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# Pt–Sn/$Al_2O_3$ catalysts: effect of catalyst preparation and chemisorption methods on $H_2$ and $O_2$ uptake

Pakornphant Chantaravitoon[a], Sumaeth Chavadej[a,*], Johannes Schwank[b]

[a] *The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA*

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## Abstract

Pulse and static hydrogen and oxygen chemisorption techniques for determining the platinum dispersion in bimetallic Pt–Sn catalysts were carried out and compared for a monometallic Pt/$Al_2O_3$ catalyst and a series of coimpregnated Pt–Sn catalysts containing 1 wt.% of Pt. The pulse chemisorption method gave lower uptakes of hydrogen and oxygen compared to the static volumetric chemisorption method. The differences in hydrogen and oxygen gas uptake behavior can be attributed to the different equilibration times provided by the two chemisorption methods. In the coimpregnated catalyst series, the O/Pt ratio increased with increasing Sn content. The H/Pt ratio, on the other hand, reached the maximum value at 0.1 wt.% Sn.

Pulse chemisorption was then used to evaluate how the preparation method affects platinum dispersion and chemisorption behavior. The alumina-supported catalyst series prepared by coimpregnation of Pt and Sn was compared with a series of catalysts prepared by sequential impregnation with tin first, followed by platinum as second component. Coimpregnation of the $Al_2O_3$ support with platinum and small amounts of tin facilitates high Pt dispersion, while sequential impregnation of the support with Sn first, followed by Pt, leads to much lower Pt dispersion.

*Keywords:* Platinum–tin; Bimetallic; Pulse chemisorption; Hydrogen adsorption; Catalyst preparation; Coimpregnation; Sequential impregnation

## 1. Introduction

Adding tin to platinum catalysts has proven to be beneficial for activity maintenance in applications such as catalytic reforming. The catalyst preparation method, especially the impregnation sequence, is known to affect the interaction of tin and platinum. Sexton et al. [1] found that a catalyst prepared by coprecipitation of Sn with alumina followed by impregnation of platinum achieved the maximum contact between Pt and ionic tin. This catalyst also had a uniform distribution of both species. Moreover, it gave the highest activity and selectivity in methylcyclopentane and cyclohexane conversion. Dautzenberg et al. [2] observed that the sequence of metal impregnation was an important factor at low tin content. They concluded that the modification of Pt–Sn alloy was more important than the effect of interaction of Pt with a tin(oxide)-modified support. Baronetti et al. [3] used three different preparation techniques for Pt–Sn/$Al_2O_3$ catalysts and characterized the samples by diffuse reflectance spectroscopy and temperature programmed reduction (TPR). Their results indicated that there was a strong interaction between Pt and Sn in catalysts prepared by coimpregnation and in catalysts prepared by sequential impregnation with Pt first, where a complex of $(PtCl_2(SnCl_3)_2)^{2-}$ was deposited on the alumina surface. However, when the catalysts were prepared by sequential impregnation with Sn first, the complex formation did not occur, and only Pt(IV) and Sn(IV) species were observed on the alumina surface. The TPR profile of a sequentially impregnated catalyst was similar to the sum of TPR profiles of the two monometallic samples ($Pt/Al_2O_3 + Sn/Al_2O_3$). They explained that Sn(II) deposited during the initial impregnation step was oxidized to Sn(IV) in the drying step, thereby preventing the formation of the $(PtCl_2(SnCl_3)_2)^{2-}$ complex when Pt(IV) was added as the second component, due to the weak interaction between $(PtCl_6)^{2-}$ and $(SnCl_6)^{2-}$ species.

Many research groups have worked on the characterization of the state of Sn, using various characterization methods such as chemisorption by static or pulse techniques [4–14], X-ray diffraction (XRD) [15], X-ray photoelectron spectroscopy (XPS) [1,8,16], Mössbauer spectroscopy [17,18], and TPR [19,20]. Srinivasan et al. [15] observed

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[*] Corresponding author. Tel.: +662-2184139; fax: +662-2154459.
*E-mail addresses:* sumaeth.c@chula.ac.th (S. Chavadej), schwank@engin.umich.edu (J. Schwank).

