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## **APPENDICES**

## APPENDIX A

### CALCULATION OF CATALYST PREPARATION

The sample calculation shown below is for 0.3wt%Pt/0.3wt%Sn-0.6wt%K/SiO<sub>2</sub>. The hydrochloric acid is also added to the impregnation solution by 5% wt the silica support. The silica support weight used for all preparation is 2 grams.

If X grams of silica support is used, so each 100 grams of the catalyst is composed of

Platinum	0.3	g
Tin	0.3	g
Potassium	0.6	g
Hydrochloric acid	0.05×X	g
Silica support	X	g
Then	$0.3 + 0.3 + 0.6 + (0.05X) + X = 100$	g
	$X = 94.0952$	g

The Platinum compound used is chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), its molecular weight is 517.92, and the platinum content in the compound is 37.67 % wt. The stock solution of chloroplatinic acid has the concentration of 1 g in 25 ml of water.

The tin compound used is stannous chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O), its molecular weight is 118.69, and the tin content in the compound is 51.02 %wt.

The potassium compound used is potassium nitrate (KNO<sub>3</sub>), its molecular weight is 101, and potassium content is 38.61 %wt. The stock solution of potassium nitrate has the concentration 3 g in 25 ml of water

Concentration of hydrochloric acid solution is 37% vol by vol, its density is 1.19 kilogram per liter.

The calculation procedure of the amount of each ingredient for the required composition of 0.3wt.%Pt/0.3wt.%Sn-0.6wt.%K/SiO<sub>2</sub>catalyst shows below.

For two grams of alumina support used:

1) Platinum required	= (0.3×2)/94.100	g
	= 6.37×10 <sup>-3</sup>	g
Chloroplatinic acid required	= 6.37×10 <sup>-3</sup> ×100×25/37.67	ml
	= 0.4232	ml
2) Tin required	= 2×0.3/94.0952	g
	= 6.376×10 <sup>-3</sup>	g
Stannous chloride dihydrate required	= 6.376×10 <sup>-3</sup> ×100/51.02	g
	= 0.0125	g
3) Potassium required	= 2×0.6/94.0952	g
	= 0.0128	g
Potassium nitrate required	= 0.0128×100×25/(38.61×3)	ml
	= 0.2763	ml
4) Hydrochloric and solution required		
	= 2×0.05	g
	= 0.1	g
The amount of hydrochloric and by volume		
	= 0.1/(1.190×0.37)	ml
	= 0.2271	ml

As the pore volume of the silica support is 1 ml/g, the total volume of impregnating solution that must be used is 2 ml by the requirement of dry impregnation method, the de-ionized water is added until the volume of impregnating solution is 2 ml as equal to the volume of the silica pore volume.

**APPENDIX B**  
**CALCULATION OF TEMPERATURE IN SATURATOR**

Set the vapor pressure of reactants to the requirement by adjust the temperature of saturator following the antoine equation [198]:

$$\text{Log } P = A - \frac{B}{(t + C)}$$

When  $P$  = vapor pressure of reactant, mm Hg

$t$  = temperature, °C

$A$ ,  $B$  and  $C$  = constants

The values of constants are in Table B-1

**Table B-1** The value of constant

Reactant	A	B	C
n-Pentane	15.8333	2477.07	-39.94
1-Pentene	15.7646	2405.96	-39.63
n-Hexane	15.8366	2697.55	-48.78
1-Hexene	15.8089	2654.81	-47.30
n-Heptane	15.8737	2911.32	-56.51
1-Heptene	15.8894	2895.51	-53.97
n-Octane	15.9426	3120.29	-63.63
1-Octene	15.9630	3116.52	-60.39

**APPENDIX C**  
**CALCULATION OF FLOW H<sub>2</sub> AND HYDROCARBON WHEN VARIED**  
**H<sub>2</sub>/HC RATIO**

At ratio of H<sub>2</sub>/HC = 1

From C<sub>3</sub>H<sub>8</sub> 20% balance with

$$C_3H_8/N_2 = 20/80$$

$$= 1/4$$

$$4C_3H_8 = N_2$$

Feed input is 30 ml./min.

Thus,

$$C_3H_8 + N_2 + H_2 = 30 \quad \text{ml/min}$$

$$C_3H_8 + 4 C_3H_8 + C_3H_8 = 30 \quad \text{ml/min}$$

$$C_3H_8 = 30/6 \quad \text{ml/min}$$

$$= 5 \quad \text{ml/min}$$

Consequently, flow rate of hydrogen = 5 ml/min

flow rate of C<sub>3</sub>H<sub>8</sub> = 25 ml/min



**APPENDIX D**  
**CALIBRATION CURVE OF CARBON DIOXIDE CONTENT**

**Table D-1** Detected area and estimated weight of carbon by feeding 100%CO<sub>2</sub> 0.405 ml/min mixed with helium in various flow rate through porapak Q column on GC 8AIT at 110°C detector temperature and 90°C column temperature, using (1.5ml) sampling loop

Carbon content (mg)	Average area (a.u.)
0.001293	2218
0.002138	3738
0.004051	7079
0.005375	9379
0.007239	12587

The assumption of gas content calculation was based on the ideal gas law. Therefore, the data fitted with linear equation can be expressed below;

