THE STUDY OF HIGHLY DISPERSED METAL OXIDE OVER SILICA AS A CATALYST FOR ETHYLBENZENE OXIDATION USING HYDROGEN PEROXIDE AS AN ENVIRONMENTALLY FRIENDLY OXIDANT

NATTAPOL YODCOME

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Students	Mr. Nattapol Yodcome Student ID 58050472
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Advisor	Dr. Kittisak Choojun
Co-advisors	Prof. Dr. Tawan Sooknoi

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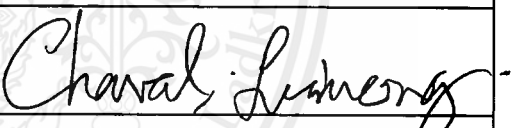
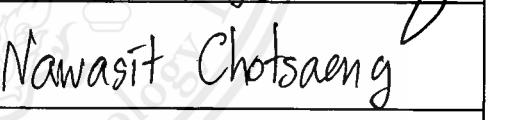
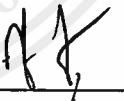
Committees	Signatures
Dr. Chaval Sriwong Chairperson	
Asst. Prof. Dr. Nawasit Chotsaeng Committee	
Dr. Kittisak Choojun Committee and Advisor	
Prof. Dr. Tawan Sooknai Committee and Co-advisor	

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ABSTRACT

In this work, ethylbenzene oxidation was studied using supported metal oxide including Cr, Fe, Mo, and Co over SiO_2 as a catalyst and H_2O_2 as an oxidant. The effect of preparation method (impregnation (IM) and strong electrostatic adsorption (SEA), metal loading, types of metal, and contact time on the oxidation of ethylbenzene were also investigated. For the impregnation method, the mixture of metal oxide species including isolated Mn^{n+} tetrahedral, polymeric, and bulk were observed. In addition, the fraction of isolated and polymeric species is more than bulk in low loading (<1%wt.). On the other hand, isolated and polymeric metal oxide are retained for all %loading of catalysts prepared by SEA. The use of Cr/SiO_2(IM) as a catalyst significantly improves the activity more than 34 times than those thermal process with acetophenone as a major product. The pathway is believed to be the Lewis acid-assisted radical mechanism. As the increase of Cr loading prepared by IM, the reaction rate seems to be retarded due to the aggregation of chromium oxide (bulk species). Besides, H_2O_2 decomposition is also predominant. However, the aggregation of bulk Cr_2O_3 is also found in spent catalyst. Once Cr/SiO_2(SEA) is used, the activity is consecutively enhanced with Cr loading indicating the important of isolated chromium species for ethylbenzene oxidation. The activity dependent on Lewis acid character; in the order of Cr > Fe > Mo > Co. Although, Mo has the valence state close to Cr, but

it is less charge density. Unfortunately, Fe, Mo (IM) and especially Co (either of IM and SEA) is also responsible for H_2O_2 decomposition.

Keywords: Ethylbenzene oxidation, single-site catalysts, highly dispersed metal oxide, strong electrostatic adsorption, green chemistry

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Mr. Nattapol Yodcome

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CHAPTER 1
INTRODUCTION

1.1 Motivation

Acetophenone is one of the important chemicals used as a solvent and reactant in plastic and pharmaceutical industry [1]. Typically, acetophenone can be prepared by ethylbenzene oxidation involving in the cleavage of C-H bond and addition of oxygen atom. This process requires high temperature and high pressure. In the past, homogeneous catalysts, for example Fe(III) [20], Cr(VI) [21], Mn(VII) [27], and Os(VII) complexes [27] are used with strong oxidants, such as $KMnO_4$, $NaIO_4$, *tert*-butyl hydroperoxide (TBHP). This reaction has oxygenated hydrocarbons as an intermediate [2]. Though, the difficulty and complicated product separation raise the concern of an environment problem from hazardous wastes. Furthermore, the non-reusable of catalysts are the main disadvantages of this process.

Heterogeneous catalyst, on the other, is easy to separate from the reaction mixtures and can be recycled, which has been applied in various industrial processes. Supported metal oxides are widely used in the oxidation reaction [22-26]. Though, most of them still requires a strong oxidizing agent which results in the toxic waste. In sharp contrast, hydrogen peroxide is an alternative oxidizing agent since it is an environmentally friendly chemical producing water as a byproduct [3]. Several supported metal oxides, such as, Ti(IV) , Zr(IV) , Hf(IV), V(V), Nb(V), Ta(V), Fe(III), and Mo(VI), has been reported for the use of oxidation reaction with H_2O_2 [2]. The key step once metal oxide reacts with the oxidant, is the generation of peroxymetal species - the important intermediates during the oxidation reaction [2]. Furthermore, oxides of Cr, Fe, Mo, and Co has been reported for the oxidation using H_2O_2 as an oxidant. The activity of oxidation reaction does not only depend on the type of metals, but it also relies on the dispersion of metal oxide which plays a significant role in the reaction. Strong electrostatic adsorption and impregnation have been reported to prepare the highly dispersed metal oxide, such as Cr [5], Fe [3], Mo [4], Co [2]. The higher the dispersion, the higher the activity.

With those regards, this research aims to evaluate the preparation and activity of supported metal oxide including, Cr(III), Co(II), Mo(VI), Fe(III) over SiO_2 for the

oxidation of ethylbenzene using hydrogen peroxide as a green oxidizing agent. The catalysts were prepared by impregnation and strong electrostatic adsorption. The effect of reaction temperatures, amount of catalysts, time profile, and reaction mechanism were also investigated.

1.2 Objectives

1.2.1 To evaluate the use of supported metal oxide including Cr(III), Co(II), Mo(VI), and Fe(III) for oxidation reaction using H_2O_2 as an oxidant

1.2.2 To compare the activity of supported metal oxide prepared by impregnation and strong electrostatic adsorption

1.2.3 To study ethylbenzene oxidation using H_2O_2 as an environmentally oxidant

1.3 Scope of this study

1.3.1 Preparation metal oxide including Cr(III), Co(II), Mo(VI), and Fe(III) using silica as a support via strong electrostatic adsorption methodology and the wetness impregnation

1.3.2 Characterization of catalysts by, inductively coupled plasma optical emission spectrometry (ICP-OES), UV-vis spectroscopy and Diffuse Reflectance Spectroscopy (DR-UV)

1.3.3 Testing the catalytic activity by ethylbenzene oxidation using hydrogen peroxide as an oxidant

1.3.4 Investigation on the effect of %loading (1, 3, 5 and 10 %wt.), contact time (200, 400, and 600 mg.h/mol), activity of supported Cr(III), Co(II), Mo(VI), and Fe(III)

1.3.5 Analysis and quantification of gas products by online gas chromatography with flame ionization detector (GC-FID)

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1.4.1 Catalyst which have high activity and selectivity for the reaction.

1.4.2 Approach to oxidized C-H bond with environmentally friendly approach.

CHAPTER 2

LITERATURE REVIEWS AND THEORY

2.1 Catalysts

2.1.1 Types of catalysts

2.1.1.1 Homogeneous catalysts [8]

Homogeneous catalyst is a catalyst in the similar media as reactants. The mechanistic principles in heterogeneous catalysts are generally applicable. One example of the homogeneous catalysis relates the influence of H^+ on the esterification of acetic acid and ethanol forming ethyl acetate. The major weak point is the separation of homogeneous catalyst from the reaction, which cannot be recovered and reused. As the result, it is not preferable in industry.

2.1.1.2 Heterogeneous catalysts [8]

Heterogeneous catalysts act in different phase as the reactants. General reaction relates a solid catalyst with the reactants as either liquids or gases. The diverse mechanisms for reactions on surfaces are known, depending on the adsorption [29]. The total surface area of solid is important to the reaction rate. The catalyst particle are small, it has a large surface area makes the reaction goes faster. Main advantages of heterogeneous catalysts are easy and cheap for catalyst's recovery and have a good thermal stability. However, the main disadvantages is the selectivity which depends on multiple active sites.

2.1.1.3 Single-site heterogeneous catalysts

The single-site heterogeneous catalysts are classified as a type of heterogeneous catalysts. However, it also behaves like homogeneous catalyst where the pocket site of the active site can be controlled by the environmentally surrounding on a support. The "single site" (catalytically active center) may consist of one or more atoms. Such single sites are spatially isolated from one another with no other cross-link between such sites. The example of single-site heterogeneous catalyst is a monometallic linked to support by having tetrahedral structure [28]. This catalyst has a discrete active site which is believed to be significant for their

low coke formation and greater selectivity to the desired products than those observed over non-single-site heterogeneous catalysts of the similar composition.

The example of the single-site heterogeneous support on silica catalysts which are single-site Co^{2+} [9], single-site Ta [10] single-site Zr [11] and single-site Zn^{2+} [12]. The preparation of single-site heterogeneous catalysts generally requires controlled synthetic techniques. Some of them need to use the semi-stable compound as a reactant which requires inert environment. One of the interesting technique is called strong electrostatic adsorption methodology (SEA) is easier to manage. This method uses charge balance to bind a cation complex to a negatively charged silica surface in the basic solution.

2.2 Oxidation [13]

Some oxidations are defined as the interaction between oxygen molecules and other different substances. In the oxidation reaction, it always comes along with the reduction reaction which called redox reaction. The substance that acts as an electron donor is called a reducing agent and a substance that acts as an electron acceptor is called oxidizing agent.

2.2.1 Oxidation agents (Oxidant)

2.2.1.1 Air, Oxygen, Ozone and electrolysis

Air is the cheapest oxidant, used only small amount with no photoirradiation and catalysts. The examples of oxidation relating an air are the conversion of aldehydes into carboxylic acids and the oxidation of acyloins to α-diketones [30]. Oxygen in excited state can be classified as single and triplet oxygen. Singlet oxygen is a name given to several higher-energy species of molecular O_2 in which all the electron spins are paired. It reacts with organic compounds in the same way as singlet oxygen generated chemically by several reaction. Furthermore, the treatment of hydrogen peroxide in alkaline medium with sodium hypochlorite or bromine could generate the singlet oxygen.

The illustration of the oxidation using a singlet oxygen are the conversions of alkenes into epoxides, secondary alcohol into ketones via alcohol hydroperoxides and the oxidative degradation of tertiary amines to secondary amines [31].

Ground-state oxygen does not much relate in the oxidation. Classical example is the autoxidation of benzaldehyde to benzoic acid, normally yielding the undesirable products even in dark. The oxidation by the combination of oxygen and catalysts are used for

the conversion of alkanes into alcohol, ketones, or acids, the epoxidation of alkenes, and the oxidation of aromatic compounds to quinones or carboxylic acids [13].

Ozone is a blue gas or a dark blue liquid used in a mixture of oxygen. Such mixture is commercially available. It is normally prepared in the laboratories. The oxidation using ozone as an oxidant is called " ozonization" , carried out by passing ozone-containing oxygen through solutions of organic compounds in the solvent that doesn't react with ozone at low temperature. The most common reaction of ozone is with alkenes as shown in **Equation 2.1.**

Equation 2.1 The reaction of alkene with ozone [13].

The electrolytic oxidation occurs at the anode of an electrolytic cell, may or may not contain a diaphragm to separate cathodic and anodic spaces. The anode needs to be made of a metal that resists oxidation reaction which are lead and platinum [16]. The reported electrolytic oxidation is the epoxidation of alkenes, the synthesis of ketones from alkenes, and the conversion of primary alcohols and, secondary alcohol to carboxylic acids and ketones, respectively.

2.2.1.2 Hydrogen Peroxide and Its Derivatives

Hydrogen peroxide, H_2O_2, is commercially available in aqueous solutions with the concentration of 30% to 90%. The 30% hydrogen peroxide is a colorless liquid stabilized against the decomposition. The oxidation with hydrogen peroxide includes the oxidation of aldehydes to acids, carboxylic acids to peroxy acids, sulfides to sulfoxides or sulfones, primary amines to nitroso compounds, secondary amines to hydroxylamines and tertiary amines to amine oxides [32].

Potassium permanganate, $KMnO_4$, is a strong oxidizing agent. It dissolves in water to give intensely pink or purple solutions, the evaporation of which leaves prismatic

purplish-black glistening crystals. The conversion of aldehydes to carboxylic acids as shown in **Equation 2.2** [14].

$$5\ C_6H_{13}CHO + 2\ KMnO_4 + 3\ H_2SO_4 \longrightarrow 5\ C_6H_{13}COOH + 3\ H_2O + K_2SO_4 + 2\ MnSO_4$$

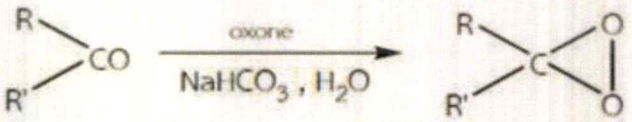
Equation 2.2 benzaldehyde oxidation with strong oxidizing agent [14]

Sodium peroxide (Na_2O_2), a pale-yellow solid, is very rarely used. The conversion of aldoximes into carboxylic acids and the oxidation of ketones to esters are examples of this type of reactions.

