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Temperature-programmed desorption of methanol and oxidation of methanol on Pt–Sn/Al_2O_3 catalysts

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Abstract

The temperature-programmed desorption (TPD) of methanol, a widely used solvent contributing to industrial VOC emissions, was studied on two different series of Pt–Sn/Al_2O_3 catalysts that were prepared by coimpregnation and sequential impregnation with Sn first. TPD results showed that methanol decomposed primarily to hydrogen and carbon monoxide. Hydrogen desorbed first, followed by carbon monoxide at higher temperatures. Adding Sn to Pt shifted the desorption peaks of both H_2 and CO to higher temperatures. For the coimpregnated Pt–Sn catalysts, the temperature difference between the H_2 and CO desorption peak maxima increased systematically with increasing Sn content; for the sequentially impregnated catalysts, the temperature difference remained nearly constant. An exception was the catalyst containing 5 wt.% Sn, where the peaks shifted upward by 150 °C. In both catalyst series, the temperature difference between the hydrogen and the carbon monoxide desorption peak maxima increased with increasing Sn content. This study has demonstrated that the adsorption/desorption behavior of methanol on platinum is strongly modified by the presence of tin.

The oxidation of methanol over the monometallic Pt and bimetallic Pt–Sn on alumina support was studied in the temperature range 35–300 °C and initial concentrations of methanol in the range 500–1200 ppm and excess oxygen (21% O_2). The experimental results showed that the monometallic Pt catalyst were much more active than the bimetallic catalysts. The coimpregnated catalysts were more active than the sequentially impregnated catalysts. CO_2 and methyl formate (CH_3OCHO) were the only carbon-containing products of methanol oxidation. Methyl formate was the principle product at low temperatures, while CO_2 was the principle product at high temperatures. The reaction order of methanol oxidation was 1.15 ± 0.05. The apparent activation energy of the monometallic platinum catalyst was 14.4 kJ/mol. For the coimpregnated catalysts, addition of tin increased the apparent activation energy while in the sequentially impregnated Pt–Sn the apparent activation energy remained essentially constant over the range 0.6–1.5 wt.% Sn, then shifted to 66.8 kJ/mol for 5 wt.% Sn.

Keywords: Methanol; Oxidation; Platinum–tin; Bimetallic; TPD

1. Introduction

Emissions of volatile organic compounds (VOCs) are a concern in solvent-intensive operations in many manufacturing processes. Gaseous effluents and contaminated exhaust air containing VOCs enter the atmosphere, where they contribute to environmental pollution. Incineration is an energy efficient method to destroy VOCs. This proceeds in the presence of a catalyst and excess oxygen at temperatures higher than 700 °C, depending on the nature of the VOCs. However, incineration is energy intensive and requires expensive materials to withstand corrosion and high temperatures. In order to reduce capital investments and fuel costs, there is a need for development of a catalyst that can oxidize VOCs at lower temperatures. Research on heterogeneous catalytic oxidation of low concentrations of VOCs with air should focus on identifying active catalysts that yield environmentally benign reaction products at lower temperatures, most desirably H_2O and CO_2. Heterogeneous catalytic oxidation of VOCs has been reviewed by Spivey [1]. The most common catalysts used for VOC abatement are metals or metal oxides such as Pt, Pd, Rh, and V_2O_5 dispersed on high surface area supports such as Al_2O_3, SiO_2, TiO_2, etc. [2–7].

Methanol has been used widely to represent VOCs in oxidation studies because of its simple chemical structure. Methanol oxidation yields various products, e.g., formaldehyde and CO_2, depending on the type of catalysts and operating conditions. Davies and Mariotti [8] studied the temperature-programmed desorption (TPD) of methanol on Cu(1 1 0) surfaces. They proposed that the reaction pathway

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was sensitive to the local structure of the methoxy/oxygen adlayer. They also confirmed the presence of two states of methoxy at the Cu(1 1 0)/O(a) surface and assigned them to methoxy species with and without stabilization by surface oxygen. Farneth et al. [9] investigated the partial oxidation of methanol over MoO_3. Their values of the number of active sites and of the Arrhenius parameters for the rate-limiting C–H bond cleavage, determined by TPD under high vacuum with simultaneous microbalance and mass spectrometry detection, were used to predict heterogeneous reaction rates that were in excellent agreement with the reaction data. Yao et al. [10] studied the kinetics of methanol oxidation over SiO_2 in the temperature range 400–600 °C to determine the oxidation pathway of methanol. They found that methanol was oxidized primarily to formaldehyde and then CO. CO_2 was produced mainly from the oxidation of intermediate species products from dehydrogenation of formaldehyde on SiO_2.

Methanol oxidation is also utilized to produce intermediates for the synthesis of several commercial products such as formaldehyde, methyl formate and as an alternative hydrocarbon fuel. Cheng [11] found that on MoO_3, methanol was partially oxidized to formaldehyde because water and methanol blocked the catalytic adsorption sites for further oxidation. IR results showed that formaldehyde, methanol, and water competed for the same adsorption sites on MoO_3. Busca et al. [12] conducted flow reactor studies using FT-IR spectroscopy to reveal the mechanism of the selective oxidation of methanol to formaldehyde, dimethoxymethane, formic acid, and methyl formate over vanadium oxide and titanium oxide catalysts, prepared by impregnation and coprecipitation. Niwa and Igarachi [13] studied the role of solid acids over MoO_3 loaded on SnO_2 in the selective oxidation of methanol to formaldehyde. They found that methanol was adsorbed more weakly on the acid sites than on the exposed surface of SnO_2 resulting in the formation of formaldehyde. Elmi et al. [14] concluded that the ability of coprecipitated vanadium–titanium oxides to catalyze the oxidation of methanol to methyl formate was correlated with the existence of dioxymethylene species with an intermediate stability not found in reactions catalyzed by pure titania or vanadia. Hydrogen production by partial oxidation of methanol on ZnO and ZrO_2 supported Pd catalysts was studied by Cubeiro and Fierro [15]. The results showed that the Pd catalysts can compete with the commercial low-temperature-methanol-synthesis catalysts, $Cu/ZnO(Al_2O_3)$, when used under the specific conditions for the partial oxidation of methanol.