$$\text{Amount of carbon (mg), } Y = 5.7410 \times 10^{-7}$$

Where least square error,  $R^2 = 0.9999$

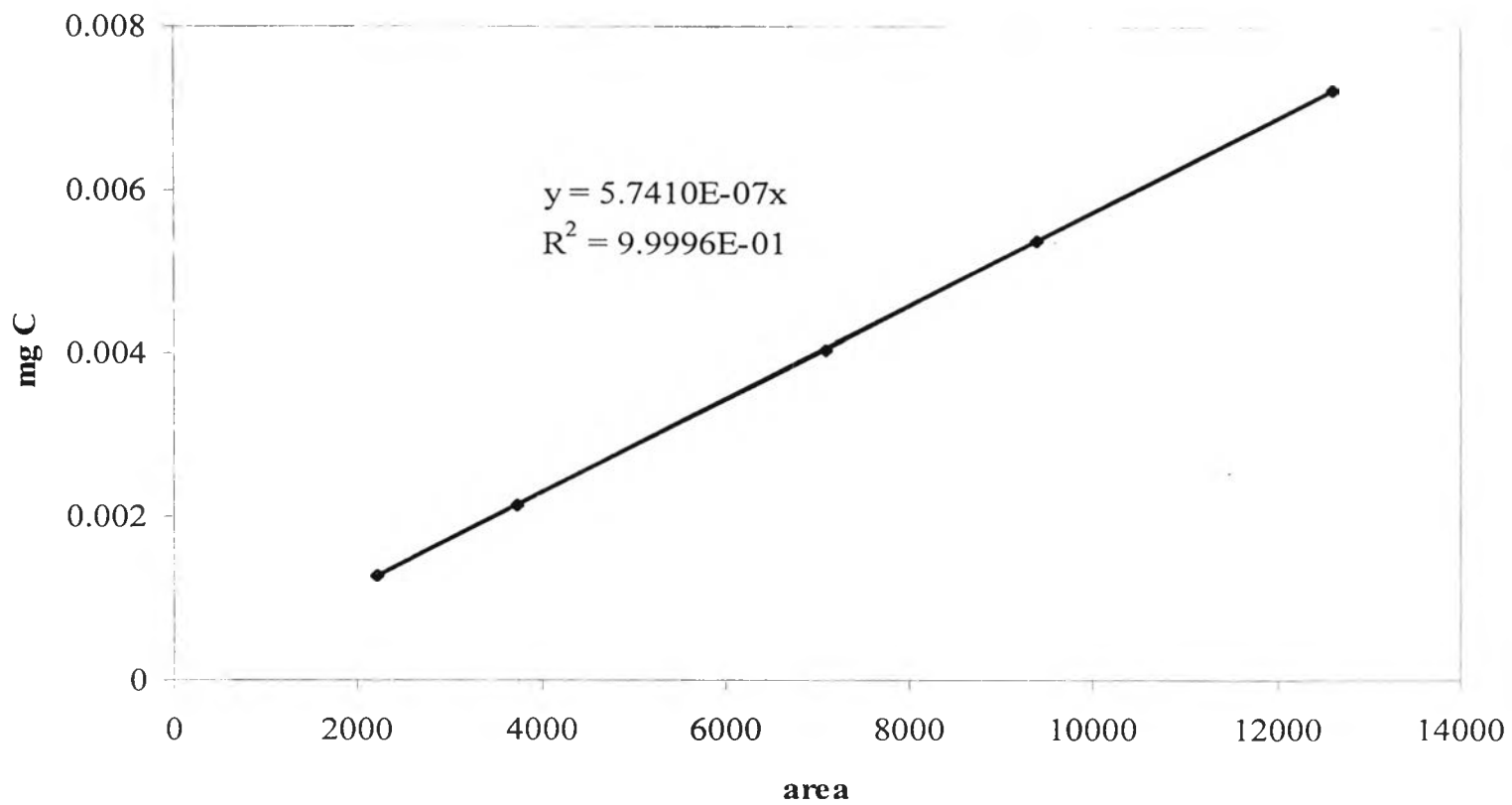


Figure D.1 Calibration curve of carbon dioxide on GC 8AIT

**APPENDIX E**  
**CALCULATION OF METAL ACTIVE SITES**

To calculation metal active sites of the catalyst by purity CO adsorption at room temperature have the procedure as follows:

Let the weight of catalyst used	= W	g
Height of CO peak after adsorption	= A	unit
Height of 40 l. standard CO peak	= B	unit
Amounts of CO adsorbed on catalyst	= B-A	unit
Volume of CO adsorbed on catalyst	= [(B-A)/B](40)	
Volume of gas 1 mole at 30°C	= 24.86×10 <sup>6</sup>	
Mole of CO adsorbed on catalyst	= [(B-A)/B][40/24.86×10 <sup>6</sup> ]	mole
Molecule of CO adsorbed on catalyst	= 1.61×10 <sup>-6</sup> [(B-A)/B][6.02×10 <sup>23</sup> ]	molecules
Metal active sites	= 9.68×10 <sup>17</sup> [(B-A)/BW]	molecules of CO/g.cat.

For Flame Ionization Detector

$$\text{Normalized Weight percent} = \frac{\text{Peak area}}{\text{Relative sensitivity}}$$

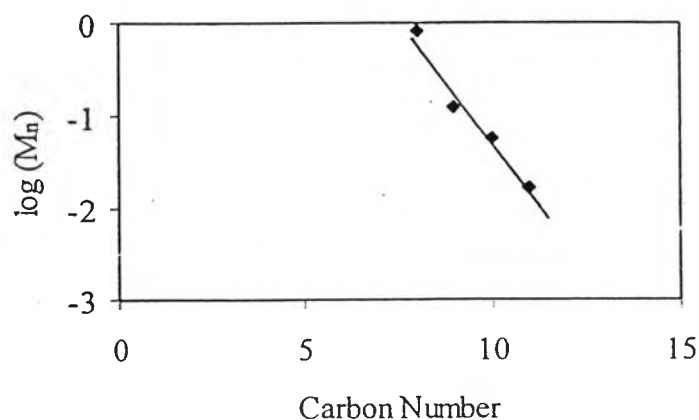
In this compound, it would be suggested that they are aromatic compound. Relative sensitivity is about 1. Thus, peak area is assumed to equal to normalized weight.