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alloy formation with a Pt:Sn stoichiometry of 1:1 by in situ XRD. Li et al. [17] showed that the fraction of Pt present in an alloy phase increased with increasing tin content, and an alloy richer in Sn than Pt:Sn = 1 : 1 was present on the silica support. Verbeek and Sachtler [21] investigated the surface composition of alloys of platinum and tin by adsorption and temperature programmed desorption (TPD) of deuterium and carbon monoxide. Based on TPD results, they referred to the ligand effect, which caused weakening of the chemisorptive bond of deuterium and carbon monoxide when the proportion of tin in the alloys increased. Static chemisorption of hydrogen and oxygen was used for investigating the surface of catalysts by several researchers. For example, Otter and Dautzenberg [12] studied the effect of hydrogen treatment at high temperatures (>500 °C) on $Pt/Al_2O_3$ catalysts. They attributed the decreasing amount of hydrogen chemisorption after reduction at high temperatures on highly dispersed platinum particles forming an alloy with the alumina support. Muller et al. [13] observed that the amount of oxygen adsorption on the Pt–Sn bimetallic catalysts was proportional to both the percentages of platinum and tin on the alumina support. They found no evidence for the metallic states of Sn or Pt–Sn alloys.

The first objective of this paper was to carry out and compare the accuracy of pulse and static hydrogen and oxygen chemisorption techniques on a monometallic $Pt/Al_2O_3$ catalyst and a series of coimpregnated Pt–Sn catalysts. The second objective was to evaluate how the preparation method affects Pt dispersion and chemisorption behavior, comparing alumina-supported catalysts prepared by coimpregnation of Pt and Sn with catalysts prepared by sequential impregnation with tin first.

## 2. Experimental methods

### 2.1. Catalyst preparation

In this work, two series of $Pt–Sn/Al_2O_3$ catalysts were investigated. The first series was prepared by coimpregnation of Degussa nonporous fumed alumina (BET surface area of 90 $m^2/g$) with acetone solution of $H_2PtCl_2$ (Aldrich) and $SnCl_2$ (Aldrich). This coimpregnated catalyst series has been extensively characterized [8]. The second series was prepared by sequential impregnation of the $Al_2O_3$ support with Sn first, followed by Pt, using the same precursors and solvent as in the previous work [8]. The nominal platinum loading was kept constant at 1 wt.% in all catalysts. In the coimpregnated series, the nominal tin loading varied from 0.1 to 1.0 wt.%. In the sequentially impregnated series, the nominal tin loading varied from 0.6 to 5 wt.%. Following impregnation, the catalysts were dried at 393 K and then calcined in air at 773 K for 2 h. After calcination, the catalysts were reduced for 5 h in flowing hydrogen at 673 K. The actual platinum, tin and chlorine contents of the catalysts were quantified by neutron activation analysis at the University of Michigan nuclear reactor laboratory. The catalyst samples were delivered via pneumatic tube to a location with an average neutron flux rate of $2.13 \times 10^{12}$ n/(cm$^2$ s) and exposed to irradiation for 1 min, followed by a 500 s count of gamma-activity after a 20 min decay. Calculations of elemental concentrations were based on comparisons with high-purity single-element standard reference materials. A summary of the results of neutron activation analysis is shown in Table 1.

Table 1
The metal loadings and chlorine content of Pt–Sn catalysts as determined by neutron activation analysis

| Catalyst (nominal wt.%) | Impregnation method | Component (wt.%) | | |
|---|---|---|---|---|
| | | Pt | Sn | Cl |
| 1.0 $Pt/Al_2O_3$ | | 0.99 | 0 | 0.72 |
| 1.0 Pt–0.1 $Sn/Al_2O_3$ | Coimpregnation | 0.96 | 0.14 | 0.97 |
| 1.0 Pt–0.5 $Sn/Al_2O_3$ | Coimpregnation | 1.00 | 0.53 | 1.00 |
| 1.0 Pt–1.0 $Sn/Al_2O_3$ | Coimpregnation | 0.89 | 0.99 | 0.97 |
| 1.0 Pt–0.6 $Sn/Al_2O_3$ | Sequential | 1.04 | 0.85 | 1.09 |
| 1.0 Pt–0.9 $Sn/Al_2O_3$ | Sequential | 1.03 | 0.96 | 1.05 |
| 1.0 Pt–1.5 $Sn/Al_2O_3$ | Sequential | 1.03 | 1.52 | 1.24 |
| 1.0 Pt–5.0 $Sn/Al_2O_3$ | Sequential | 1.12 | 4.18 | 1.01 |

