



Research Article

Characterization of Industrial Pt-Sn/Al₂O₃ Catalyst and Transient Product Formations during Propane Dehydrogenation

Kah Sing Ho, Joanna Jo Ean Chye, Sim Yee Chin, Chin Kui Cheng*

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang,
Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

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Abstract

The major problem plaguing propane dehydrogenation process is the coke formation on the Pt-Sn/Al₂O₃ catalyst which leads to catalyst deactivation. Due to information paucity, the physicochemical characteristics of the commercially obtained regenerated Pt-Sn/Al₂O₃ catalyst (operated in moving bed reactor) and coke formation at different temperatures of reaction were discussed. The physicochemical characterization of regenerated catalyst gave a BET surface area of 104.0 m²/g with graphitic carbon content of 8.0% indicative of incomplete carbon gasification during the industrial propylene production. Effect of temperatures on coke formation was identified by studying the product yield via temperature-programmed reaction carried out at 500 °C, 600 °C and 700 °C. It was found that ethylene was precursor to carbon laydown while propylene tends to crack into methane. Post reaction, the spent catalyst possessed relatively lower surface area and pore radius whilst exhibited higher carbon content (31.80% at 700 °C) compared to the regenerated catalyst. Significantly, current studies also found that higher reaction temperatures favoured the coke formation. Consequently, the propylene yield has decreased with reaction temperature. © 2013 BCREC UNDIP. All rights reserved

Keywords: Carbon formation; Industrial Pt-Sn/Al₂O₃ catalyst; Propane dehydrogenation

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1. Introduction

Propene, also known as propylene, is widely used in the production of downstream petrochemical products. It is produced via propane dehydrogenation (PDH) process [1]. From thermodynamic perspective, the reaction is highly endothermic which requires elevated temperature and low pres-

sure to obtain a meaningful conversion.

During propane dehydrogenation process, carbonaceous deposit identified as coke is normally formed [2]. The onset of other side reactions may also increase the presence of carbon precursors that ultimately leads to the coke/ carbon formation. The main and side reactions during PDH are proposed as follows [3]:

Main reaction:



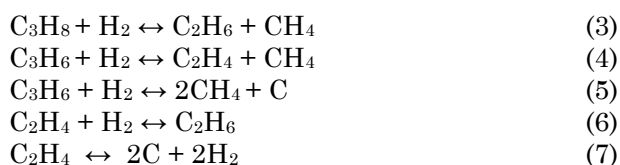
Side reactions:



* Corresponding Author.

E-mail: chinkui@ump.edu.my (C. Cheng)

Tel: +60-9-5492896, Fax: +60-9-5492889



Significantly, reports on physicochemical of industrial Sn-Pt/Al₂O₃ catalyst and its transient kinetic trend are scarcely available in the open literature. Therefore the current work is dedicated to the characterization of commercially-obtained regenerated Pt-Sn/Al₂O₃ catalyst (in spherical pellet form) and the analyses of reaction trend as well as coke formation during PDH. Characterization is necessary to establish the relation of the structural feature and the performance of the catalyst before and post-PDH.

2. Materials and Methods

2.1. Fresh Regenerated Catalyst Characterization

The characterization of the obtained regenerated catalyst was carried out without any pre-treatment. X-ray photoelectron spectroscopy (XPS) was used to carry out the elemental studies with its atomic concentration percentage by determining the binding energy of the element. In addition, the oxidation state of Sn was also sought from XPS. Fourier transformed infrared spectroscopy (FTIR) was employed to determine the functional groups attributed to the catalyst and field emission scanning electron microscopy (FESEM) to capture the morphology the catalyst. Besides, nitrogen adsorption analyzer was used in determining the surface area of catalysts through Brunauer-Emmett-Teller (BET) method and pore radius was obtained from Barrett-Joyner-Halenda (BJH) correlation. The crystallite size for the catalyst was determined from X-Ray Diffraction (XRD) with 2θ range of 20° to 90°.

