reactivity of the adsorbed hydrocarbon species seemed to us of interest and was expected to throw light on the correlation between the above-mentioned effects.

In the present work we studied the adsorption and hydrogenation of ethylene, 1-hexene, and benzene on alumina-supported Pt and Pt–Sn catalysts. Data concerning coke formation are also presented. For this purpose gravimetric and chemisorption measurements and catalytic experiments in a flow system were employed. Infrared spectra of adsorbed carbon monoxide and 1-hexene were recorded in order to obtain more information about the surface properties of the investigated catalysts.

EXPERIMENTAL

Catalysts

The support used in this study was a nonporous δ-alumina, Degussa P110 C1, with a BET surface area of about 90 m^2/g. Platinum alone or platinum and tin were de-

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posited by impregnation from aqueous solutions of H_2PtCl_6 and $SnCl_2$. The monometallic platinum and the bimetallic Pt–Sn catalysts thus prepared were heated in air for 2 h at 500°C. Reduction was carried out "*in situ*" under flowing hydrogen at 400°C for 5 h.

Gravimetric Measurements

The gravimetric measurements were performed at room temperature by means of a Sartorius Type 4102 electronic microbalance. Each hydrocarbon was admitted to the cell at the pressure of 10 Torr (1 Torr = 133.3 N m^{-2}). Prior to an adsorption run, the catalysts were oxidized at 400°C, reduced in a stream of hydrogen at 400°C, and evacuated at 420°C to 1×10^{-5} Torr. More details can be found in Ref. (*3*).

Combined Chemisorption and Infrared Measurements

The infrared and chemisorption measurements were performed at room temperature in one and the same conventional vacuum apparatus equipped with calibrated volumes and a calibrated Pirani gauge. The Pirani gauge operated at constant filament temperature with a self-balancing control unit. The infrared cell employed in this study was similar in design to the one described earlier (*4*). Carbon monoxide, hydrogen, and oxygen gases were used for the chemisorption measurements. The total uptakes were measured by stepwise adsorption of the corresponding gas up to a residual pressure of about 5×10^{-2} Torr. Higher pressures were not applied mainly because of the insufficient accuracy of the vacuum gauge above this pressure range. The reversible uptakes were determined by stepwise readsorption onto samples saturated in advance with gas at 5×10^{-2} Torr and evacuated at the temperature of adsorption down to 1×10^{-5} Torr.

Catalyst pellets (20 × 15 mm) for the IR transmission and chemisorption experiments were prepared by pressing the powder, each pellet weighed about 0.08–0.1 g. The samples were reactivated under the conditions used for the gravimetric measurements.

The infrared spectra were recorded on a Carl Zeiss UR-10 double-beam spectrometer applying reference beam screening to obtain suitable baselines.

Experiments with Catalyst Samples Covered by Coke

Coke-poisoned Pt and Pt–Sn samples were studied by IR spectroscopy combined with chemisorption measurements. In these experiments *n*-hexane was used as a source of carbonaceous species. Coke was deposited in the following way. The IR sample was oxidized and reduced at 400°C. After that it was annealed at 400°C in *n*-hexane vapor, at a pressure of about 1×10^{-1} Torr, for 30 or 90 min. Finally, the cell was evacuated at 400°C to 1×10^{-5} Torr and cooled to room temperature. Carbon monoxide and hydrogen chemisorption were measured by stepwise adsorption at room temperature on a freshly reduced sample or after coke deposition. The carbon monoxide adsorption was also monitored through the infrared spectra of the clean and coked samples.

Catalytic Activity

The experiments were performed in a continuous flow reactor and the catalytic activity was expressed as the reaction rate in mol g^{-1} h^{-1}. The following reaction conditions were used. With each catalyst the rates were determined at 5 different temperatures in the ranges 50–95, 30–55, and 60–140°C for ethylene, 1-hexene, and benzene, respectively. The rates thus obtained were plotted as Arrhenius diagrams and the values of log r_0 shown in Fig. 3 were taken from these diagrams at constant temperature selected for each reaction. For ethylene and 1-hexene hydrogenation 2 mg of catalyst were mixed with 400 mg of γ-Al_2O_3. In both cases hydrogen flow rates were 2.26 liters/h whereas the ethylene flow rate was 0.5 liter/h (partial pressure of

138 Torr). Hydrogen was saturated with 10 Torr of 1-hexene. Benzene hydrogenation was carried out with 100 mg of catalyst mixed with 300 mg of γ-Al_2O_3. Hydrogen, at a flow rate of 4.52 liters/h, was saturated with 60 Torr of benzene.

Gases, Chemicals, and Their Purification

Carbon monoxide (Matheson Research Grade) was used without further purification. Electrolytic hydrogen was passed through a Deoxo unit (Heraeus) followed by a liquid-nitrogen trap. Oxygen was prepared by thermal decomposition of potassium permanganate under vacuum. Ethylene and benzene from Merck and 1-hexene from Fluka, all puriss grades, were used as obtained.

