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Method for Metal Dispersion Measurements in Bimetallic Pt–Sn/Al_2O_3 Catalysts

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A method for metal dispersion measurement in bimetallic Pt–Sn/Al_2O_3 catalysts using a combination of nonactivated and activated H_2/O_2 chemisorptive titrations has been attempted. Fractions of dispersed, unalloyed Pt, Pt(U), alloyed Pt, Pt(A) and alloyed Sn, Sn(A) may be determined by this method. The Pt(A) and Sn(A) contents of the catalysts correspond to a mole ratio (Pt/Sn) ≈ 1, (for catalysts containing 0.4 wt% Pt and Sn content ranging such that the atomic ratio of Sn to Pt varies from 0.25–8, in steps) indicating possible formation of an alloy phase, PtSn (1 : 1 mole basis). Turnover numbers for dehydrogenation of *n*-dodecane indicate that Sn increases overall dispersion of Pt by dilution/ensemble effects. Increasing the Sn : Pt ratio to 16 results in decreased dispersion. Typical trends in H_2/O_2 uptakes with respect to titration cycles for bimetallic Pt–Sn catalysts vis a vis monometallic Pt/Al_2O_3 catalysts are discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Pt–Sn bimetallic catalysts are widely used for reforming and dehydrogenation of hydrocarbons because of their better performance in terms of activity and stability when compared to monometallic Pt/Al_2O_3 catalysts. Method for determination of dispersion of Pt by H_2/O_2 titration is reasonably well established in the case of monometallic Pt/Al_2O_3 catalysts (1). Application of the same, to bimetallic Pt–Sn/Al_2O_3 catalysts, as reported in literature, results in markedly lower uptake of H_2, suggesting lower Pt metal dispersion, whereas other techniques viz. TEM (2), in contrast, show a much higher dispersion than for the monometallic catalyst. Several other studies as described below, pertain to Pt–Sn catalysts that vary widely with respect to metal loadings and preparation techniques and bring out some interesting aspects.

Trends in H_2 and O_2 titration at ambient temperature. Volter *et al.* (3, 4), report a lower H_2 uptake in bimetallic Pt–Sn catalysts (Pt 0.5% w/w, Sn/Pt, atomic, 0–4, prepared by coimpregnation) than on monometallic Pt/Al_2O_3 catalysts. Results of Gault *et al.* (Pt 10%, Sn 0.2–5% w/w, prepared by successive impregnation) (2) and Balakrishnan and Schwank (Pt 1%, Sn 0.1–5% w/w, prepared by coimpregnation) (5) show that, H_2 uptake passes through a maximum with increasing Sn : Pt ratio. The decrease in H_2 uptake is attributed to alloying of part of the Sn with Pt resulting in dilution/ensemble effects by these authors. Oxygen uptakes, much higher than those for Pt/Al_2O_3, are reported with increasing Sn content. Where this uptake is irreversible, it has been considered to be by reduced Sn. Muller *et al.* (Pt 0.35%, Sn 0–1.4% w/w, prepared by successive impregnation) (6), however, have observed a linear reversible increase in O_2 uptake, with cycles and attribute it to reaction with H_2 spilled over from Pt to Sn.

Oxidation state of Sn. Sn is reported to be stabilized as Sn(II) on Al_2O_3 by Gault *et al.* (2), Sexton *et al.* (Pt 0.5%, Sn 0.2–6.3% w/w, prepared by successive impregnation) (7) and Balakrishnan and Schwank (5), whereas it is reported to reduce to Sn(0) on SiO_2, by the latter as well as by Dautzenberg *et al.* (8). Lieske and Volter (Pt 0.5–1.0%, Sn 0.3–1.2% w/w, prepared by coimpregnation) (9) attribute presence of Sn(0) to weak metal-support interaction, and Sn(II) to strong interaction.

Alloy formation between Pt and Sn. Muller *et al.* (6) report absence of alloy formation, while several others have identified Pt–Sn alloys, through various techniques. Davis and co-workers have identified Pt–Sn alloys in Pt–Sn/Al_2O_3 catalyst by electron microdiffraction (Pt : Sn 1 : 3, prepared by coimpregnation and coprecipitation) (10), in situ XRD (Pt 0.6% w/w, coimpregnated as Pt–Sn complex) (11), (Pt : Sn 1 : 1 to 1 : 8, prepared by coimpregnation) (12), XPS (Pt : Sn 1 : 1 to 1 : 8 prepared by coimpregnation) (13) and Mossbauer studies (Pt 1% w/w, Pt/Sn 1–8 prepared by coimpregnation) (14), and observe that the Pt_xSn_y (where $x = y = 1$) alloy content increases with Sn content of the catalyst. Sinfelt and co-workers (Pt 1.1%, Sn 1.2% w/w, prepared by cogelling of Sn with alumina followed by Pt impregnation) (15) using EXAFS technique report that Pt clusters are finely dispersed on an overlayer of Sn(II) on Al_2O_3, whereas bimetallic Pt–Sn entities are formed on SiO_2. Castro *et al.* (16) observe formation of Pt–Sn alloy on successive oxidation–reduc-

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tion, in catalysts prepared by coimpregnation, deposition of Pt–Sn complex and by successive impregnation in which Pt is loaded first followed by Sn (Pt 0.2–0.3%, Sn 0.3% w/w). Patents on Pt–Sn catalysts also describe the use of preparation methods like coprecipitation, coimpregnation, and Pt–Sn complex routes to obtain catalysts with better performance (17).