### 2.2. Pulse chemisorption

Prior to pulse chemisorption, all samples were reduced in purified hydrogen at a flow rate of 15 ml/min for 2 h at 673 K. The temperature was controlled to ±1 °C by a temperature controller (Omega CN8000). The reduced samples were purged in purified nitrogen at 673 K for 30 min and then cooled to room temperature in nitrogen atmosphere. The chemisorption of hydrogen and oxygen was measured by using a gas chromatograph (HP 5890) with a thermal conductivity detector (TCD). Gas mixtures of 5% $H_2/N_2$ and 5% $O_2/N_2$ were used as adsorbates. Injections of these gas mixtures into a $N_2$ carrier gas stream flowing at 30 ml/min were made in 5 min intervals until no further gas uptake by the catalyst was observed as indicated by constant peak areas of the last few injections. The total amount of adsorption was calculated by adding the gas uptake observed in the series of gas injections until saturation was reached.

### 2.3. Static volumetric chemisorption

The details of the static volumetric chemisorption experiments have been described previously [8]. The catalysts were pre-reduced in a hydrogen flow of 15 cm$^3$/min at 673 K, followed by evacuation and static reduction at 673 K in a partial pressure of 33.3 kPa of research-grade $H_2$ for 3 h, followed by evacuation and a second exposure to 33.3 kPa of $H_2$ for 10 h at 673 K. Hydrogen was removed from the catalyst surface by evacuation at 693 K, followed by cooling of the catalyst sample to ambient temperature under dynamic vacuum. For both $H_2$ and $O_2$, two adsorption isotherms were collected. The first isotherm represented the total $H_2$ or $O_2$ uptake at 298 K. The second isotherm was obtained after removing the weakly adsorbed hydrogen or oxygen by evacuation at 298 K for 1 h.

## 3. Results and discussion

### *3.1. Comparison of pulse chemisorption and static chemisorption*

Table 2 shows the summary results of the amounts of hydrogen and oxygen adsorbed on the two series of Pt–Sn/$Al_2O_3$ catalysts using pulse chemisorption technique. The H/Pt ratio in the monometallic Pt/$Al_2O_3$ catalyst was 0.28. The coimpregnated sample containing 0.1 wt.% Sn exhibited a much larger hydrogen uptake, giving a H/Pt ratio of about 0.46, assuming that all the chemisorbed hydrogen is located on platinum surface sites. However, with further increase of tin content, the hydrogen uptake decreased, giving H/Pt ratios of about 0.3. These results show the same overall trends for hydrogen uptake versus tin content as the previous static volumetric chemisorption data reported by Balakrishnan and Schwank [8] for the same coimpregnated catalyst series. However, the amount of hydrogen uptake measured by the pulse chemisorption method was consistently lower by 10–20% than the uptake obtained by the static volumetric method (Fig. 1). These findings are in good agreement with Buyanova et al. [4,5] who compared a frontal chromatographic method with the static adsorption method. They found that on Pt/$Al_2O_3$ catalysts with Pt loadings of 0.50 and 0.45 wt.%, the hydrogen uptake determined from the chromatographic method was 6–19% smaller than that obtained by the static method.

Some of the differences in hydrogen uptake between the pulse and static methods may be attributed to small errors in the integration of the pulse chemisorption peak areas due to slight baseline drift. However, error analysis showed that in a worst-case scenario, these integration errors could cause not more than a 5% discrepancy. The remaining difference, therefore, would be inherently to the chemisorption method used. One of the differences accounting for the larger hydrogen uptake in static volumetric experiments could be the longer equilibration time provided. In Balakrishnan and Schwank's work [8], a significant portion of the adsorbed hydrogen was found to be weakly adsorbed. In their experiments, 40–45% of the adsorbed hydrogen was removed by