RESULTS

Gravimetric Chemisorption Measurements

The results of the gravimetric measurements are summarized in Table 1. Blank experiments demonstrated that the addition of tin had not a notable influence on the adsorptive properties of alumina towards the hydrocarbons. Alumina alone adsorbed irreversibly not more than 5% of the irreversibly adsorbed amounts of olefins on the monometallic catalyst. An irreversible benzene adsorption on the carrier was not detected. The irreversibly adsorbed amounts, referred to as "irrev," were measured after admitting the hydrocarbon to the cell and evacuating to 1×10^{-5} Torr. The chemisorbed species could be hydrogenated at room temperature by admitting 100 Torr of hydrogen. The hydrogenated species desorbing from the surface during evacuation to 1×10^{-4} Torr is denoted as "des." Its portion was determined by the difference between the irreversibly adsorbed species prior to hydrogenation and the remaining species on the surface after hydrogenation. As seen, a small concentration of tin caused a strong reduction of ethylene and 1-hexene uptakes and unexpected enhancement of benzene chemisorption. The chemisorbed species from ethylene was readily hydrogenated on single platinum whereas the hydrogenation of preadsorbed benzene on the bimetallic samples was suppressed.

Combined Chemisorption and Infrared Measurements

Data on hydrogen, carbon monoxide, and oxygen chemisorption are shown in Table 2 where total and reversible uptakes as well as CO : O ratios are presented. An appreciable adsorption of CO and H_2 was not found on Al_2O_3 and Sn/Al_2O_3 under the experimental conditions employed in this

TABLE 1

Gravimetric Chemisorption Measurements of Hydrocarbons on Alumina-Supported Pt and Pt–Sn Catalysts

Hydrocarbon	Catalyst sample					
	5% Pt		5% Pt + 2% Sn		5% Pt + 5% Sn	
	Irrev[a] (mg/g Pt)	Des[b] (%)	Irrev (mg/g Pt)	Des (%)	Irrev (mg/g Pt)	Des (%)
Ethylene	18.2	50	6.2	36	13.0	ND[c]
1-Hexene	32.2	38	8.3	37	14.6	33
Benzene	27.3	30	31.6	0	21.6	6

[a] Amount of irreversibly adsorbed species.

[b] Portion of desorbed products after hydrogen treatment.

[c] Not determined.

TABLE 2

Chemisorbed Amounts of Carbon Monoxide, Oxygen, and Hydrogen on Alumina-Supported Pt, Pt–Sn, and Pt–Pb Catalysts

Catalyst	CO^{tot} (molecules/g Pt)	CO^{rev} (%)	H^{tot} (atoms/g Pt)	O^{tot} (atoms/g Pt)	O^{rev} (%)	CO : O
5% Pt	7.5×10^{20}	12	6.8×10^{20}	11.0×10^{20}	—	0.68
5% Pt + 2% Sn	2.1×10^{20}	22	1.1×10^{20}	9.6×10^{20}	8	0.22
5% Pt + 5% Sn	0.7×10^{20}	48	0.27×10^{20}	7.2×10^{20}	14	0.1
5% Pt + 2% Pb	2.0×10^{20}	19	1.4×10^{20}	ND	ND	ND
5% Pt + 5% Pb	0.8×10^{20}	51	0.37×10^{20}	ND	ND	ND

study. Results of hydrogen and carbon monoxide chemisorption on platinum–lead catalysts are also given. Addition of tin or lead to platinum and an increase in their concentration gave rise to decreased gas uptakes on the investigated samples. Reversible uptakes of CO were found to increase due to the presence of tin and lead while the CO : O ratios rapidly decreased at the same time. No reversible oxygen adsorption was measured with the monometallic sample.

In the IR spectra from adsorbed carbon monoxide a very intense band at 2090 cm^{-1} was observed with the Pt/Al_2O_3 sample. Addition of tin to the platinum catalyst caused a significant shift toward lower frequencies. This shift became larger as the tin concentration was increased (Table 3). Spectra were also taken at a certain residual coverage defined as the adsorbed amount of CO remaining on the surface after desorption at a particular temperature (Table 3). Desorption temperatures were chosen in a way to obtain still detectable and uniformly intense bands for all the IR samples. Desorption from the monometallic catalyst resulted in a 32-cm^{-1} frequency fall, whereas the shift was smaller for the modified samples and was dependent upon the concentration of the inactive metal (Table 3). Coadsorption of carbon monoxide ($\theta_{CO} = 0.3$) with ethylene on the monometallic platinum sample produced a 40-cm^{-1} red shift. The same procedure performed on the Pt–Sn samples caused a smaller shift toward lower frequencies (Table 3).