Compound	Peak area	mol	mol fraction ( $M_n$ )	$\log M_n$
C <sub>8</sub>	36362	378.77	0.364	-0.44
C <sub>9</sub>	48839	452.21	0.434	-0.36
C <sub>10</sub>	23761	198.01	0.190	-0.72
C <sub>11</sub>	731	5.53	0.005	-2.27
C <sub>12</sub>	956	6.64	0.006	-2.20
Total	91176	1041.17		

From Schulz-Flory Distribution

$$\text{Log}(M_n) = n \log(\alpha) + \log((1-\alpha)/\alpha)$$

Subsequently, plot  $\log(M_n)$  versus n

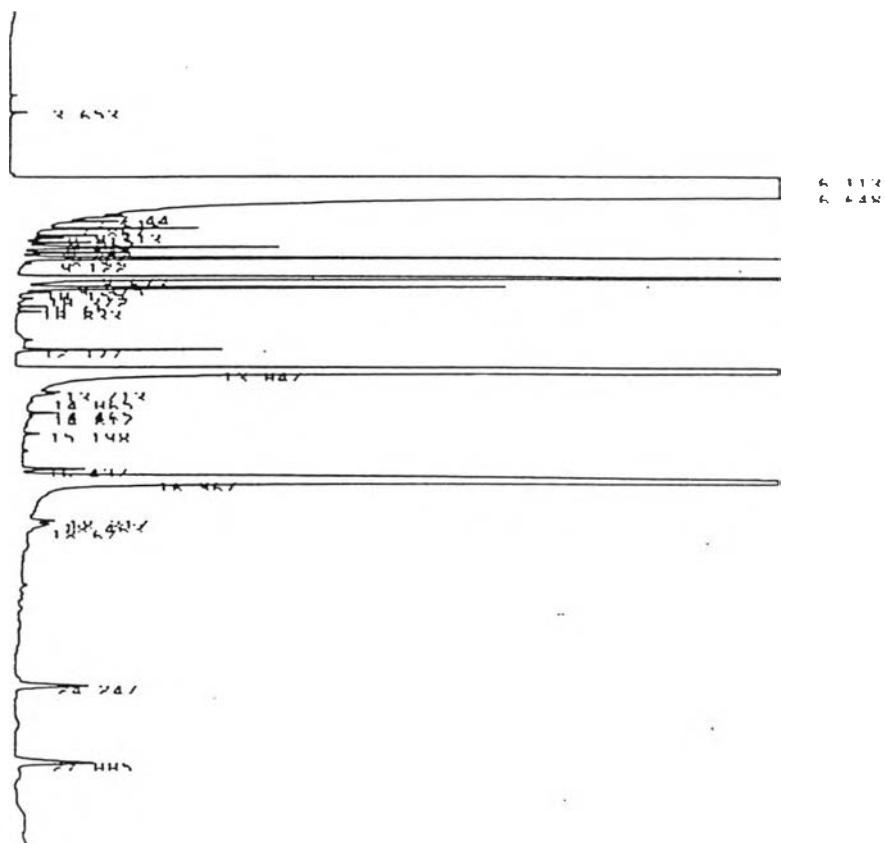


From this graph, slope =  $\log \alpha$

$$\text{Probability of chain growth } \alpha = 10^{\text{slope}} = 0.29$$

## APPENDIX F

### CALCULATION OF PROBABILITY OF CHAIN GROWTH ( $\alpha$ )



PKNO	TIME	AREA	MC	TIME	CHNO	NAME
1	3.652	54			H 0028	
2	6.112	54962			2 864	
3	6.648	1752312	SM		91 2618	toluene
4	7.44	114	I		0 0059	
5	7.612	178	I		0 0088	
6	7.867	565	I		0 0294	
7	8.112	270	I		0 012	
8	8.215	122	IV		0 0064	
9	8.257	251	I		0 0131	
10	8.545	1158	IV		0 0599	
11	8.717	442	IV		0 023	
12	8.843	5522	IV		0 2878	
13	8.122	56	IV		0 0029	
14	9.672	24246	I		1 2634	
15	9.875	3128	IV		0 1626	
16	10.155	167	IV		0 0087	
17	10.272	182	IV		0 0052	
18	10.65	121	IV		0 0062	
19	10.823	97	IV		0 0051	
20	12.177	815			0 0424	
21	12.847	47675	S		2 4842	
22	12.712	176	I		0 0092	
23	14.065	27	I		0 0012	
24	14.465	118	I		0 0062	
25	14.617	22	IV		0 0017	
26	15.198	99			0 0052	
27	16.437	767			0 0191	
28	16.867	22819			1 1891	
29	18.217	206			0 0107	
30	18.463	227	V		0 0118	
31	18.67	43	V		0 0022	
32	28.247	731			0 0391	
33	27.005	596			0 0429	
TOTAL		1418025				

## Response Factors for Gas Chromatographic analysis

**Table F-1** Relative sensitivity data for Flame Ionization Dectector [199]

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Normal Paraffins		3,3-Dimethylheptane	1.00
Methane	0.97	2,4-Dimethyl-3-ethylpentane	0.99
Ethane	0.97	2,2,3-Trimethylhexane	1.01
Propane	0.98	2,2,4-Trimethylhexane	0.99
Butane	1.09	2,2,5-Trimethylhexane	0.99
Pentane	1.04	2,3,3-Trimethylhexane	1.00
Hexane	1.03	2,3,5-Trimethylhexane	0.96
Octane	1.00	2,4,4-Trimethylhexane	1.01
Nonane	0.97	2,2,3,3-Tetramethylpentane	1.00
Branched Paraffins	0.98	2,2,3,4-Tetramethylpentane	0.99
Isopentane	1.05	2,3,3,4-Tetramethylpentane	0.99
2,2-Dimethylbutane	1.04	3,3,5-Trimethylheptane	0.99
2,3-Dimethylbutane	1.03	2,2,3,4-Tetramethylhexane	1.01
2-Methylpentane	1.05	2,2,4,5-Tetramethylhexane	1.00
3-Methylpentane	1.04	Cyclopentanes	
2-Methylhexane	1.02	Cyclopentane	1.04
3-Methylhexane	1.02	Methylcyclopentane	1.01
2,2-Dimethylpentane	1.02	Ethylcyclopentane	1.00
2,3-Dimethylpentane	0.99	1,1-Dimethylcyclopentane	1.03
2,4-Dimethylpentane	1.02	T-1,2-Dimethylcyclopentane	1.01
3,3-Dimethylpentane	1.03	C-1,2-Dimethylcyclopentane	1.00
3-Ethylpentane	1.02	T-1,3-Dimethylcyclopentane	1.00
2,2,3-Trimethylbutane	1.02	C-1,3-Dimethylcyclopentane	1.00
2-Methylheptane	0.97	1MT2-Ethylcyclopentane	1.01
3-Methylheptane	1.01	1MC2-Ethylcyclopentane	1.00
4-Methylheptane	1.02	1MT3-Ethylcyclopentane	0.97
2,2-Dimethylhexane	1.01	1MC3-Ethylcyclopentane	1.00
2,3-Dimethylhexane	0.99	1,1,2-Trimethylcyclopentane	1.03
2,4-Dimethylhexane	0.99	1,1,3-Trimethylcyclopentane	1.04
2,5-Dimethylhexane	1.01	T-1,2C3-Trimethylcyclopentane	1.00
3,4-Dimethylhexane	0.99	T-1,2C4-Trimethylcyclopentane	0.98
3-Ethylhexane	1.00	C-1,2T3-Trimethylcyclopentane	0.98
2-Methyl-3-ethylpentane	0.98	C-1,2T4-Trimethylcyclopentane	0.99
2,2,3-Trimethylpentane	1.02	Isopropylcyclopentane	0.98
2,2,4-Trimethylpentane	1.00	n-Propylcyclopentane	0.97
2,3,3-Trimethylpentane	1.01	Cyclohexanes	
2,3,4-Trimethylpentane	0.99	Cyclohexane	1.01
2,2-Dimethylheptane	0.97	Methylcyclohexane	1.01