Sodium perborate, $NaBO_3.4H_2O$, is used for the oxidation of primary aromatic amines to azo compounds or nitro compounds and of sulfides to sulfoxides and sulfones. This reagent does not have the effect on alcohols and only slightly effect on alkenes.

Persulfuric acid (sulfomonoper acid, peroxymonosulfuric acid), H_2SO_5, is prepared in situ either from hydrogen peroxide, potassium persulfate ($K_2S_2O_8$), or ammonium persulfate [$(NH_4)_2S_2O_8$]. The reagent can convert aldehydes into esters, primary aromatic amines into azoxy, nitroso, or nitro compounds, and iodo compounds into iodoxy compounds. Currently, the use of persulfuric acid is very limited due to the toxicity.

Dioxiranes, prepared from acetone and other aliphatic ketones mixtures treated with oxone, can accomplish the oxidation that are usually not achieved by oxone itself as shown in **Equation 2.3.** Examples of these applications are epoxidations of dioxiranes and the conversion of primary amines to nitro compounds, of tertiary amines to amine oxides, and of sulfides to sulfoxides.



Equation 2.3 The reaction of ketone with ozone.

2.3 Strong Electrostatic Adsorption [15]

The idea of strong electrostatic adsorption (SEA), is to control the pH of the excess liquid so as to be at the optimal pH where metal complex–surface interaction is strongest [29]. This method uses charge balance to bind a cation complex to a negatively charged silica surface in basic solution or an anion complex to a positively charged silica surface in acidic solution. Components of an electrostatic adsorption mechanism are shown in **Figure 2.1.** An oxide surface consists of terminal hydroxyl groups that are protonated or deprotonated depending of the acidity of the impregnating solution. The pH at which the hydroxyl groups overall are neutral is termed the point of zero charge (PZC).

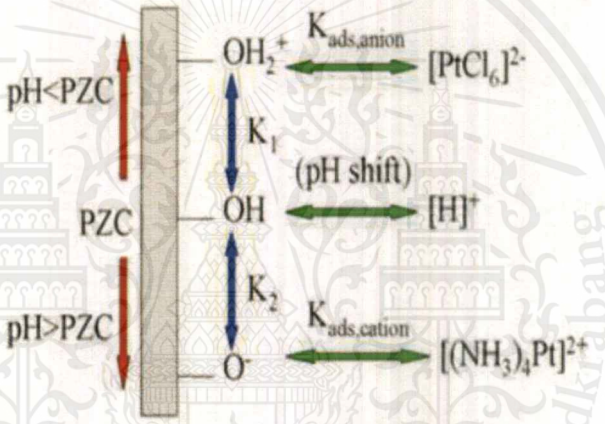


Figure 2.1 Components of an electrostatic adsorption mechanism: surface charging, metal adsorption, and proton transfer. $[M]^+$= Cationic metal complex, $[M]^-$= Anionic metal complex [15].

Below this pH (pH<PZC), the hydroxyl groups are protonated and become positively charge, and this positively surface can adsorb anionic metal complexes. On the other hand, above the PZC (pH>PZC), the hydroxyl groups are deprotonated and become negatively charge, and the surface can adsorb cationic metal complexes. The PZCs and suitable metal complexes for common supports are shown in **Figure 2.2.**

Support	PZC	Complex
MoO_3	<1	Cations
Nb_2O_5	2–2.5	Cations
SiO_2	4	Cations
Oxidized carbon black	2–4	Cations
Oxidized activated carbon	2–4	Cations
Graphitic carbon	4–5	Cations
TiO_2	4–6	Cations (or anions)
CeO_2	7	Cations or anions
ZrO_2	8	Cations or anions
Co_3O_4	7–9	Cations or anions
Al_2O_3	8.5	(Cations or) anions
Activated carbon	8–10	Anions
Carbon black	8–10	Anions

Figure 2.2 PZCs and suitable metal complexes for common supports [15].

2.4 Literature reviews

The oxidization reaction involving in the C-H bond cleavage of aromatic hydrocarbons requires high temperature, high pressure and oxidants, such, molecular oxygen, hydrogen peroxide and *tert*-butyl hydroperoxide. Lingaiah, N., *et. al.* (2009) studied the use of vanadium substituted polyoxometalate catalysts for toluene oxidation using *t*-butly hydrogen peroxide (TBHP) as an oxidant [1]. Benzaldehyde was observed as a main product. Giselle, C., *et. al.* (2016) reported the use of iron(III) complexes with H_2O_2 as an oxidant for toluene oxidation [1]. They claimed that 100% benzaldehyde selectivity was obtained with 30% conversion at 50 °C. However this homogeneous catalyst still has the main disadvantage as it's limiting of reuse and high cost of product separation.

Supported metal oxide, on the other hand, is easy to separate from the reaction mixtures and can be recycle, which has been applied in various industrial processes. Nicholas, E., *et. al.* (2015) studied the use of Ti(IV) , Zr(IV) , Hf(IV) , V(V) , Nb(V) and Ta(V) (all of group IV and V) supported on SiO_2 for alkene epoxidation using hydrogen peroxide [2]. The reaction was carried out in acetonitrile at the temperature of 45 and 65 °C. They explain that V-SiO_2 is not effective; while, Ti-SiO_2, Zr-SiO_2, Hf-SiO_2 is more active. They suggested that this is due to polyoxometal species and peroxymetal species in Ti, Zr, and Hf that are the active site for the alkene epoxidation. Similarly, Ausavasukhia, A., *et. al.* (2015) reported the use of Fe(III) in clay as a catalyst for THF oxidation using H_2O_2 as an oxidant [3]. Butyrolactone, chemical use in polymer and cosmetic industries, was obtained a main product. They observed higher activity

as the catalyst (Clay-500) treated at higher temperature. They proposed that the active oxidizing center would derive from the high-valence iron-oxo species that is formed by interaction of H_2O_2 with the dislodged Fe(III) oxides, rather than the Fenton-type species. Futhermore they suggested that Fe(III) react with H_2O_2 forming Fe^{+4}-OOH as a key active species for the THF oxidation. In similar manner, Das So *et. al.* (2003) reported the use of MoO_3 and H_2O_2 for diphylmetane oxidation [3]. This could indicate that MoO_3 could generate the peroxomolybdate. In addition, Michael, H., *et. al* (1994) reported the formation of two peroxo chromium species when Cr(VI) reacts with H_2O_2 [4].

As the metal dispersion play an important role in activity, the preparation of highly dispersed metal oxide has been developed. Regalbuto, R., *et. al.* (2008) studies the preparation of supported metal catalysts by strong electrostatic adsorption (SEA) using the noble and base ammine complexes $[Pd(NH_3)_4]^{+2}$, $[Cu(NH_3)_4]^{+2}$, $[Co(NH_3)_6]^{+3}$, $[Ru(NH_3)_6]^{+2}$, $[Ru(NH_3)_6]^{+3}$, and $[Ni(NH_3)_6]^{+2}$ [29]. It appears that the high dispersion of electrostatically adsorbed ammine metal precursors is retained during reduction; a strong correlation between adsorption and high metal dispersion has been established. The SEA method appears to be a rational procedure for the cheap, simple, and scalable preparation of highly dispersed supported catalysts, even at relatively high metal loadings.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

Chemicals	Grade of purity	Manufacturers
Silicon dioxide (SiO_2)	99.8%	SIGMA-ALDRICH
30% Ammonium hydroxide solution (NH_4OH)	30%	CARLO ERBA
Ammonium chloride (NH_4Cl)	99.00%	CARLO ERBA
Cobalt(II) chloride hexahydrate ($CoCl_2.6H_2O$)	99.00%	CARLO ERBA
Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$)	98.00%	LABORATORY REAGENT (RANKEM)
Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}$	99.00%	CARLO ERBA
Chromium(lll) nitrate nonhydrate ($Cr(NO_3)_3.9H_2O$)	97.00%	FLUKA
Chromium(VI) oxide (CrO_3)	98.00%	SIGMA-ALDRICH
Iron(III) Chloride Hexahydrate ($FeCl_3.6H_2O$)	98.00%	CARLO ERBA
Hydrogen peroxide 30%	98.00%	CARLO ERBA
Diethyl ether	98.00%	CARLO ERBA
37% Hydrochloric acid	36.90%	CARLO ERBA
70% Nitric acid (HNO_3)	69.90%	CARLO ERBA
Dodecane	97%	ALDRICH
Ethylbenzene	99.80%	Buksan
Acetonitrile(CH_3CN)	99.9%	CARLO ERBA
Deionized water	-	-
Acetone ($(CH_3)_2CO$)	-	-
Air zero gas, zero grade	99.99%	UIG
Hydrogen gas, high purity	99.99%	PRAXAIR

3.2 Material and apparatus

1. Beakers
2. Clamps
3. Condensers
4. Graduate pipettes
5. Volumetric flasks
6. Vials
7. Thermometer
8. Buchner funnel
9. Desiccator
10. Round bottom flask 25 mL
11. Filter paper diameter 70 mm
12. Hot air Oven
13. Hot Plate & Stirrer
14. Centrifuge
15. Tube furnace with a programmed temperature controller, VCTF4, Vecstar
16. pH conductivity meter
17. Gas Chromatography (GC-FID)
18. Inductively coupled plasma atomic emission spectroscopy (ICP-OES)

3.3 Preparation and Characterization of catalyst.

3.3.1 Preparation of supported catalyst on silica by impregnation methodology

3.3.1.1. 1%wt metal oxide over silica

The calculated amount of metal oxide precursor (0.26, 0.09, 0.20, and 0.24 g of $CrCl_3.6H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$, $CoCl_{2.6}H_2O$, and $FeCl_3.6H_2O$, respectively) was dissolved in 10 mL of in DI water. This solution was then slowly dropped into 4.95 g SiO_2 (devisil) and kept stirring to prevent agglomeration. Then, the obtained solid was dried at ambient temperature for 6 h, and placed in the oven at 110°C for overnight. It is then calcined at 300 °C at the heating rate of 2°C/min for 3 h using horizontal tube furnace.

The preparation of 3, 5, and 10% Cr/SiO_2 via impregnation was similarly to those with the calculated amount of $CrCl_3.6H_2O$.

3.3.2 Preparation of supported catalyst over silica by strong electrostatic adsorption (SEA)

3.3.2.1 Cr, Mo, and Fe catalysts

The Cr/SiO_2[SEA], Mo/SiO_2[SEA], and Fe/SiO_2[SEA] were prepared by strong electrostatic adsorption (SEA) method using CrO_3, $(NH_4)_6Mo_7O_{24}$, $[Fe(bipy)_3]Cl_3$ as a precursor, respectively. First, 4.76 g of silica was suspended in approximately 50.00 mL of deionized water. In a separate flask, 0.49, 1.00, and 1.50 g of CrO_3, $(NH_4)_6Mo_7O_{24}$, $[Fe(bipy)_3]Cl_3$, respectively, was dissolved in 50.00 mL of deionized water. The pH of this solution will be adjusted to 1.76. Then, this resulting solution was rapidly added to the silica and stirred for 60 min at room temperature. The solid was allowed to settle for 5 minutes. The resulting wet powder was vacuum filtered, rinsed several times with deionized water at pH 1.76, and dried at room temperature for 8 h, followed by drying in air at 125 °C for 8 h. Afterward, the catalyst was calcined in the horizontal tube furnace under the flow of air (60 mL/min) at 650 °C for 3 h with a heating rate at 2 °C/min.

3.3.2.2 Co^{2+} catalyst

The Co/SiO_2[SEA], was prepared by strong electrostatic adsorption method from the previous reported literature [17]. In a typical synthesis, silica was suspended in deionized water. The pH of the solution was adjusted to 11 using concentrated ammonium hydroxide (NH_4OH). In separate flask, 2.50 g of $[Co(NH_3)_6]Cl_3$ was dissolved in deionized water. The pH of the solution was adjusted to 11 with NH_4OH. This solution was rapidly added to the silica suspension and stirred at room temperature for 8 h. The solid will be allowed to settle. The resulting wet powder will be vacuum filtered continued with for rinsed several times with deionized water, and dried at room temperature, followed by drying in air at 125 °C for. After that, the catalyst was calcined in muffle furnace at 650 °C under air (60 ml/min) for 3 h.