It is worth noting that the CO adsorption

TABLE 3

Infrared Band Frequencies from CO Adsorbed on Clean and Coked Alumina-Supported Pt and Pt–Sn Catalysts

Catalyst	ν^1_{CO} (cm^{-1}) (P_{CO} = 10 Torr)	ν^2_{CO} (cm^{-1})	$\Delta\nu^1_{CO}$[a] (cm^{-1})	$\Delta\nu^2_{CO}$[b] (cm^{-1})
5% Pt[c]	2090	2058 (335°C; $\theta_{CO} = 0.15$)[d]	32	40
5% Pt + 2% Sn[c]	2060	2045 (220°C; $\theta_{CO} = 0.17$)[d]	15	13
5% Pt + 5% Sn[c]	2053	2045 (150°C; $\theta_{CO} = 0.33$)[d]	8	10
5% Pt[e]	2090	2030 ($\theta_{CO} \approx 0.3$)	60	ND
5% Pt + 2% Sn[e]	2060	2047 ($\theta_{CO} \approx 0.3$)	13	ND

[a] $\Delta\nu^1_{CO} = \nu^1_{CO} - \nu^2_{CO}$.

[b] $\Delta\nu^2_{CO}$: red shift due to ethylene coadsorption on a partially covered sample with CO ($\theta_{CO} = 0.3$; $P_{C_2H_4} = 5$ Torr).

[c] Clean sample.

[d] Desorption temperature at which the indicated coverage is reached.

[e] Coked sample.

on Pt/Al_2O_3 gave rise to a weak band at 1850 cm^{-1} which was not recorded with the bimetallic samples.

Figure 1 shows variations of the integrated CO band intensity (I_r) with CO surface coverage. Enhanced band intensity for equal amounts of chemisorbed carbon monoxide is clearly seen for the tin-modified platinum catalysts. These catalysts show no hysteresis between the adsorption and desorption sequences (Figs. 1b and c), while a slight hysteresis is exhibited by pure platinum (*5*). It is important to note that a marked hysteresis was found with $Pt-Pb/Al_2O_3$ catalysts (*5*). Details on the procedure of obtaining the curves shown in Fig. 1 are given in Ref. (*5*).

Infrared spectra of 1-hexene adsorbed on 5% Pt/Al_2O_3 and (5% Pt + 5% Sn)/Al_2O_3 are shown in Fig. 2. In spite of the smaller olefin amount adsorbed on the bimetallic sample (Table 1), the C—H stretching bands with the same sample are more intense, especially those from the CH_3 groups (Fig. 2). However, the bands due to the CH_2 and CH_3 stretching modes are displaced to higher frequencies with the bimetallic catalyst.

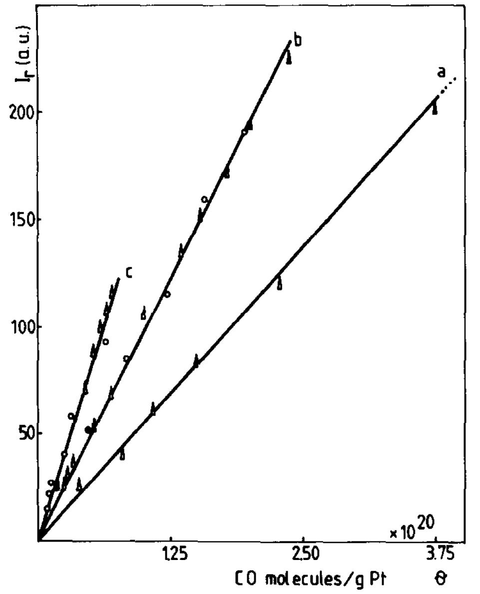


FIG. 1. Integrated CO band intensities (I_r, arbitrary units) versus CO coverage (θ_{CO}) within adsorption and desorption sequences: (a) 5% Pt, (b) 5% Pt + 2% Sn, (c) 5% Pt + 5% Sn; Δ, adsorption; O, desorption. Only part of the adsorption curve with Pt/Al_2O_3 is shown here, for the sake of simplicity.

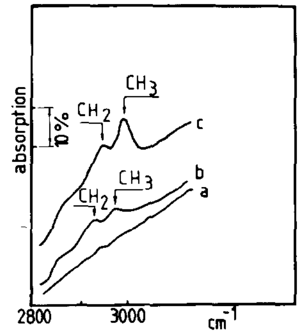


FIG. 2. IR spectra of 1-hexene adsorbed on 5% Pt/Al_2O_3 (curve b) and 5% Pt + 5% Sn/Al_2O_3 (curve c); background (curve a). Samples were saturated with olefin at the pressure of 10 Torr and then the cell was evacuated to 1 × 10^{-5} Torr.

Catalytic Activity

A strong decrease in the rate of benzene hydrogenation was observed with the bimetallic catalysts (Fig. 3). Ethylene and 1-hexene hydrogenation rates were not so severely affected by the presence of tin. The fall with the olefins was of the same order of magnitude (Fig. 3).