Obviously, the catalytic oxidation of trace concentrations of VOCs in air is more economical when the reaction is carried out at lower temperatures. To do this, high activity, high selectivity, low activation energies and high durability of VOC oxidation catalysts are required. The present study provides information about methanol oxidation on Pt and Pt–Sn catalysts to lead to a better understanding of the mechanistic aspects of VOC oxidation catalysis. The objective of this work was to investigate the oxidation of methanol on two different series of $Pt–Sn/Al_2O_3$ catalysts. Adding tin to platinum catalysts has been proven to be beneficial for activity maintenance in applications such as catalytic reforming [16,17]. One of the factors that affects the interaction of tin and platinum is the preparation methods of the catalysts. Thus, in this study, one series of catalysts was prepared by coimpregnation and a second series was prepared by sequential impregnation with Sn followed by Pt.

2. Experimental methods

2.1. Catalyst preparation

Fumed alumina (Degussa; BET surface area $= 90\,m^2/g$) with a chlorine content of about 0.35 wt.% was used as the catalyst support. The primary alumina phase was the γ-phase. Most commercial aluminas tend to give undesirable contrast effects in high-resolution microscopy due to the various overlaying crystalline planes of alumina. This particular Degussa support has been proved to be more conducive to characterization by electron microscopy as it can minimize the contrast effects that might obscure the observation of small metal particles. A comparison with Pt–Sn catalysts supported on high surface area, porous γ-alumina (BET surface area $= 250\,m^2/g$) did not show significant differences in particle size distribution and elemental composition.

The first series of $Pt–Sn/Al_2O_3$ catalysts was prepared by coimpregnation with acetone solution of H_2PtCl_2 (Aldrich) and $SnCl_2$ (Aldrich). The nominal platinum loading was maintained constant at 1 wt.% for all catalysts and the nominal tin loading was varied from 0.1 to 1.0 wt.%. This coimpregnated catalyst series has been the subject of extensive characterization [18–21]. A second series was prepared by sequential impregnation with Sn first, followed by Pt, using the same precursors and solvent as described previously [18]. For the sequentially impregnated series, the nominal platinum loading was kept constant at 1 wt.% and the nominal tin loading was varied from 0.6 to 5 wt.%. Following the impregnation step, the catalysts were dried at 100 °C and then calcined in air at 500 °C for 2 h. Portions of these calcined catalysts were reduced overnight in flowing hydrogen at 400 °C. Neutron activation analysis was performed after the calcination and reduction steps to verify the actual metal compositions and to determine the chlorine content of the catalyst samples. The prepared catalysts were characterized by hydrogen and oxygen chemisorption, XPS, HREM, and TPD as reported in a related study [19].

2.2. TPD of methanol

The TPD experiments were conducted in two parts: first, the quantitative determination of the amount of gas desorption by thermal conductivity detection of effluent gas;

second, mass spectrometric identification of the molecular species contributing to each TPD peak.

2.2.1. Quantitative TPD experiments

A fresh catalyst sample of 50 mg was placed into a quartz tube reactor, which was externally heated by a tube furnace. Prior to TPD, all samples were reduced for 2 h at 400 °C with a stream of ultra-high purity hydrogen at a flow rate of 25 cm^3/min. After completing the reduction step, the catalysts were cooled down to room temperature by introducing a stream of ultra-high purity nitrogen. TPD was performed using a TPD/TPR unit (Micromeritics, 2900). The temperatures of the thermal conductivity detector (TCD), valve and injection loop were maintained at 100, 100, and 75 °C, respectively. Ultra-high purity nitrogen was selected as carrier gas at a 50 cm^3/min flow rate. The detector current was 55 mA. The experimental setup contained three gas lines. The first line served as a pretreatment line, the second provided carrier and reference gases, while the third was used for carrying the solvent vapor to the injection loop. Once the adsorption step was complete, the temperature controller was set to ramp the furnace temperature up to 800 °C at a linear ramp rate of 10 °C/min. As the temperature increased, the surface species began to desorb and the signal of the desorbed species from the TCD was displayed as a function of temperature. Typically, the TPD/TPR data are represented as peaks in signal vs. time plots and temperature vs. time plots. The location of peaks on the temperature axis depicts the strength of adsorption. For simple adsorbates that do not undergo decomposition during TPD, the number of peaks can indicate the number of energetically distinct surface sites. The area under each peak represents the quantity of adsorbed species on a given type of surface site. The adsorbate used in this study, however, is likely to undergo decomposition at elevated temperatures, and this can lead to additional peaks in the TPD spectrum.

2.2.2. Qualitative TPD experiments

These experiments were performed on 100–250 mg of catalyst. The catalyst was placed in a 1.2 cm o.d. tubular quartz reactor. Prior to TPD, the catalyst sample was again reduced at 400 °C for 2 h in flowing purified hydrogen. After reduction, the catalyst was flushed with ultra-high purity helium at 400 °C for 30 min and then cooled down to room temperature (25 °C) in a flow of helium. After that, 20 cm^3/min of helium was switched and sent to a Pyrex glass saturator, which contained methyl alcohol at room temperature. The helium stream containing methyl alcohol vapor then passed through the catalyst bed for 30 min. The catalyst bed was purged with pure helium until there was no longer any trace of methyl alcohol observed by mass spectrometry. Then the reactor was heated with a linear temperature rise of 40 °C/min to 600 °C in a He flow of 100 cm^3/min. The temperature of the furnace was controlled by an OMEGA CN8500 controller and recorded using a computer data acquisition system with LabVIEW software. The effluent gas from the reactor was split using a packless two-way valve (Nupro, SS-BNVCR4). A small portion of the effluent was sent into a UHV system, operating at a base pressure $<10^{-9}$ Torr, through a variable leak valve (Varian, 1000). Both valves were heated at 60 °C to avoid condensation of methyl alcohol. A Micromass PC Residual Gas Analyzer (RGA), from VG Quadrupoles, was used for analyzing the gases desorbing from the surface of the catalysts. The RGA was placed in the ultra-high vacuum system, which was pumped by a turbomolecular pump (Balzers, TPU 420). The pressure was detected by an ionization gauge tube (Varian). During TPD experiments, the pressure in the UHV chamber was kept at 7×10^{-6} Torr.

