

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Static and Pulse Chemisorption

The results of actual metal loading in the prepared catalyst samples, which were obtained by the neutron activation analysis, are shown in Table 4.1. The summary results of the amount of hydrogen and oxygen pulse chemisorption are provided in Table 4.2. The H/Pt ratio in the monometallic Pt/Al₂O₃ 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 for the same coimpregnated catalyst series (Balakrishnan and Schwank, 1991). 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 (Figure 4.1). These findings are in good agreement with Buyanova *et al.* (1969) who compared a frontal chromatographic method with the static adsorption method. They found that on Pt/Al₂O₃ 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 due 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.

Table 4.1 The metal loading of series of Pt-Sn catalysts as determined by Neutron Activation Analysis

Catalyst (nominal wt%)	Impregnation Method	Component weight %		
		Pt	Sn	Cl
1.0%Pt/Al ₂ O ₃		0.99	0	0.72
1.0%Pt-0.1%Sn/Al ₂ O ₃	coimpregnation	0.96	0.14	0.97
1.0%Pt-0.5%Sn/Al ₂ O ₃	coimpregnation	1.00	0.53	1.00
1.0%Pt-1.0%Sn/Al ₂ O ₃	coimpregnation	0.89	0.99	0.97
1.0%Pt- 0.6%Sn/Al ₂ O ₃	sequential	1.04	0.85	1.09
1.0%Pt-0.9%Sn/Al ₂ O ₃	sequential	1.03	0.96	1.05
1.0%Pt-1.5%Sn/Al ₂ O ₃	sequential	1.03	1.52	1.24
1.0%Pt-5.0%Sn/Al ₂ O ₃	sequential	1.12	4.18	1.01

Table 4.2 Composition and pulse chemisorption of hydrogen and oxygen results

	Metal (wt%)	Sn (atom%)	Sn/Pt (atomic ratio)	Gas uptake (cc STP/g cat)		H/Pt	O/Pt
				H ₂	O ₂		
1.0 Pt/Al ₂ O ₃	0.99	0	0.00	0.1577	0.1115	0.2774	0.1962
Coimpregnation							
1.0 Pt-0.1 Sn/Al ₂ O ₃	1.1	19	0.23	0.2533	0.2674	0.4596	0.4852
1.0 Pt-0.5 Sn/Al ₂ O ₃	1.53	47	0.89	0.1843	0.3645	0.3210	0.6349
1.0 Pt-1.0 Sn/Al ₂ O 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 ₂ O ₃	1.89	57	1.33	0.0839	0.1391	0.1405	0.2330
1.0 Pt-0.9 Sn/Al ₂ O ₃	1.99	61	1.56	0.1073	0.2329	0.1815	0.3939
1.0 Pt-1.5 Sn/Al ₂ O ₃	2.55	71	2.45	0.0881	0.3075	0.1490	0.5201
1.0 Pt-5.0 Sn/Al ₂ O ₃	5.3	86	6.14	0.0278	0.0616	0.0433	0.0957

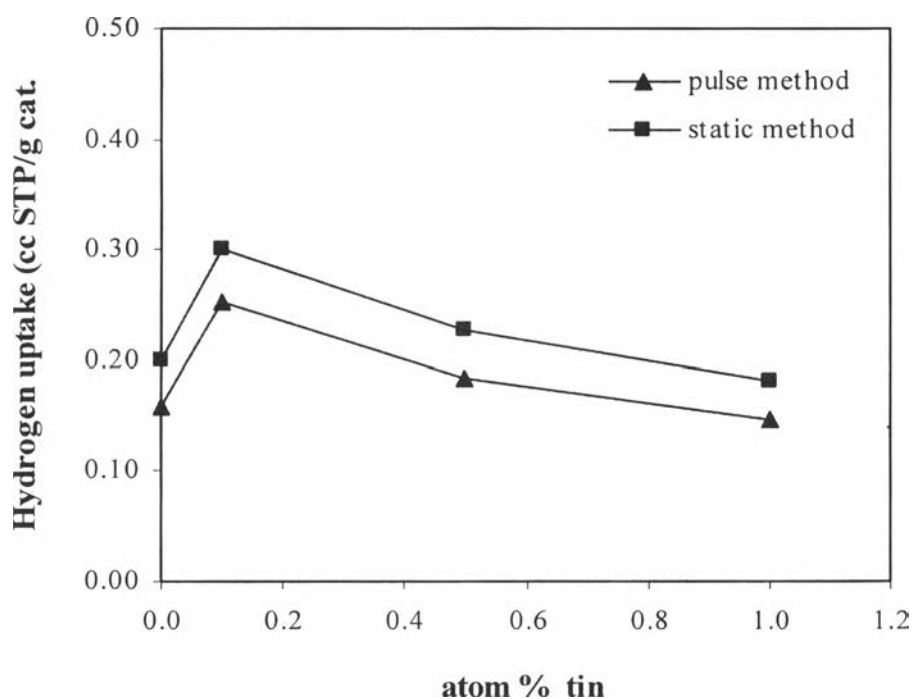


Figure 4.1 Comparison of hydrogen uptake measured by the pulse and static volumetric chemisorption methods as a function of nominal tin loading.

In Balakrishnan and Schwank's work (1991), 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 evacuation for 1 hour at room temperature. In the pulse experiments, the catalyst samples were flushed in flowing N_2 at room temperature for about 5 minutes 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 earlier work by O'Rear *et al.* (1990) reporting an O_{ads}/H_{ads} ratio of 0.65 on

unsupported platinum powder, and by Balakrishnan *et al.* (1990) giving an O_{ads}/H_{ads} ratio of 0.68 on Pt/SiO₂. Since a large fraction of the adsorbed hydrogen was weakly adsorbed (Balakrishnan and Schwank, 1991), these weakly adsorbed hydrogen species should have higher mobility than the more strongly adsorbed oxygen.

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) (Balakrishnan and Schwank, 1991). 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 (Figure 4.2).

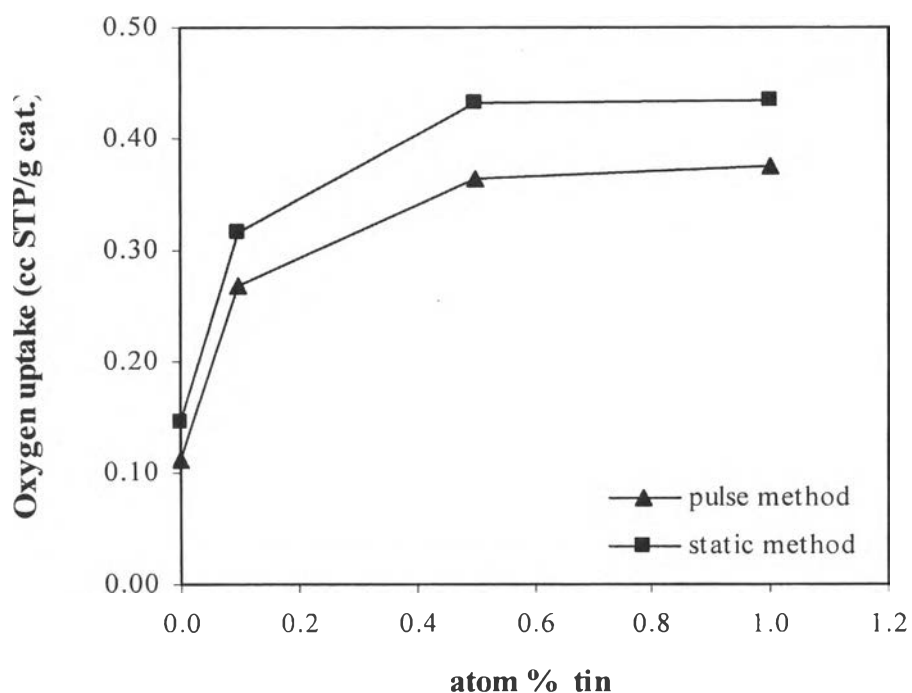


Figure 4.2 Comparison of oxygen uptake measured by the pulse and static volumetric chemisorption methods as a function of nominal tin loading.

In contrast to our pulse chemisorption results, the chromatographic method used by Buyanova *et al.* (1969) 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.* (1969) 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 method showed a systematic increase of oxygen uptake (Figure 4.2). 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 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 (1984) proposed 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 (Balakrishnan and Schwank, 1991) 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.