H_2/O_2 titration at temperatures higher than ambient. Volter *et al.* (3, 4) have attempted titrations at temperatures up to 573 K, in addition to ambient temperature. A small increase in H_2 uptake observed by them at higher temperature, is attributed to a small increase in dispersity or spill over to Sn. Van der Avoird (18) has shown that an increase in distance between adjacent Pt atoms shifts the mechanism of deuterium (or hydrogen) chemisorption from a nonactivated to activated process (the potential well becoming less favorable for nonactivated dissociative chemisorption). Verbeek and Sachtler (19) have studied chemisorption of D_2 on ordered Pt–Sn alloy phases Pt_3Sn, PtSn, and $PtSn_2$ and report low coverage of deuterium on these alloys due to either (i) change in mechanism from nonactivated to activated chemisorption or (ii) a strong ligand effect due to electron transfer from Sn to Pt. They favor the latter factor on the basis of their observation that the amount of deuterium absorbed being half that of ethene adsorbed (when the expected value should have been equal), had the former factor been the cause for lower chemisorption of D_2).

Thus a review of literature shows: (i) partial alloy formation between Pt and Sn, in bimetallic Pt–Sn/Al_2O_3 catalysts, preferably when the catalyst is prepared by coimpregnation of Pt and Sn (ii) differences in extent of uptakes of H_2/O_2 when compared with monometallic Pt–Al_2O_3 catalysts, attributed to alloying, (iii) higher uptakes of H_2 when measured at temperatures higher than ambient, possibly due to activated chemisorption. These studies, while revealing important insights into bimetallic catalysts, however, do not yield a reliable method for metal dispersion measurement in bimetallic Pt–Sn/Al_2O_3 catalysts. The main reason for this appears to be attempts at measuring dispersion by titration at ambient temperature, like in the case of monometallic Pt catalysts. Volter *et al.* (4), and Burch (20) have attempted to correlate the amount of H_2 chemisorbed dissociatively, between 273 and 573 K (activated chemisorption), with catalytic activity. The latter has linked higher H_2 uptakes at temperatures above ambient to higher metal dispersion. However, attempts have not been made in the direction of combining the results of nonactivated chemisorption (at ambient temperature) with those of activated chemisorption (at a suitable higher temperature) and to analyze these data in terms of different or additional species reacting at the higher temperature.

The present work describes such a method. It allows for determination of dispersion of alloyed Pt, alloyed Sn and unalloyed Pt and Sn in bimetallic Pt–Sn/Al_2O_3 catalysts. Typical trends in amount of H_2/O_2 chemisorption as a function of Sn/Pt atomic ratio of the catalyst are discussed. An attempt has also been made to determine the fractions of alloyed metals (Pt and Sn) and hence the alloy composition. It has also been attempted to correlate the dispersion of Pt, as determined by the method described in this work, with catalytic activity for dehydrogenation of higher paraffins.

METHODS

Catalyst preparation. Catalysts of composition 0.4 wt% Pt – x wt% Sn/γ–Al_2O_3 were prepared, where x varies as 0.0, 0.06, 0.12, 0.24, 0.49, 0.9, 1.94, and 3.88. Chloride content of the catalysts was between 1.6–1.8 wt%. The catalysts were coded S-1 to S-7 and S-9. Another catalyst S-8, containing 0.49 wt% Sn on alumina was also prepared. Spheroidal alumina (SMR-14-2141), supplied by Davison Chemicals (Baltimore, MD), was used as the support. Its particle diameter was 1.4–1.7 mm, bulk density 0.38 g/ml and BET surface area 203 m^2/g. Source of Pt was H_2PtCl_6 (aq). Sn was used as a solution of the metal, purity 99.99%, in A.R Grade HCl. The incipient wetness method, involving coimpregnation of the active phase precursors onto the support was adopted. An acidic mixture of the salt solutions of Pt and Sn (in the proportion required for the desired composition of the catalyst) along with distilled water to makeup for the pore volume was impregnated onto the alumina. This was followed by drying at 110°C for 4 h and calcination in flowing air at 500°C for 4 h.