3.3.3 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The solution to analyze is conducted by a peristaltic pump though a nebulizer into a spray chamber. The produced aerosol is lead into an argon plasma. Plasma is the forth state of matter, next to the solid, liquid and gaseous state. In the ICP-OES the plasma is generated at the end of a quarts torch by a cooled induction coil through which a high frequency

alternate current flows. As a consequence, an alternate magnetic field is induced which accelerated electrons into a circular trajectory. Due to collision between the argon atom and the electrons ionization occurs, giving rise to a stable plasma. The plasma is extremely hot, 6000-7000 K. In the induction zone it can even reach 10000 K. In the torch de-solvation, atomization and ionizations of the sample takes place. Due to the thermic energy taken up by the electrons, they reach a higher "excited" state. When the electrons drop back to ground level energy is liberated as light (photons). Each element has an own characteristic emission spectrum that is measured with a spectrometer. The light intensity on the wavelength is measured and with the calibration calculated into a concentration.

3.3.4 Ultraviolet–visible spectroscopy (UV-VIS)

Ultraviolet–visible spectroscopy (UV-VIS) was used to determine the Cr, Fe, Mo and Co loading amount, using deionized water is adjusted pH 1.76 and pH 11 for Co was used as solvent for baseline correction. The sample solution is taken to adjust the volume to a certain volumé. The calibration curve was prepared with a sample standard in different concentrations. The samples were measured using a UV–Vis Spectrophotometer (PG instruments limited, T60 U, 50-60 Hz, 150 W), with a wavelength of maximum absorbance. The results were calculated for finding the Cr, Fe, Mo and Co loading amount.

3.3.5 UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS)

Reflectance spectroscopy is very closely related to UV/Vis spectroscopy, in that both of these techniques use visible light to excite valence electrons to empty orbitals. The difference in these techniques is that in UV/Vis spectroscopy one measures the relative change of transmittance of light as it passes through a solution, whereas in diffuse reflectance, one measures the relative change in the amount of reflected light off of a surface.

3.4 Catalytic Testing

3.4.1 The oxidation of ethylbenzene

The reactions were performed in the rounded bottle flask equipped with condenser. 1.00 mL of ethylbenzene were mixed with 10 mL CH_3CN and transferred to rounded-bottle flask. 0.4 g Catalyst and 30%H_2O_2 0.8 mL were then introduced. After that, the mixtures were

heated to 60 °C for 24 hours. After the reaction, this mixture was centrifuged at 8500 rpm for 5 min to separate the solid particle (catalysts). The filtrates were then pipetted for 1.00 mL. To this amount of pipetted volume, the mixture of 0.10 mL of dodecane (internal standard), 1.00 mL of CH_3CN, and 1.00 mL of Et_2O were introduced. The products in organic solvent were collected from the separation funnel. These products were then analyzed by Gas chromatography equipped with flame ionization detector (FID) using capillary1 column. The condition of GC was as the following: injector 220 °C, N_2 flow 1.5 mL/min, column 70 °C hold 2 min to 180°C rate 20 °C/min, detector 220 °C, pressure 16.4 psi, linear velocity 36.1 cm/sec.

The remaining hydrogen peroxide was determined by titration. 1.00 mL of sample was mixed with 2.50 ml 10%wt KI solution and 5.00 mL 1 M H_2SO_4. The mixture was then titrated using 0.1M $Na_2S_2O_3$ and starch an indicator.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 Amount of metal oxide supported on SiO_2

Metal oxides supported SiO_2 were prepared two following methods; impregnation (IM) and strong electrostatic adsorption (SEA). Inorganic metallic salts were used as a precursor for IM; while, the complexes were used for SEA. The metal oxide contents over SiO_2 are summarized in **Table 4.1**.

Table 4.1 Metal content on the catalysts

Catalysts	Method	Precursor	Concentration (M)	%Metal[a] (%wt.)
0.27%Cr/SiO_2	IM	$CrCl_3.6H_2O$	-	0.27
1%Cr/SiO_2		$CrCl_3.6H_2O$	-	0.97
3%Cr/SiO_2		$CrCl_3.6H_2O$	-	3[b]
5%Cr/SiO_2		$CrCl_3.6H_2O$	-	5[b]
10%Cr/SiO_2		$CrCl_3.6H_2O$	-	10[b]
1%Fe/SiO_2		$FeCl_3.6H_2O$	-	1.00
1%Mo/SiO_2		$(NH_4)_6Mo_7O_{24}$	-	0.85
1%Co/SiO_2		$Co(NO_3)_2.6H_2O$	-	0.80
0.27%Cr/SiO_2	SEA	CrO_3	0.100	0.27
0.37%Cr/SiO_2		CrO_3	0.200	0.37
0.40%Cr/SiO_2		CrO_3	0.300	0.40
0.17%Fe/SiO_2		$[Fe(bipy)_3]SO_4$	0.045	0.16
0.16%Mo/SiO_2		$(NH_4)_6Mo_7O_{24}$	0.100	0.16
0.59%Co/SiO_2		$[Co(NH_3)_6]Cl_3$	0.100	0.59

[a] determined by ICP-OES, [b] estimated from the calculation

The amount of metal content for all IM catalysts are in agreement with the expectation. This is typical for impregnation as the loaded metal precursor would remain on support's surface. For catalysts prepared by SEA, they are depending on the nature of the complex, e.g. formal charge of it ionic cluster, size, and ligand. For Cr/SiO_2(SEA) and Mo/SiO_2(SEA), both of these precursors exist as an anion cluster as CrO_4^{2-} and MoO_4^{2-} at pH=3, respectively. With the similar concentration at 0.100 M, the resulting. catalysts after SEA were 0.27% and 0.16% for Cr and Mo, respectively. This suggests that the molybdate species tend to be less adsorbed than CrO_4^{2-} at pH = 3. Once increase the concentration of chromium precursor for the SEA, the amount of chromium is increased as depicted in **Figure 4.1**.

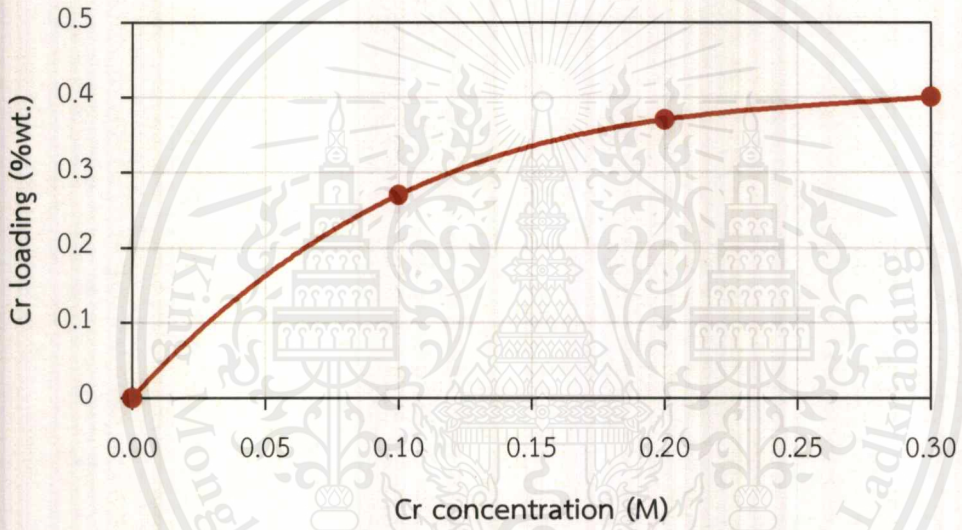


Figure 4.1 Adsorption profile of chromium with various concentration of CrO_3

It can be seen from **Figure 4.1** that Cr adsorptivity is rapidly increased from 0.27 to 0.37 % at the concentration of 0.10 and 0.20 M, respectively. Subsequently, the adsorption curve reaches an equilibrium at 0.30 M yielding 0.40%Cr/SiO_2[SEA] catalyst. This adsorption characteristic is in accordance with Langmuir adsorption (monomer form). According to this, the maximum adsorption at equilibrium point is ~0.4%wt. of Cr. This could be limited by the number of accessible Si-OH^{2+}on SiO_2 at pH = 3.

For $[Fe(bipy)_3]SO_4$ and $\{Co(NH_3)_6]Cl_3$, these are considered as the cationic precursor. The obtained catalysts after SEA are 0.16 and 0.59%wt, for Fe and Co, respectively. The lower %loading of Fe could contribute to the lower concentration use as compared to Co complex.

4.1.2 Metal oxide species over SiO_2

4.1.2.1 Cr oxide

To monitor the Cr species formed once impregnated various Cr loadings, DR-UV spectroscopy was investigated. The result is shown in **Figure 4.2**

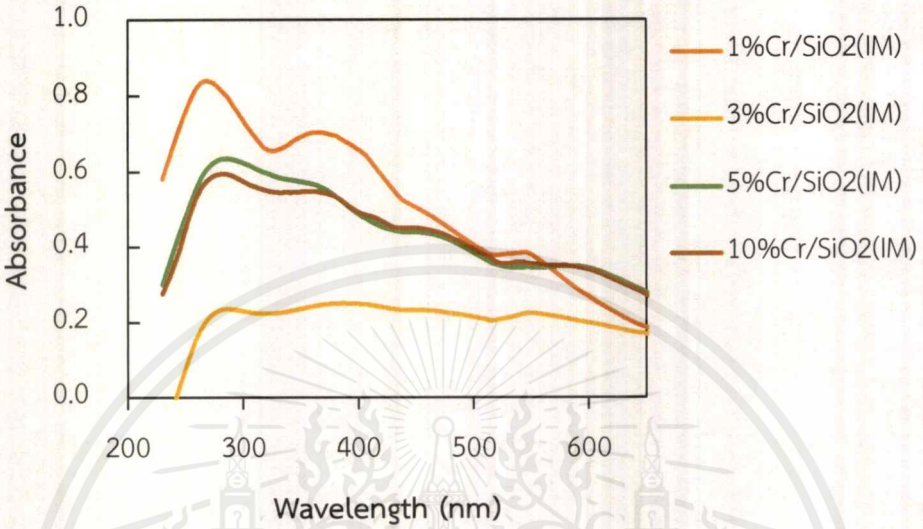
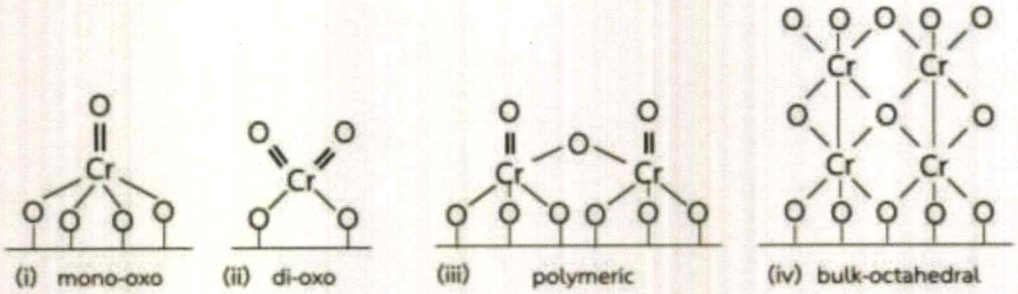


Figure 4.2 DRS UV-Vis spectra of various Cr loading supported on SiO_2 prepared by impregnation

As can be seen in **Figure 4.2**, all impregnated chromium samples show absorption peaks at 280, 375, 450 and 550 nm. According to Edward L. Lee *et. al.*[34], peaks at 280 and 375 nm correspond to the isolated tetrahedral chromium species (**i** and **ii**); while the peak at 450 and 596 nm refer to polymeric chromium species (**iii**) and Cr^{3+} in octahedral environment, such as bulk Cr_2O_3 species (**iv**), respectively as shown in **Scheme 4. 1** [17]. However, 1%Cr/SiO_2(IM) shows very low λ_{max} at 450 and 596 nm as compared to 3%, 5%, and 10%Cr/SiO_2(IM). This suggests that the isolated tetrahedral species (**i** and **ii**) are more predominant at low %loading. Thus, the higher dispersion of 1%Cr/SiO_2 (IM) could be more as compared to others.