Table 2
Pulse chemisorption of hydrogen and oxygen on two series of Pt–Sn/$Al_2O_3$ catalysts compared with Pt/$Al_2O_3$ catalyst

| | Metal (wt.%) | Sn (at.%) | Sn/Pt (atomic ratio) | Gas uptake (cm$^3$ STP/g cat.) | | H/Pt | O/Pt |
|---|---|---|---|---|---|---|---|
| | | | | $H_2$ | $O_2$ | | |
| 1.0 Pt/$Al_2O_3$ | 0.99 | 0 | 0.00 | 0.1577 | 0.1115 | 0.2774 | 0.1962 |
| Coimpregnation | | | | | | | |
| 1.0 Pt–0.1 Sn/$Al_2O_3$ | 1.1 | 19 | 0.23 | 0.2533 | 0.2674 | 0.4596 | 0.4852 |
| 1.0 Pt–0.5 Sn/$Al_2O_3$ | 1.53 | 47 | 0.89 | 0.1843 | 0.3645 | 0.3210 | 0.6349 |
| 1.0 Pt–1.0 Sn/$Al_2O_3$ | 1.88 | 65 | 1.86 | 0.1467 | 0.3744 | 0.2872 | 0.7327 |
| Sequential impregnation (Sn first) | | | | | | | |
| 1.0 Pt–0.6 Sn/$Al_2O_3$ | 1.89 | 57 | 1.33 | 0.0839 | 0.1391 | 0.1405 | 0.2330 |
| 1.0 Pt–0.9 Sn/$Al_2O_3$ | 1.99 | 61 | 1.56 | 0.1073 | 0.2329 | 0.1815 | 0.3939 |
| 1.0 Pt–1.5 Sn/$Al_2O_3$ | 2.55 | 71 | 2.45 | 0.0881 | 0.3075 | 0.1490 | 0.5201 |
| 1.0 Pt–5.0 Sn/$Al_2O_3$ | 5.3 | 86 | 6.14 | 0.0278 | 0.0616 | 0.0433 | 0.0957 |

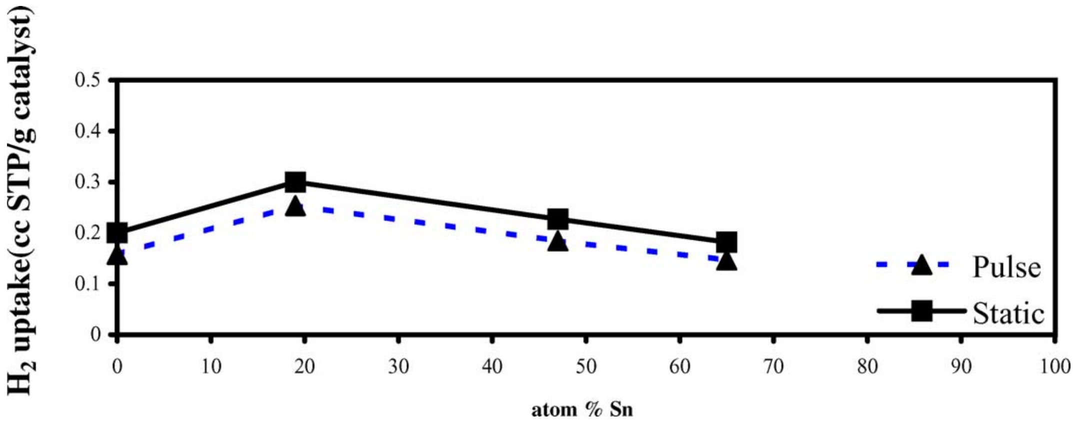

Fig. 1. Comparison of hydrogen uptake measured by the pulse and static volumetric chemisorption methods as a function of nominal tin loading.

evacuation for 1 h at room temperature. In the pulse experiments, the catalyst samples were flushed in flowing $N_2$ at room temperature for about 5 min between pulses of hydrogen. This means there is no equilibration time in pulse chemisorption. Given the relatively large fraction of weakly adsorbed hydrogen observed by static volumetric methods, it is conceivable that the experimental conditions in the pulse method might lead to different degrees of surface coverage of weakly adsorbed hydrogen.