For the sequentially impregnated (Sn first) catalysts, with increasing tin content a much lower hydrogen uptake was observed, as compared to the coimpregnated catalysts (Figure 4.3). The H/Pt atomic ratios for 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 indicated that deposition of tin as first component on the alumina support was detrimental for the dispersion of platinum, while coimpregnation appears to facilitate high platinum dispersions. After reduction in H₂ at 400 °C the sequentially impregnated catalysts contained a slightly higher amount of residual chlorine, compared to the coimpregnated catalysts (see Table 1.1). However, these small differences in chlorine content should not have significant effects on the chemisorption behavior and platinum dispersion.

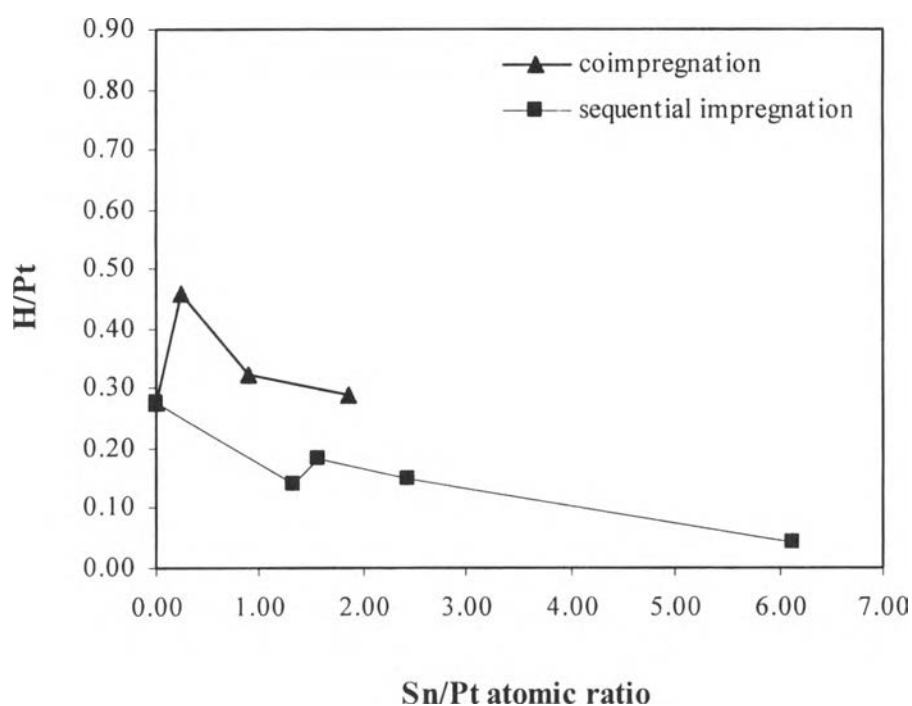


Figure 4.3 Effect of catalyst preparation method on platinum dispersion, as measured by hydrogen pulse chemisorption.

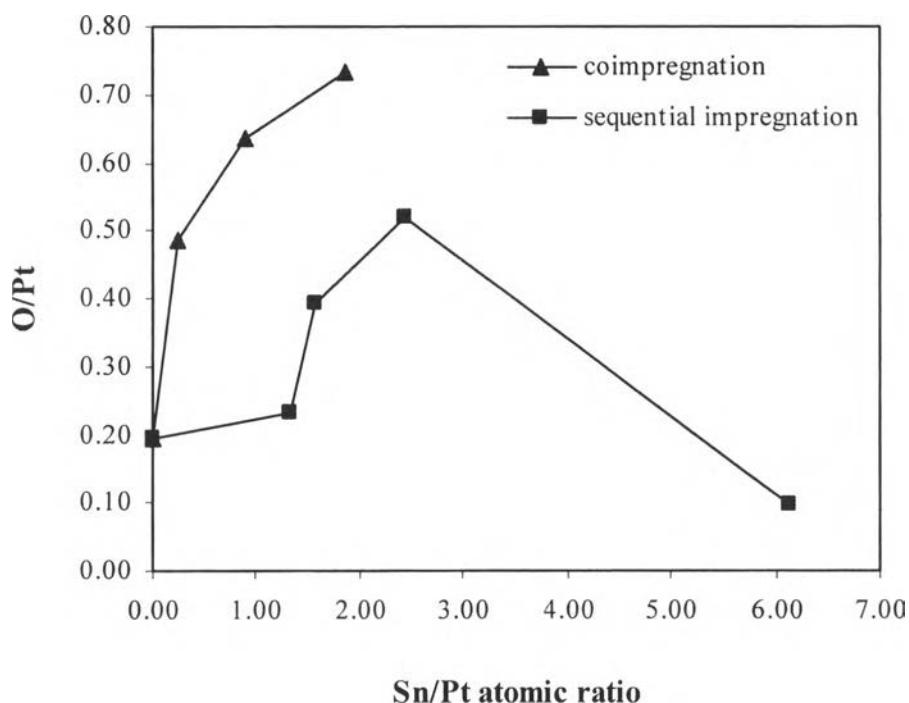


Figure 4.4 Effect of catalyst preparation method on O/Pt ratio measured by oxygen pulse chemisorption.

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 (Figure 4.4). On the catalyst sample with very large Sn content (1.0Pt-5.0Sn/Al₂O₃), 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.

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) (Balakrishnan and Schwank, 1991).

4.2 Temperature Programmed Desorption of Methanol

The TPD profiles of methanol on the monometallic Pt/Al₂O₃ and the coimpregnated Pt-Sn/Al₂O₃ catalyst series are shown in Figure 4.5. The TPD profiles for the sequentially impregnated catalysts are summarized in Figure 4.6.

Blank experiments were carried out using the Al₂O₃ support alone, which had been subjected to the same pretreatment as the experimental catalysts. After exposing the blank Al₂O₃ to methanol at 25°C, no desorption peak feature was observed over the entire temperature range up to 700°C, suggesting that the support did not adsorb methanol to any significant extent. Moreover, the hydrogen and oxygen adsorption behavior of 2% Sn/Al₂O₃ also did in the previous work (Balakrishnan and Schwank, 1991). The results showed there was no adsorption of hydrogen and small amount of oxygen adsorption (0.026 cm³ STP/g cat.). This is in marked contrast to the observations made by Cordi and Falconer (1996) who found substantial activity of blank alumina for decomposition and dehydration of methanol. They reported that a small amount of methanol desorbed over a broad temperature range, while most of the methanol decomposed during TPD between 330 and 630°C, giving primarily CO and H₂, with CO₂ as a minor reaction product. In addition, less than 40 % of the methanol dehydrated, giving dimethylether between 270 and 620°C. They carried out their experiments on Kaiser A-201 Al₂O₃, which had been pretreated in O₂ at 600°C to dehydrate it before each experiment. Kaiser Al₂O₃ has a pore volume of 0.46 cm³/g, an average pore radius of 41 Å, and a surface area of 200 m²/g. Our investigation was carried out on non-porous fumed alumina (Degussa) which has a surface area of 90 m²/g and is mainly in the gamma phase with some in the delta phase. The chlorine content of the alumina is less than 0.5 %. Furthermore, the catalysts used in this study were pretreated with H₂ at 400°C, followed by cooling in nitrogen. Thus, the resulting alumina surface was not dehydrated.

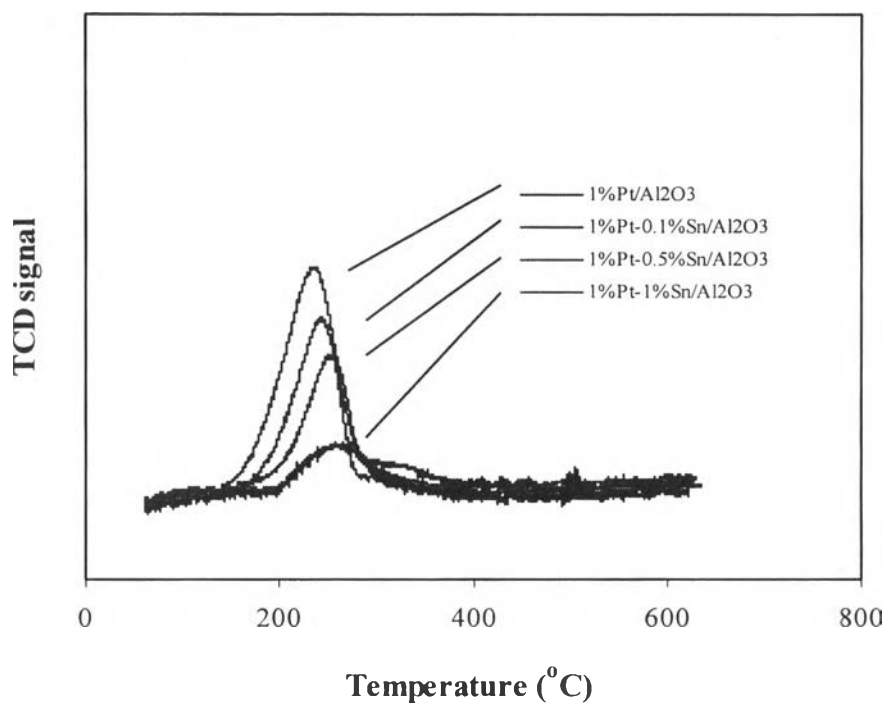


Figure 4.5 Temperature-programmed desorption profiles of coimpregnated Pt-Sn catalyst series.