2.2. Transient Kinetic Profiles

PDH process over the Pt-Sn/Al₂O₃ catalyst was monitored online using temperature programmed reaction (TPR) instrument model TPRO 1100 SE-RIES by subjecting the regenerated Pt-Sn/Al₂O₃ catalyst with propane flowing at a fixed rate of 15 ml/min at different reaction temperatures. Compositions of gaseous products formed at 500 °C, 600 °C and 700 °C was detected by mass spectrometer.

2.3. Used Catalyst Characterization

Comparisons on physicochemical properties were also sought for the used Pt-Sn/Al₂O₃ catalyst (also termed as spent) post-propane dehydrogena-

tion in elucidating some critical observations. XPS was used to compare the atomic concentration percentage of carbon. Liquid nitrogen adsorption method was also employed to determine the surface area and pore radius. The crystallite size for the carbon was determined by using XRD while FESEM was used to study on the surface structure and morphology of the spent catalyst.

3. Results and Discussion

3.1 XPS and FTIR Characterization

Table 1 presents the percentage of atomic concentration for the elements detected in XPS analysis. XPS results confirmed the presence of platinum, Pt (*undisclosed*) catalyst promoted by stannum, Sn (*undisclosed*) and supported by alumina (86.87%), Al and oxygen. Alumina accounts for a large fraction of oxygen detected and a small fraction is due to the tin oxide. Significantly, a substantial percentage of carbon (7.75%) was also detected in the regenerated catalyst pellet. The presence of carbon was due to the poor regeneration technique employed in the existing industrial moving bed reactor. Consequently, failure to completely remove the carbonaceous deposits over the extended period of reaction time has led to the accumulation of these polymerized carbonaceous species at the core of the pellet culminating in higher energy requirement to disintegrate the compound.

A small percentage of chlorine was found in the catalyst and this may be related to the history of catalyst preparation itself. Pt-Sn/Al₂O₃ catalyst is normally synthesized from the impregnation of the tin (IV) chloride and hexachloroplatinic acid as metal precursors into the alumina solid.

In addition, the detection of sulphur (S) was due to the purification of the natural gas from impuri-

Table 1. Quantification result of regenerated Pt-Sn/Al₂O₃ catalyst

Detected Element	Core Level	Binding Energy (eV)	Percentage of Atomic Composition (%)
C	1s	284.5	7.75
O	1s	531.0	47.68
F	1s	685.0	1.76
Al	2p ³	74.2	39.19
S	2p ³	169.0	undisclosed
Cl	2p ³	198.8	0.80
K	2p ³	293.5	undisclosed
Sn	3d ⁵	486.5	undisclosed
Pt	4d ⁵	333.0	undisclosed

ties. One of the byproducts of this process is H₂S which is further converted into sulphur. It is also a common practice to add sulphur as an odorant for leak detection. It can also be seen from Table 1 that potassium (K) element was detected. Once again, this can be attributed to the formulation of the catalyst where the potassium was incorporated for basicity increment.

Information pertaining to the types of chemical bonding present on catalyst surface was obtained via FTIR scanning and the identified peaks are presented in Table 2. Peaks appeared at 829.58 cm⁻¹ and 1384.36 cm⁻¹ indicate the presence of alkane group. Significantly, carbon species of the olefinic type was deposited on the catalyst as shown by the double bond detected at 1636.43 cm⁻¹. This finding was consistent with XPS analysis where detection of carbon/ coke was reported.