Metal dispersion measurement. The pulse gas chromatographic technique was used. The assembly was all stainless steel (SS 316). The pulse volume was 0.080 ml. It was ascertained by carrying out blank runs that the steel reactor neither chemisorbed nor desorbed measurable quantities of the reactant gases at the temperatures of measurement. The H_2 and O_2 used for the study were all high purity gases, 99.999%, supplied by M/s Indian Oxygen Ltd. (Bombay). Argon (used as carrier gas) supplied by M/s GSFC Baroda, India, with purity 99.99% was further purified by passage through a copper trap to free it from trace O_2 impurities. The following abbreviations have been adopted in the subsequent text. $(HT\#)_\$$ and $(OT\#)_\$$ represent H_2 and O_2 titers respectively, the numeral # within the brackets refers to the cycle number and the numeral subscript \$ refers to the temperature at which the said titration was conducted viz. 25 or 150°C. The term dispersion, as used in the text, refers to the fraction of metal atoms accessible to H_2/O_2 titration.

For dispersion measurement the catalyst samples were reduced in flowing H_2 at 150°C, 5 h and 470°C, 1 h prior to cooling to 25°C. Titration OT1, with O_2 was carried out first until surface saturation (as detected from the gas

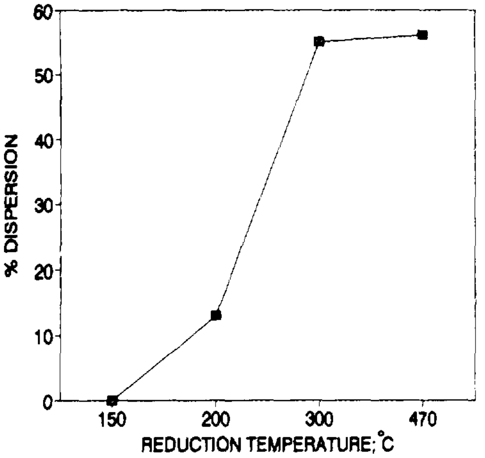

FIG. 1. Effect of reduction temperature on metal dispersion in monometallic Pt/Al_2O_3 catalyst.

TABLE 1

H_2/O_2 Uptakes, (ml NTP/g Catalyst) at 25 and 150°C as a Function of Sn : Pt (Atomic)

Catalyst code	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Sn/Pt	0	0.25	0.5	1.0	2.0	4.0	8.0		16.0
Uptake at 25°C									
HTI	0.345	0.363	0.292	0.338	0.292	0.290	0.260	0	0.085
OT1	0.191	0.307	0.317	0.397	0.337	0.437	0.455	0.025	0.404
OT2	0.201	0.209	0.197	0.218	0.144	0.199	0.164	0	0.078
Uptake at 150°C									
HT1	0.388	0.524	0.462	0.619	0.593	0.657	0.733	0	0.433
OT1	0.215	0.392	0.407	0.545	0.484	0.613	0.686	0.06	0.554
OT2	0.223	0.299	0.294	0.346	0.291	0.373	0.402	0	0.271

chromatographic results of the gas exiting the reactor). This was followed by titration with H_2, HT1. Six such separate H_2/O_2 cycles were carried out alternately for each catalyst at 25°C. After this the catalyst was rereduced at 470°C in flowing H_2 for 1 h and cooled to 150°C for titration with H_2/O_2. It was ascertained with a freshly reduced sample (cooled straight to 150°C, for H_2/O_2 titration), that rereduction did not affect chemisorption properties of the sample. Chemisorption measurement at temperatures higher than 25°C was considered on the basis of literature (2, 4) and after independent observation that Pt–Sn bimetallic catalysts chemisorb larger quantities of H_2/O_2 at higher temperatures than monometallic Pt/Al_2O_3 catalysts, possibly due to activated chemisorption.

Catalytic activity. A fixed bed tubular, continuous, axial flow reactor was used for this purpose. The catalyst (0.6 g) was reduced in pure H_2 at 470°C for 2 h prior to feeding the reactant. Reaction conditions were: temperature 450°C, liquid hourly space velocity (LHSV) 30 h^{-1}, H_2 : HC 6 (molar), pressure atmospheric. The products were analyzed with a GLC using a 9 m × 1/8″ SS column packed with 25% Poly phenyl ether on Chromosorb P 80-100 mesh. Turnover number (TON) of the catalysts for dehydrogenation of n-dodecane was calculated from initial rate data.

RESULTS AND DISCUSSION

Monometallic Pt–Al_2O_3 catalysts. Dispersion of Pt, when measured as a function of the reduction temperature of the catalyst (Fig. 1), increases with reduction temperature up to 300°C beyond which it remains constant $(H/Pt)_{25°C} \approx 0.53$ up to 470°C, (reduction temperature used in this work). The ratio HT : OT is the same at titration temperatures 25 and 150°C, therefore it can be safely assumed that the chemisorption process is the same at temperatures $\leq 150°C$. Since the amount of gas chemisorbed at 25°C and 150°C is comparable (refer to Table 1), activated chemisorption on monometallic catalysts is very little, at least up to 150°C.