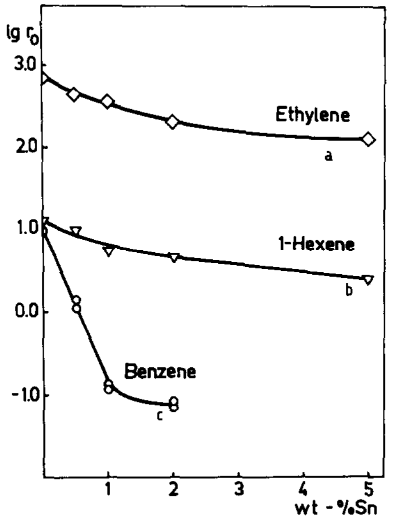


FIG. 3. Hydrogenation rates (mol g^{-1} h^{-1}) vs tin content for catalysts of 5 wt% Pt: (a) ethylene at 60°C, (b) 1-hexene at 30°C, (c) benzene at 90°C.

Experiments with Catalyst Samples Covered by Coke

Gas uptakes were decreased due to coke formation on the platinum surface. The amount of deposited coke was time-dependent. Carbonaceous deposits on platinum led to diminished H : CO ratios with Pt/Al_2O_3 whereas these ratios were nearly the same with the Pt–Sn catalysts (Fig. 4).

Coke formation was also studied through the IR spectra of CO chemisorbed on the investigated samples (Table 3). The adsorption of carbon monoxide on a platinum surface covered by coke resulted in the appearance of a single band situated above 2000 cm^{-1} and assigned to linearly bonded species (*5*). The weak band at 1850 cm^{-1}, attributed to bridged species on bare platinum (*5*), was not detected on the coked surface. Admission of small does of CO (θ_{CO} = 0.3) gave rise to a weak band at about 2030 cm^{-1} (Table 3). However, at complete coverage (P_{CO} = 10 Torr) the band moved to the frequency of the bare Pt sample (2090 cm^{-1}). Low CO coverages on the clean (5% Pt + 2% Sn)/Al_2O_3 sample produced a band at 2045 cm^{-1} which shifted to 2060 cm^{-1} at 10 Torr of CO (Table 3). At low coverage on the coked Pt–Sn sample the frequency differed by 2 cm^{-1} whereas it was the same at complete coverage relative to the clean sample (Table 3).

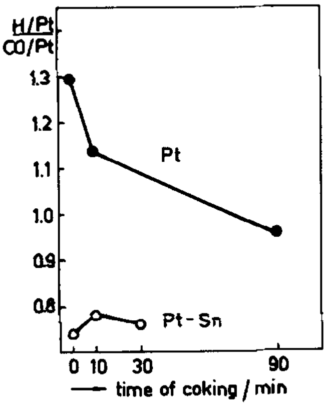
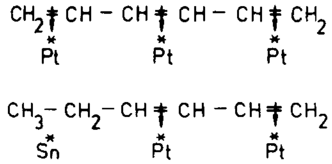


FIG. 4. Ratio between adsorbed hydrogen and carbon monoxide per gram of platinum as a function of coking time with catalysts containing 5 wt% Pt and 5 wt% Pt + 2 wt% Sn.

DISCUSSION

As already stated, ethylene and 1-hexene chemisorption was strongly suppressed on the Pt–Sn/Al_2O_3 samples whereas the benzene uptake was slightly increased with (5% Pt + 2% Sn)/Al_2O_3 (Table 1). This finding was somewhat unexpected since selective CO and H_2 chemisorption on the bimetallic catalysts showed very low values which is consistent with a reduced number of exposed platinum atoms on the surface of the Pt–Sn system (Table 2). It is relevant to assume that the unusual benzene uptake on Pt–Sn/Al_2O_3 is concerned with changes of the nature of bonding between benzene and platinum. At present it is generally accepted that the benzene molecule is bonded to one platinum atom through a π-complex on the surface of Pt/Al_2O_3 (*6*). We suppose that the mode of bonding between platinum and benzene on the bimetallic surface is changed and consider σ-bonding as primarily involved. σ-Bonding implies that the benzene ring should be perpendicular or slightly tilted with respect to the surface. Benzene molecules in a flat position relative to the surface, i.e., π-bonded species, should block all the nearest neighbor surface atoms, with the result that a large area of the platinum surface becomes inaccessible for adsorption. Therefore, due to the steric effects, π-bonded species should occupy more sites per unit platinum surface than σ-complexes. Examples of π- to σ-rearrangements in organometallic chemistry are well known (*7, 8*) and they are related to an increased number of organic ligands per metal center. Also, this model is consistent with the concept of Haaland (*9*) that benzene molecules on platinum surfaces perturbed by ordered carbon residues form both π- and σ-bonded species. It should be emphasized that the model discussed above requires modification not only of the geometry but also of the electronic properties of the platinum surface in the Pt–Sn system. Since the π-complex of benzene occupies one Pt atom, the increase in the benzene uptake on (5% Pt + 2% Sn)/Al_2O_3 cannot be rationalized on pure geometric grounds. In view of this we propose the formation of σ-bonded benzene species on an electronically perturbed platinum surface. The same speculations are also valid for the (5% Pt + 5% Sn)/Al_2O_3 catalyst. However, the benzene uptake is lower than that on 5% Pt/Al_2O_3 (Table 1) because the enhancement of the benzene chemisorption in this case is not sufficient to compensate for the very strong decrease in the number of exposed Pt atoms (Table 2).