2.3. Methanol oxidation experiments

The oxidation of methanol was carried out in a Pyrex vertical tube reactor. Catalyst powder (50–100 mg) was placed between layers of glass wool. Prior to oxidation, the catalyst sample was pretreated in flowing hydrogen at 400 °C for 2 h and purged in a helium stream at 400 °C for 30 min. Then the catalyst sample was cooled down to the desired reaction temperature, that was varied from room temperature to 100 °C. Methanol was vaporized by passing helium through a bubbler containing liquid methanol at 5 °C. The methanol-laden helium was then mixed with the oxygen and the second helium lines to give gas mixtures having 1200, 1000, 770, and 500 ppm of methanol with 21% O_2 and balance with He. The flow rates of gases were controlled by mass flow controllers (Sierra series 840 Side-Trak). The feed mixture gas was passed upward through the reactor. The total flow rate through the reactor was 260 cm^3/min giving a space velocity of 20,000 h^{-1}. The catalytic reaction was performed using a continuous flow method at atmospheric pressure. The compositions of the feed gas and the outlet gas were principally analyzed by a gas chromatograph (Perkin-Elmer, Autosystem XL) equipped with a flame ionization detector (FID) and a Carbopack B/3% SP-1500 column, and with a TCD with a 60/80 Carboxen-1000 column. The temperatures of the FID and TCD were 120 and 200 °C, respectively. The gas chromatographic separations were carried out isothermally at 60 °C.

3. Results and discussion

Table 1 shows the actual loadings of Pt and Sn as well as chlorine content of two series of Pt–Sn catalysts in the study. The TPD profiles of methanol on the monometallic Pt/Al_2O_3 and the coimpregnated Pt–Sn/Al_2O_3 catalyst series are shown in Fig. 1. The TPD profiles for the sequentially impregnated catalysts are summarized in Fig. 2.

Blank experiments were carried out using the Al_2O_3 support alone, which had been subjected to the same pretreatment as the experimental catalysts. After exposing the blank Al_2O_3 to methanol at 25 °C, no desorption peak feature was observed over the entire temperature range up to

Table 1
The metal loading of series 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

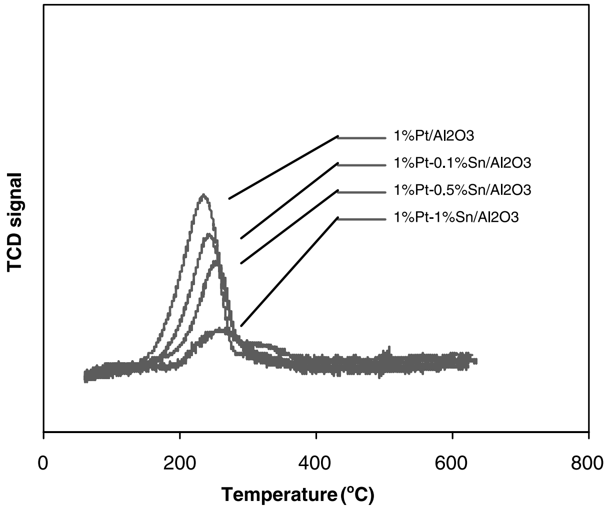

Fig. 1. TPD profiles of coimpregnated Pt–Sn catalyst series.

700 °C, suggesting that the support did not adsorb methanol to any significant extent. Moreover, the hydrogen and oxygen adsorption behavior of 2 wt.% Sn/Al_2O_3 also did in the previous work [18]. The results showed that there was no adsorption of hydrogen and small amount of oxygen adsorption (0.026 cm^3 STP/g cat.). This is in marked contrast to the observations made by Cordi and Falconer [22], 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 H_2, with CO_2 as a minor reaction product. In addition, less than 40% of the methanol dehydrated, giving dimethyl ether between 270 and 620 °C. They carried out their experiments on Kaiser A-201 Al_2O_3, which had been pretreated in O_2 at 600 °C to dehydrate it before each experiment. Kaiser Al_2O_3 has a pore volume of 0.46 cm^3/g, an average pore radius of 41 Å, and a surface area of 200 m^2/g [22]. Our investigation was carried out on non-porous fumed alumina (Degussa) which has a surface area of 90 m^2/g and is mainly in the gamma phase with some in the δ-phase. The chlorine content of the alumina is less than 0.5 wt.%. Furthermore, the catalysts used in this study were pretreated with H_2 at 400 °C, followed by cooling in nitrogen. Thus, the resulting alumina surface was not dehydrated.

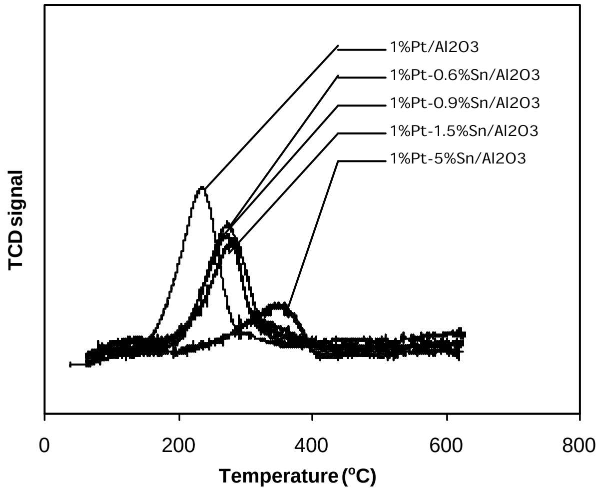

Fig. 2. TPD profiles of sequential impregnated Pt–Sn catalyst series (with Sn first).