Sn–Al_2O_3 catalysts. Catalyst S-8, containing 0.49 wt% Sn on alumina, did not show any uptake of H_2 at 25°C and 150°C after reduction at 470°C. However, small extent of O_2 uptake ≈ 0.065 ml NTP/g was observed. Experiment with alumina alone showed that this uptake is due to impurities in alumina. A correction was made for this uptake for other catalysts studied in this work. When reduced at 550°C, this catalyst showed O_2 uptake, indicating reduction of Sn. The bimetallic catalysts (Pt–Sn/Al_2O_3) however, showed good uptakes of both H_2/O_2 after reduction at 470°C. Thus, Pt seems to be essential for the reduction of Sn on alumina at temperatures up to 470°C.

Pt–Sn/Al_2O_3 bimetallic catalysts. The reaction stoichiometries for Pt and Sn are shown below in brackets alongside the chemical equations. Different possible stoichiometric reactions were considered in the case of Sn.

OT1; O_2 titration (first cycle)
$2\,Pt \ldots H + 1.5\,O_2 \rightarrow 2\,Pt \ldots O + H_2O$ (OT : Pt 0.75 : 1)
$Sn^0 + 0.5\,O_2 \rightarrow SnO$ (OT : Sn 0.5 : 1)
$Sn^0 + O_2 \rightarrow SnO_2$ (OT : Sn 1 : 1)
$2\,Sn \ldots H + 1.5\,O_2 \rightarrow 2\,SnO + H_2O$ (OT : Sn 0.75 : 1)
$2\,Sn \ldots H + 2.5\,O_2 \rightarrow 2\,SnO_2 + H_2O$ (OT : Sn 1.25 : 1)
$SnO + 0.5\,O_2 \rightarrow SnO_2$ (OT : Sn 0.5 : 1)
HT1; H_2 titration (first cycle)
$Pt \ldots O + 1.5\,H_2 \rightarrow Pt \ldots H + H_2O$ (HT : Pt 1.5 : 1)
OT2; O_2 titration (second cycle)
$2\,Pt \ldots H + 1.5\,O_2 \rightarrow 2\,Pt \ldots O + H_2O$ (OT : Pt 0.75 : 1)

The following assumptions have been made:

(i) Part of the Pt and Sn form an alloy on reduction of the catalyst in H_2 at 470°C. This has been amply demonstrated in literature (10–14, 16) and further confirmed by experiments on physical mixtures (last paragraph of results and discussion section). The catalyst, on reduction could possibly contain unalloyed Pt, unalloyed Sn, alloyed Pt–Sn (Pt_xSn_y) on Al_2O_3.

(ii) Based on the chemisorption behavior exhibited by the bimetallic Pt–Sn/Al_2O_3 catalyst, the above phases are assumed to react with H_2/O_2 in the manner shown below.

Titer	At 25°C	At 150°C
OT1	Unalloyed Pt + Alloyed Sn	Unalloyed Pt + alloyed Pt + alloyed Sn
HT1	Unalloyed Pt	Unalloyed Pt + alloyed Pt
OT2	Unalloyed Pt	Unalloyed Pt + alloyed Pt

Method for computation of metal dispersion. From the reaction scheme shown above the following procedure is adopted for determining the dispersion of Pt–Sn/Al_2O_3 catalyst:

1. Measure Pt(U) (fraction of dispersed unalloyed Pt) from $(HT1)_{25}$, i.e., HT1 at 25°C.
2. Measure Pt(A) (fraction of dispersed alloyed Pt) from the difference $(HT1)_{150}$–$(HT1)_{25}$.
3. Measure Pt(A) (fraction of dispersed alloyed Pt) from $(OT1)_{150}$–$(OT1)_{25}$ and also from $(OT2)_{150}$–$(OT2)_{25}$ and compare these values with the value estimated from the difference $(HT1)_{150}$–$(HT1)_{25}$ in step 2 above. The three values should match. This serves as confirmation.
4. Measure Pt(T), (fraction of total dispersed Pt, both alloyed and unalloyed) independently, from the titer $(HT1)_{150}$. This value should match the sum of individual dispersions of unalloyed Pt, Pt(U) (calculated from step 1) and alloyed Pt, Pt(A) (calculated from step 3, O_2 titer).
5. Measure Sn(A) (fraction of dispersed alloyed Sn) from the difference $(OT1)_{25}$–$(OT2)_{25}$ and also from $(OT1)_{150}$–$(OT2)_{150}$ and compare the two for confirmation. These two values should match.
6. Balance Sn is considered to be unalloyed Sn.

Dispersion of Pt at 25 and 150°C was calculated from the H_2/O_2 titration data using the relation HT : OT : Pt $\approx$ 1.5 : 0.75 : 1 established by Boudart and co-workers (1), for chemisorption on monometallic Pt catalysts at room temperature (25°C). The same stoichiometry was used for computation of both unalloyed and alloyed Pt.