The adsorption of 1-hexene on the mono- and bimetallic samples showed considerable differences in the IR spectra. Chemisorbed species gave rise to more intense bands in the C—H stretching region with the Pt–Sn catalyst (Fig. 2) which is at variance with the gravimetric data. It was pointed out that olefin irreversible uptakes were strongly decreased on the Pt–Sn samples (Table 1). Consequently the portion of methyl and methylene groups, not bonded to the surface, should be larger with the tin-containing catalysts due to the dilution of the platinum atoms by tin. On platinum, hexene is easily dehydrogenated to a polyolefinic species via multiple bonding with the surface resulting in a flat adsorption of the molecule (*10*). On the other hand, it is known that the dehydrogenation activity of platinum is strongly suppressed by tin (*11*). On Pt–Sn/Al_2O_3, therefore, an appreciable part of the hexene molecules should be bonded through the original double bond to one Pt atom or to a smaller number of Pt atoms relative to the monometallic catalyst. For example, compare the possible structures of chemisorbed hexene shown in Scheme 1. The rest of the molecule may be situated in a tilted position with respect to the surface tin atoms thus giving rise to comparatively intense CH stretching bands (Fig. 2). Suppressed dissociative olefin adsorption on Ni–Au and Ni–Cu alloy films has also been reported by Franken and Ponec (*12*).



$$\mathrm{CH_2 \underset{\overset{*}{Pt}}{\mid} CH - CH \underset{\overset{*}{Pt}}{\mid} CH - CH \underset{\overset{*}{Pt}}{\mid} CH_2}$$

$$\mathrm{\underset{\overset{*}{Sn}}{CH_3} - CH_2 - CH \underset{\overset{*}{Pt}}{\mid} CH - CH \underset{\overset{*}{Pt}}{\mid} CH_2}$$

SCHEME 1

In the present experiments with samples containing 5 wt% Pt, 1-hexene adsorption was decreased by tin addition (Table 1). However, an enhanced adsorption has recently been reported with tin-lean catalysts of 1 wt% Pt (*13*). This is surprising because Sn/Pt atomic ratios were nearly the same in both series of experiments; only the total metal content was different. In Fig. 5 the ratio between oxygen and hydrogen uptakes (per gram of Pt) is plotted as a function of the Sn/Pt ratio. It is seen that the O/H ratios are only slightly increased for samples containing 0.5 wt% Pt and very drastically with 5 wt% Pt. The relative increase in oxygen adsorption is a measure of

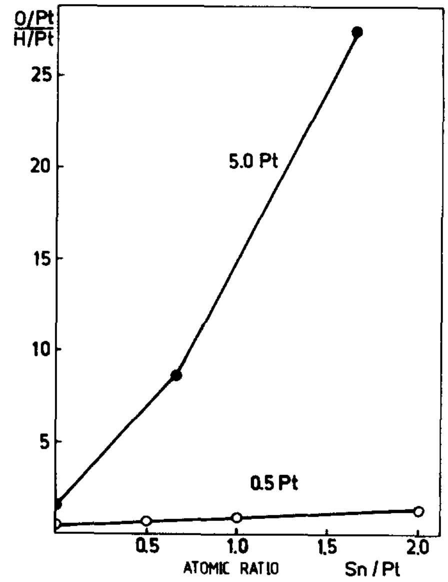


FIG. 5. Ratio between adsorbed oxygen and hydrogen per gram of Pt as a function of the Sn/Pt ratio in catalysts containing 5 wt% Pt (this study) and 0.5 wt% Pt (*11*).

enhanced interaction between Pt and Sn because alloyed tin adsorbs only oxygen whereas hydrogen is selectively adsorbed on platinum (*14*). One must conclude that the interaction is much stronger in metal-rich than in metal-lean catalysts. Hence the observed differences in 1-hexene uptakes on metal-rich and metal-lean tin-modified samples can reasonably be explained by the extent of interaction between platinum and tin.

Another question arising from the gravimetric measurements is why the promoting effect of tin on the adsorption of benzene and 1-hexene is exhibited in a different way: after tin addition the amount of adsorbed benzene was increased whereas 1-hexene adsorption was strongly suppressed (Table 1). Most probably the single-atom site adsorption of σ-bonded benzene is less sensitive to alloying than the π-type or two-atom site σ-adsorption of 1-hexene. The decrease in ethylene adsorption on (5% Pt + 2% Sn)/Al_2O_3 should be due to the same reason as the decrease in 1-hexene adsorption. However, at present we do not have sufficient data to explain the increase in the olefin uptakes as the tin content is increased to 5 wt% (Table 1). Experiments with (5% Pt + 7% Sn)/Al_2O_3 demonstrated a significant decrease in the olefin uptakes compared to the other two bimetallic samples.