As seen in Figs. 1 and 2, 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 wt.% Sn. This indicates that the bond strength between the adsorbed species and the Pt sites is the weakest for the monometallic 1.0 wt.% Pt/Al_2O_3 and increases with addition of tin. For the sequentially impregnated catalyst series, the maximum temperature peak shifted significantly from 230 to 290 °C when tin was added, but did not change much with further increase of the tin content from 0.6 to 1.5 wt.%. However at a tin content of 5 wt.%, 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 Figs. 3 and 4. For all catalysts, the peaks observed by mass spectrometry were in agreement with the TPD spectra obtained by TCD. From the mass spectra, the H_2/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

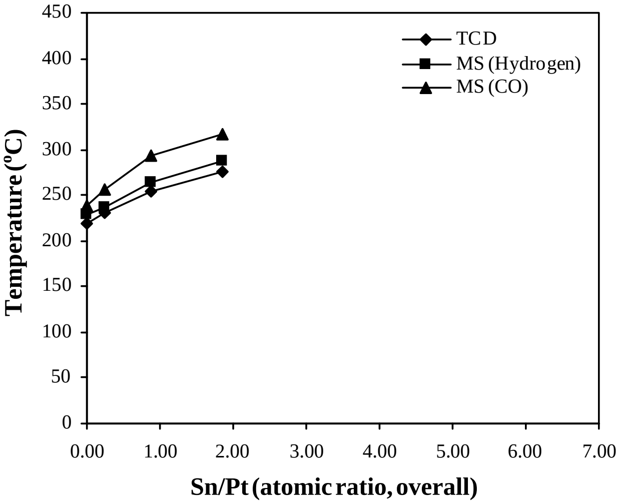

Fig. 3. The maximum peak temperature from TCD and MS versus Sn/Pt atomic ratio for coimpregnated Pt–Sn catalysts.

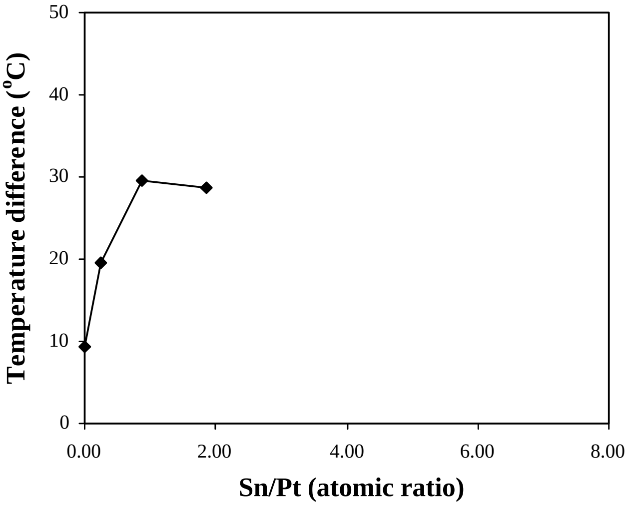

Fig. 5. The difference of hydrogen and carbon monoxide maximum peak temperatures versus Sn/Pt atomic ratio for coimpregnated Pt–Sn catalysts.

carbon monoxide peaks, as shown in Figs. 5 and 6. 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.

In a previous chemisorption study [18], it was found that CO adsorption on monometallic Sn/Al_2O_3 catalysts was completely reversible, with 100% of the adsorbed CO weakly held and removable by evacuation. On monometallic Pt/Al_2O_3, 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 [18], it appears that Pt particles in contact with tin–aluminate complexes exhibit a stronger CO bonding than that of CO on Pt/Al_2O_3. This trend towards a stronger CO bonding on $Pt–Sn/Al_2O_3$ catalysts with increasing tin content also manifests itself in the shift of the methanol decomposition to H_2 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

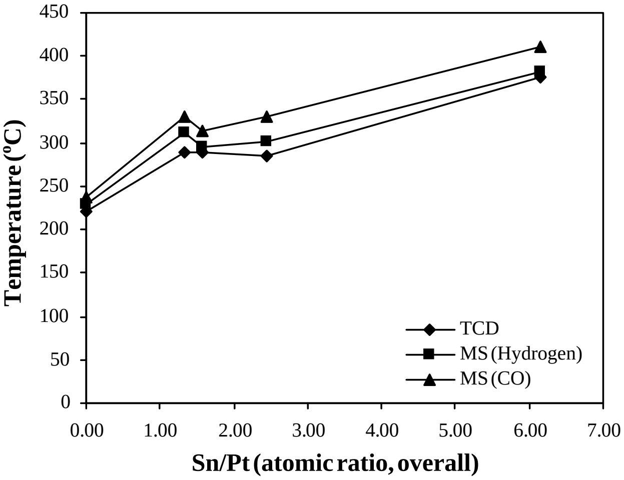

Fig. 4. The maximum peak temperature from TCD and MS versus Sn/Pt atomic ratio for sequentially impregnated Pt–Sn catalysts.