As shown in Fig. 2, titer HT1, at 25°C the quantity of H_2 chemisorbed on the bimetallic Pt–Sn/Al_2O_3 catalysts decreases with increasing Sn : Pt atomic ratio of the catalyst, whereas at 150°C the amount increases. The second cycle O_2 uptake, Fig. 3, titer OT2, attributed to uptake by Pt alone, also shows a similar trend. It decreases with Sn : Pt ratio at 25°C but increases at 150°C. These observations could be explained on the basis of a transition from nonactivated to an activated mechanism of chemisorption. Hence in the above scheme only unalloyed Pt is assumed to react at 25°C, whereas both alloyed and unalloyed Pt react at 150°C with H_2.The uptake in the first cycle oxygen titer, OT1, in Fig. 3, shows an increasing trend with Sn : Pt (atomic) ratio of the catalyst, at both 25 and 150°C, which is attributed to uptake by alloyed Sn, in addition to Pt.

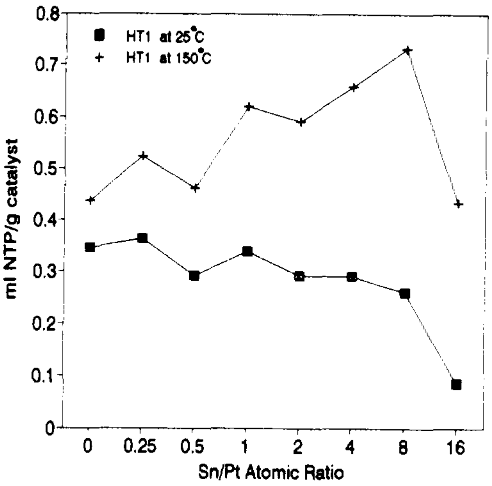

FIG. 2. First cycle H_2 uptake, at 25 and 150°C, as a function of Sn : Pt atomic ratio of catalyst.

In Pt–Sn bimetallic catalysts with composition Sn : Pt (atomic) in the range 0.5–8, dispersion of unalloyed Pt, Pt(U), as measured from $(HT1)_{25}$ is observed to be less by $\approx$10–12% vis a vis Pt/Al_2O_3 (Sn : Pt 0), refer to (Table

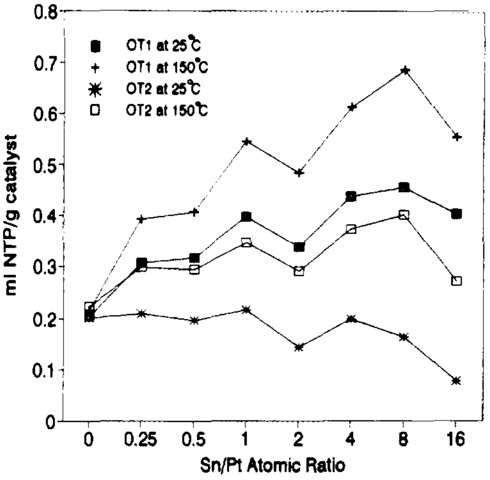

FIG. 3. First and second cycle O_2 uptakes at 25 and 150°C as a function of Sn : Pt atomic ratio of catalyst.

TABLE 2

Comparison of Dispersion of Pt and Sn Calculated from Various Proposed Equations

Sn/Pt (atomic) of catalyst	Fraction of dispersed metal						
	Unalloyed Pt, Pt(U)	Alloyed Pt Pt(A)			Total Pt Pt(T)	Alloyed Sn Sn(A)	
	Eq. [1]	Eq. [2]	Eq. [3]	Eq. [4]	Eq [7]	Eq. [5]	Eq. [6]
0.00	0.53	0.00	0.00	0.00	0.53	0.00	0.00
0.25	0.52	0.23	0.25	0.26	0.76	0.86	0.82
0.50	0.42	0.25	0.26	0.28	0.67	0.53	0.50
1.0	0.49	0.41	0.43	0.37	0.90	0.39	0.44
2.0	0.42	0.44	0.43	0.42	0.86	0.21	0.21
4.0	0.42	0.53	0.51	0.50	0.95	0.13	0.13
8.0	0.38	0.68	0.67	0.69	1.06	0.08	0.08
16.0	0.12	0.51	0.44	0.56	0.64	0.04	0.04

$(HT1)_{25} = Pt(U)$ Eq. [1]
$(HT1)_{150}-(HT1)_{25} = Pt(A)$ Eq. [2]
$(OT1)_{150}-(OT1)_{25} = Pt(A)$ Eq. [3]
$(OT2)_{150}-(OT2)_{25} = Pt(A)$ Eq. [4]
$(OT1)_{25}-(OT2)_{25} = Sn(A)$ Eq. [5]
$(OT1)_{150}-(OT2)_{150} = Sn(A)$ Eq. [6]
$(HT1)_{150} = Pt(T)$ Eq. [7]

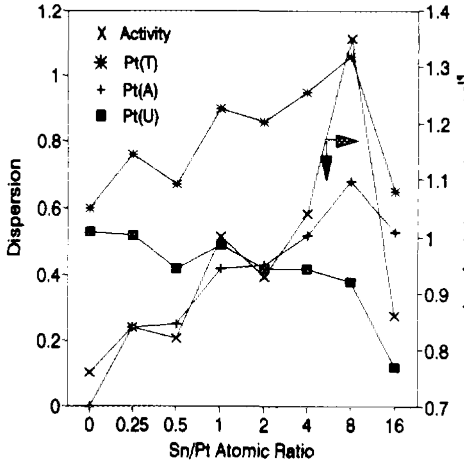

FIG. 4. Pt metal dispersion and activity for dehydrogenation of *n*-dodecane as a function of Sn : Pt atomic ratio of catalyst.