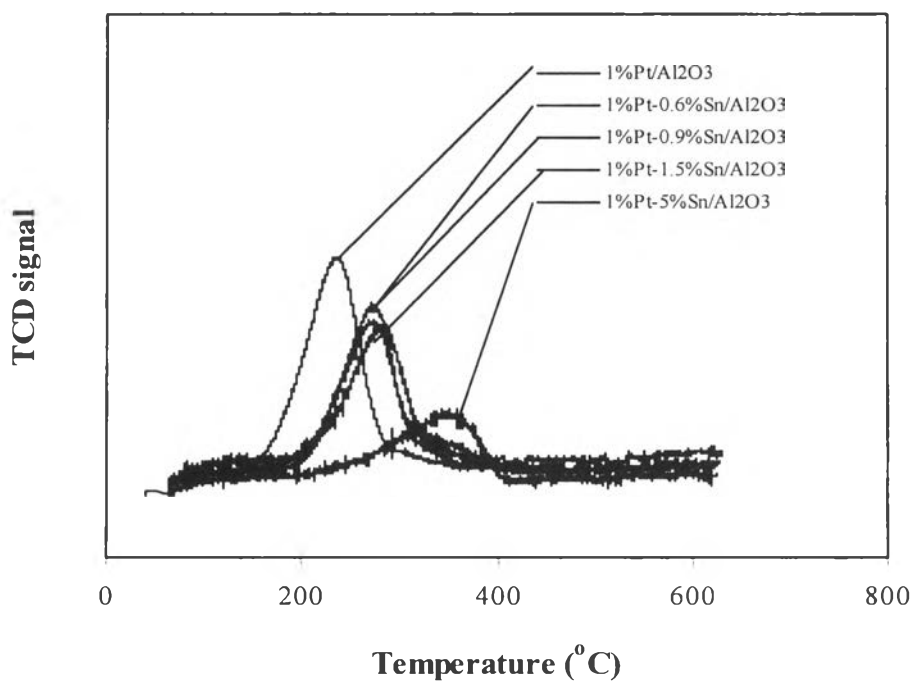


Figure 4.6 Temperature-programmed desorption profiles of sequential impregnated Pt-Sn catalyst series (with Sn first).

As seen in Figures 4.5 and 4.6, the TPD profiles detected by TCD on all Pt-Sn catalyst samples had only one major peak. For the coimpregnated catalyst series, the maximum temperature peak increased with increasing tin content from 220°C for the monometallic Pt to 275°C for the sample with 1% Sn. This indicates that the bond strength between the adsorbed species and the Pt sites is the weakest for the monometallic 1.0Pt/Al₂O₃ and increases with addition of tin. For the sequentially impregnated catalyst series, the maximum temperature peak shifted significantly from 230°C to 290°C when tin was added, but did not change much with further increase of the tin content from 0.6%-1.5%. However at a tin content of 5%, the maximum peak temperature increased dramatically to 375°C.

The major products identified by mass spectrometry in the TPD of methanol were hydrogen, and carbon monoxide. Only a small amount of weakly adsorbed methanol was found to desorb intact at the beginning of temperature ramping, along with small amounts of formaldehyde and water. The results indicate that the dehydrogenation of methanol on Pt sites appears to be the dominant pathway of methanol decomposition.

The peak maximum temperatures of hydrogen and carbon monoxide on the two series of catalysts are presented in Figure 4.7 and 4.8. For all catalysts, the peaks observed by mass spectrometry were in agreement with the TPD spectra obtained by TCD. From the mass spectra, the H₂/CO peak area ratios of the monometallic catalysts were consistently larger than 1.5, and for most of the bimetallic catalysts, the ratio exceeded a value of 2. This indicates that carbon monoxide is more strongly bonded on the surface of the bimetallic catalysts than on the monometallic platinum catalysts. This conclusion is consistent with the significant differences seen in the desorption peak maxima for the hydrogen and carbon monoxide peaks, as shown in Figure 4.9 and 4.10. After the decomposition of methanol on the catalyst surface, hydrogen is released before the release of carbon monoxide, indicating that carbon monoxide is adsorbed more strongly than hydrogen. Moreover, the difference between the hydrogen and carbon monoxide peak maxima temperature increased with increasing tin content in both series of catalysts. It appears that the presence of tin enhances the differences in adsorption strength of hydrogen and carbon monoxide.

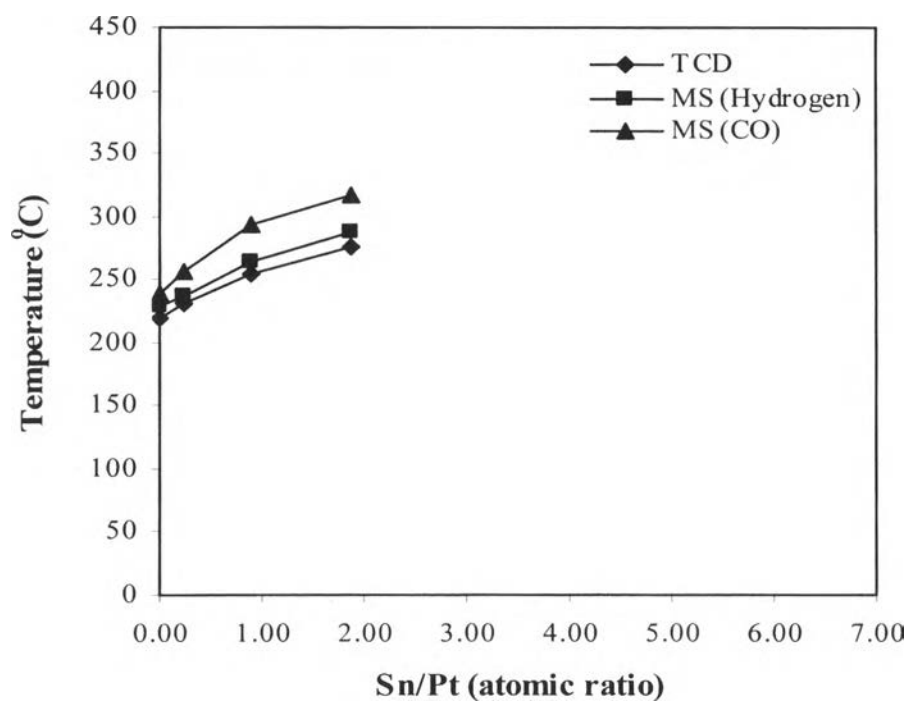


Figure 4.7 The maximum peak temperature from TCD and MS versus Sn/Pt atomic ratio for coimpregnation Pt-Sn catalysts.

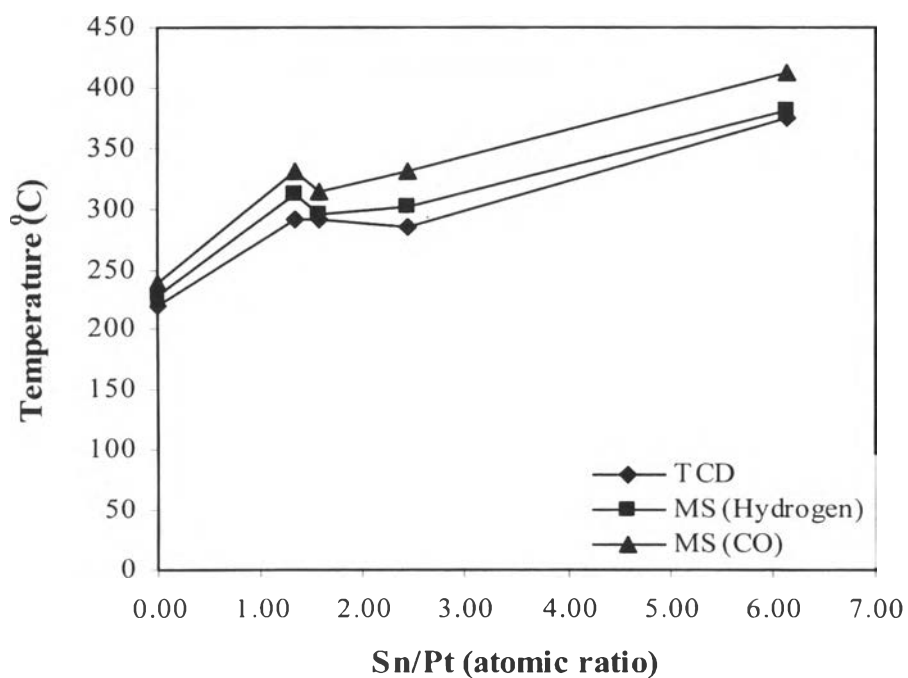


Figure 4.8 The maximum peak temperature from TCD and MS versus Sn/Pt atomic ratio for sequential impregnation Pt-Sn catalysts.