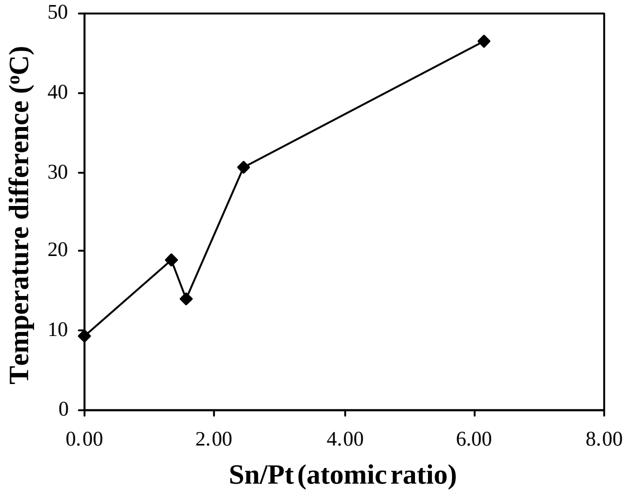

Fig. 6. The difference of hydrogen and carbon monoxide maximum peak temperatures versus Sn/Pt atomic ratio for sequential impregnated Pt–Sn catalysts.

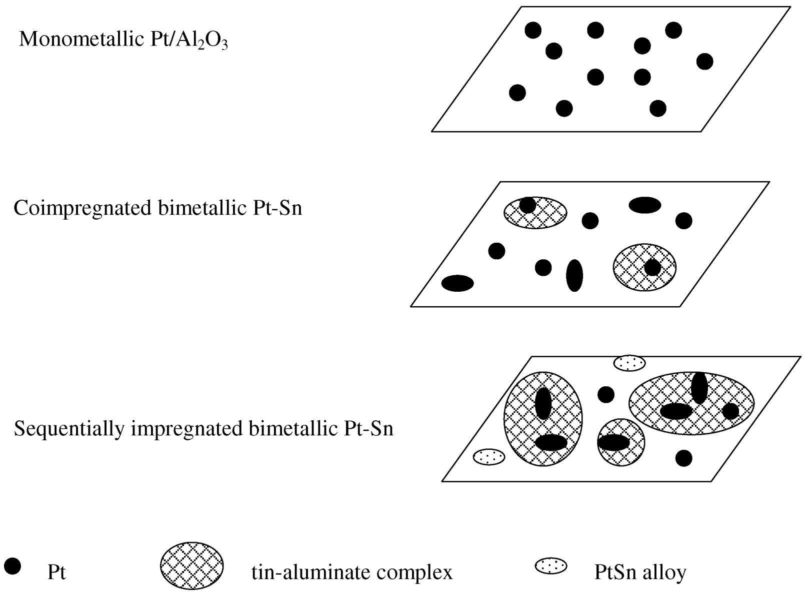

Fig. 7. The schematic describing the microstructural properties of studied catalysts.

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 H_2 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 tin-alumina 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 [18–21], a schematic describing the microstructure properties of the studied catalysts is sketched in Fig. 7. The monometallic Pt/Al_2O_3 catalyst structure is quite straightforward as the metal particles are highly dispersed and the particle size is mostly smaller than 10 Å with some proportion of the particles in the range of 10–20 Å. 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 proportion of particles are smaller than 10 Å. 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 wt.% Pt–1 wt.% Sn/Al_2O_3). 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.

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. Fig. 8 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

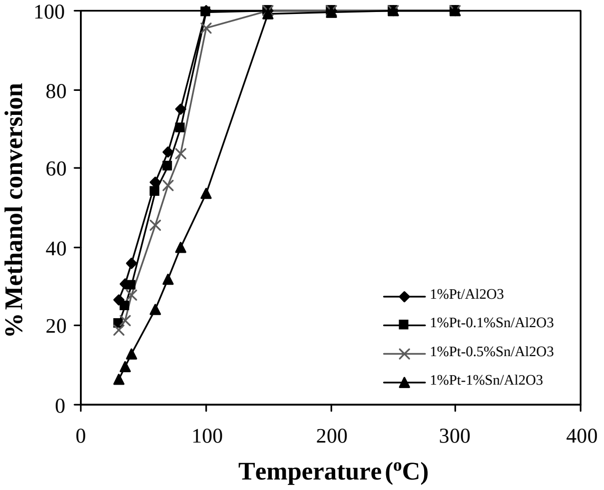

Fig. 8. Effect of temperature on methanol conversion for coimpregnated catalysts series. The feed contained 1200 ppm of methanol and 21% O_2 in helium carrier at a volumetric space velocity of 20,000 h^{-1}.

methanol was observed at room temperature for all catalysts and complete conversion was achieved at 100 °C for the 1 wt.% Pt/Al_2O_3 catalyst. The coimpregnated catalysts were also very active and reached 100% methanol conversion near 100 °C, except for the 1 wt.% Pt–1 wt.% Sn/Al_2O_3 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 [19]. According to the hydrogen chemisorption results, the 1 wt.% Pt–0.1 wt.% Sn/Al_2O_3 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. 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 [23], who found that in electrochemical oxidation of methanol, alloy surfaces of Pt–Sn exhibited lower catalytic activity than pure platinum surfaces.

The results of methanol oxidation over the sequentially impregnated catalysts are markedly different from those over the coimpregnated catalysts as shown in Fig. 9. 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, an increased Sn content slightly decreased 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 H_2 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, CO_2 and methyl formate were the only carbon-containing products of methanol oxidation over the monometallic Pt catalyst, as shown in Fig. 10. Methyl formate was the principle product at low temperatures, but its content decreased sharply with increasing temperature, with concomitant increase in the production of CO_2, 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:

$$2CH_3OH + O_2 \xrightarrow[\text{low temperature}]{\text{Pt and Pt–Sn catalyst}} CH_3OCHO + 2H_2O$$

$$2CH_3OH + 3O_2 \xrightarrow[\text{high temperature}]{\text{Pt and Pt–Sn catalyst}} 2CO_2 + 4H_2O$$

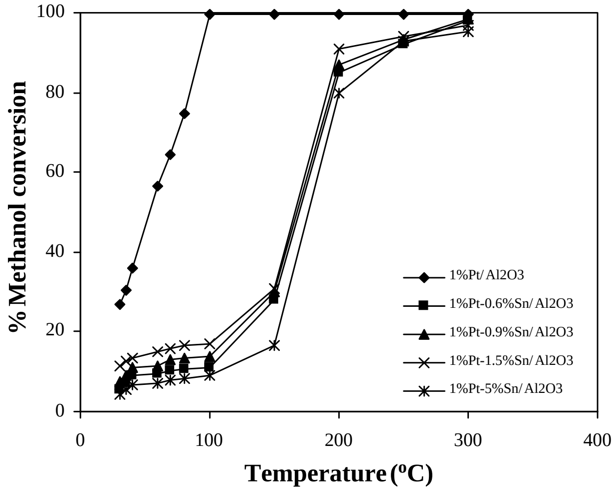

Fig. 9. Effect of temperature on methanol conversion for sequentially impregnated catalysts series. The feed contained 1200 ppm of methanol and 21% O_2 in helium carrier at a volumetric space velocity of 20,000 h^{-1}.