2). However, the bimetallic catalysts exhibit higher conversions (Table 3) for dehydrogenation of n-dodecane. The fraction of dispersed alloyed Pt, Pt(A), as calculated from the difference in H_2/O_2 uptakes viz. $(HT1)_{150}-(HT1)_{25}$ or $(OT1)_{150}-(OT1)_{25}$ (Table 2, Eqs. [2–4]) exhibits an increasing trend with Sn : Pt ratio, ≈0.25 at Sn : Pt 0.25 to 0.5, followed by a steady increase to ≈0.68 at Sn : Pt 8. Dispersion of total Pt, Pt(T) (both unalloyed and alloyed Pt included) calculated from titration $(HT1)_{150}$ (Table 2, Eq. [7]) also increases with Sn : Pt ratio. This increase was observed to take place in two stages, from ≈0.53 in the case of Pt/Al$_2$O$_3$ (Sn : Pt = 0) to up to ≈0.70 for Sn : Pt atomic ratio in the range 0.25 to 0.5 and further to ≈1.0 at Sn : Pt 8. As seen from Fig. 4 catalytic activity for dehydrogenation of *n*-dodecane also increases steadily with Sn : Pt ratio of the catalyst.

TABLE 3

Pt–Sn Alloy Composition and Turnover Number for *n*-Dodecane Dehydrogenation as a Function of Sn : Pt Atomic Ratio of Catalyst

	Catalyst code								
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Pt wt%	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.	0.4
Sn wt %	0	0.06	0.12	0.24	0.49	0.97	1.94	0.49	3.88
Sn : Pt (atomic)	0	0.25	0.50	1.0	2.0	4.0	8.0	—	16.0
Pt(A)/Sn(A) (mole)	—	1.15	0.98	1.01	1.03	1.01	1.09	—	0.83
Conversion, %	10.6	11.8	11.4	14.0	13.0	14.6	18.9		12.0
N_p	Molecules reacting/s/g cat. × 10^{18}								
	7.60	8.46	8.16	10.03	9.33	10.46	13.56	—	8.59
TON	Turnover number, molecules/site/s								
	1.02	0.90	0.98	0.90	0.88	0.89	1.03	—	1.07

Further increase in the Sn : Pt atomic ratio to 16 leads to a drastic decrease in dispersion of Pt(U) to 0.12, Pt(A) to 0.52 and Pt(T) to 0.64 (Table 2). It is seen from Table 3 that the mole ratio of alloyed Pt : alloyed Sn, Pt(A)/Sn(A), (computed from the catalyst composition and the dispersion) which remains almost constant at ≈1.0 (over the catalyst composition range of Sn : Pt, atomic 0.25 to 8) drops to 0.83 at Sn : Pt ≈ 16. From these results it is inferred that in Pt–Sn/Al$_2$O$_3$ catalysts, prepared by coimpregnation, an alloy phase Pt_xSn_y (where $x = y = 1$), active for dehydrogenation, is formed in increasing concentration over the catalyst composition range Sn : Pt, (atomic), from 0.25 to 8. On further increasing the Sn : Pt (atomic) ratio to 16, (catalyst S-9) other alloy phases Pt_xSn_y (where $y > x$) also seem to form, resulting in a drop in Pt(A)/Sn(A) mole ratio to 0.83 (Table 3). The catalyst activity N_p (Table 3) also decreases but the turnover number, TON, remains constant, indicating that Sn rich alloys Pt_xSn_y ($y > x$) may be inactive for dehydrogenation. A slight deviation in the case of catalyst S-5, Sn : Pt 2, (which shows lower activity than S-4 Sn : Pt 1) was found to be reproducible but lacks explanation. The results are in very good agreement with those of Davis and co-workers (10, 21) who, recently, by using EMD and other techniques (other than H_2/O_2 titration), have detected the alloy phase to be predominantly PtSn (hcp structure), in addition to small quantities of $PtSn_2$ and Pt_2Sn_3.