In the following text the gravimetric data are compared with the catalytic activities. First of all there exists no direct correlation between the amount of irreversibly adsorbed hydrocarbons and the catalytic activity. For example, added tin slightly increases the adsorption of benzene (Table 1) but dramatically decreases its hydrogenation rate (Fig. 3). Of specific interest, however, is the portion of chemisorbed species which is removed from the surface after hydrogen treatment. Hydrogenation of the olefinic species was not significantly affected by tin while the benzene species was hardly eliminated from the bimetallic samples (Table 1). This is consistent with the catalytic effect of tin. Ethylene and 1-hexene hydrogenation was only slightly inhibited whereas benzene hydrogenation was strongly suppressed. Thus the reactivity to hydrogen of the chemisorbed species can be directly correlated with the catalytic activity in hydrogenation. This correlation is logically explained by the proposed mode of adsorption of the chemisorbed species. It is known that benzene, adsorbed on platinum, forms a stable π-complex which readily reacts with hydrogen and gives rise to desorption of cyclohexane (*6*). The gravimetric experiments with benzene indicate that the amount of the desorbing species after hydrogenation is negligible with Pt–Sn/Al_2O_3 whereas the irreversibly adsorbed quantities prior to hydrogen treatment are almost unaffected by tin (Table 1). Apparently, in hydrogenation the bimetallic surface is mostly covered by the unreactive σ-bonded benzene species. The nature of olefin bonding is not drastically changed by tin and the catalytic activity in hydrogenation reactions is not so severely inhibited. Olefin hydrogenation rates were decreased by about a factor of 10 in agreement with the decrease in the platinum surface according to the chemisorption data (cf. Table 2 and Fig. 3). However, the rate of benzene hydrogenation on (5% Pt + 5% Sn)/Al_2O_3 was diminished by two orders of magnitude (Fig. 3). We believe that in this case electronic effects are mainly concerned which cause changes of the bonding modes between benzene and platinum.

Information about the state of tin in the bimetallic catalysts can be obtained from the chemisorption measurements. It has been established by Muller *et al.* (*15*) that tin in Sn/Al_2O_3 is tightly bonded to the alumina support and is in the +2 oxidation state after reduction at 510°C. The same authors (*15*) also found a lack of irreversible adsorption of oxygen at room temperature on nonmetallic tin. The results shown in Table 2 indicate the presence of reversible adsorption of oxygen on the bimetallic catalysts; however, it is rather low. At the same time the $CO^{tot} : O^{tot}$ ratios were significantly decreased with the increase in tin content (Table 2), i.e., an appreciable irreversible oxygen adsorption does occur on the $Pt-Sn/Al_2O_3$ system. This is strong evidence that platinum promotes the formation of metallic tin on which oxygen is irreversibly adsorbed. The conclusion is in accordance with TPR and chemisorption experiments with $Pt-Sn/Al_2O_3$ catalysts of 0.5 wt% Pt in which the content of metallic tin was found to be in the 10–30% range (*14*). Recently, however, Sexton *et al.* (*16*) published XPS and TPR data on the same bimetallic system and claimed that no metallic tin was formed. The discrepancy becomes understandable, considering that (i) Pt and Sn were more inhomogeneously distributed in most of the catalysts of Sexton *et al.* (*16*), thus restricting the interaction between the two metals, and (ii) small amounts of metallic tin are difficult to detect due to the limited sensitivity of the applied techniques.

The IR results obtained from CO adsorption are consistent with electronic modification of the platinum surface by tin. The downward shift of the CO band (Table 3, ν_{CO}^1 and ν_{CO}^2) indicates an electron transfer from tin to platinum similar to that observed with the $Pt-Pb/Al_2O_3$ catalysts (*5*); however, the red shift with $Pt-Sn/Al_2O_3$ is smaller. On the other hand, the amounts of chemisorbed CO and hydrogen on the corresponding Pt–Sn and Pt–Pb samples of equal metal concentrations are nearly the same (Table 2). This implies that if electronic factors were absent and platinum cluster sizes of the respective bimetallic samples of both series of catalysts were of the same order, the CO band frequencies from platinum surfaces of equal magnitude should have close values.

The reversible CO adsorption is strongly enhanced by the presence of tin or lead (Table 2). The bond between the CO molecules and the bimetallic catalysts is weakened as a result of a chemical modification of the platinum surface. Definitely the weakening of the bond cannot be correlated with geometrical changes (*17*). Lowering of ν_{CO}^2 due to the increased content of Sn or Pb (Table 3) is consistent with an enhanced electron transfer from the platinum *d*-orbitals to the unoccupied $2\pi^*$ antibonding CO molecular orbitals, i.e., with a decrease in the C—O bond strength. This will strengthen the $d-\pi^*$ dative bond and one should expect a further strengthening of the metal–CO bond. However, the experimental data show just the opposite (Table 2), namely, an increased reversible adsorption due to loosening of the chemisorption bond. Therefore the σ-component of the metal–CO bond has to be significantly weakened. Furthermore, in catalysis the activity in benzene hydrogenation is decreased (Fig. 3) together with the increase in the reversible CO adsorption (Table 2), i.e., the chemical modification of Pt is primarily responsible for the catalytic activity of the bimetallic catalysts in the investigated reaction. However, this may not be the case with reactions of different type, for example dehydrogenation.