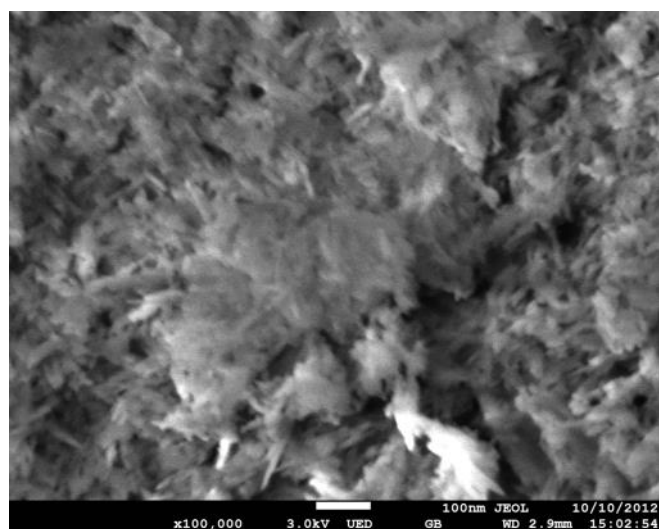
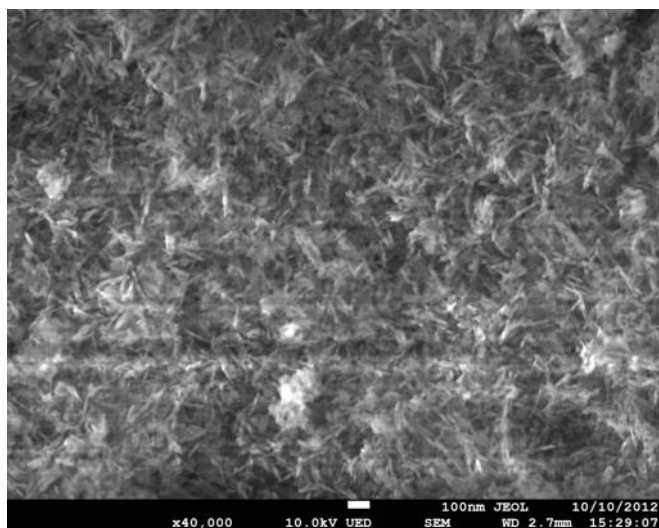


Figure 1. FESEM images on regenerated catalyst at magnifications (from left) 40000X and 100000X

The presence of hydroxyl group (broad peak at 3444.05 cm⁻¹) was probably due to the moisture captured from the ambient after the catalyst sample has been left at ambient condition for an extended time. The catalyst is a hygroscopic substance, hence possess tendency to absorb moisture from the environment.

3.2 FESEM Analysis

Figure 1 shows the images snapped from FESEM instrument at magnifications of 40000X and 100000X respectively. It can be seen that there are two distinct regions; the lighter region was attributed to the metals while the darker region can be attributed to the carbon residue. In addition, the structural feature observed from FESEM suggests homogenous dispersion of metal over the alumina support.

The catalyst also exhibited non-spherical shape with high porosity. High porosity of the catalyst increased the surface area yielding more active sites for the reaction to take place. Besides, the darker region which was attributed to the carbonaceous deposits displayed a filamentous structure (cf. Figure 1).

3.3 Liquid Nitrogen Physisorption and XRD Pattern

Liquid nitrogen adsorption was used to determine the surface area, median pore size and maximum pore size profiles of catalyst. Table 3 shows the results.

Table 2. Peaks identified from FTIR

Wavelength (cm ⁻¹)	Possible Compounds
3444.05	Hydroxyl groups
1636.43	Alkenes
1384.36	Alkanes
829.58	Alkanes

Table 3. Physical properties of Pt-Sn/Al₂O₃ catalyst

Physical property	Values	Remarks
Surface area (m ² /g)	103.55	BET
Median pore radius (nm)	12.70	Mesopores
Max. pore radius (nm)	13.55	Mesopores
Pore volume (cm ³ g ⁻¹)	0.79	Mesopores

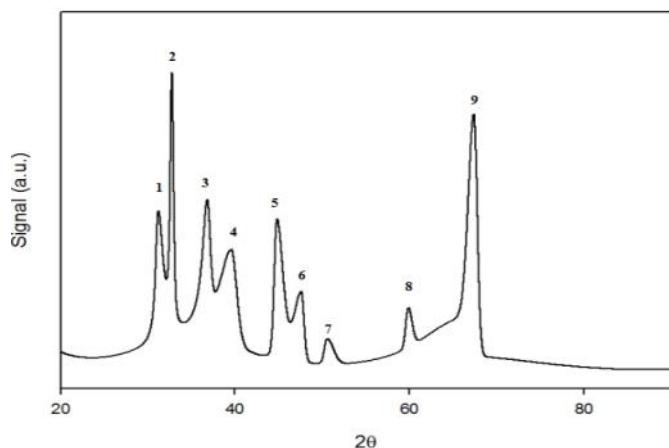


Figure 2. XRD pattern of regenerated catalyst

The pore radius was determined from the Barrett-Joyner-Halenda (BJH) method which used the desorption branch of nitrogen isotherm pore size distribution estimation. BJH method gave a median pore radius of 12.70 nm. BJH method is suitable for pore size greater than 2 nm and therefore it is valid for the current result. Furthermore, it can be concluded that the catalyst possessed mesopores as the diameter is within 2 to 50 nm.