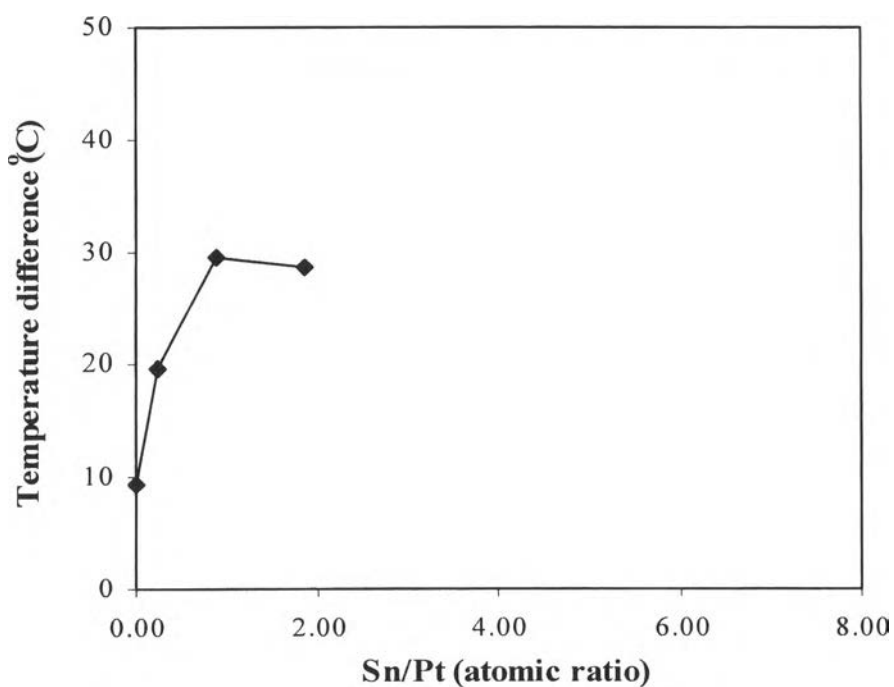


Figure 4.9 The difference of hydrogen and carbon monoxide maximum peak temperatures versus Sn/Pt atomic ratio for coimpregnation Pt-Sn catalysts.

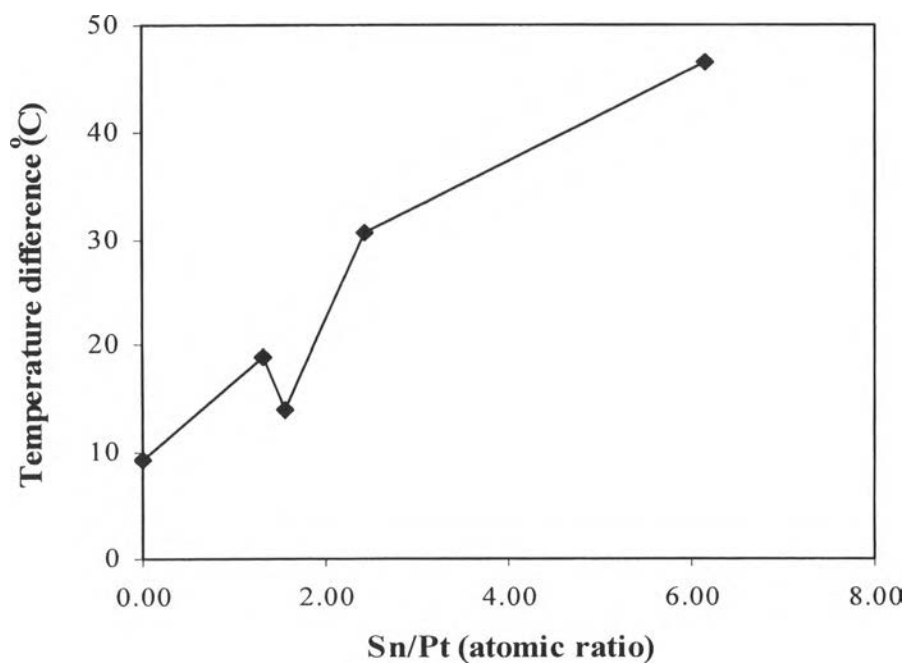


Figure 4.10 The difference of hydrogen and carbon monoxide maximum peak temperatures versus Sn/Pt atomic ratio for sequential impregnated Pt-Sn catalysts.

In a previous chemisorption study (Balakrishnan and Schwank, 1991), it was found that CO adsorption on monometallic Sn/Al₂O₃ catalysts was completely reversible, with 100 % of the adsorbed CO weakly held and removable by evacuation. On monometallic Pt/Al₂O₃, on the other hand, 32% of the adsorbed CO was weakly held. One would expect that adding Sn to Pt would lead to a percentage of weakly held CO somewhere between 32% and 100 %. However, this was not the case in the present experiments. Adding Sn to Pt actually decreased the amount of weakly held CO to 16-17%. From the earlier chemisorption results (Balakrishnan and Schwank, 1991), it appears that Pt particles in contact with tin-aluminate complexes exhibit a stronger CO bonding than that of CO on Pt/Al₂O₃. This trend towards a stronger CO bonding on Pt-Sn/ Al₂O₃ catalysts with increasing tin content also manifests itself in the shift of the methanol decomposition to H₂ and CO to higher temperatures.

The bimetallic catalysts are predominantly made up of platinum particles located in tin containing regions. On these bimetallic catalysts, methanol decomposition, as evidenced by the evolution of hydrogen and CO, requires higher temperatures as compared to monometallic platinum catalysts.

Furthermore, the increased concentration of ionic tin species as a function of tin loading causes the desorption peak for CO to shift progressively to higher temperatures, thus increasing the temperature gap between H₂ and CO desorption. This could mean that CO interacts more strongly with the interface where platinum particles are in direct contact with ionic tin species or tin-aluminates. There is a possibility of a dual-site adsorption of methanol molecules by the C-O bond of methanol may interact with SnO and C-H bond of methanol contact on Pt crystallites. Therefore, catalysts may be located at the interface between SnO and Pt crystallites.

Based on the present TPD results and by comparing with the previous characterization of catalysts by chemisorption, high resolution electron microscopy, and X-ray energy dispersive spectroscopy (Sachdev, 1989) a schematic describing the microstructure properties of the studied catalysts is sketched in Figure 4.11. The monometallic Pt/Al₂O₃ catalyst structure is quite straightforward as the metal particles are highly dispersed and the particle size is mostly smaller than 10Å with

some proportion of the particles in the range of 10-20Å. The structures of the coimpregnated bimetallic catalysts and of the sequentially impregnated bimetallic catalysts are more complex in terms of particle size distribution, structure and composition. The size distribution for the coimpregnated bimetallic catalysts indicates that the largest proportions of particles are smaller than 10Å. These consist of either elemental platinum alone or both platinum and tin. None of the particles analyzed were comprised of solely tin. There was no evidence of alloy formation or zero valent tin in catalysts except in the high loading of tin catalysts (1%Pt-1%Sn/Al₂O₃). Most of the platinum particles are associated with tin, so it can be postulated that tin exists in an alumina stabilized ionic state and that the platinum particles are located within or near it. For the sequentially impregnated catalysts, a certain proportion of the metal particles were somewhat larger and there was evidence of the formation of Pt-Sn alloy.