In Table 3 the correlation of the dispersion, as measured by this method, with catalytic activity for dehydrogenation of *n*-dodecane, expressed as turnover number (TON), is shown. TON is defined as molecules reacting per active site per unit time. Since both the monometallic Pt/Al_2O_3 and bimetallic Pt–Sn/Al_2O_3 catalysts exhibit activity for dehydrogenation, total Pt dispersion Pt(T) was used in the calculation. As seen from Table 3, TON does not differ significantly from monometallic Pt/Al_2O_3 catalyst (S-1) to bimetallic Pt–Sn/Al_2O_3 catalysts (S2–S-9), over the entire range of catalyst composition Sn : Pt (atomic) 0–16. This indicates that Sn increases total Pt dispersion up to Sn : Pt (atomic) 8, (by dilution/ensemble effect), thereby increasing the activity of the catalyst for dehydrogenation of *n*-dodecane due to an increase in number of active sites, rather than by modification of specific activity. Ligand and electronic effects may be playing a role in improving stability of the catalyst. It is well known that Sn increases the stability of catalysts by suppressing deactivation (9). In the present work, increase in Sn content of the catalyst was observed to markedly improve stability as shown below. The activity of the catalysts at the 9th hour on stream (relative to initial activity) increased with increasing Sn : Pt as follows:

Catalyst:	S-1	S-2	S-3	S-4	S-5	S-6	S-7
Sn : Pt (atomic):	0	0.25	0.5	1.0	2.0	4.0	8.0
Activity 9th hour:	0.32	0.34	0.34	0.50	0.47	0.79	0.79

Podkletnova *et al.* (22) have used ESCA to show a partial transfer of electron density from Pt to the promoter in bimetallic Pt–Sn/alumina catalysts. Kogan *et al.* (23) have attributed the promotion effect of Sn to result in a shift in mechanism of coke formation on both metal (Pt) and support, to one predominantly on the support (alumina).

Amongst other interesting observations, was a decrease in H_2/O_2 uptakes with increasing number of titration cycles. The uptake could be restored to that in the first cycle by heating the catalyst in inert carrier, Argon, at 400°C for 1 h or at 150°C for 4 h. Muller *et al.* (6) report that the H_2O formed during the titration deactivates some of the Pt towards reaction with H_2/O_2. We believe this is responsible for the decrease in H_2 (after the first cycle, HT1) and O_2 uptakes (after the second cycle, OT2) with increasing cycles. Typical trends are shown in Figs. 5a and 5b for hydrogen and oxygen respectively. The decrease in uptakes is gradual. Similar behavior was also observed with monometallic Pt/Al_2O_3 catalysts, but over much longer cycle numbers compared to the alumina supported bimetallic Pt–Sn catalysts. Therefore only the first H_2 titer, $(HT1)_{150}$–$(HT1)_{25}$ yields the correct uptake of H_2 by alloyed Pt.

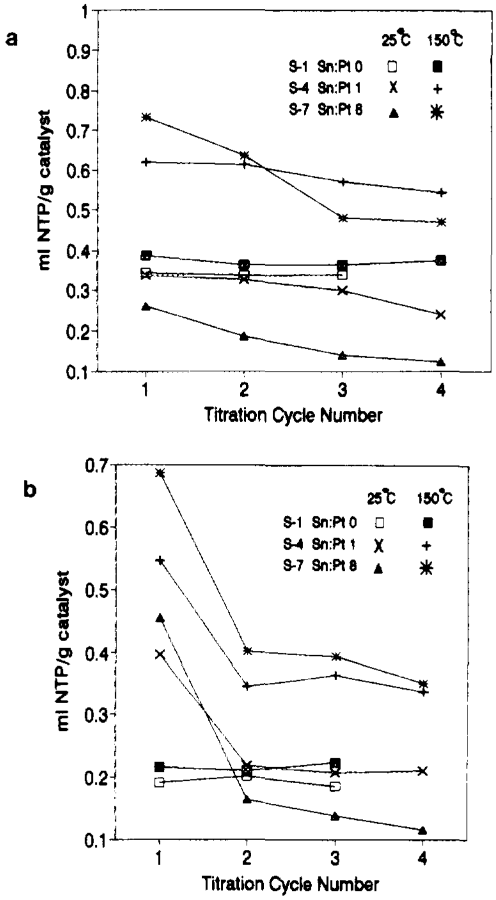

FIG. 5. (a) Typical trends in H_2 uptake by catalysts at 25 and 150°C with increasing titration cycle number. (b) Typical trends in O_2 uptake by catalysts at 25 and at 150°C with increasing titration cycle number.

Assumption for irreversible titration of alloyed Sn in titer OT1 is based on the observation of a sharp decrease in O_2 uptake between the first (OT1) and second (OT2) cycles, at both 25° and 150°C, leading to a "L" shaped curve (Fig. 5b). This aspect was further confirmed through an experiment wherein the catalyst was not rereduced between measurements at 25 and 150°C, but directly heated to 150°C in Ar for 1 h (after titration at 25°C). Subsequent titrations at 150°C showed only a slight difference between the O_2 uptakes at the first (OT1) and second (OT2) cycles at 150°C. Hence, dispersion of alloyed Sn may be calculated from the difference in O_2 uptake in the first and second cycles viz. (OT1–OT2) at both 25 and 150°C. The results of dispersion calculations, refer to Table 4, suggest that the reoxidation of Sn involves principally $Sn^0 \longrightarrow SnO_2$ step, because, assumption of $Sn^0 \longrightarrow SnO$ yields dispersion $\gg$ 100% for catalysts with low Sn content, i.e., Pt : Sn > 2 (viz. S-2 and S-3). The other mechanisms have been ruled out because chemisorption of H on Sn (Sn . . . H) is neither reported nor was it observed on Sn/Al_2O_3 (catalyst S-8) in this work. This experiment also shows that the decrease in H_2 uptake with cycles and O_2 uptakes after the first cycle involve only Pt and not Sn.