Scheme 4.1 Schematic of molecular structures surface chromium species in [IM] Cr/SiO_2 1% wt. catalyst (i) mono-oxo, (ii) di-oxo, (iii) polymeric and (iv) bulk-octahedral chromium oxide [18,19]

The comparison of chromium species formation using IM and SEA was evaluated by the DR-UV spectra of 0.27%Cr/SiO_2 (IM) and 0.27%Cr/SiO_2 (SEA) as shown in **Figure 4.3.**

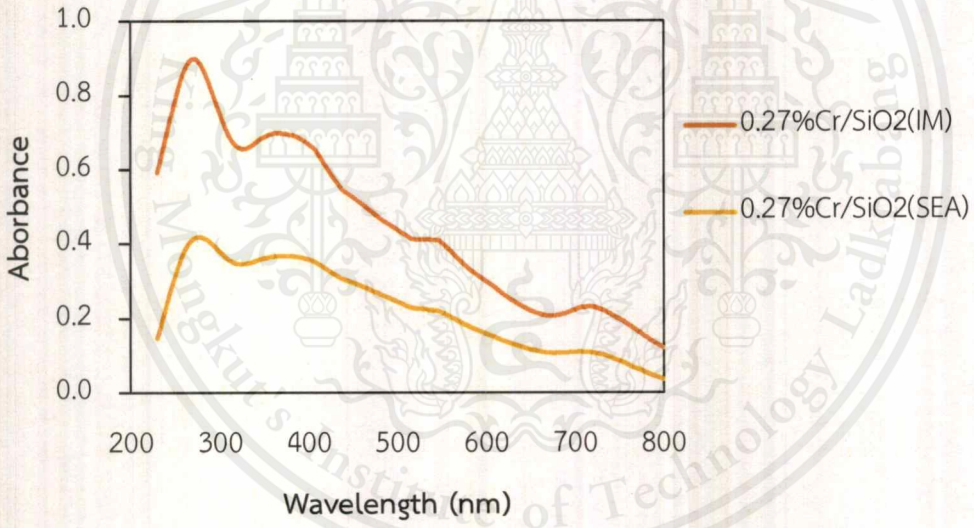


Figure 4.3 DR-UV spectra of Cr oxide supported SiO_2 prepared from impregnation and adsorption

It is obviously seen that weak absorption peak at 590 nm was observed in both catalysts indicating the low bulk Cr_2O_3 content. This suggests the high dispersion of these two catalysts. Furthermore, the fraction of chromium in tetrahedral (isolated) over in octahedral (bulk) evaluating from the $\lambda_{375}/\lambda_{550}$ of 0.27%Cr/SiO_2(SEA) (1.8) has more than 0.27%Cr/SiO_2(IM)

(1.75). This suggests that there is more isolated species respected to bulk Cr_2O_3 in SEA than those in IM.

Once increase the amount of Cr/SiO_2(SEA) by the increase of concentration of CrO_3, the sample absorbance is in the order of 0.27%, 0.37%, and 0.40%Cr/SiO_2(SEA), respectively as shown in **Figure 4.4.** This could due to the higher chromium content. In addition, the $\lambda_{375}/\lambda_{596}$ found to be 2.3, 2.3, and 3.2 for 0.27%, 0.37%, and 0.40%Cr/SiO_2(SEA), respectively. This suggests that the increase of chromium by SEA yields predominantly isolated chromium species. Though, the amount of bulk species is also enhanced.

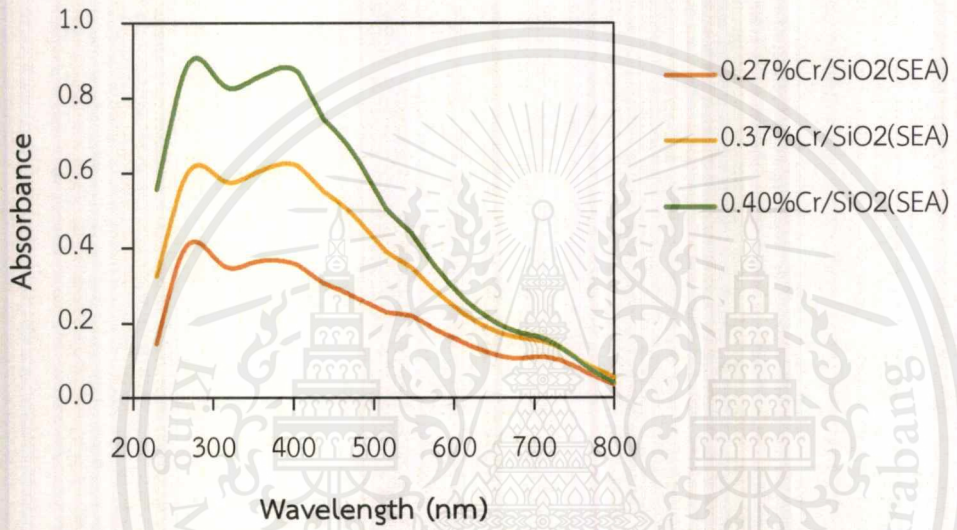


Figure 4.4 DR-UV of Cr/SiO_2 (SEA) at various Cr concentration

4.1.2.2 Fe oxide

The comparative DR-UV spectra of Fe oxide supported SiO_2 prepared by IM and SEA are depicted in **Figure 4.5.**

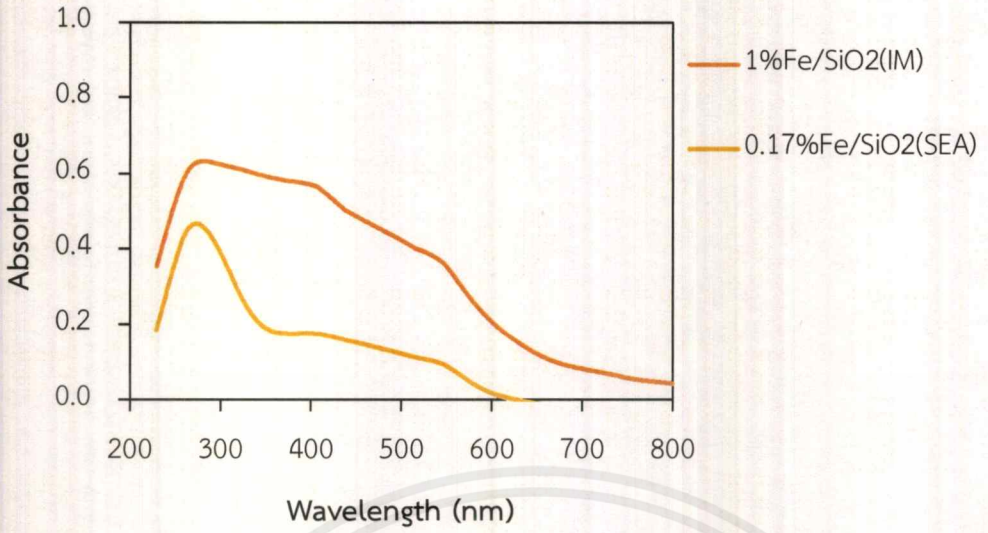


Figure 4.5 DR-UV spectra of Fe oxide supported SiO_2 prepared from impregnation and adsorption

The spectra show an intense band at 280 nm and a strong absorption in range of 360-600 nm. Dapurkar, S.E., et. al., reported that the absorption bands at ~ 250 nm could be assigned to Fe_2O_3 nanoparticles which is owing to the quantum size effect; while the broad spectra is attributed to an agglomerated Fe_2O_3. In line with this observation, Fe/SiO_2 prepared by SEA could attribute to the small size of Fe_2O_3 and/or the isolate Fe^{3+} referring as a highly dispersed Fe_2O_3; whereas IM provides both highly-dispersed Fe and bulks Fe_2O_3.

4.1.2.3 Mo oxide

DRUV spectra of molybdenum oxide supported SiO_2 prepared by IM and SEA are depicted in **Figure 4.6**.

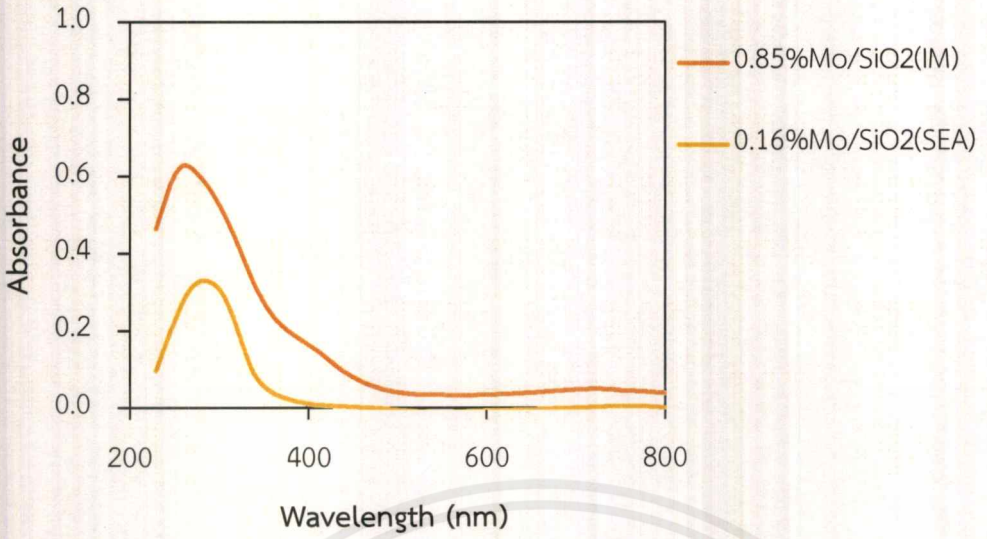


Figure 4.6 DR-UV spectra of Mo oxide supported SiO_2 prepared from impregnation and adsorption

Considering 0.85%Mo/SiO_2(IM), the intense absorption peaks are at 267 nm and 400 nm. Though, the shoulder at ~290 nm is also observed. According to Radu Dorin Andrei *et. al.* [33], the first peak is attributed to highly-disperse MoO_3 monomers and the higher wavelength are the absorption of octahedral MoO_x and small-crystalline α-MoO_3 [33]. For 0.16%Mo/SiO_2(SEA), the absorption band is less intense than the impregnated catalyst due to the lower amount of MoO_x. Though, the intense peak at ~290 nm was observed as compared to those at 400 nm. It is suggested the same that Mo/SiO_2 prepared by SEA provides isolated MoO_3 and IM facilitates the formation both monomeric and bulk MoO_x.

4.1.2.4 Co oxide

DRUV spectra of cobalt oxide supported SiO_2 prepared by IM and SEA are depicted in **Figure 4.7**.

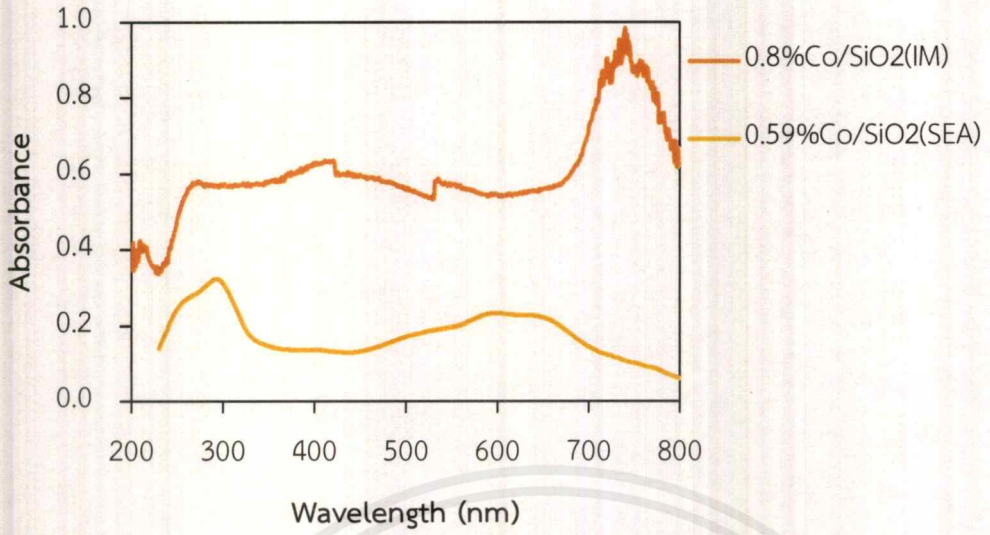


Figure 4.7 DR-UV spectra of Co oxide over SiO_2 prepared from impregnation and adsorption

According to **Figure 4.7,** the intense peak at ~740 nm was detected in 0.80%Co/SiO_2(IM); while, peaks at 300 and ~ 650 nm was observed in 0.59%Co/SiO_2 (SEA). This suggests that the cobalt catalysts prepared by SEA gives the different cobalt species as compared to the impregnation. Our lab had been reported that the preparation of cobalt catalysts by SEA using the same precursor would yield "single-site Co(II) species." However, with the impregnation method, the bulk Co_2O_3 would be obtained. This thus could contribute the different in DR-UV.