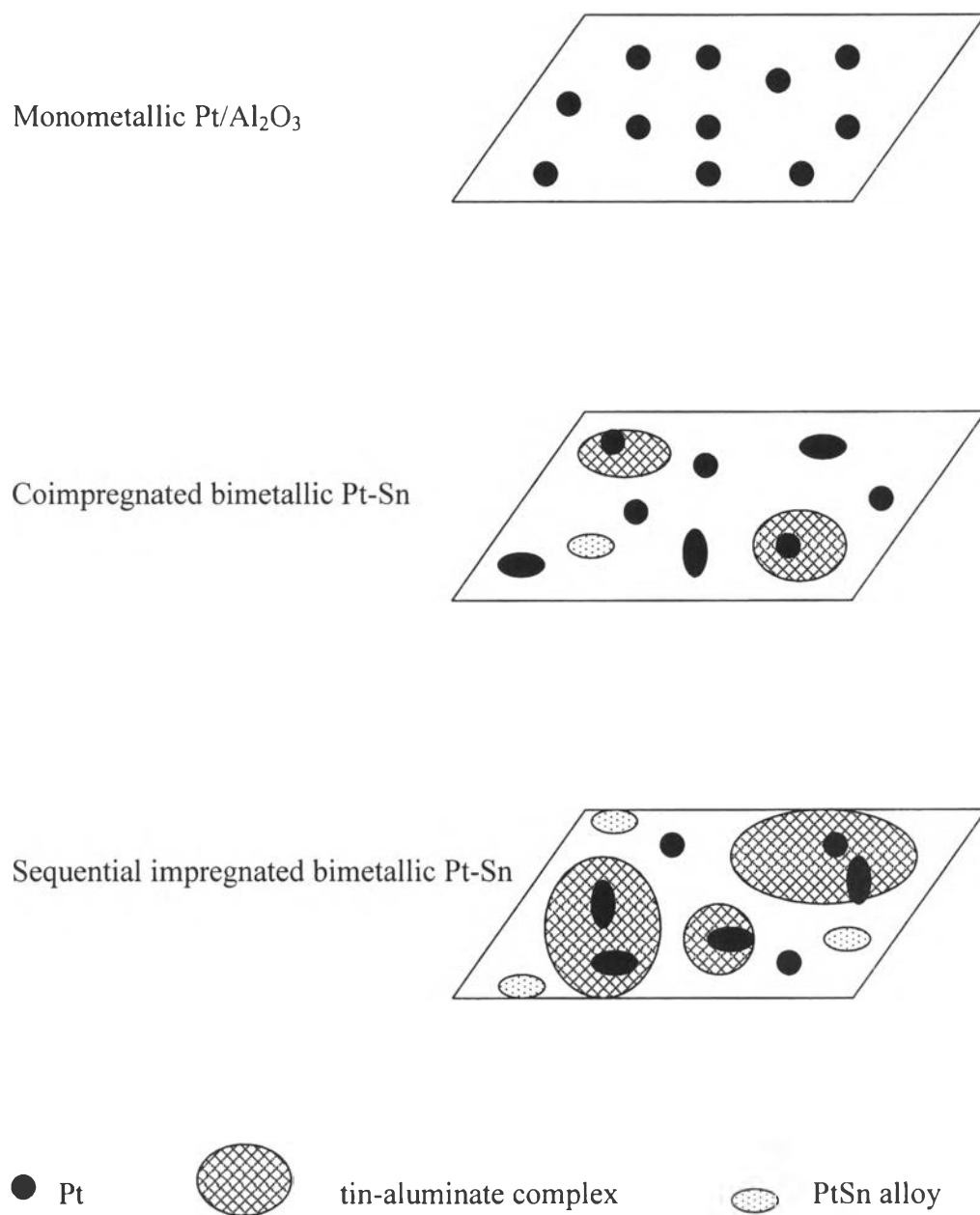


Figure 4.11 The schematic describing in the microstructure properties of catalysts.

4.3 Methanol Oxidation

The conversion of methanol was immeasurable in the empty reactor in the studied temperature range (room temperature to 200°C). For each run, it took about 15 h for the system to reach steady state. Figure 4.12 shows steady-state methanol conversion as a function of temperature for the monometallic Pt and bimetallic Pt-Sn catalysts prepared by the coimpregnation method. The monometallic platinum catalyst was found extremely active. Significant conversion of methanol was observed at room temperature for all catalysts and complete conversion was achieved at 100°C for the 1%Pt/Al₂O₃ catalyst. The coimpregnated catalysts were also very active and reached 100% methanol conversion near 100°C, except for the 1%Pt-1%Sn/Al₂O₃ catalyst, which required 150°C to achieve 100% methanol conversion. For any given methanol conversion, the reaction temperature was increased with increasing tin content. The reaction results agree very well with the hydrogen and oxygen chemisorption data on monometallic and the bimetallic Pt-Sn catalysts prepared by coimpregnation and sequential impregnation with Sn first. According to the hydrogen chemisorption results, the 1%Pt-0.1%Sn/Al₂O₃ has better Pt dispersion than the monometallic Pt catalyst. The Pt dispersion decreases with increasing tin loading in the bimetallic Pt-Sn catalysts. For the methanol oxidation reaction, the monometallic Pt catalyst was the most active and the overall conversion shifted to higher temperature with increasing tin content. The increased reaction temperature of bimetallic Pt-Sn may not be attributed simply to a dispersion effect. The oxygen chemisorption results indicated that increasing Sn content of the Pt catalyst increases the oxygen uptake and further addition of tin gave the increasing oxygen uptake decreased the extent of methanol conversion decreased significantly with increasing tin content. Thus, the enhanced oxygen uptake can be attributed to adsorption of oxygen on Sn surface atoms. But an increasing amount of oxidized tin does not seem to favor the conversion of methanol. Tin oxide may block Pt sites responsible for methanol oxidation. The results of the present study are in good agreement with the study of Haner and Ross (1991), who found that in electrochemical oxidation of methanol, alloy surfaces of Pt-Sn exhibited lower catalytic activity than pure platinum surfaces.

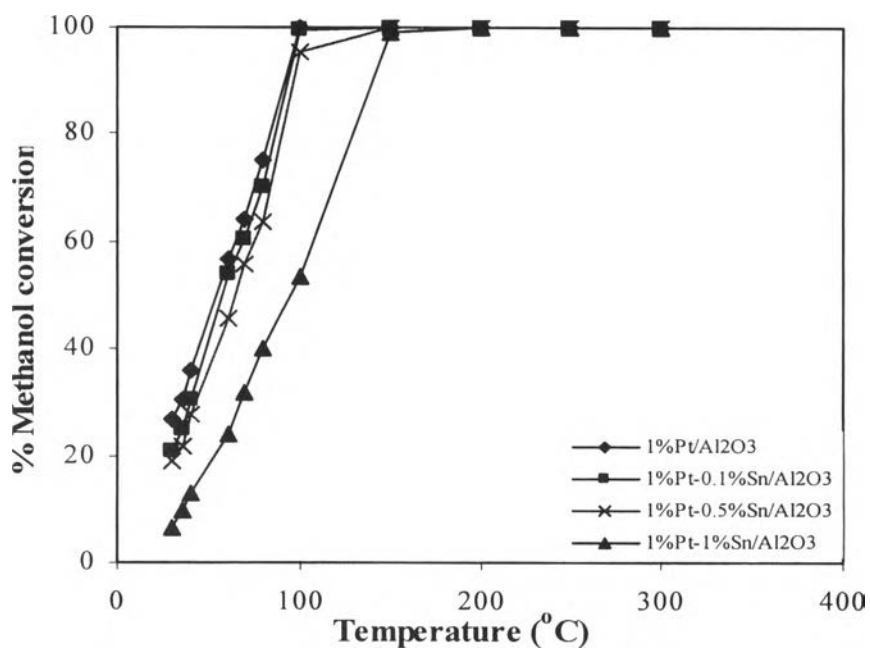


Figure 4.12. Effect of temperature on methanol conversion for coimpregnated catalysts series. The feed contained 1,200 ppm of methanol and 21% O₂ in helium carrier at a volumetric space velocity of 20,000 h⁻¹.