TABLE 4

Dispersion of Sn Calculated at 25 and 150°C Assuming Various Stoichiometric Reactions

Catalyst code	Sn/Pt atomic	Fraction dispersed			
		$Sn^0 \rightarrow SnO$	$SnH \rightarrow SnO$	$Sn^0 \rightarrow SnO_2$	$SnH \rightarrow SnO_2$
		Temperature 25°C			
S-2	0.25	1.73	1.15	0.86	0.69
S-3	0.50	1.06	0.70	0.53	0.42
S-4	1.0	0.79	0.53	0.39	0.32
S-5	2.0	0.42	0.28	0.21	0.17
S-6	4.0	0.32	0.21	0.13	0.13
S-7	8.0	0.16	0.11	0.08	0.06
S-9	16.0	0.09	0.06	0.04	0.04
		Temperature 150°C			
S-2	0.25	1.64	1.09	0.82	0.65
S-3	0.50	0.99	0.66	0.50	0.40
S-4	1.0	0.88	0.59	0.44	0.35
S-5	2.0	0.42	0.28	0.21	0.17
S-6	4.0	0.31	0.20	0.13	0.12
S-7	8.0	0.15	0.10	0.08	0.06
S-9	16.0	0.08	0.05	0.04	0.03

Validity of the reaction scheme. Although the method has inherent limitations viz. relying only on the first H_2 (HT1) cycle and the first two (OT1, OT2) O_2 cycles, the method has advantages of calculation of alloyed metal contents from two separate data $(OT1\text{–}OT2)_{25}$ and $(OT1\text{–}OT2)_{150}$ for Sn and three separate data $((HT1)_{150}\text{–}(HT1)_{25})$ as well as $((OT1)_{150}\text{–}(OT1)_{25})$ or $((OT2)_{150}\text{–}(OT2)_{25})$ for Pt. The results in Table 2 show a good match between the fraction of alloyed Sn, Sn(A) (calculated using two different titer data, from Eq. (5) and (6) and for dispersed alloyed Pt content Pt(A) (calculated from Eqs. (2–4). The values of total Pt dispersion, Pt(T), as measured independently, from the titer $(HT1)_{150}$ are in good agreement with the sum of values Pt(U) (unalloyed Pt) and Pt(A) (alloyed Pt), each calculated from independent titer data. (Table 2). A good correlation is obtained between the measured dispersion and activity for *n*-dodecane dehydrogenation.

Physical mixtures of monometallic catalysts. Experiments were carried out with physical mixtures of the monometallic catalysts Pt-Al_2O_3 (S-1) and Sn-Al_2O_3 (S-8). The catalysts were taken in a 1 : 1 weight ratio (corresponding to a 1 : 2 Pt : Sn atomic ratio). Two sets of such mixtures were prepared. In the first set the catalysts were separately prereduced in H_2 at 470°C for 2 h prior to mixing and grinding. In the second set the fresh catalysts were mixed, ground, and subsequently reduced in H_2. H_2/O_2 titrations were carried out at both 25 and 150°C. The results for both sets of mixtures were identical to those obtained with the monometallic catalyst, Pt–Al_2O_3 alone, further strengthening the observation that difference in behavior of the bimetallic Pt–Sn catalyst is due to interaction between Pt and Sn, probably due to alloy formation and not due to physical interaction. This observation also rules out the possibility of spillover of H_2 from Pt to Sn or to the Al_2O_3 support.

CONCLUSIONS

In conclusion, dispersion of Pt–Sn bimetallic catalysts is readily measured from a combination of nonactivated (at 25°C) and activated (at 150°C) chemisorption data, rather than from the former alone. Reason apparently being the nonreactivity of alloyed Pt towards H_2/O_2 at ambient temperature. From the analysis of data, fractions of alloyed Pt, unalloyed Pt and alloyed Sn can be determined. The results can be confirmed by more than one independent data sets and hence seem to be reliable. Based on the molar quantities of Pt(A) and Sn(A) the stoichiometric composition of the alloy phase appears to be Pt–Sn (Pt : Sn 1 : 1) in this case. This alloy phase also catalyses dehydrogenation of paraffins. The turnover numbers for dehydrogenation of *n*-dodecane on monometallic Pt/Al_2O_3 and bimetallic Pt–Sn/Al_2O_3 catalysts are comparable, as shown in this work, and activity improvement is due, mainly to increased metal dispersion than improved specific activity. Typical trends in H_2/O_2 uptakes, viz. suppression in uptake of H_2 at 25°C, increased uptake at 150°C, increased uptakes of O_2 (first cycle) at both temperatures in Pt–Sn/alumina bimetallic catalysts are indicative of metallic interaction, through either alloying or dilution/ensemble effects between Pt and Sn.

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