4.2 Catalytic testing

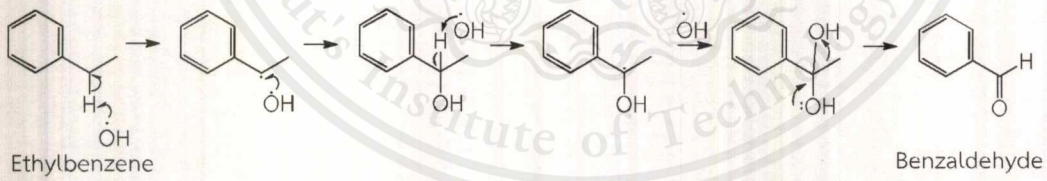
The ethylbenzene oxidation was primarily studied using chromium catalysts prepared by impregnation. Their activity as compared to thermal oxidation and SiO_2 (blank) is summarized in **Table 4.2**.

Table 4.2 Ethylbenzene oxidation using various Cr loading sample (IM)

Catalysts	Conversion (%)	Yield (%)						H_2O_2 Initial (mmol)	H_2O_2 remain (mmol)	TON
		Benzaldehyde	1-Phenylethanol	Acetophenone	Methyl benzoate	2-ethylphenol	3-ethylphenol			
Thermal	0.4	0.1	0.3	0.0	0.0	0.0	0.0	8.2	7.8	-
SiO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.2	7.2	-
1%Cr/SiO_2(IM)	14.0	0.7	2.6	5.2	0.4	2.3	2.7	8.2	0.1	14.9
3%Cr/SiO_2(IM)	12.4	0.6	1.9	4.6	0.1	2.5	2.6	8.2	0.1	4.4
5%Cr/SiO_2(IM)	11.9	0.6	2.7	4.3	0.3	1.9	2.0	8.2	0.1	2.5
10%Cr/SiO_2(IM)	10.2	0.5	2.3	3.8	0.1	1.7	1.8	8.2	0.1	1.1

1.00 mL of ethylbenzene, 10 mL CH_3CN, 0.4 g of catalyst, 0.8 ml of 30% H_2O_2, 60°C, 24 hours

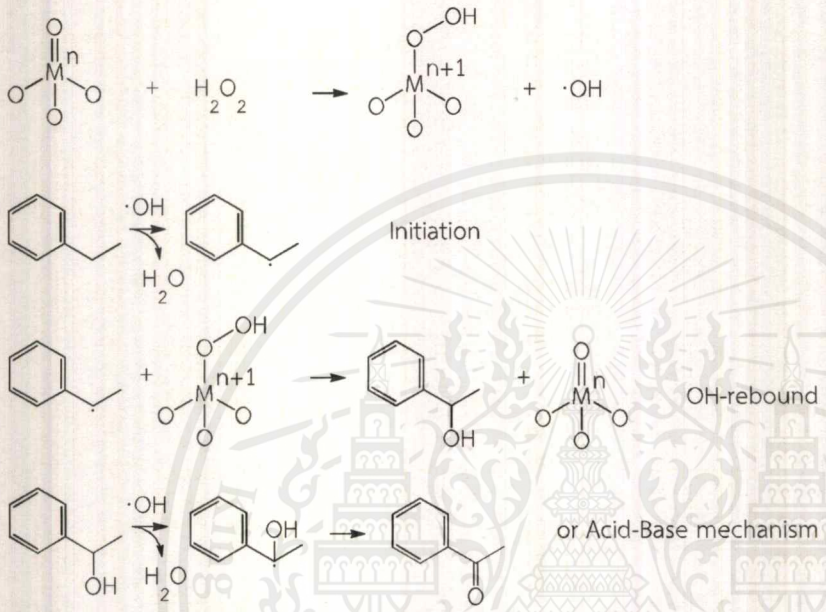
Ethylbenzene oxidation by thermal process gives conversion 0.4% and slightly yield of benzaldehyde (0.3%) and 1-phenylethanol (0.1%). Benzaldehyde a major majority indicating the C-C cleavage during the oxidation which could take place via radical mechanism as shown in **Scheme 4.1**.



Scheme 4.1 The oxidation of ethylbenzene via radical mechanism.

However, the oxidation using pure SiO_2 as material blank shows none of ethyl benzene conversion. It is suggested that OH radical can be fixed by the weak Lewis acid character of SiO_2 surface, then decomposed to O_2 and H_2O as reported by Manos Mavrikakis's group [35]. When the ethylbenzene was carried out using 1%wt. Cr/SiO_2 (IM) as a catalyst, the conversion is promoted up to 34 times (14%) than that of the thermal oxidation. This indicates that chromium species promote the C-H cleavage at benzylic position via push-pull mechanism. Furthermore, the major product is changed to acetophenone (5.2%); while, benzaldehyde is

retained at 0.7%. In addition, 1-phenylethanol (2.6%), methylbenzoate (0.4), 2-methylpenol (0.3), 3-methylphenol (0.7) were slightly produced. These changes in product distribution and the presence of methylbenzoate indicate the Lewis acid assisted-mechanism (instead of common radical mechanism). The mechanism has been wildly reported in the literatures [36] that it is participated in metal-peroxo species as in **Scheme 4.2**.



Scheme 4.2 Mechanism for ethylbenzene oxidation [36]

Furthermore, it has seen that the conversion and TON decrease as the Cr loading increase (14.0, 12.4, 11.9, and 10.2% of conversion and 14.9, 4.4, 2.5 and 1.1 for TON for 1, 3, 5, and10%Cr, respectively). In addition, the H_2O_2 remaining after the reaction was almost demolished for 3%, 5%, and 10%Cr/SiO_2(IM). This indicates the large decomposition of hydrogen peroxide in these catalysts. This could attribute to the bulk chromium oxide as presence more in high Cr content. As such, it is suggested that Cr tends to be agglomerated at high loading and the surface exposed Cr is thus corresponded to oxidation ability, in agreement to those DRUV spectra in **Section 4.1.2.1**. The active species could be the isolated chromium species. Though, the product selectivity is not significantly different.

To evaluate the change in chromium species before and after the reaction, DR-UV spectra of the spent 1%wt. Cr/SiO_2(IM) was determined as shown in **Figure 4.8**.

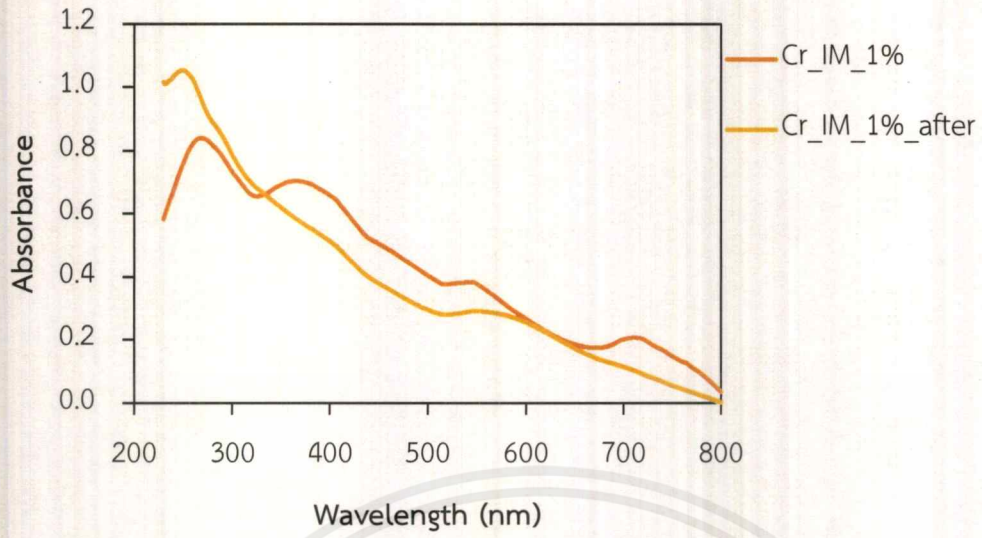


Figure 4.8 DR-UV spectra of fresh and spent 1%wt. Cr/SiO_2

The spectra of spent 1%wt. Cr/SiO_2(IM) catalyst show the intense band at 230, 370 and 590 nm similar to the fresh one. However, the peak intensity at 370 nm that represents to polymeric form is diminished with the ascendance of the intensity at 230 and 590 nm. It is suggested that Cr oxide cannot localized at the precise position on SiO_2 surface. It tends to be re-dispersed to form aggregated Cr_2O_3 via Oswald ripening mechanism [37]. Though, it could be leached out during the reaction as well.

The use of 0.27%Cr/SiO_2(SEA) as a catalyst for ethylbenzene oxidation compared with 0.27%Cr/SiO_2(IM) is summarized in **Table 4.3**.

Table 4.3 Ethylbenzene oxidation using various Cr loading sample (SEA)

catalysts	Conversion (%).	Yield (%)						H_2O_2 initial	H_2O_2 remain	TON
		Benzaldehyde	1-Phenylethanol	Acetophenone	Methyl benzoate	2-ethylphenol	3-ethylphenol			
0.27%Cr/SiO_2(IM)	10.4	0.5	2.2	3.4	0.3	2.1	0.7	8.2	1.4	41.0
0.27%Cr/SiO_2(SEA)	11.7	0.5	2.3	3.3	0.4	1.6	2.0	8.2	2.6	46.3
0.37%Cr/SiO_2(SEA)	13.2	0.6	2.5	3.8	0.3	2.0	2.6	8.2	0.7	38.2
0.40%Cr/SiO_2(SEA)	13.0	0.5	2.2	3.2	0.3	2.4	2.6	8.2	0.5	34.6

1.00 mL of ethylbenzene, 10 mL CH_3CN, 0.4 g of catalyst, 0.8 mL of 30% H_2O_2, 60 °C, 24 hours

In comparison between 0.27%wt.Cr/SiO_2(SEA) to 0.27%Cr/SiO_2(IM), the conversion of 0.27%Cr/SiO_2(SEA) is slightly higher than impregnation (11.7% and 10.4% for 0.27%wt.Cr/SiO_2(SEA) to 0.27%Cr/SiO_2(IM), respectively). This thus causes the slightly higher TON in 0.27%Cr/SiO_2(SEA) (46.3) as compared to 0.27%Cr/SiO_2(IM) (41.0). It is because these two samples possess the similar fraction of monomeric and polymeric form (see DRUV spectroscopy **Figure 4.3**). In term of product distribution, they all provide the similar products. However, 0.27%Cr/SiO_2(IM) yielded more 2-ethylphenol which is the side products. Furthermore, the hydrogen peroxide used in 0.27%Cr/SiO_2(IM) is higher than those SEA even at their lower conversion. This indicates that 0.27%Cr/SiO_2(IM) has more hydrogen decomposition than SEA. It could attribute to the higher bulk chromium in IM than SEA as discussed earlier. Thus, this suggests that the isolated chromium species are more active than those in bulk.

The increase of chromium loading by SEA were prepared using the different concentration of chromium precursor during the adsorption. As can be seen in **Table 4.3**, once the Cr %loading increase from 0.27% to 0.37%, the %conversion is also enhanced (11.7 and 13.2%, respectively. Furthermore, yield of acetophenone is increased. This could attribute to the higher amount of isolated chromium species as evidenced by the DR-UV. However, at 0.40%wt Cr, the conversion is slightly dropped and the H_2O_2 consumption is more than others. This suggests the lower metal dispersion with the higher amount of bulk as discussed in DR-UV causing the more decomposition of hydrogen peroxide.

To investigate the reaction mechanism, 0.27%Cr/SiO_2 (SEA) was selected as a catalyst for ethylbenzene oxidation in which it was carried out with the different amount of the catalyst. The result is shown in **Figure 4.9**.