XRD was employed to determine the crystallite species present on the regenerated Pt-Sn/Al₂O₃ catalyst. Figure 2 shows the resulting XRD pattern.

It can be seen that only alumina crystallite of γ -phase are being identified from the XRD analysis. Metals of other elements were not detected most likely due to the fine dispersion within the alumina matrix. This concurs with the obtained FESEM images. Table 4 summarizes the crystallite identified from XRD analysis.

3.4 PDH Reaction and Coke Formation Studies

From the equilibrium constant ($K_{\text{equilibrium}}$) calculation, propane dehydrogenation to produce propene increases with temperature due to the endothermicity nature. However, Figure 3 shows that the highest yield of propylene was obtained at 500°C (lowest temperature employed in the current study). This is in total contradiction to the theoretical thermodynamic prediction. One of the reasons for the discrepancy was probably due to the hydrocarbon thermal cracking which causes coke deposition on the catalyst. It is a common knowledge that olefinic species is a coke-precursor.

In addition, it can be observed that the propylene yield exhibits a rapid transient ascension in particular for the first 300 s before attaining a steady state (cf. Figure 3). At the onset of reaction, propane dehydrogenation took place on the surface of catalyst with high catalytic activity. During the

Table 4. Summary of crystallites from XRD pattern

Peak	Theta (2 θ)	Crystallite size (nm)	Compound
1	31.0	8.70	Alumina
2	32.8	20.0	Alumina
3	36.8	8.20	Alumina
4	39.6	3.56	Alumina
5	44.8	7.70	Alumina
6	47.6	6.60	Alumina
7	50.5	7.60	Alumina
8	59.8	11.80	Alumina
9	66.1	1.74	Alumina

reaction, not all propylene formed would have desorbed immediately from the catalyst. Subsequently, further competing side reaction such as thermal cracking may occur to produce shorter chain olefinic species *i.e.* ethylene or even C₁ species (methane). This may have contributed to the drop of propylene yield post-1800 s. The propene yield loss was most prominent at higher reaction temperatures (600 and 700 °C respectively).

As propene yield was lowest at highest reaction temperature in the current investigation, further analysis was carried out to elucidate the transient product distribution at 700°C. Figure 4 shows that products detected were propylene, ethylene, ethane and methane. No other gaseous products were detected. Significantly, it can be observed that ethylene formation was faster than propylene. This has indicated that propane easily underwent thermal cracking to form ethylene and methane (cf. Equation (2)), in a parallel reaction with propane dehydrogenation (cf. Equation (1)). Nonetheless, ethylene yield decreased thereafter whilst propylene increased and holding steady before eventually decreased. It is generally accepted that ethylene is a coke precursor over an acidic site. Consequently, coke formation over Pt-Sn/Al₂O₃ catalyst was primarily originating from ethylene cracking (cf. Equation (7)) and to some extent from propylene cracking (cf. Equation (5)). The qualitative trend shown in Figure 4 has indicated that most likely, propylene was a prime candidate for methane formation.

It can be seen that methane showed gradual increase in the region of propylene decay (cf. Figure 4). From 1800 seconds onwards, there is a sharp increase in methane yield. This was corroborated with substantial decrease of propylene composition.

The used/spent catalysts were then collected and subjected to another round of physicochemical

characterization and the results were compared with the regenerated catalyst. From XPS analysis, same elements were detected for both the regenerated and spent catalyst. However, it is important to stress that the percentage of elemental concentration for carbon in spent catalyst was considerably higher than the regenerated catalyst. Table 5 compares the percentage of carbon detected in spent catalysts post-reaction.