On the monometallic 1% $Pt/Al_2O_3$ catalyst, the static volumetric method gave an atomic ratio of adsorbed oxygen to adsorbed hydrogen ($O_{ads}/H_{ads}$) equal to 0.73. In the pulse chemisorption method, the $O_{ads}/H_{ads}$ ratio was 0.71, showing good agreement between the two methods. It appears that the saturation coverage of oxygen on platinum is smaller than that of hydrogen. This observation agrees with the earlier work by Boudart and coworkers [22] reporting an $O_{ads}/H_{ads}$ ratio of 0.65 on unsupported platinum powder, and by Balakrishnan et al. [23] giving an $O_{ads}/H_{ads}$ ratio of 0.68 on $Pt/SiO_2$. Since a large fraction of the adsorbed hydrogen was weakly adsorbed [8], these weakly adsorbed hydrogen species should have higher mobility than the more strongly adsorbed oxygen [24].

While in the pulse chemisorption experiments hydrogen adsorption required several pulses to reach saturation, oxygen adsorption reached saturation already during the first pulse of gas. Subsequent pulses of oxygen did not lead to additional uptakes of oxygen. These differences between hydrogen and oxygen adsorption might be linked to the different degrees of weak adsorption (40–45% of weakly held hydrogen, and only 1–2% weakly held oxygen) [8]. The oxygen uptake values measured by the pulse method on all the bimetallic Pt–Sn samples were again lower than those observed by static chemisorption experiments, similar to the observation made in hydrogen chemisorption (Fig. 2).

In contrast to our pulse chemisorption results, the chromatographic method used by Buyanova et al. [5] gave a slightly higher amount of adsorbed oxygen than the static method. The main difference between the static method and the chromatographic method is that the chromatographic method exposes the catalyst to flowing oxygen at essentially constant partial pressure. In a static adsorption experiment, on the other hand, the partial pressure of oxygen will gradually decrease, until adsorption equilibrium is established. Buyanova et al. [5] mentioned that their frontal chromatographic method could only be used for rough estimates.

With increasing tin content of the coimpregnated catalysts, both the static and the pulse methods showed a systematic increase of oxygen uptake (Fig. 2). The increased oxygen uptake as a function of tin content may be attributed to several possible reasons. One possibility is that chemisorbed oxygen can spill over from platinum sites to adjacent tin sites, which may be present in the form of tin–aluminate surface complexes. Another possibility may be that the adsorption stoichiometry for oxygen on platinum is changed by the presence of adjacent tin ions. Furthermore, it is well known that oxygen can be adsorbed on metallic tin, but not on ionic tin. One could argue that the increased oxygen uptake with increasing tin content may be due to increased levels of metallic tin in the catalysts with higher tin loading. Lieske and Völter [7] purposed the formation of platinum–tin alloy by assuming that metallic tin is transformed into SnO by oxidation and that the presence of tin does not affect the oxygen adsorption on the platinum sites. They concluded that the amount of platinum–tin alloy increases with the addition of tin. However, the XPS results obtained on our coimpregnated Pt–Sn catalyst series [8] did not give evidence for the presence of zero valent tin. It is likely that tin–aluminate complexes are present, which could change the oxygen adsorption characteristics compared to catalysts where there is no interaction of alumina and tin. Similarly, platinum–tin alloy particles may adsorb oxygen in a different way compared to individual particles of metallic platinum and tin.

### 3.2. Comparison of the coimpregnated and sequentially impregnated Pt–Sn catalysts

For the sequentially impregnated (Sn first) catalysts, with increasing tin content a much lower hydrogen uptake was