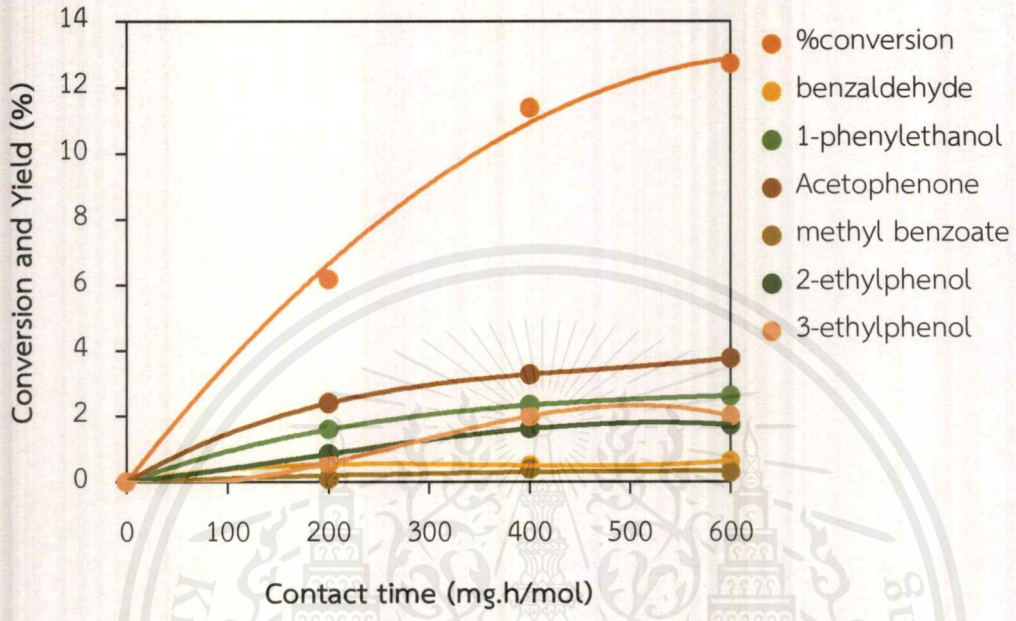
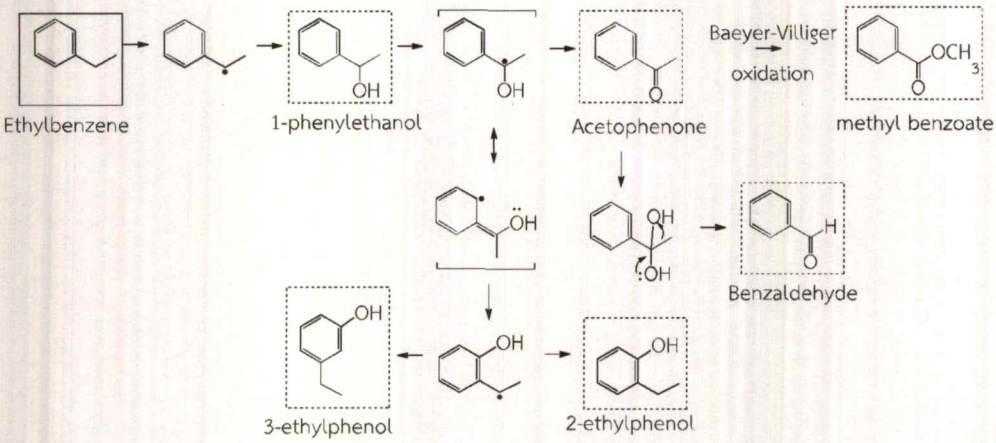


Figure 4.9 the reaction time profile of 0.27%Cr/SiO_2 (SEA); 1.00 mL of ethylbenzene, 10 mL CH_3CN, 0.4 g of catalyst, 0.8 mL of 30% H_2O_2, 60 °C.

The conversion is increased with contact time and tends to stable after 600 mg.h/mol. This is suggested that the activity is not limit by amount of H_2O_2. Acetophenone is major product that is highly gained up at the initial contact time and slightly increased until 600 mg.h/mol. 1-phenylethanol seems to be produced in first short-time period and keep stable. Other products e.g. methylbenzoate, 2-ethylphenol, 3-ethylphenol and benzaldehyde shows a spline s-curve that is a characteristic of secondary product. Therefore, the ethylbenzene oxidation profile can be summarized in **Scheme 4.3**.



Scheme 4.3 summarized ehthylbenzene oxidation pathway using Cr/SiO_2 (SEA)

As mention throughout this work the ethylbenzene oxidation though metal-peroxo species is the strategy beyond thermal oxidation, the type of metal is also screened for the best choice. Ability of each metal for ethylbenzene oxidation is showed in **Table 4.4**.

Table 4.4 the screening of metal for ethylbenzene oxidation

Catalysts	Conversion (%).	Yield (%)						H_2O_2 initial	H_2O_2 remain	TON
		Benzaldehyde	1-Phenylethanol	Acetophenone	Methyl	2-ethylphenol	3-ethylphenol			
0.27%Cr/SiO_2(IM)	10.4	0.5	2.2	3.4	0.3	2.1	0.7	8.2	1.4	41.0
0.27%Cr/SiO_2(SEA)	11.7	0.5	2.3	3.3	0.4	1.6	2.0	8.2	2.6	46.3
1%Fe/SiO_2(IM)	2.8	0.2	0.5	1.0	0.0	0.6	0.3	8.2	3.8	3.2
0.17%Fe/SiO_2(SEA)	3.8	0.3	0.7	1.3	0.1	0.7	0.3	8.2	2.6	24.1
0.85%Mo/SiO_2(IM)	0.6	0.1	0.2	0.3	0.0	0.0	0.0	8.2	5.9	1.3
0.16%Mo/SiO_2(SEA)	0.4	0.1	0.1	0.2	0.0	0.0	0.0	8.2	7.0	4.9
0.80%Co/SiO_2(IM)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.2	0.1	0.0
0.59%Co/SiO_2(SEA)	0.1	0.0	0.1	0.1	0.0	0.0	0.0	8.2	0.1	0.3

1.00 mL of ethylbenzene, 10 mL CH_3CN, 0.4 g of catalyst, 0.8 mL of 30% H_2O_2, 60 °C, 24 hours

It can be seen in **Table 4.4** that the ethylbenzene conversion over the catalysts prepared by SEA is higher than that of IM in all cases (even at lower %loading). This emphasizes

that SEA method provides highly dispersed metal oxide and/or higher isolated amount of metal oxide species.

Considering Co catalysts, no activity of ethyl benzene oxidation was observed in 0.80%Co/SiO_2(IM) in contrast with the hydrogen peroxide consumption. This could attribute to the facile hydrogen decomposition of Co_2O_3 as reported in literatures. However, the very low conversion of 0.80%Co/SiO_2(SEA) catalyst (0.1%) was detected indicating that this catalyst can act as oxidation reaction. Though, it would prefer the hydrogen peroxide decomposition.

For Mo catalysts, they showed higher activity than Co catalysts but lower than those of Cr catalyst. Interestingly, both 0.85%Mo/SiO_2(IM) and 0.16%wt Mo/SiO_2(SEA) showed the lowest hydrogen peroxide consumption regardless to their conversion. This suggests that molybdenum catalyst does not active towards hydrogen peroxide decomposition.

Considering Fe catalysts, 0.17%Fe/SiO_2(SEA) shows conversion lower than 0.27%Cr/SiO_2(SEA). However, the TON of 0.17%Fe/SiO_2(SEA) is higher as compared to others.

It is indicating that its activity dependent on Lewis acid character; in the order of Cr > Fe > Mo > Co. Although, Mo has the valence state close to Cr, but its large cationic size affects to the less charge density. Moreover, Fe, Mo (IM) and Co (either of IM and SEA) is much responsible for H_2O_2 decomposition. The mole of H_2O_2 lost during the oxidation is twice; while the conversion is slightly changed. It is suggested that there is the competitive formation between metal-peroxo and metal-OH species. The last one is unstable and end up to couple with neighboring one to liberate O_2 and H_2O. Furthermore, all product selectivity is remained in the similar pattern (both IM and SEA). Acetophenone is yet the major product. It is all indicated that tetrahedrally isolated and polymeric metal oxide is much more favorable for ethylbenzene oxidation with the selectivity toward acetophenone.

CHAPTER 5
CONCLUSION AND SUGGESTIONS

5.1 Conclusions

In this work, ethylbenzene was studied using metal oxide including Cr, Fe, Mo, and Co supported SiO_2 as a catalysts with H_2O_2 as an oxidant. The catalysts were prepared from both impregnation (IM) and strong electrostatic adsorption (SEA) in comparison. The effect of preparation method, metal loading, type of metal, and contact time on the oxidation of ethylbenzene are also investigated. Amount of metal oxide supported SiO_2(IM) are in agreement with the expectation. While, the number of metal oxides supported SiO_2(SEA) are depended on formal charge, ionic cluster size and ligand. Cr and Mo which are existed in negatively charged cluster favored to adsorbed at the precise Si-OH^{2+} position (at pH=3), rather than those Fe and Co where the cluster is cationic charges. In addition, the metal oxide species are also varied with the preparation method and metal loading. The Cr species for IM only possessed in the mixture of tetrahedral isolated and polymeric form at low Cr loading. As the loading is increased, the fraction of bulk Cr_2O_3 is also a consequence. On the other hand, isolated and polymeric Cr are retained for Cr/SiO_2(SEA) throughout. In similarly, the other SEA catalysts (Fe, Mo and Co) highly also provide an isolated over than those bulk oxide compared to IM.

The ethylbenzene oxidation was carried out under ambient condition at 60 °C for 24 h. The thermal oxidation provides low conversion and benzaldehyde majority via C-C cleavage through radical process. However, no activity is observed for pure SiO_2 and else H_2O_2 tends to be decomposed due to its acidity. The use of Cr/SiO_2(IM) as a catalyst can promote the conversion up to 34 times and also yield acetophonone as a major product via Lewis acid-assisted radical mechanism. As the Cr loading is increased, the reaction rate seems to be decreased and beside; H_2O_2 decomposition is also increased in account of the Cr oxide aggregation and physio-chemical property of bulk Cr_2O_3. Furthermore, isolated and polymeric Cr oxide tends to be re-dispersed to form bulk Cr_2O_3 via Ostwald ripening mechanism during the oxidation. Once Cr/SiO_2(SEA) which is possessed only isolated and polymeric Cr is used, the activity is consecutively enhanced with Cr loading. In conclusion, tetrahedrally isolated and polymeric Cr oxide are responsible for ethylbenzene oxidation while the bulk Cr_2O_3 additionally level up H_2O_2 decomposition. For the other metal oxide, the activity dependent

on Lewis acid character; in the order of Cr > Fe > Mo > Co. Although, Mo has the valence state close to Cr, but its large cationic size affects to the less charge density. Moreover, Fe, Mo (IM) and Co (either of IM and SEA) is much responsible for H_2O_2 decomposition. In overall elementary steps, the oxidation of ethylbenzene firstly provides 1-phenylethanol as an intermediate that can be conversed to both acetophenone and ethylphenol in parallel. The ketone can subsequently form benzaldehyde and methylbenzoate via Baeyer- Villiger keto oxidation, respectively.

5.2 Suggestion

5.2.1 The activity and selectivity can be also enhanced by the use of metal complexes with the different ligand.

5.2.2 Alternatively, the oxidation of ethylbenzene can be carried out using the application of air as an oxidant to overcome an environmental issue.