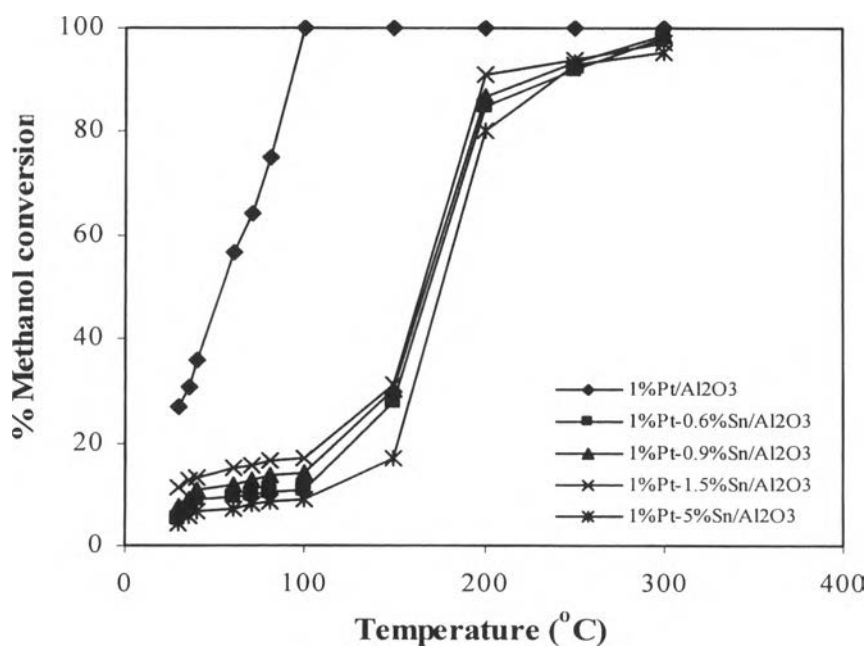
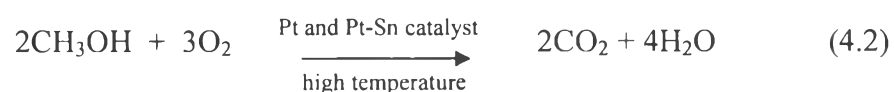
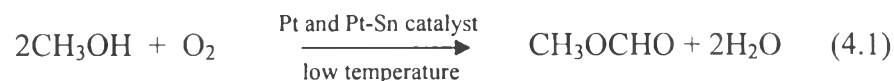


Figure 4.13 Effect of temperature on methanol conversion for sequentially impregnated catalysts series. The feed contained 1,200 ppm of methanol and 21% O₂ in helium carrier at a volumetric space velocity of 20,000 h⁻¹.

The results of methanol oxidation over the sequentially impregnated catalysts are markedly different from those over the coimpregnated catalysts as shown in Figure 4.13. For a temperature up to 100°C, the activity was very low with conversions of less than 20 % for all Pt-Sn catalysts. At higher temperatures, the activity increased steeply reaching 80–90 % conversion at 200°C. It was also found that for any given reaction temperature, the methanol conversion dropped markedly in the presence of tin as compared to the monometallic Pt catalyst. For the bimetallic Pt-Sn catalysts, increased Sn decreased slightly the methanol conversion. As stated previously, the TPD results on the sequentially impregnated catalysts showed a significant shift to higher desorption temperatures for CO and H₂ formed during thermal decomposition of methanol compared to both monometallic Pt and the coimpregnated catalysts. This suggests that Pt particles deposited on Sn tend to adsorb methanol more strongly than Pt in the coimpregnated catalysts. Thus, it is not surprising to see much lower oxidation activities of the sequentially impregnated catalysts as compared to the coimpregnated catalysts. It is noteworthy that there was good correlation between the maximum desorption peak temperature of methanol and the methanol oxidation temperature in both of the catalyst series tested. Moreover, CO₂ and methyl formate were the only carbon-containing products of methanol oxidation over the monometallic Pt catalyst, as shown in Figure 4.14. Methyl formate was the principle product at low temperatures, but its content decreased sharply with increasing temperature, with concomitant increase in the production of CO₂, which became the principle product at high temperatures. The two proposed main reactions of methanol oxidation over the monometallic Pt and bimetallic Pt-Sn catalysts are shown below:



These results are in good agreement with the previous work reported by McCabe and Mitchell (1986) who studied methanol oxidation over alumina-supported catalysts containing highly dispersed Rh, Pd, Pt, Ag or Cu-Cr. They also found that methyl

formate, CO_2 and H_2CO were the only carbon-containing products of methanol oxidation over the Pt catalyst. Further, methanol oxidation over the Pd catalyst was similar to that over the Pt catalyst, but there was more H_2CO formed over Pd than over Pt. The Rh catalyst was much less active than Pt and Pd and dimethyl ether and H_2CO were the principle partial oxidation products over the Rh catalyst.

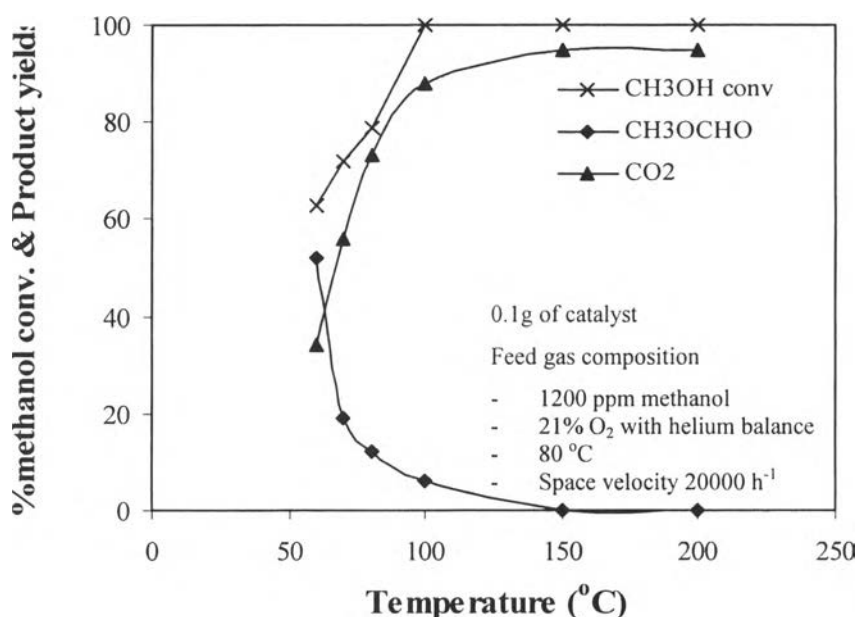


Figure 4.14 Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over the monometallic Pt catalyst.

For the coimpregnated catalysts, the reaction products are similar to those using the monometallic Pt catalyst (Figures 4.15-4.17). Similarly, methyl formate was the principle product in the low temperature range, but decreased dramatically with increasing reaction temperature. CO_2 became dominant at high temperatures. Addition of tin decreased the amount of methyl formate.

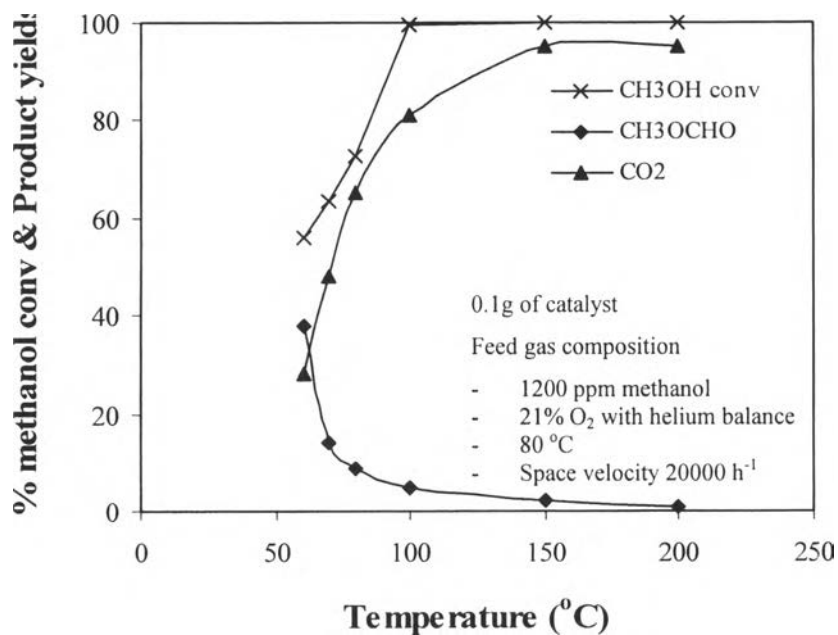


Figure 4.15 Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over 1%Pt-0.1%Sn/Al₂O₃ catalyst.