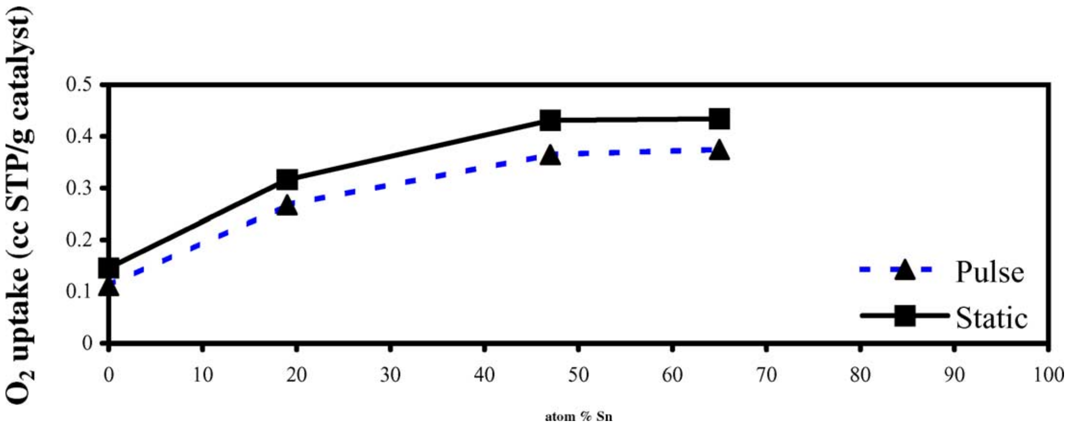

Fig. 2. Comparison of oxygen uptake measured by the pulse and static volumetric chemisorption methods as a function of nominal tin loading.

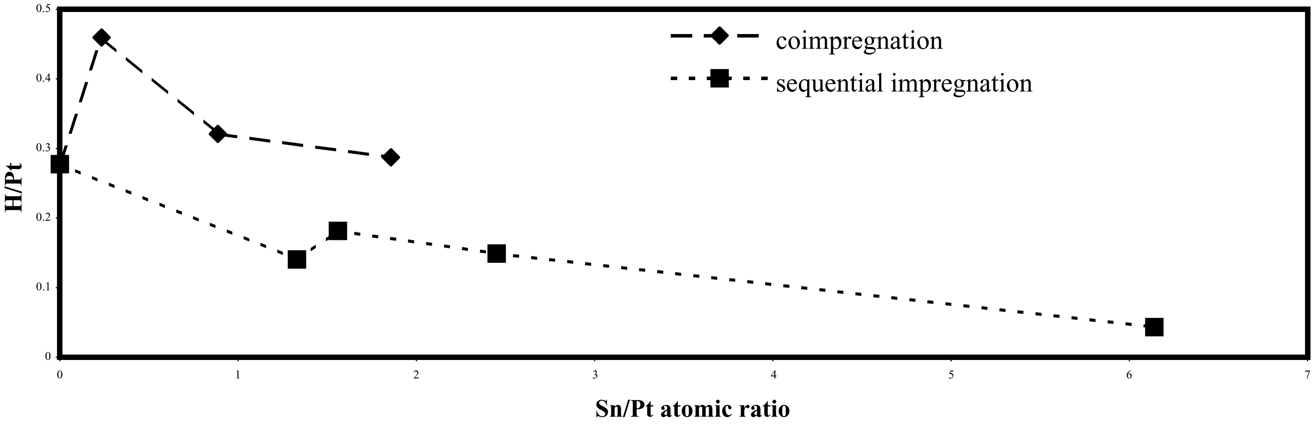

Fig. 3. Effect of catalyst preparation method on platinum dispersion, as measured by hydrogen pulse chemisorption.

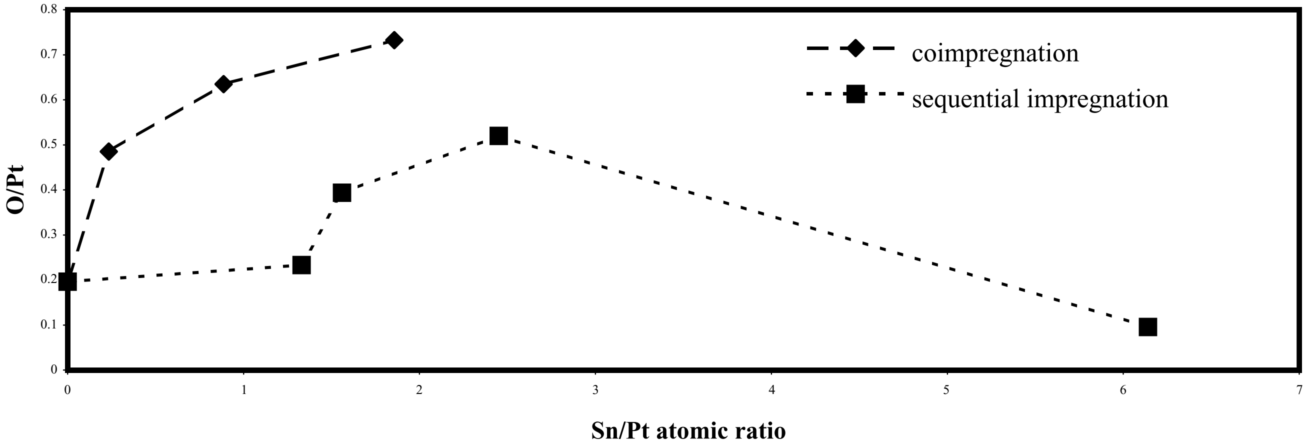

Fig. 4. Effect of catalyst preparation method on O/Pt ratio measured by oxygen pulse chemisorption.