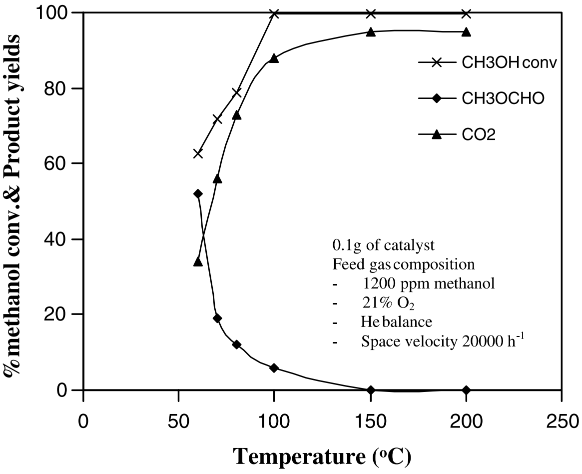

Fig. 10. Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over the monometallic Pt catalyst.

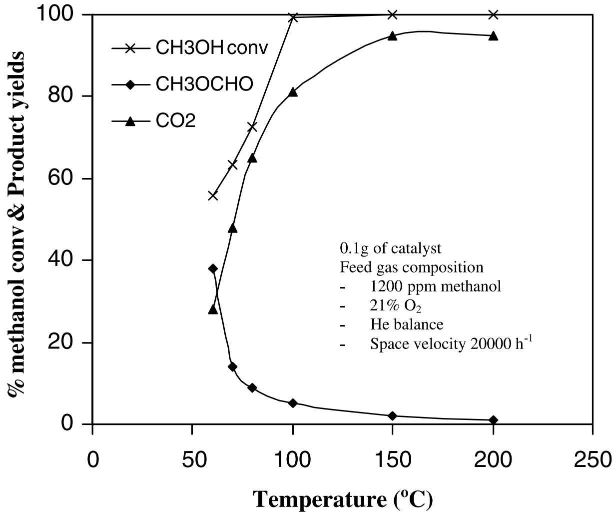

Fig. 11. Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over 1 wt.% Pt–0.1 wt.% Sn/Al_2O_3 catalyst.

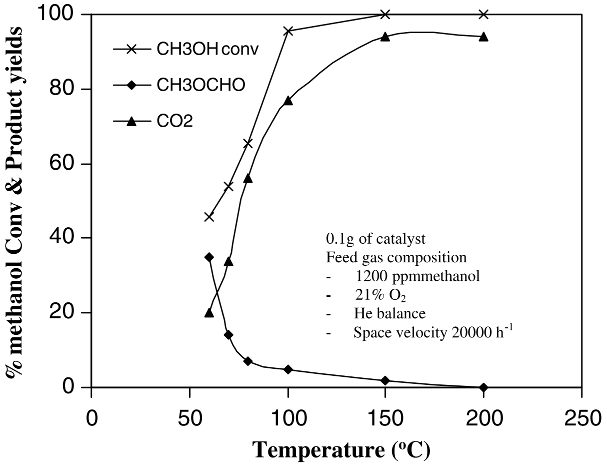

Fig. 12. Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over 1 wt.% Pt–0.5 wt.% Sn/Al_2O_3 catalyst.

These results are in good agreement with the previous work reported by McCabe and Mitchell [24] 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. Furthermore, 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.

For the coimpregnated catalysts, the reaction products are similar to those using the monometallic Pt catalyst (Figs. 11–13). 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.

As shown in Figs. 14 and 15 and Table 2, 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 [22]. Arrhenius plots were established to calculate the activation energy for methanol oxidation (Figs. 16 and 17). As shown in Table 2, 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 wt.%, but it shifted to 66.8 kJ/mol for 1 wt.% Pt–5 wt.% Sn/Al_2O_3 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

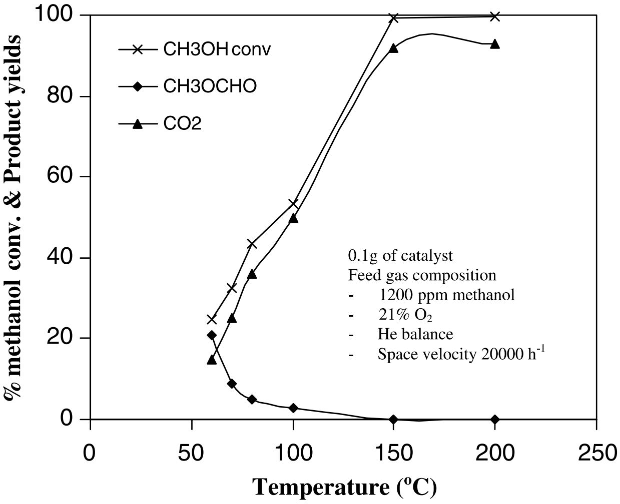

Fig. 13. Percentage of methanol conversion and selectivity of carbon-containing products as a function of temperature over 1 wt.% Pt–1 wt.% Sn/Al_2O_3 catalyst.