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APPENDIXCES

APPENDIX A

CALCULATION

Calculation of ethylbenzene conversion, acetophenone selectivity and reaction yield

Table A1 The area of all product of ethylbenzene oxidation[a]

catalysts	Area						
		Product					
	EB[b]	Benzaldehyde	1-Phenylethanol	Acetophenone	Methyl benzoate	2-ethylphenol	3-ethylphenol
0.37%Cr/SiO_2(SEA)	23181.7	151.7	669.2	1004.2	92.7	538.8	687.8

a reaction condition : *1.00 mL of ethylbenzene, 10 mL CH_3CN, 0.4 g of catalyst, 0.8 mL of 30% H_2O_2, 60 °C, 24 hours*

b EB : ethylbenzene

Calculation of conversion

Conversion can be calculated from the following equation:

$$\text{Conversion (\%)} = \frac{\text{(Area feed of EB/IS feed)} - \text{(Area product of EB/IS)} \times 100}{\text{(Area feed of EB/IS)}}$$

For example;

ethylbenzene Conversion (%) of 0.37%Cr/SiO_2(SEA)

$$\text{Conversion (\%)} = \frac{(23402.5/24402.7) - (23181.7/27929) \times 100}{(23402.50/24402.7)} = 13.2\ \%$$

Calculation of Yield

Calculate the percent yield of each component in sample as follow:

$$\% \text{ Yield in each product} = \frac{(\text{Area product/IS}) \times 100}{(\text{Area feed of EB/IS})}$$

For example;

Acetophenone yield (%) of 0.37%Cr/SiO_2 (SEA)

$$\% \text{ Yield of acetophenone} = \frac{(1004.2/27929) \times 100}{(23402.50/24402.7)} = 3.8\ \%$$

Calculation of selectivity

% Selectivity can be obtained from the following equation:

$$\% \text{ Selectivity in each product} = \frac{\text{Area product} \times 100}{\text{Total area of total product}}$$

For example;

acetophenone selectivity (%) of 0.37%Cr/SiO_2 (SEA)

$$\% \text{ Selectivity} = \frac{1004.2 \times 100}{(151.7+669.2+1004.2+92.7+538.8+687.8)} = 31.90\ \%$$

APPENDIX B

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY (ICP-OES) REFERENCE

Table B1 Metal content on the catalysts determined by ICP-OES

Catalysts	%Metal (%wt.)
0.27%Cr/SiO_2(IM)	0.27
1%Cr/SiO_2(IM)	0.98
3%Cr/SiO_2(IM)	1.35[a]
5%Cr/SiO_2(IM)	1.46[a]
10%Cr/SiO_2(IM)	1.14[a]
1%Fe/SiO_2(IM)	1.04
1%Mo/SiO_2(IM)	0.85
1%Co/SiO_2(IM)	0.80
0.27%Cr/SiO_2(SEA)	0.27
0.37%Cr/SiO_2(SEA)	0.37
0.40%Cr/SiO_2(SEA)	0.40
0.17%Fe/SiO_2(SEA)	0.17
0.16%Mo/SiO_2(SEA)	0.16
0.59%Co/SiO_2(SEA)	0.59

a : estimated from the calculation

APPENDIX C

DR-UV reflectance spectra

DR-UV of catalysts Before run and after run

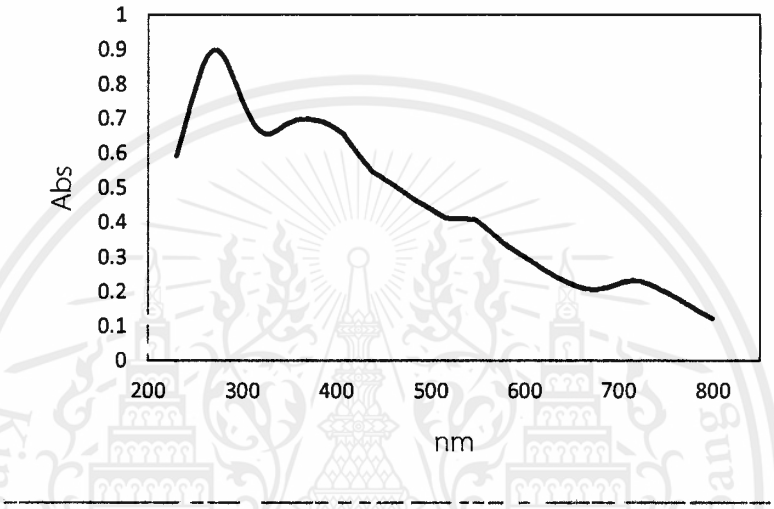

Figure C1 0.27%Cr/SiO_2 (IM) before run.