Table F-1 Relative sensitivity data for Flame Ionization Dectector

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Ethylcyclohexane	1.01	Isopropanol	0.53
1,1-Dimethylcyclohexane	1.03	n-Butanol	0.66
T-1,2-Dimethylcyclohexane	1.01	Isobutanol	0.68
C-1,2-Dimethylcyclohexane	0.99	sec.-Butanol	0.63
T-1,4-Dimethylcyclohexane	0.99	tert.-Butanol	0.74
1MT4-Ethylcyclohexane	0.98	Amyl alcohol	0.71
1MC4-Ethylcyclohexane	0.96	Methylisobutylcarbinol	0.74
1,1,2-Trimethylcyclohexane	1.01	Methylamyl alcohol	0.65
Isopropylcyclohexane	0.98	Hexyl alcohol	0.74
Cycloheptane	1.01	Octyl alcohol	0.85
Aromatics		Decyl alcohol	0.84
Benzene	1.12	Pentoxol	0.60
Toluene	1.07	Aldehydes	
Ethylbenzene	1.03	Butyraldehyde	0.62
para-Xylene	1.00	Heptanoic aldehyde	0.77
meta-Xylene	1.04	Octaldehyde	0.78
ortho-Xylene	1.02	Capric aldehyde	0.80
1M2-Ethylbenzene	1.02	Acids	
1M3-Ethylbenzene	1.01	Formic	0.01
1M4-Ethylbenzene	1.00	Acetic	0.24
1,2,3-Trimethylbenzene	0.98	Propionic	0.40
1,2,4-Trimethylbenzene	0.97	Butyric	0.48
1,3,5-Trimethylbenzene	0.98	Hexanoic	0.63
Isopropylbenzene	0.97	Heptanoic	0.61
n-Propylbenzene	1.01	Octanoic	0.65
1M2-Isopropylbenzene	0.99	Esters	
1M3-Isopropylbenzene	1.01	Methylacetate	0.20
1M4-Isopropylbenzene	0.99	Ethylacetate	0.38
sec.-Butylbenzene	1.00	Isopropylacetate	0.49
tert.-Butylbenzene	1.02	sec.-Butylacetate	0.52
n-Butylbenzene	0.98	Isobutylacetate	0.54
Unsaturates		n-Butylacetate	0.55
Acetylene	1.07	Isoamylacetate	0.62
Ethylene	1.02	Methylamylacetate	0.63
Hexene-1	0.99	Ethyl-(2)-ethylhexanoate	0.72
Octene-1	1.03	Hexylcaproate	0.78
Decene-1	1.01	Cellosolve acetate	0.50
Alcohols		Nitrogen Compounds	
Methanol	0.23	Acetonitrile	0.39
Ethanol	0.46	Trimethylamine	0.46
n-Propanol	0.60	tert.-Butylamine	0.54

Table F-1 Relative sensitivity data for Flame Ionization Dectector

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Diethylamine	0.61	Pentoxone	0.56
Aniline	0.75	Others (Solvents)	
di-n-Butylamine	0.75	Cellosolve	0.45
Ketone		Butyl cellosolve	0.62
Acetone	0.49	Isophorone	0.85
Methylethylketone	0.61	Thiophane	0.57
Methylisobutylketone	0.71		
Ethylbutylketone	0.71		
Diisobutylketone	0.72		
Ethylamylketone	0.80		
Cyclohexane	0.72		



**APPENDIX G**  
**SPECIFICATION OF ALUMINA SUPPORT (Al<sub>2</sub>O<sub>3</sub>) TYPE KNH-3**

Chemical Composition	Weight percent
Al <sub>2</sub> O <sub>3</sub>	60-70
SiO <sub>2</sub>	30-35
Fe <sub>2</sub> O <sub>3</sub>	0.3-0.5
TiO <sub>2</sub>	0.5-0.7
CaO	0.1-0.2
MgO	0.2-0.4
Na <sub>2</sub> O	0.3-0.4
K <sub>2</sub> O	0.2-0.3
ZrO <sub>2</sub> + HfO <sub>2</sub>	0.03-0.04

Physical properties	
Bulk Density (g/ml)	1.3-1.5
Apparent Specific Gravity	3.1-3.3
Packing Density (lb/ft <sup>3</sup> )	20-25
Pore Volume (ml/g)	1.0-1.3
Surface Area (m <sup>2</sup> /g)	340-350