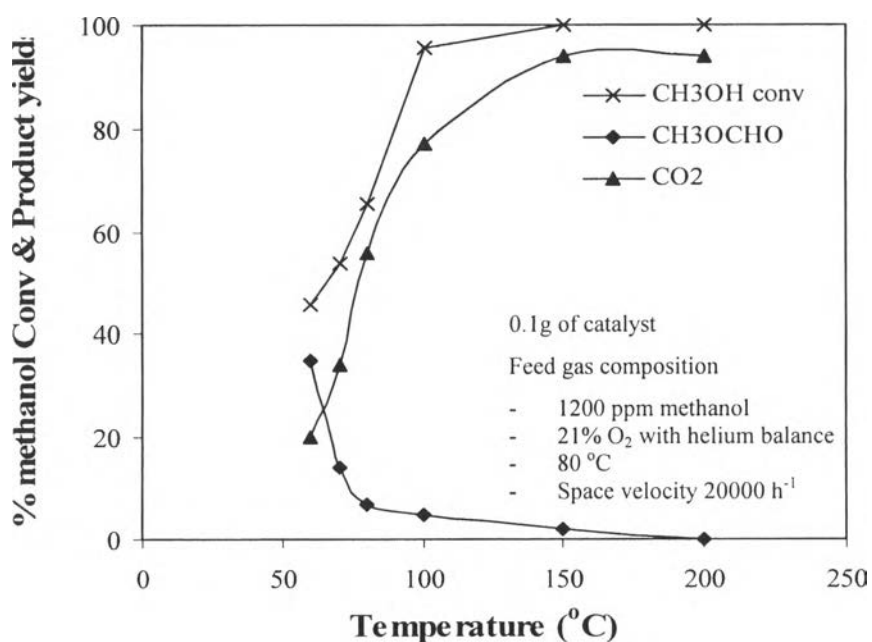


Figure 4.16 Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over 1%Pt-0.5%Sn/Al₂O₃ catalyst.

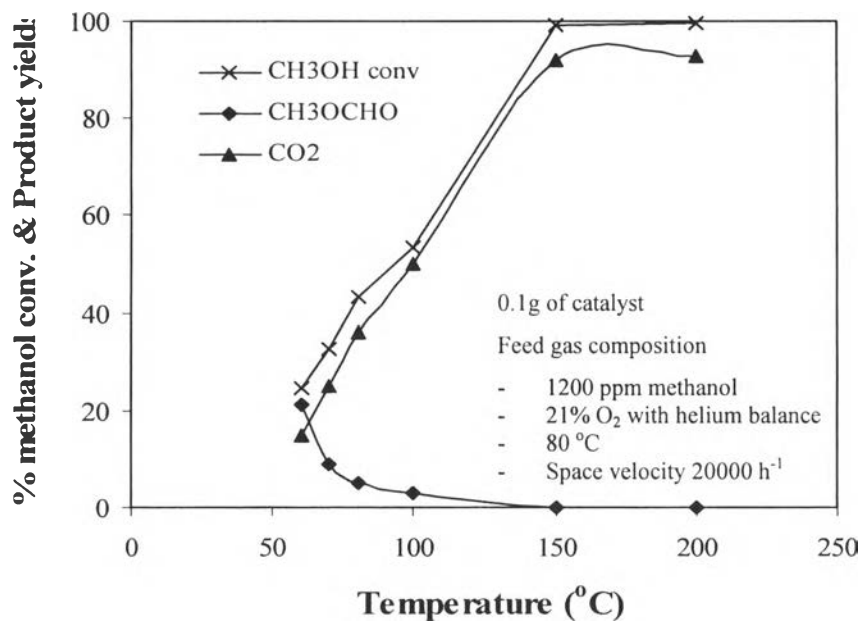


Figure 4.17 Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over 1%Pt-1%Sn/Al₂O₃ catalyst.

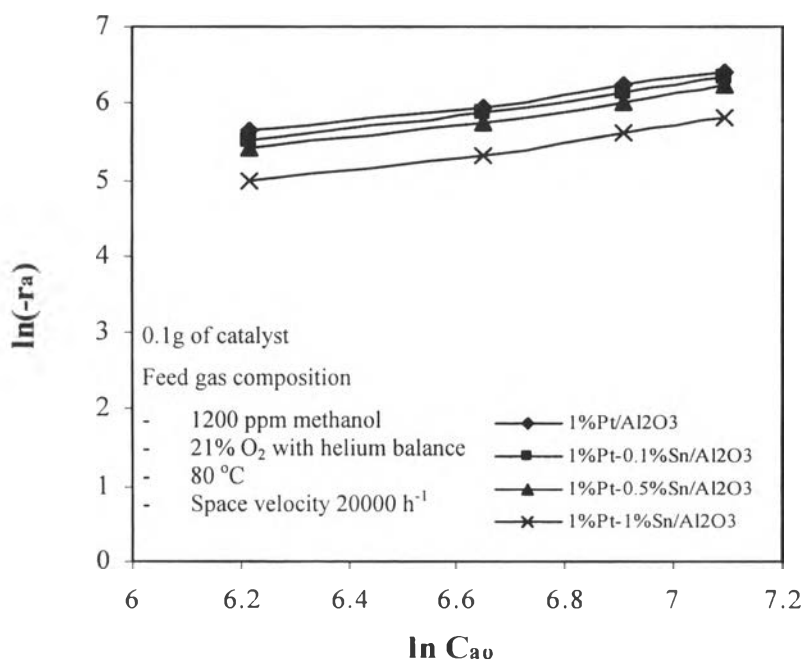


Figure 4.18 Relation of rate of reaction and initial methanol concentration for coimpregnated catalysts series.

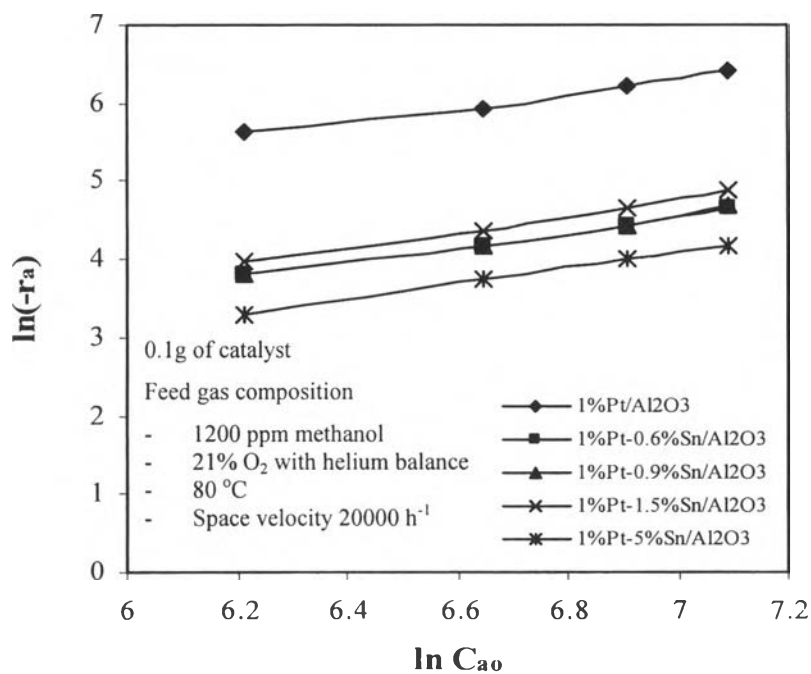


Figure 4.19 Relation of rate of reaction and initial methanol concentration for sequentially impregnated catalysts series.

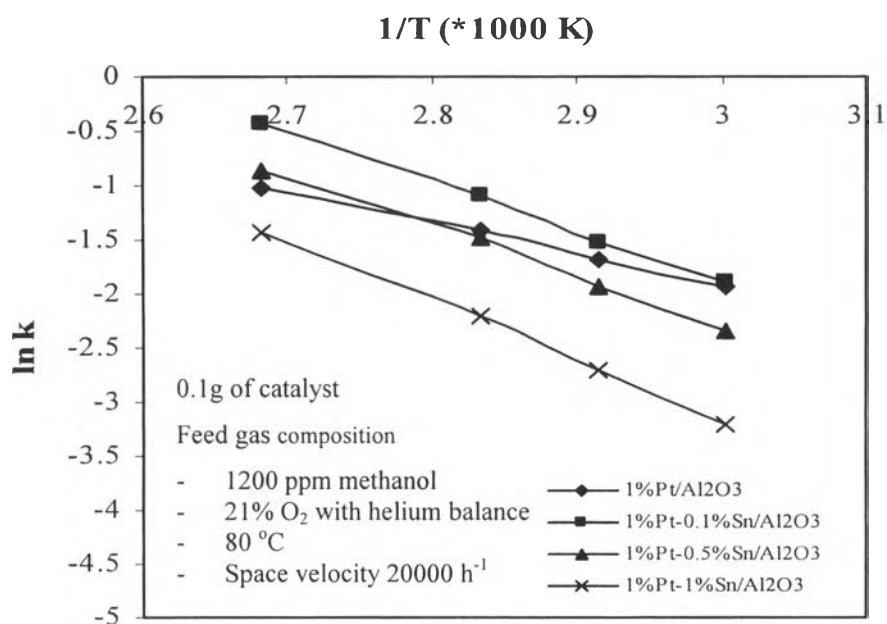


Figure 4.20 Arrhenius plot for coimpregnated catalysts series.