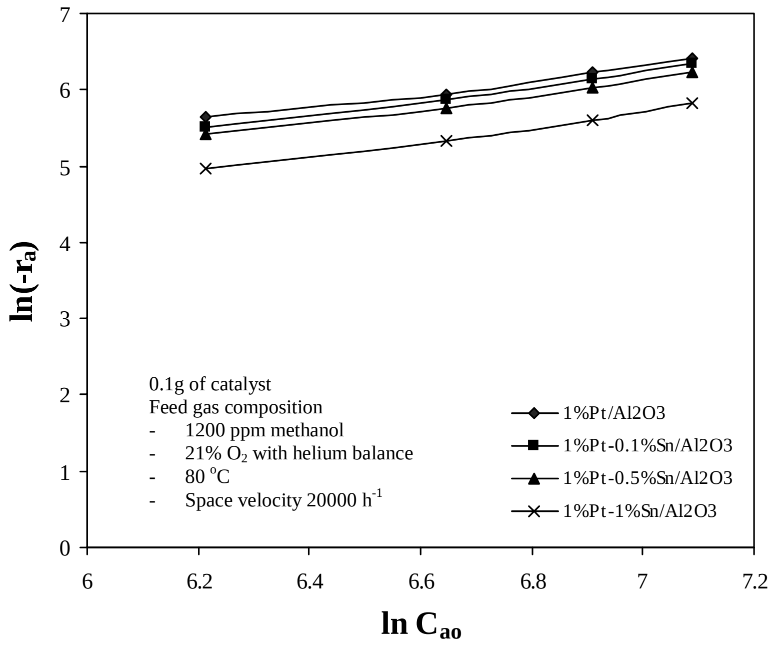

Fig. 14. Relation between rate of reaction and initial methanol concentration for coimpregnated catalysts series.

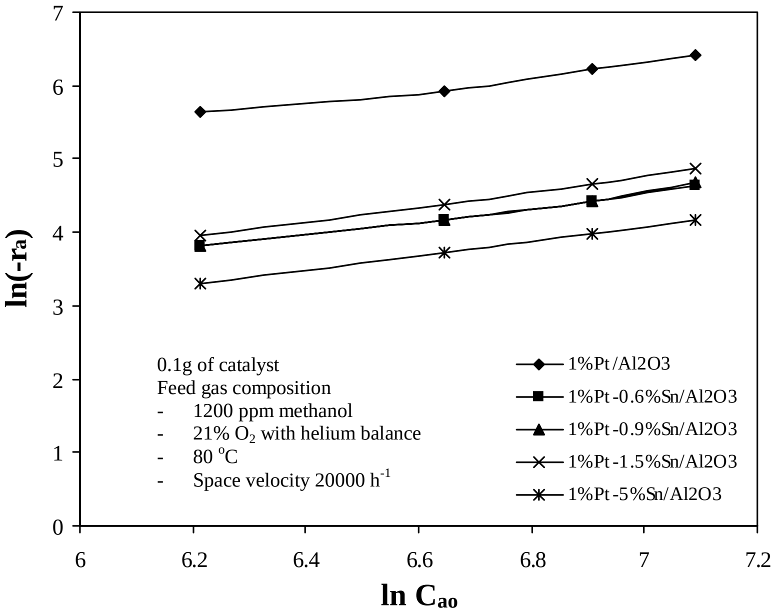

Fig. 15. Relation between rate of reaction and initial methanol concentration for sequentially impregnated catalysts series.

Table 2
Calculated values of reaction orders and activation energies

Catalyst (wt.%)	Impregnation method	Reaction order	E_a (kJ/mol)
0.99 Pt/Al_2O_3	–	1.12	25.9
0.96 Pt–0.14 Sn/Al_2O_3	Coimpregnation	1.12	38.9
1.00 Pt–0.53 Sn/Al_2O_3	Coimpregnation	1.13	41.8
0.89 Pt–0.99Sn/Al_2O_3	Coimpregnation	1.16	48.7
1.04 Pt–0.85 Sn/Al_2O_3	Sequential	1.15	54.5
1.03 Pt–0.96 Sn/Al_2O_3	Sequential	1.16	55.1
1.03 Pt–1.52 Sn/Al_2O_3	Sequential	1.13	54.9
1.12 Pt–4.18 Sn/Al_2O_3	Sequential	1.17	66.8

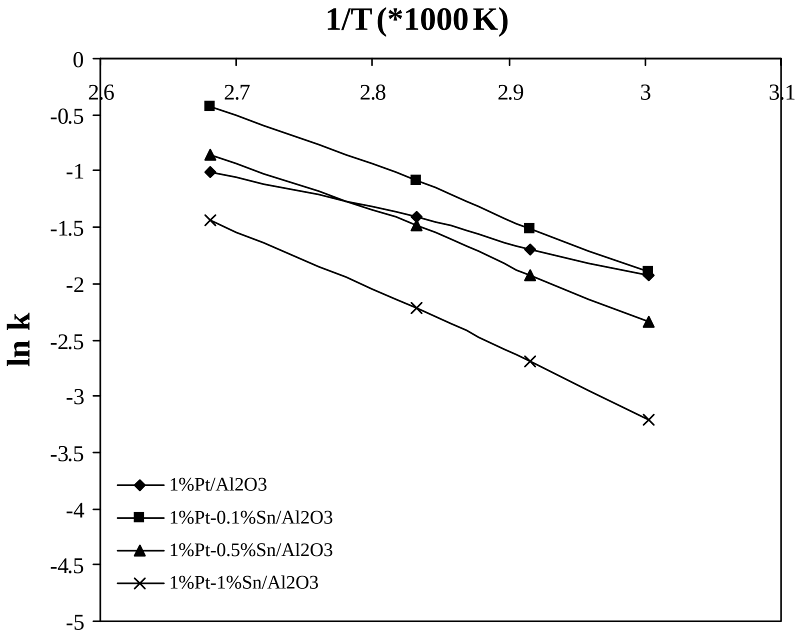

Fig. 16. Arrhenius plot for coimpregnated catalysts series.