**APPENDIX H**  
**LIST OF PUBLICATIONS**

1. Sunee Srihiranpullop, Piyasan Prasertthdam and Tharathon Mongkhonsi, "Deactivation of the metal and acidic functions for Pt, Pt-Sn and Pt-Sn-K using physically mixed catalysts", the Korean Journal of Chemical Engineering, 17(5), 548-552 (2000).
2. Sunee Srihiranpullop, Piyasan Prasertthdam and Tharathon Mongkhonsi, "Cooperative effect of platinum and alumina on catalyst deactivation for dehydrogenation reaction", Reaction Kinetics and Catalysis Letters, under review.
3. Piyasan Prasertthdam, Sunee Srihiranpullop and Tharathon Mongkhonsi, "Determination of coke propagation on metal and support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by using Schulz-Flory distribution theory", Proceedings of region symposium on Chemical Engineering 1998, Manila, Philippines, Oct. 14-16, 1998, 152.
4. Piyasan Prasertthdam, Sunee Srihiranpullop and Tharathon Mongkhonsi, "Determination of coke propagation on metal and support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by using Schulz-Flory distribution theory", 15th Canadian Symposium on Catalysis 1998, Quebec, Canada, May 17-20, 1998, 43.
5. Piyasan Prasertthdam, Sunee Srihiranpullop and Tharathon Mongkhonsi, "Determination of coke propagation on metal and support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by using Schulz-Flory distribution theory", Proceedings of region symposium on Chemical Engineering 1997, Johor, Malaysia, Oct. 13-15, 1997, 549.

## Deactivation of the Metal and Acidic Functions for Pt, Pt-Sn and Pt-Sn-K Using Physically Mixed Catalysts

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**Abstract**—The effect of K addition on the amount and dispersion of carbon deposition on metal sites and support sites was investigated on a physical mixture for hexane dehydrogenation. TPO, BET and ESR experiments were used for characterization. The K addition significantly decreases catalyst deactivation involving the amount of coke deposits and the density of carbon radicals on the metal and support sites because of ensemble and electronic effects, especially on the metal sites. Coke on the metal sites associated with carbonaceous species rich in hydrogen is less polymerized than coke on the support sites, corresponding to a more graphitic-like carbon.

**Key words:** Deactivation, Pt-based Catalyst,  $\gamma$ -based Catalyst Modified with Sn and/or K, Physically Mixed Catalyst

### INTRODUCTION

Catalytic processing of many industrial feedstocks is frequently accompanied by the deposition of carbonaceous deposits. For metal catalysts, supported mono- and multi-metal Pt containing catalysts are widely used for dehydrogenation in the petroleum and other industries. The addition of modifiers such as K and/or Sn into Pt-containing catalysts may change the selectivity of catalysts and can increase the resistance of carbon deposition [Rotrup-Nielsen, 1997; Trimm, 1983, 1999]. Coking on the catalyst surface has been reported to be a dynamic process [Lietz and Volter, 1984; Biswas et al., 1988; Liu et al., 1990; Bond, 1987]. Carbon deposition takes place on both the active metal sites and the support surface for supported metal catalysts. Numerous species of carbon are observed to be deposited or formed on the surface of coked catalysts, ranging from carbides or microcrystalline and amorphous species to highly aromatic/graphitic carbons apparently through polymerization reactions and rearrangement for the polymer formed to be stabilized [Trim, 1999; Biswas et al., 1988; Afonso et al., 1994]. Additionally, analysis by temperature-programmed oxidation (TPO) generally indicates two types of coke: the first one burns at low temperatures (polymeric carbon), which is associated with the metal phase and the second type burns at high temperatures (amorphous/graphitized carbon), associated with the support [Barbier, 1987; Biswas et al., 1987]. Although catalyst deactivation has been studied for many years, coke growth completely separated between coke on the metal and coke on the support sites has not been investigated sufficiently so far. In order to shed some light on this matter, physically mixed Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was used in this work as a representative catalyst of Pt/Al<sub>2</sub>O<sub>3</sub>. Since the SiO<sub>2</sub> support in Pt/SiO<sub>2</sub> has a very low acidity, its contribution to the acidic function is, therefore, negligible. The mesh sizes of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> selected for the physically mixed catalyst are based on ones that give approximately the conversion of hexane similar to that obtained from the conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalyst [Bond, 1987; Shum

et al., 1984; Inaba et al., 1996]. With this simulated catalyst associated with the presence of K and/or Sn, much debate about how the additive metal brings about the enhancement in catalytic properties should be better conceived.

Thus, this work involved a detailed study of coke deposition on Pt, Pt-Sn and Pt-Sn-K catalysts employed in a physically mixed system where silica-supported platinum, Pt/SiO<sub>2</sub>, represents the metal sites and acidic alumina, Al<sub>2</sub>O<sub>3</sub>, represents the support sites. The dehydrogenation of n-hexane was adopted to cause coked catalysts with carefully selected reaction conditions so that thermal cracking effects may be negligible. The main goal was to determine the effect of K and/or Sn on coke distribution over the metal sites and support sites in order to better understand the deactivation process of the catalysts.

### EXPERIMENTAL

#### 1. Catalyst Preparation

The alumina used in this study was obtained from Sumitomo Alumina Smelting (type NKH-3) and the silica was manufactured by Merck. They were ground and then sieved to retain particles with sizes between 60-80 mesh and 100-120 mesh, respectively. Three types of catalyst, namely, 0.3 wt% Pt/SiO<sub>2</sub>, 0.3 wt%Pt-0.3 wt%Sn/SiO<sub>2</sub> and 0.3 wt%Pt-0.3 wt%Sn-0.6 wt%K/SiO<sub>2</sub>, were employed in this work. The catalysts were prepared by impregnation method using H<sub>2</sub>PtCl<sub>6</sub>, SnCl<sub>4</sub> and KNO<sub>3</sub> as salt precursors. All chemicals used were normally analytical grade. After drying at 110 °C overnight, the catalysts were calcined in an air flow at 500 °C for 3 h.