Interaction between Pt and Sn (and between Pt and Pb) is also indicated by the correlation of the integrated intensities of the IR band from adsorbed CO and the CO surface coverage (Fig. 1 and Ref. (*5*)). In contrast to Pt/Al_2O_3 (*5*), no hysteresis was found between the adsorption and desorption sequences with the Pt–Sn system (Figs. 1b and c). A pronounced hysteresis was reported for the $Pt-Pb/Al_2O_3$ catalysts; however, it was opposite to that of the monometallic sample (*5*). Experiments with Pt/Al_2O_3 samples of various dispersion showed no variation of slope and hysteresis of the $I_r-\theta_{CO}$ curves (*5*). These results are in agreement with the conclusion that the chemical effect of tin and lead on platinum can be different. Furthermore, the coverage-induced shifts toward higher frequencies with both Pt–Sn and Pt–Pb are identical (cf. $\Delta\nu_{CO}^1$ in Table 3 and Ref. (*5*)). The blue shift is larger with the monometallic catalyst (Table 3) and some authors have stated that it is due entirely to adsorbate–

adsorbate coupling (*18*). Coadsorption of CO and ethylene on the Pt–Sn/Al_2O_3 samples produced an additional shift of the CO band to lower frequencies (Table 3) in agreement with previous coadsorption data on Pt/Al_2O_3 and Pt–Pb/Al_2O_3 catalysts (*5*). However, this shift is larger for the tin-modified samples in comparison with the lead-containing ones which is further evidence for an electron transfer (albeit variable in extent) between platinum and the Group IVB metals.

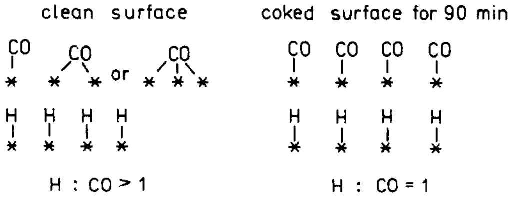
The Pt–Sn/Al_2O_3 catalysts showed enhanced intensities of the IR band from adsorbed CO compared to Pt/Al_2O_3 (Fig. 1). This is also an indication for electronic interaction between platinum and tin. For example, we can draw an analogy with the IR spectra of bulk carbonyl compounds with electron-donating substituents. Increased integrated band intensities of the C—O stretching vibration of these compounds are claimed to originate from an increase in the dipole transition moment of the carbonyl group if the latter is conjugated with electron-releasing substituents (*19*).

It is worth noting that the catalytic activities of the Pt–Sn/Al_2O_3 and Pt–Pb/Al_2O_3 catalysts in cyclohexane and *n*-heptane conversions were very similar (*20*) despite the differences in the IR spectra from adsorbed CO indicated above. We notice that the differences in the modifying abilities of Sn and Pb may not necessarily be exhibited in every catalytic reaction.

Finally, the problem of coke formation should be discussed. The IR spectra of CO on poisoned monometallic Pt and bimetallic Pt–Sn catalysts by carbonaceous deposits show several important features. Usually one band situated above 2000 cm^{-1} and attributed to linearly adsorbed species is observed (*5*). The band at 1850 cm^{-1}, commonly found in the IR spectra of CO on clean platinum surfaces (*5*), is not detected on coked platinum. At small CO coverages a downward shift of the linear band is recorded with the monometallic catalyst compared to the clean platinum surface, whereas no significant displacement is found for high coverages and with the bimetallic samples (Table 3). Recently, Bertolini and Tardy (*21*) studied the adsorption of CO on carbided (111), (100), and (110) nickel surfaces by vibrational electron energy loss spectroscopy and thermal desorption. They found a shift to higher frequencies on Ni(111) with respect to the clean surface. Also, surface carbon lowered markedly the bond strength and changed the nature of the adsorption sites (*21*). The different direction of the CO band shift with polycrystalline platinum (Table 3) and Ni(111) (*21*) may be explained by the presence of various types of carbonaceous deposits on the surface such as carbidic carbon, graphitic carbon and hydrogen-containing coke. Kiskinova and Goodman (*22*) found that carbidic carbon was formed on the Ni(100) surface following ethylene cracking at 330°C. This electronegative carbon causes a depletion of the Ni 3*d* electronic density and results in a weakening of the Ni—CO interaction. Contrary to the results with the Ni single crystals (*21, 22*), we found a red shift of the CO band which indicates that the carbonaceous deposits on Pt/Al_2O_3 have a different nature. Coke deposited under the experimental conditions applied in this study is known to consist mainly of polyaromatic hydrocarbons with poorly organized pseudographitic structures (*23*). That is why it is relevant to expect a downward shift of the CO band due to the coadsorption of carbon monoxide and the graphitic species, in agreement with data on CO coadsorption with aromatic molecules (*6*). However, the insignificant upward shift with the coked bimetallic sample (Table 3, cf. ν_{CO}^2 for the clean and coked bimetallic samples) suggests that the coke formed on the Pt–Sn surface is of different type, most probably carbidic.