observed, as compared to the coimpregnated catalysts (Fig. 3). The H/Pt atomic ratios of the sequentially impregnated catalysts show that the platinum dispersion values are relatively small as compared to those of the coimpregnated catalysts. The significantly smaller hydrogen uptake in the sequential impregnation series indicates that deposition of tin as first component on the alumina support is detrimental for the dispersion of platinum, while coimpregnation appears to facilitate high platinum dispersions. After reduction in $H_2$ at 400 °C, the sequentially impregnated catalysts contained a slightly higher amount of residual chlorine, compared to the coimpregnated catalysts (see Table 1). However, these small differences in chlorine content should not have significant effects on the chemisorption behavior and platinum dispersion.

In the sequentially impregnated catalysts, the effect of tin loading on enhanced oxygen uptake was much less pronounced as compared to the coimpregnated catalyst series (Fig. 4). On the catalyst sample with very large Sn content (1.0 wt.% Pt–5.0 wt.% $Sn/Al_2O_3$), the uptakes of both oxygen and hydrogen were very low indicating low dispersion of platinum. High resolution electron microscopy and X-ray energy dispersive spectroscopy results showed a certain proportion of the metal particles were somewhat larger and there was evidence of the formation of Pt–Sn alloy in the sequentially impregnated catalysts [25].

It appears that oxygen adsorbed on highly dispersed platinum particles can spillover onto tin–aluminate complex situating the nearby platinum atoms, thus causing larger O/Pt ratios than H/Pt ratios in the bimetallic catalysts with high Pt dispersion. This explanation is also consistent with the XPS analysis of the coimpregnated catalyst series with high Pt dispersion, indicating that in the reduced alumina-supported Pt–Sn catalysts, Sn is primarily present in a state of Sn(II) or Sn(IV) [8].

## 4. Conclusions

Comparing static volumetric chemisorption data with the pulse chemisorption data shows agreement in the qualitative trends. On monometallic $Pt/Al_2O_3$, the static method gives an $O_{ads}/H_{ads}$ ratio equal to 0.73, in excellent agreement with the pulse chemisorption method, where the $O_{ads}/H_{ads}$ ratio is 0.71. In the coimpregnated Pt–Sn/$Al_2O_3$ catalyst series, the H/Pt ratio goes through a maximum for the catalyst with 0.1 wt.% Sn, both for the static as well as the pulse method. In both methods, the O/Pt ratio increases with increasing Sn content. However, the pulse chemisorption method gives consistently lower uptakes of hydrogen and oxygen compared to the static volumetric method. These differences in gas uptake might be attributed to the different equilibration times provided by the two chemisorption methods.

The method of catalyst preparation has great influence over the metal dispersion and adsorption behavior. Coimpregnation of the $Al_2O_3$ support with platinum and small amounts of tin facilitates the formation of high Pt dispersion, exceeding the dispersion of monometallic Pt/$Al_2O_3$ catalysts with similar Pt loading. However, sequential impregnation of the $Al_2O_3$ support with Sn first, followed by Pt, leads to low Pt dispersion, as evidenced by consistently lower H/Pt and O/Pt ratios as compared to coimpregnated catalysts with similar overall Pt and Sn loading.

In the tin containing catalysts, the O/Pt ratios obtained are consistently higher than the H/Pt ratios, showing a trend towards enhanced oxygen uptake with increasing Sn content. It appears that oxygen adsorbed on highly dispersed platinum particles can migrate from the platinum sites to adjacent tin sites, populating the Sn surface. Sn is in a state of Sn(II) and/or Sn(IV), according to XPS results. This enhancement of oxygen uptake is not observed on catalysts containing large amount of tin, but low platinum dispersion, suggesting that the presence of highly dispersed platinum is required for populating nearby tin sites with oxygen.

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