#### 2. Coking Reaction

Coked catalysts were prepared from the dehydrogenation reaction of n-hexane (10% hexane in N<sub>2</sub>). The reaction was carried out by using an ordinary flow microreactor under atmospheric pressure. The ratio of physically mixed catalyst between Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was 1 : 1. About 0.2 g of catalyst was used in each run. The experiments began after a reduction of catalyst under hydrogen at 500 °C for 1 h. Then, the temperature was adjusted to the reaction temperature of 475 °C and allowed to stabilize at that tem-

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perature for 30 min before hydrocarbon was introduced. The reaction was run for 120 min on stream in absence of hydrogen. The gas composition was analyzed by GC-11A (Shimadzu) equipped with a capillary column and a flame ionization detector. Finally, the coked catalyst comprised of coked Pt/SiO<sub>2</sub> and coked Al<sub>2</sub>O<sub>3</sub> in different mesh size was sieved and separated for the characterization of coke on metal and coke on support, respectively.

### 3. Characterization

Many techniques were used to analyze both the fresh catalysts and coked catalysts. The oxygen consumed and carbon dioxide of coke were determined by temperature-programmed oxidation (TPO) using oxygen (1%O<sub>2</sub> in He). After heating at 500 °C for 1 hr to remove the adsorbed species, CO<sub>2</sub> produced was measured with a gas chromatograph equipped with a TCD and an on-line gas sampling valve. The heating rate was 10 °C/min up to 700 °C. BET surface area was measured by a surface area analyzer (Micromeritics, Model ASAP 2000). Additionally, to determine the density of carbon radicals of coke computed from the area under the curve, electron spin resonance spectra were analyzed with an X-band Jeol JES-RE2X spectrometer at room temperature.

## RESULTS AND DISCUSSION

### 1. Carbon Deposition on the Metal Sites and the Acidic Sites of the Pt, Pt-Sn and Pt-Sn-K Catalysts

Carbon depositions on Pt-based catalysts were investigated by temperature-programmed oxidation (TPO). On the active metal sites of various catalysts, Fig. 1A shows TPO profiles of Pt, Pt-Sn and Pt-Sn-K catalysts, respectively. It is observed that two peaks appear at 300 °C and 425 °C in every TPO profile. This indicates that carbon depositions on these catalysts can be divided into two types: (i) coke deposited directly on metal, and (ii) coke in the vicinity of metal centers, which correspond to other reports [Lietz and Jovanovic, 1984; Jovanovic and Putanov, 1997]. In addition, it is obvious that coke is depositing on different sites on the different catalysts and affecting deactivation to differing extents. From Fig. 1a, the difference of the modified catalysts is that, for Pt and Pt-Sn catalysts, the area of the first peak at lower temperature is less than that of the second peak at higher temperature. For the Pt-Sn-K catalyst, the situation is just opposite. Interestingly, the peak of the K-doped catalyst decreased more than any other catalysts, especially in the position at 425 °C. Previous studies [Lietz and Volter, 1984; Biswas et al., 1988; Liwu et al., 1990; Bond, 1987; Afonso et al., 1994; Barbier, 1987; Biswas et al., 1987] speculated that the active metal site was linked with the originally generated coke precursors. Consequently, K addition dramatically inhibits the production of coke intermediates, resulting in the lower area of carbonaceous compounds. It is seen that the order of their TPO areas is as follows: Pt>Pt-Sn>Pt-Sn-K. Furthermore, the total carbon accumulate on the metal sites of different catalysts listed in Table 1 was determined from the areas under the TPO profiles. The order of decreasing amount of carbon per gram is Pt>Pt-Sn>Pt-Sn-K. The areas of the TPO peaks were found to increase with the amount of carbon deposition for the Pt-based catalysts.

On the other hand, Fig. 1b exhibits spectra of TPO on the acidic sites of Pt, Pt-Sn and Pt-Sn-K catalysts. It is observed that a single peak appears on the spectra of TPO for the modified catalysts.

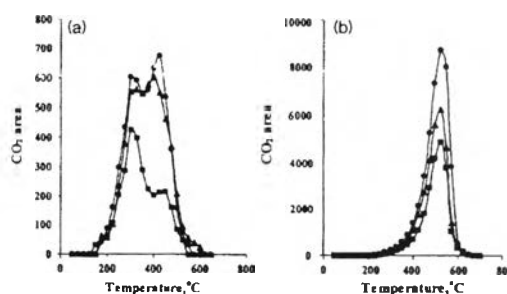


Fig. 1. (a) Temperature Programmed Oxidation of carbonaceous deposits produced on the metal sites with different catalysts. (b) Temperature Programmed Oxidation of carbonaceous deposits produced on the support sites with different catalysts.

Symbols: ● the Pt catalyst, ▲ the Pt-Sn catalyst and ■ the Pt-Sn-K catalyst.

Table 1. The amount of carbon deposited on the catalysts

Catalysts	Coke on the metal sites %C	Coke on the support sites %C
Pt catalyst	0.35	2.50
Pt-Sn catalyst	0.32	1.73
Pt-Sn-K catalyst	0.21	1.26

Coke burns off at higher temperature, about 525 °C, compared with coke on the metal sites. This implies that the peak shifts to a higher temperature because of a larger degree of polymerization of coke [Padro et al., 1997]. Moreover, the TPO area of the Pt catalyst is diminished by the addition of Sn and especially in combination with K. As presented above, it is relevant to note that the surface coverage has different compositions, which are summarized in Table 1. The amount of coke on both the metal sites and support sites decreased significantly by the addition of Sn and/or K.