All three catalyst samples showed significantly higher carbon content compared to the regenerated catalyst (cf. Table 1) indicating severe coking during propane dehydrogenation. Nonetheless, the

carbon peak possessed similar binding energy suggesting that similar carbon species were detected. In addition, carbon deposition seems to increase with reaction temperature, consistent with earlier proposition that olefinic species such as ethylene have dehydrogenated further into coke that covered the catalyst and rendered the catalyst inactive. Consequently, propylene yield has decreased with reaction temperature due to the blockage of access to the active sites.

Figure 5 illustrates the comparison of peak picked up by XRD for both the regenerated and spent catalyst.

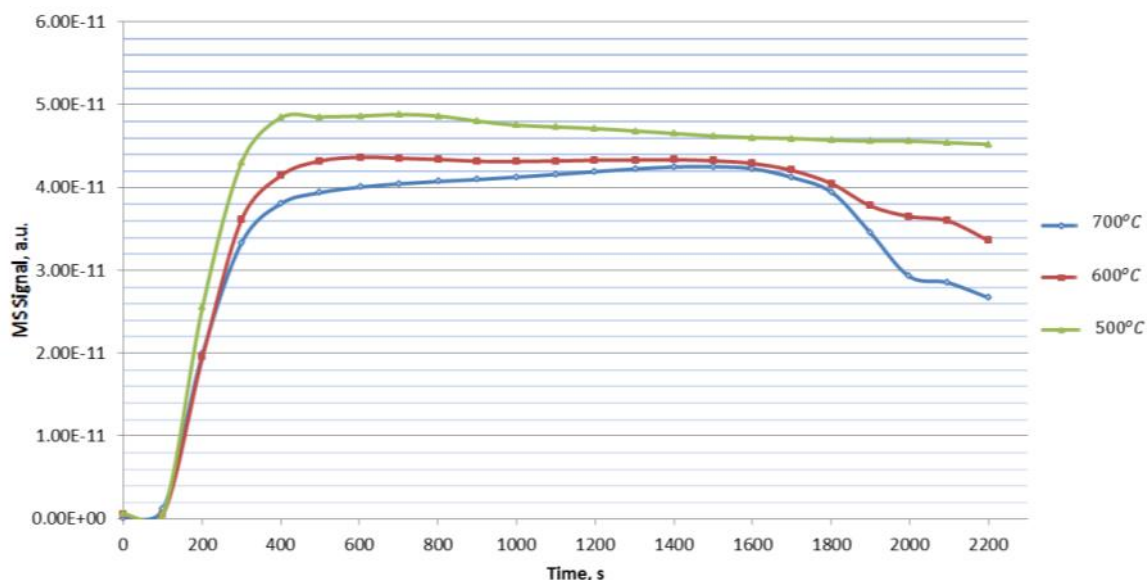


Figure 3. Transient propylene yield at various temperatures

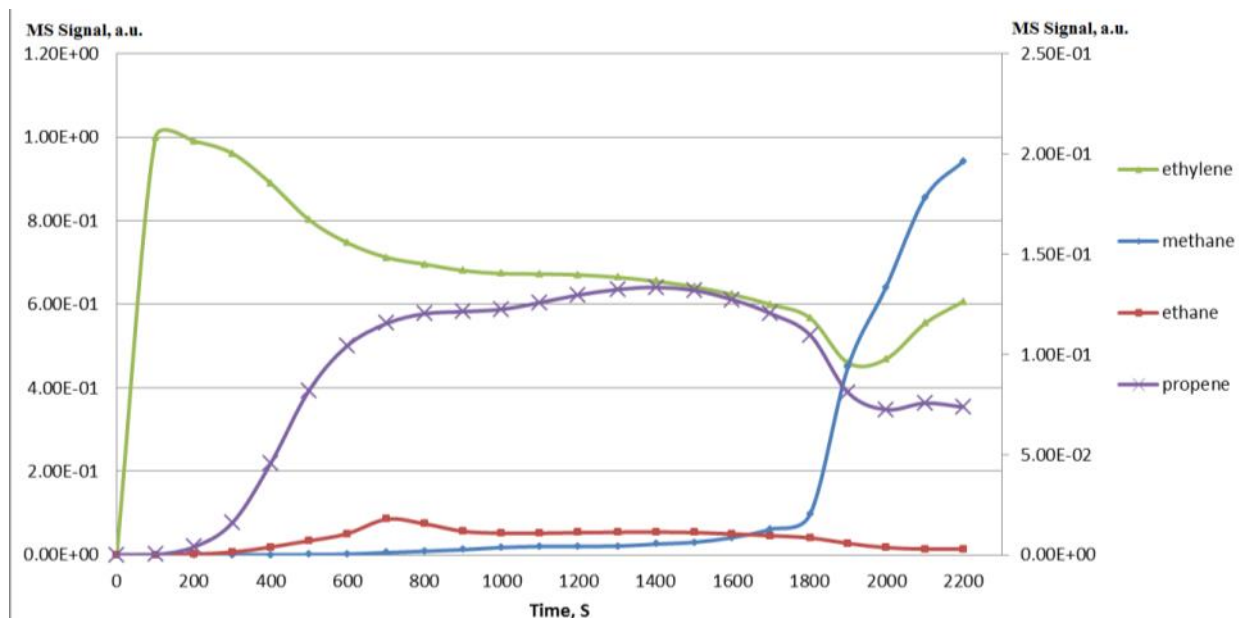


Figure 4. Qualitative transient trend of product formations at 700 °C

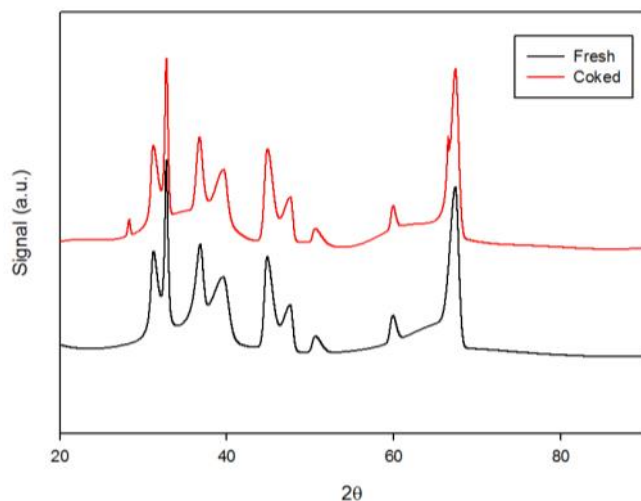


Figure 5. XRD pattern for regenerated and spent catalyst (at 700 °C)

It can be seen that another peak was detected at 2θ of approximately 25° and this was attributed to the presence of the carbonaceous compound. The detected carbon was graphitic type with crystallite size of approximately 257 nm.

In addition, from the liquid nitrogen adsorption method, a great reduction in surface area, mean pore size and median pore size was observed. Table 6 compares the findings between regenerated catalyst and spent catalyst post propane dehydrogenation reaction at 700 °C.