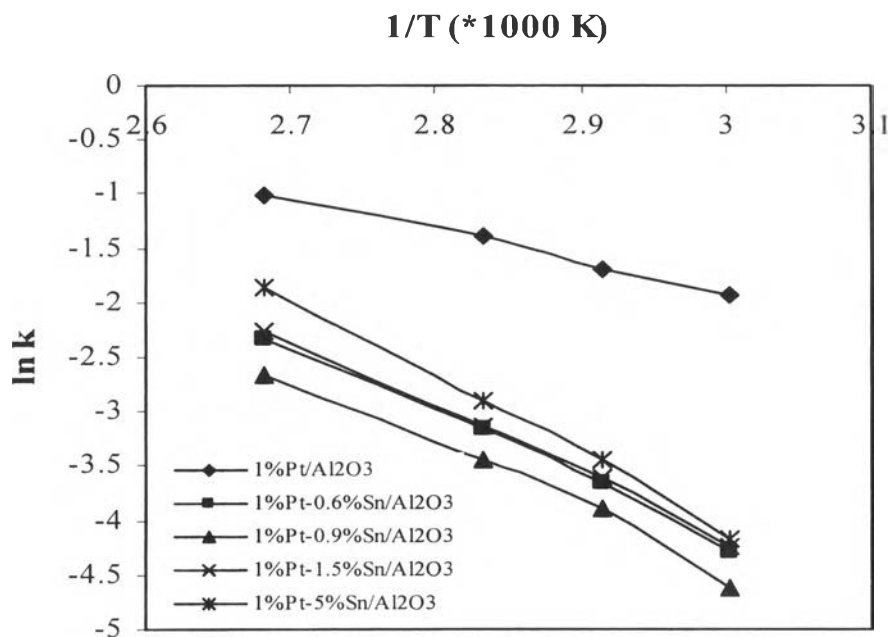


Figure 4.21 Arrhenius plot for sequentially impregnated catalysts series.

As shown in Figures 4.18-4.19 and Table 4.3, the reaction order calculated from the experimental data with respect to the rate of methanol oxidation over both the monometallic and bimetallic Pt-Sn catalysts is 1.15 ± 0.05 , which is in good agreement with the reported value of a first-order reaction for methanol oxidation (Cordi and Falconer, 1996). Arrhenius plots were established to calculate the activation energy for methanol oxidation (Figures 4.20-4.21). As shown in Table 4.3, the apparent activation energy increases significantly with increasing tin content for the coimpregnated catalysts. For the sequentially impregnated catalysts, the apparent activation energy was almost unchanged with tin contents in the range of 0.6 % – 1.5 %, but it shifted to 66.81 kJ/mol for 1% Pt -5% Sn/Al₂O₃ catalyst. For both catalysts series, the trend toward higher desorption temperature for CO with increasing tin content indicates that the presence of tin can decrease methanol oxidation activity. The effect of tin is more pronounced in the sequentially impregnated catalysts since Pt is deposited on top of oxidized Sn. The nature of the microstructures formed during sequential impregnation was not investigated. It does appear that the

sequentially impregnated catalysts have lower platinum dispersion compared to the coimpregnated catalysts. Based on the result from the coimpregnated series, it is not likely that the observed trends in CO bond strength and in methanol oxidation activity can be attributed simply to the Pt dispersion effects. Based on the evidence of the microstructures of the studied catalysts, it can be concluded that the strength of the CO bonds on the surface is significantly increased by the interaction between Pt and Sn. Consequently, the reactivity of these catalysts for oxidation of methanol, which might involve adsorbed CO intermediates, is significantly decreased.

The results of deactivation study (Figure 4.22) showed a small drop in the activity of the monometallic Pt catalyst, but less drop in the activity was found over the 0.96%Pt-0.14%Sn/Al₂O₃ catalyst. The activity decreased considerably when the tin loading was further increased. The 0.92%Pt-0.14%Sn/Al₂O₃ catalyst did not show any signs of deactivation over 2 days, while 0.99%Pt/Al₂O₃ catalyst lost about 2% activity per day. Extrapolation of these results indicate that the 0.99%Pt/Al₂O₃ catalyst would lose its activity completely after 39 days on stream. However, the results indicate that the activity of platinum catalysts can be maintained by the addition of an appropriate amounts of tin.

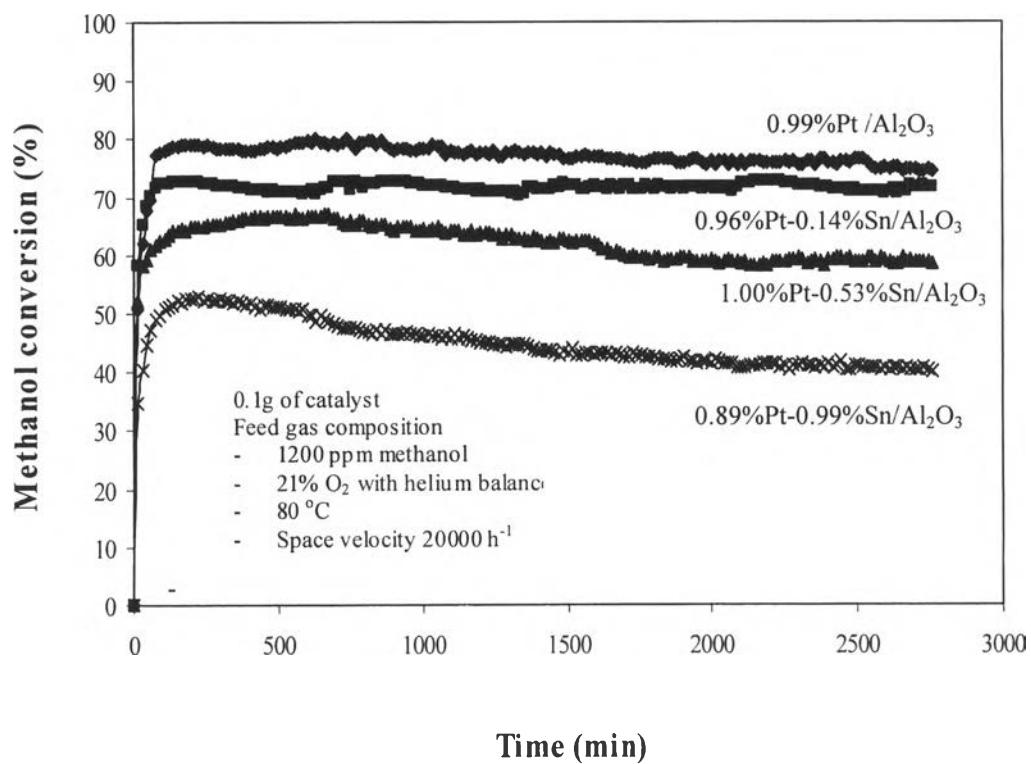


Figure 4.22 The long-running experimental for observing the deactivation of the coimpregnated catalysts series.

Table 4.3 Calculation values of reaction orders and activation energies

Catalyst (wt%)	Impregnation Method	Reaction order	E _a (kJ/mol)
0.99 Pt/Al ₂ O ₃	-	1.12	25.9
0.96 Pt-0.14 Sn/Al ₂ O ₃	coimpregnation	1.12	38.9
1.00 Pt-0.53 Sn/Al ₂ O ₃	coimpregnation	1.13	41.8
0.89 Pt-0.99Sn/Al ₂ O ₃	coimpregnation	1.16	48.7
1.04 Pt- 0.85 Sn/Al ₂ O ₃	sequential	1.15	54.5
1.03 Pt-0.96 Sn/Al ₂ O ₃	sequential	1.16	55.1
1.03 Pt-1.52 Sn/Al ₂ O ₃	sequential	1.13	54.9
1.12 Pt-4.18 Sn/Al ₂ O ₃	sequential	1.17	66.8