As mentioned above, carbonaceous materials deposit either on the active metal sites or on the acidic alumina support surface. The migration of coke precursor from one type of sites to another may possibly occur. Hence, a model of coking is proposed in Fig. 2. Hydrocarbons first undergo dehydrogenation and cracking on the active metal surface to form precursors of coke deposits. In general, unsaturated reaction intermediates such as monocyclic diolefins are formed and then reversibly adsorbed to form coke on the metal and in its direct vicinity. However, they can migrate to acid

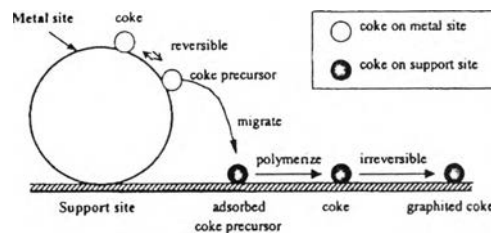


Fig. 2. Coking mechanism on both sites of catalyst.

sites and become polymerized to the more graphite-like material. Additionally, when comparing the amount of coke on the metal sites and the support sites as shown in Table 1, it is obvious that a small part of coke is located on the metal sites, whereas the major fraction is accumulated on the acidic sites. These results imply that coke deposits on the metal sites are less dehydrogenated and correspond to species rich in hydrogen in accordance with the literature reviews [Tao et al., 1991; Beltrami and Trimm, 1987]. Accordingly, the H/C ratio of coke deposits on metal sites is higher than that of the coke deposits on acidic support sites. This displays the different nature of coke between the metal sites and alumina. Finally, the modifications of Pt catalyst by addition of Sn and K are able to reduce the amount of coke on both sites.

### 2. Carbon Radicals of Coke on the Metal Sites and the Acidic Sites of the Pt, Pt-Sn and Pt-Sn-K Catalysts

In order to examine the effect of Sn and K addition on coke formation with both sites in more detail, Electron Spin Resonance (ESR) has long been an effective technique to estimate the radical density of coke. ESR spectra are obtained by measuring the intensity vs. wavelength (or frequency) of a beam of electromagnetic radiation as it passes through a sample of matter, which is presented in a derivative trace of absorption curve. Then, the radical density can be computed from the integrated area of the spectra obtained [Werle and Bolton, 1972; Lunsford, 1972]. Further coke radicals are representative of the overall coke, for both its nature and its amount because the amount of olefin or allylic radicals is characteristic of carbonaceous matter as introduced elsewhere [Butt and Peterson, 1988; Guisnet and Magnoux, 1989; Lange and Gutsze, 1988; Lange et al., 1988a, b]. In an earlier study, Karge et al. [Butt and Peterson, 1988; Guisnet and Magnoux, 1989] investigated low temperature coke (below about 500 K) and high temperature coke radicals (above about 500 K). They found that olefinic or allylic oligomeric species were low-temperature coke radicals while highly unsaturated species were high-temperature coke radicals. Consequently, the formation of radicals enables us to discriminate between individual coke of various catalysts including coke

**Table 2. The density of carbon radicals of coke per gram catalyst**

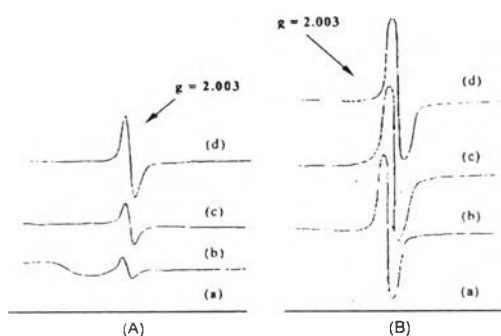
Catalysts	The metal sites	The support sites
Pt catalyst	$8.55 \times 10^6$	$3.02 \times 10^6$
Pt-Sn catalyst	$5.18 \times 10^6$	$2.07 \times 10^6$
Pt-Sn-K catalyst	$3.17 \times 10^6$	$1.83 \times 10^6$

on the metal sites and the support surface. In this study, Fig. 3(A) shows the ESR spectra of coke radicals for various catalysts on the metal sites. The carbon radical's density computed from the total peak area is given in Table 2. The g value of coke radicals is estimated to be 2.003 in agreement with earlier literature [Lange et al., 1988; Gutsze et al., 1997]. It is found that the modification of catalysts displays a dominant role in reducing the intensity of carbonaceous radicals as well as reducing the amount of coke precursors. Interestingly, the K-doped sample has a sharply lower amount of radicals of coke, by 27 times, compared with the Pt catalyst, resulting in the lowest amount of coke shown in Table 1. Another modification of the Pt catalyst diminishes carbonaceous radicals about 1.7 times. A comparison between ESR results and TPO results, which are described above, exhibits a good correlation between the number of radicals and the amount of coke.

For the acidic alumina, the ESR spectra of radicals are illustrated in Fig. 3(B) with the Pt-based catalysts. Table 2 also lists their intensity on these sites. This characteristic of carbon radicals is similar to that already reported above. However, the density of coke radicals is greater on the alumina sites than on the active metal sites. It is clear that the amount of radicals compared with the carbonaceous radicals intensity of Pt catalyst is reduced by 1.45 times for Sn modification and 1.65 times for K addition. As mentioned above, this indicates that the metal sites are relevant for generating coke intermediates, which are adsorbed to form coke on this site and can migrate to the acidic support sites. Thus, if the modification of catalysts inhibits the production of coke precursors on the metal sites, then the amount of carbonaceous compounds is consequently decreased. From the result shown in Table 2, it is obvious that the K-doped sample dramatically reduces coke radicals concerned with coke species on the active metal sites. Accordingly, a lower amount of coke deposits is produced as shown by the TPO results.

### 3. The Changes of Textural Properties and the Dispersion Factors of Coke on the Metal Sites and the Acidic Sites of the Pt, Pt-Sn and Pt-Sn-K Catalysts

Coking is claimed to be responsible for a decrease in the specific surface, pore surface and pore volume depending on a limitation of diffusion (dispersion) and nature of coke deposits. As a result, we investigated texture changes in surface area before and after coke deposition of Pt-based catalysts. Jovanovic and Putanov [Jovanovic and Putanov, 1997] introduced the dispersion factor to consider catalyst degradation of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Re/Al<sub>2</sub>O<sub>3</sub>. The dispersion factor is the ratio of change of surface area to the quantity of carbon deposits. Higher values of dispersion factor proved that carbon deposited on this catalyst is better dispersed with the fine small grain structure. In this work, the dispersion factor of carbonaceous deposit defined as the ratio of change of surface area to the amount of coke was investigated on Pt, Pt-Sn and Pt-Sn-K catalysts. Table 3 summarizes the textural properties of catalyst