Table 6 shows that the surface area and pore radius of the regenerated catalyst was much higher compared to the spent catalyst. Lower surface area and pore radius in the spent catalyst was due to the deposition of carbonaceous compound that has blocked the catalyst's pores.

4. Conclusions

Commercially-obtained regenerated Pt-Sn/Al₂O₃ catalyst has been subjected to a series of physicochemical property examinations. A substantial reduction of surface area was observed for the spent catalyst (surface area of 78.9 m²/g with pore radius of 101.15 nm) compared to the regenerated catalyst (surface area of 103.5 m²/g and pore radius of 12.70 m²/g). In addition, XPS analysis confirmed that the carbon content for spent catalyst (31.75%) post reaction was higher compared to the regenerated catalyst (7.75%). Propane dehydrogenation studies suggest that the highest yield was detected at 500 °C, followed by 600 °C and 700 °C. Likewise, the carbon laydown also increased with the temperature. This may explained the decrease of propylene yield with temperature.

Table 5. Atomic composition of carbon in spent catalyst

Catalyst	Temp (°C)	Atomic Conc. (%)
Spent	500	15.50
	600	24.30
	700	31.75

Table 6. Comparison of physicochemical properties of regenerated and spent catalysts (700 °C)

	Regenerated Catalyst	Spent Catalyst
Surface area (m ² /g)	103.55	78.9
Mean pore radius (nm)	12.70	10.15
Maximum pore radius (nm)	13.55	11.17

Acknowledgements

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