As stated above, tin or lead added to coke-free platinum also produced shifts of the CO band to lower frequencies due to electronic interaction between the two metal components. We note that platinum is modified by coke in a similar way. On the other hand, high coverages on coked platinum shift back the CO band frequency to the value with clean Pt at high coverages (Table 3, cf. ν^1_{CO} for the clean and coked monometallic catalysts). These results are consistent with the proposed model of a working Pt catalyst (*24*). In our experiments the first doses of CO are adsorbed on modified Pt atoms (these may be individual atoms or peripheral ones in Pt ensembles of sites). As platinum ensembles are saturated by carbon monoxide (P_{CO} = 10 Torr) the red shift is compensated by a coverage-induced shift to higher frequencies and the IR spectrum resembles that of clean platinum. With the bimetallic catalysts no appreciable shift due to coke deposits was found (Table 3, cf. ν^2_{CO} for the clean and coked bimetallic samples). It may be assumed that the modification of platinum by coke is obscured in this case by the interaction between platinum and tin.

Chemisorption and IR data on the coked catalysts can be correlated with a simple geometric model. As already mentioned, the IR spectra of CO adsorbed on the Pt–Sn/Al_2O_3 catalysts are characterized by the absence of the 1850-cm^{-1} band which is attributed to multiply bonded CO molecuels. According to the geometric effect, the multiple-atom sites are destroyed by the inactive metal, whereas smaller ensembles remain more or less unchanged. The band at 1850 cm^{-1} was not observed on the coked monometallic catalyst either, and hence one has to conclude that coke acts in a similar manner to tin. This conclusion is confirmed by the behavior of the H_{ad}/CO_{ad} ratios with both the mono- and bimetallic catalysts after coking. Predominant blocking of multiple-atom sites should increase the total number of adsorbed CO molecules with respect to the hydrogen atoms which occupy only single-atom sites, as shown in Scheme 2.



SCHEME 2

Therefore the H_{ad}/CO_{ad} ratios should decrease with increased coking on Pt/Al_2O_3 (Fig. 4). Moreover with the bimetallic catalyst the sites for multiply bonded CO are destroyed by alloying. Hence the H_{ad}/CO_{ad} ratios with the clean bimetallic catalyst should be lower than those with the monometallic catalyst and should not be affected by coking (Fig. 4). These results indicate that the geometry of the platinum surface is modified by tin and by carbon in a similar way. This is in accordance with previous conclusions (*25, 26*).

CONCLUSIONS

1. Gravimetric measurements show interesting features concerning the chemisorption of ethylene, 1-hexene, and benzene on alumina-supported Pt and Pt–Sn catalysts. Thus benzene chemisorption is slightly enhanced while ethylene and 1-hexene uptakes are decreased with the Pt–Sn catalysts as compared with the monometallic sample. An adsorption model for benzene is proposed with flat and tilted chemisorbed species on Pt and Pt–Sn, respectively.

2. From gravimetric measurements and catalytic experiments a correlation was found between the reactivity of the adsorbed hydrocarbon species towards hydrogen and the hydrogenation rates of the same hydrocarbons on Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts. This is an example of how chemisorption data can provide direct information about the behavior of certain compounds in a particular catalytic reaction.

3. Combined infrared and chemisorption studies of CO adsorption on alumina-supported Pt–Sn and Pt–Pb catalysts (*5*) reveal a number of results which cannot be ex-

plained by a model of simple dilution of the platinum atoms by another metal (*27*). In the main these results are:

(i) A variable red shift of the CO band with the Pt–Sn and Pt–Pb catalysts for platinum surfaces of similar magnitude with respect to carbon monoxide and hydrogen chemisorption;

(ii) increased reversible CO adsorption consistent with changes of the nature of the Pt–CO chemisorption bond;

(iii) difference in the hysteresis of the I_r–θ_{CO} curves between the adsorption and desorption sequences with Pt–Sn/Al_2O_3 and Pt–Pb/Al_2O_3 samples;

(iv) the effect of CO and ethylene coadsorption on the CO band frequency is more pronounced with Pt–Sn/Al_2O_3 than Pt–Pb/Al_2O_3;

(v) enhanced integrated intensities of the CO band with the bimetallic catalysts relative to the monometallic sample.

On the other hand, the IR results from both 1-hexene and CO adsorption demonstrate that geometric effects are also operating with the bimetallic catalysts. Unlike some authors (*28*), we believe that the geometric factors in catalysis should not be disregarded. Both the electronic and geometric effects play a definite role and they are in a close relation. Their separation, very frequently used in the catalytic terminology, is only conventional.

4. The most active sites for hydrocarbon decomposition on the platinum surface are the same as those on which CO is multiply bonded. They are blocked by carbon as well as by tin. The IR results concerning CO adsorption on coked platinum surfaces are consistent with the model of a working platinum catalyst proposed by Davis *et al.* (*24*).

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