**Fig. 3. (A) ESR spectra of coke on the metal sites; (a) reference spectrum before coking reaction (b) coke on Pt-Sn-K catalyst (c) coke on Pt-Sn catalyst and (d) coke on Pt catalyst. (B) ESR spectra of coke on the support sites; (a) reference spectrum before coking reaction (b) coke on Pt-Sn-K catalyst (c) coke on Pt-Sn catalyst and (d) coke on Pt catalyst.**

**Table 3. The textural properties of catalysts samples before and after testing and dispersion factor**

Catalysts	The metal sites			The support sites		
	SA (m <sup>2</sup> /g)		Dispersion factor	SA (m <sup>2</sup> /g)		Dispersion factor
	Fresh	Used		Fresh	Used	
Pt catalyst	447	386	171	390	343	19
Pt-Sn catalyst	417	325	291	390	330	35
Pt-Sn-K catalyst	380	283	462	390	283	85

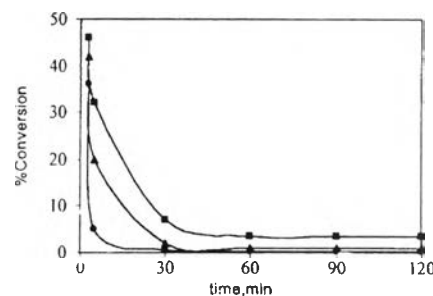
samples before and after coking and the dispersion factor, which is separated into the metal sites and the acidic alumina in each catalyst. The change of surface area may be attributed to the blockage of catalysts by coke, though thermal sintering and the other factor except coking should not be ruled out. It has been found that the modified catalyst lost their surface area after the reaction more than the unmodified one containing only platinum. This might be due to the fine structure of coke readily occurring in the case of Pt catalysts with the presence of Sn and/or K, which easily block the existing porous area of the catalyst. The results obtained were consistent with the report of fine small grain structure of coke deposits for the modification catalysts suggested in literature reviews [Lange and Gutze, 1988; Kirszenstejn et al., 1991; Mann, 1997]. Moreover, noticeably higher values of dispersion factors are obtained from the Pt-Sn and particularly Pt-Sn-K catalysts as illustrated in Table 3. Compared with the Pt catalyst, the dispersion factor of the Pt-Sn catalyst is about 1.7 times on the metal sites and about 1.8 times on the acidic sites. In the case of K addition, dispersion factors on the metal sites and on the support sites are about 2.4 times and 4.5 times compared with Pt catalyst, respectively.

#### 4. The Influence of Sn and K Addition on Coke Formation

The main theories put forward to account for the improved properties of multi-metallic catalysts tend to involve either geometric or electronic effects. Coke formation is known to require relatively large clusters or ensembles of adjacent metal atoms. For the Sn addition, the presence of Sn improves the diluting of the active metal surface into smaller ensembles, which enhances the catalysts' resistance to deactivation. The addition of Sn to Pt catalyst forms substitutional surface alloys, and it has been shown that Sn interacts with platinum on silica to form a Pt/Sn alloy [Rostrup-Nielsen, 1997; Trimm, 1983, 1999; Hill et al., 1998; Macleod et al., 1998]. Thus, carbon intermediates cannot readily form multiple carbon-metal bonds. Furthermore, this inhibits the formation of highly dehydrogenated surface species that are intermediates for coking. According to Padro et al. and Larsson et al. [Padro et al., 1997; Larsson et al., 1996], one reason is that coke deposits bind more strongly to the Pt catalyst than to the Pt-Sn catalyst.

From TPO profiles and ESR spectra of the metal sites, the less strong attachment of the adsorbed species to the metal surface would be explained by the significant minimizing of these sites and promotion of the migration of coke precursors to the carrier. These effects are evident by the change in the heights of peaks in the TPO profiles and ESR spectra.

The addition of K into bimetallic Pt-Sn catalyst produces a significant decrease in the catalyst deactivation as shown in Fig. 4, illustrating the conversion of hexane as a function of time. The de-

**Fig. 4. % conversion of hexane dehydrogenation for physically mixed catalysts.**

Symbols: ● the Pt catalyst, ▲ the Pt-Sn catalyst and ■ the Pt-Sn-K catalyst.

cline in conversion is slower for catalysts containing tin and potassium than for catalysts containing platinum only because less coke was formed on the modified catalysts. In Fig. 4 and Table 1, it is obvious that Pt catalyst deactivates quickly and a considerable amount of coke was formed. This may be related to the incorporation of tin into the surface of platinum through the formation of a substituted alloy, while potassium may be present on top of the platinum surface. As described elsewhere [Padro et al., 1997; Hill et al., 1998], it was found that K-doped catalyst significantly decreases the activation energy of CH dehydrogenation, which would suggest that K effect diminishes the interaction between Pt and Sn. This modification in the interaction between both metal components could be due either to a direct addition of K on the metal phase or to an indirect effect of the alkali metal addition to support, which could change the metal-support and the metal-metal interactions, as suggested in the literature [Hill et al., 1998; Larsson et al., 1996; Cortright and Dumesic, 1995]. This results in a weakening of Pt-C bond strength to make the catalyst less susceptible to deactivation by deposition of carbonaceous species on both sites as illustrated in Fig. 1, Table 1, Fig. 3 and Table 2. This is known as an electronic effect [Rostrup-Nielsen, 1997; Trimm, 1983, 1999; Cortright and Dumesic, 1995].

#### CONCLUSION

The addition of Sn and K resists coke formation both on the metal sites and on the support sites. It seems due to the ensemble and electronic effects. They also reduce the density of carbon radicals and affect the nature of coke. For textural properties, noticeably higher values of dispersion factor were obtained on Pt-Sn and Pt-Sn-K catalysts than on Pt catalysts. This can indicate that coke on the Pt-Sn and Pt-Sn-K catalysts has a softer coke nature. Specifically, K addition significantly inhibits coking. Comparing coke on the metal sites and on the support sites, it can be concluded that coke on the metal is soft in nature, rich in hydrogen and has a lower degree of polymerization.

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