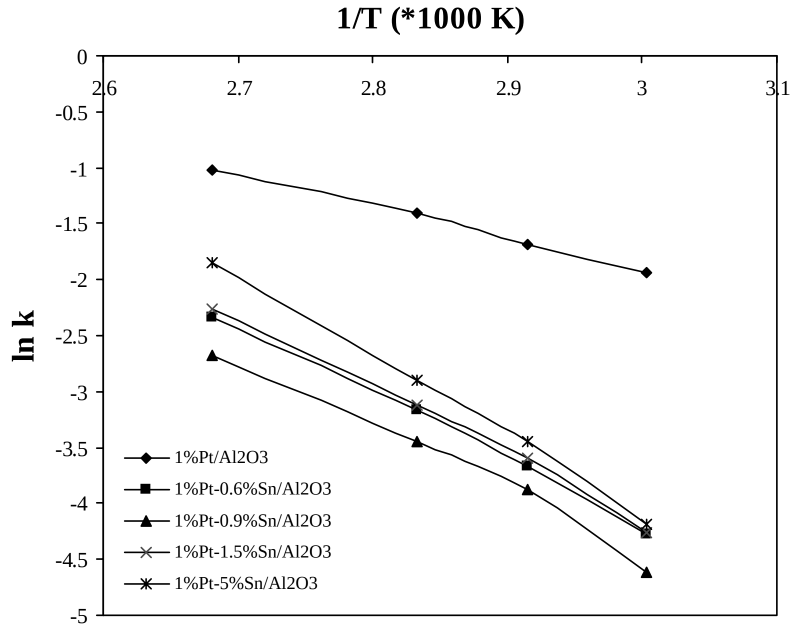

Fig. 17. Arrhenius plot for sequentially impregnated catalysts series.

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 (Fig. 18) showed a small drop in the activity of the monometallic Pt catalyst, but less drop in the activity was found over the 0.96 wt.% Pt–0.14 wt.% Sn/Al_2O_3 catalyst. The activity decreased considerably when the tin loading was further increased. The 0.96 wt.% Pt–0.14 wt.% Sn/Al_2O_3 catalyst did not show any signs of deactivation over 2 days, while 0.99 wt.% Pt/Al_2O_3 catalyst lost about 2% activity per day. Extrapolation of these results indicates that the 0.99 wt.% Pt/Al_2O_3 catalyst would lose its activity completely after 39 days on stream. However, the results indicate that the activity of platinum catalysts can be

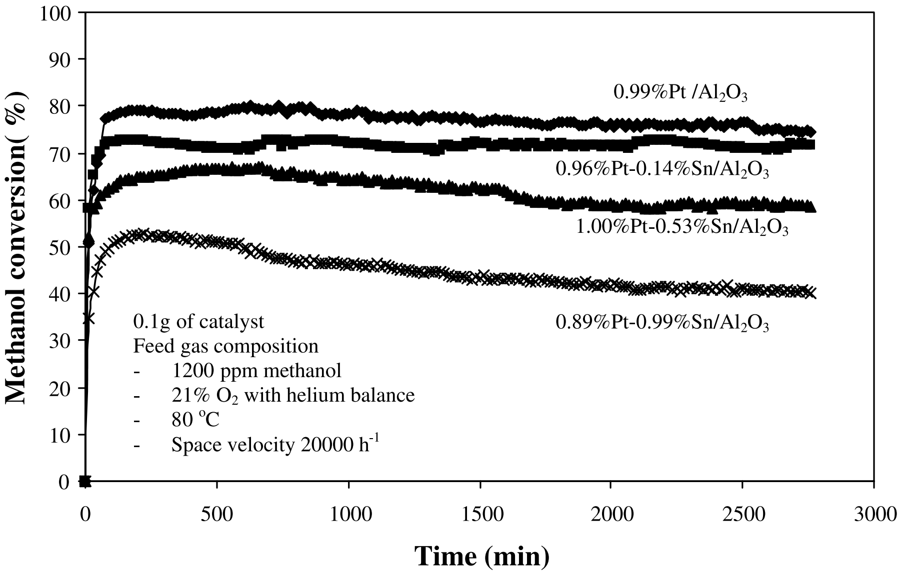

Fig. 18. The long-running experiment for observing the deactivation of the coimpregnated catalysts series.

maintained by the addition of an appropriate amount of tin.

4. Conclusions

From the TPD results of methanol oxidation on the bimetallic Pt–Sn/Al$_2$O$_3$ catalysts, methanol decomposes primarily into hydrogen and carbon monoxide. Hydrogen desorbs first followed by desorption of carbon monoxide at higher temperatures. In the coimpregnated catalyst series, the desorption peaks of both H$_2$ and CO were found to gradually shift to higher temperatures with increasing Sn content. In the sequentially impregnated catalyst series, the same results were observed for all Sn containing samples, except for the catalyst containing 5 wt.% Sn, where the shift was significantly larger than for all other samples. The temperature difference between the H$_2$ and CO desorption peak maxima increased significantly with increasing Sn content in both catalyst series. This study has demonstrated that the adsorption and decomposition behavior of methanol on platinum is strongly modified by the presence of tin. The relative distribution of Sn to particles of different size and nature, such as alloy particles or partially oxidized Sn species interacting with the alumina support, influences the strength of adsorption of both H$_2$ and CO. This has been shown by a schematic describing the microstructure of catalysts.

The alumina-supported monometallic Pt catalyst was found to be the most active methanol oxidation catalyst. The trend in oxidation temperature was similar to the maximum peak temperature as seen from the TPD results. The main carbon-containing products of methanol oxidation over the alumina-supported monometallic Pt and bimetallic Pt–Sn catalysts were found to be CO$_2$ and methyl formate (CH$_3$OCHO). A small amount of tin can counteract the deactivation of platinum catalyst.

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