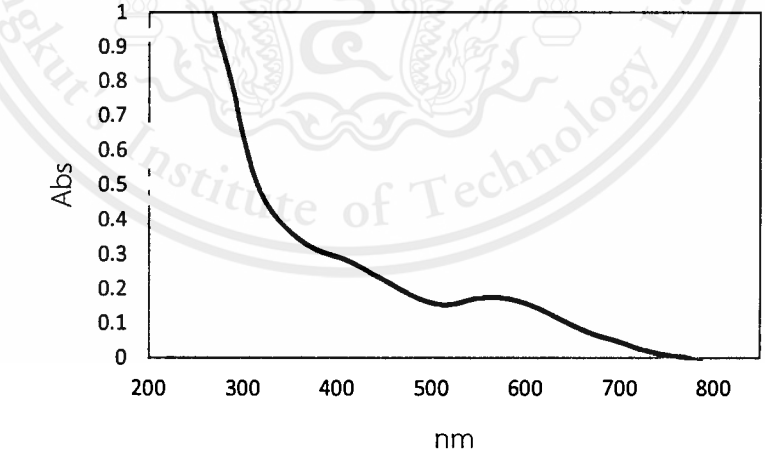

Figure C2 0.27%Cr/SiO_2 (IM) after run

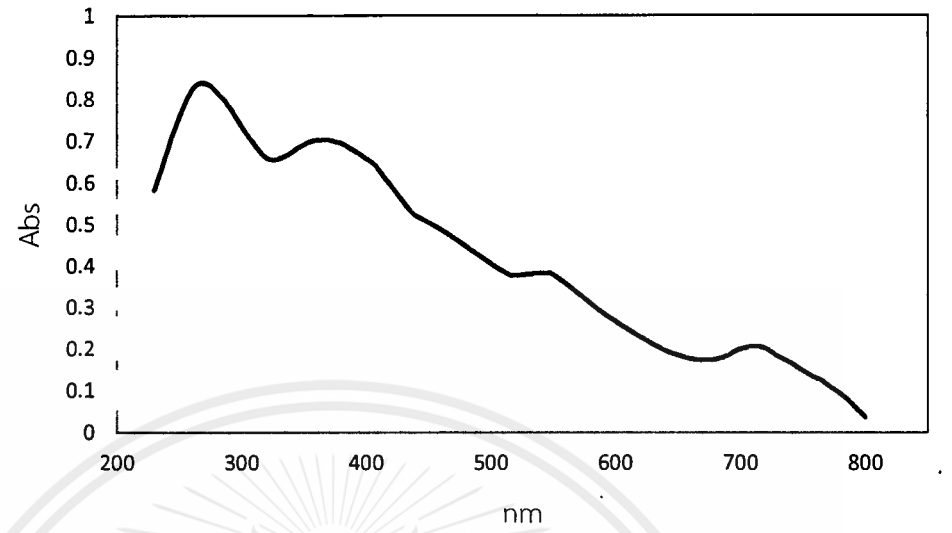

Figure C3 1%Cr/SiO_2 (IM) before run

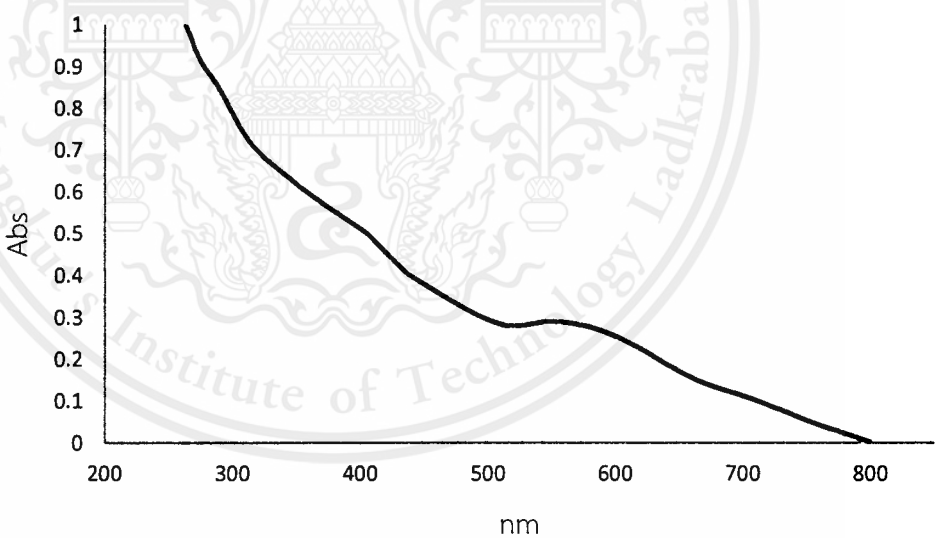

Figure C4 1%Cr/SiO_2 (IM) after run

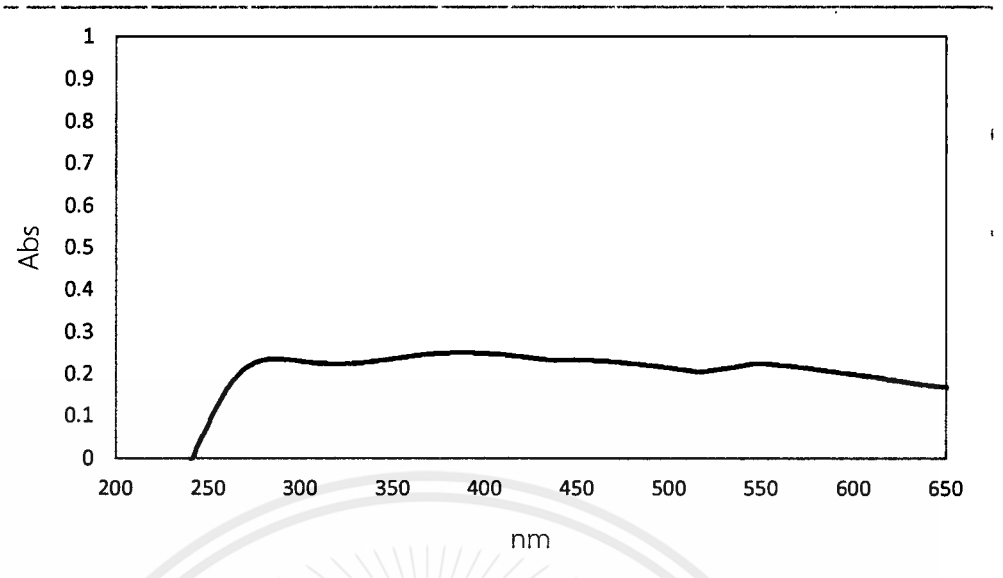

Figure C5 3%Cr/SiO_2 (IM) before run

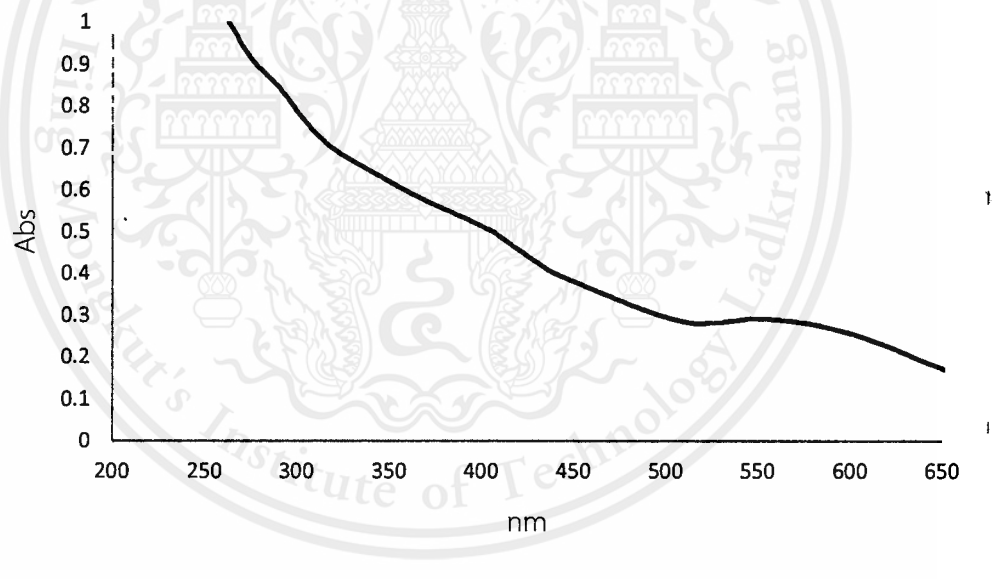

Figure C6 3%Cr/SiO_2 (IM) after run

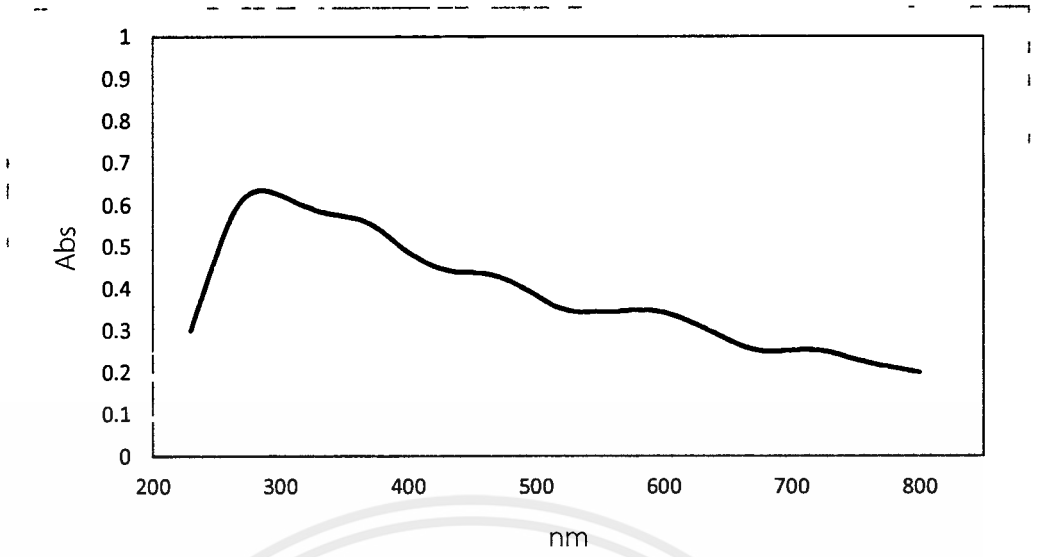

Figure C7 5%Cr/SiO_2 (IM) before run

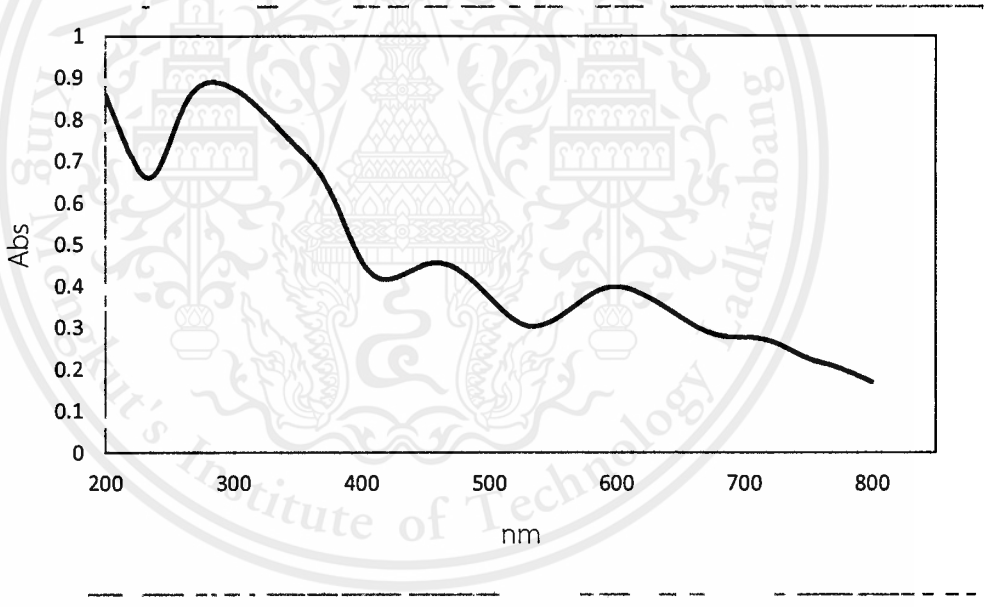

Figure C8 5%Cr/SiO_2 (IM) after run

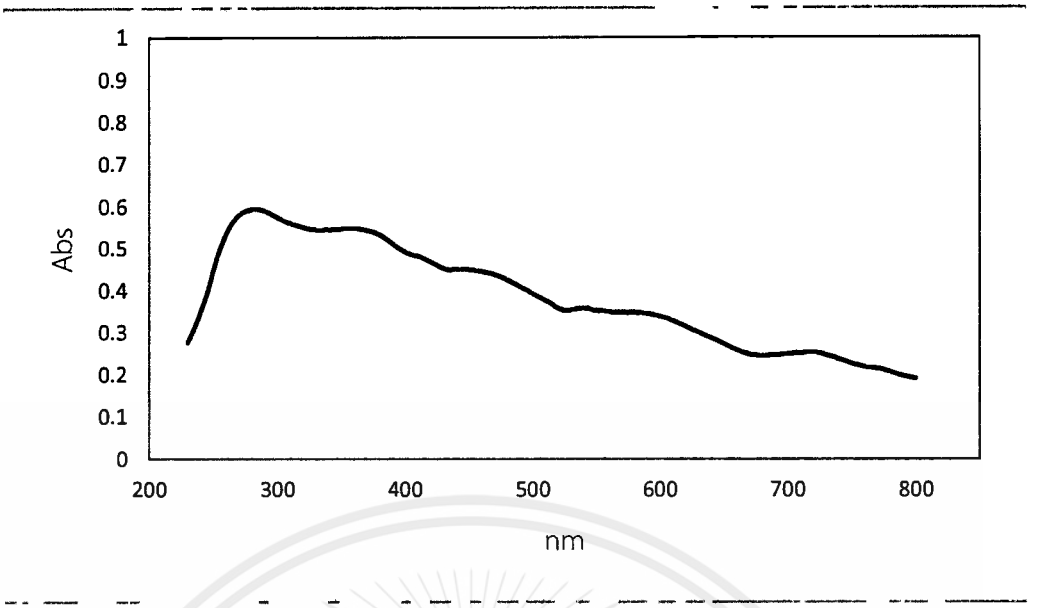

Figure C9 10%Cr/SiO_2 (IM) before run

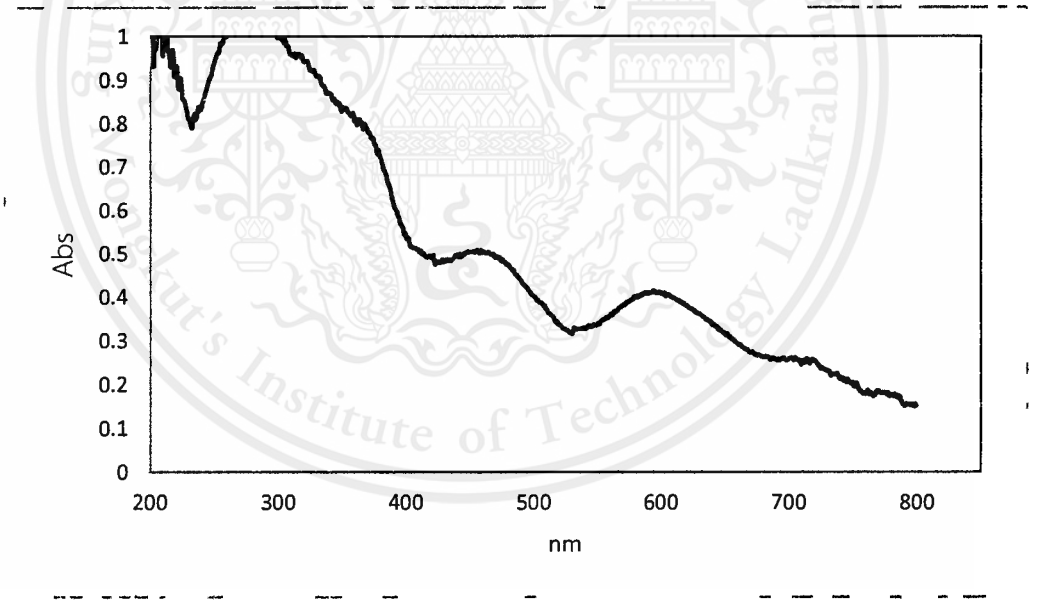

Figure C10 10%Cr/SiO_2 (IM) after run

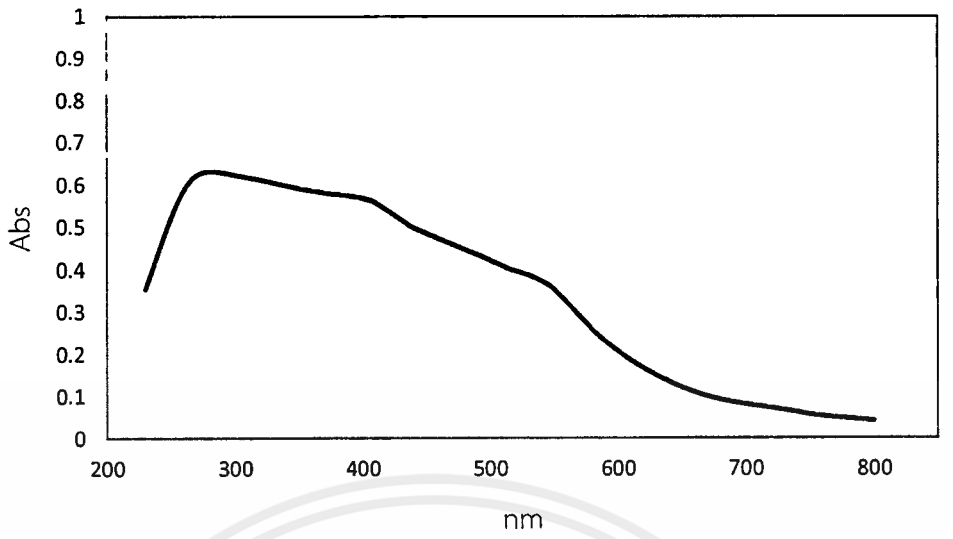

Figure C11 1%Fe/SiO_2 (IM) before run

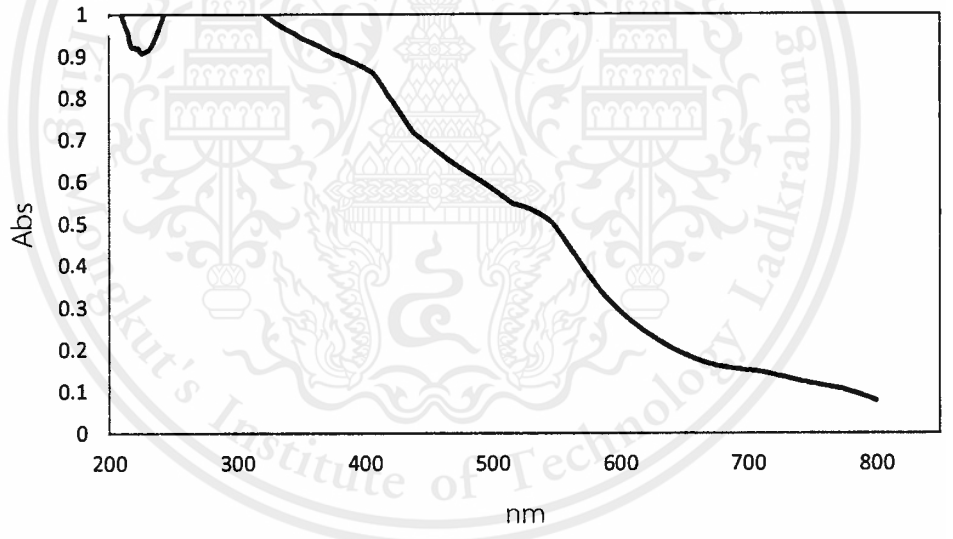

Figure C12 1%Fe/SiO_2 (IM) after run

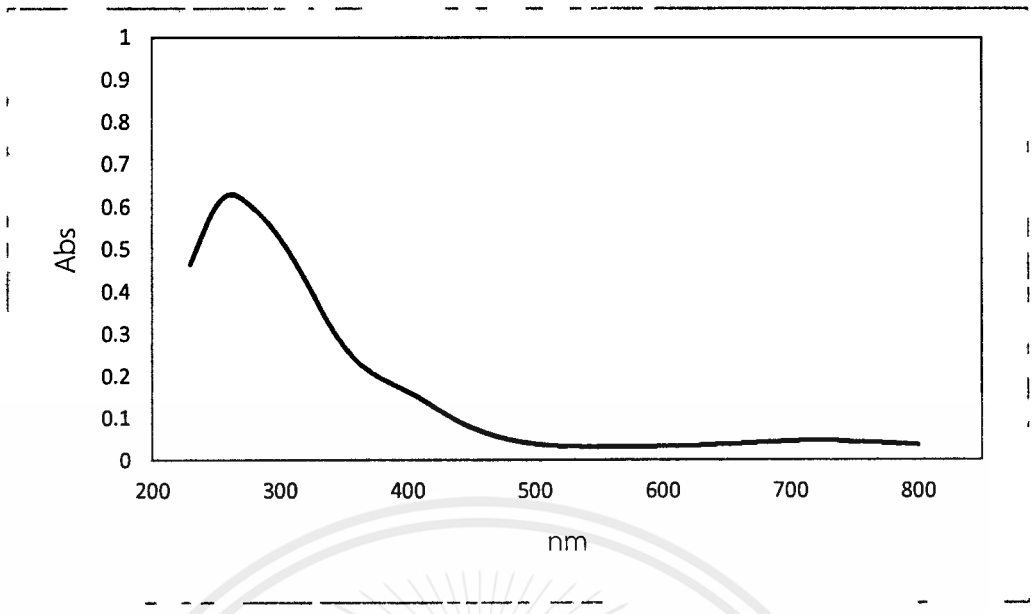

Figure C13 0.85%Mo/SiO_2 (IM) before run

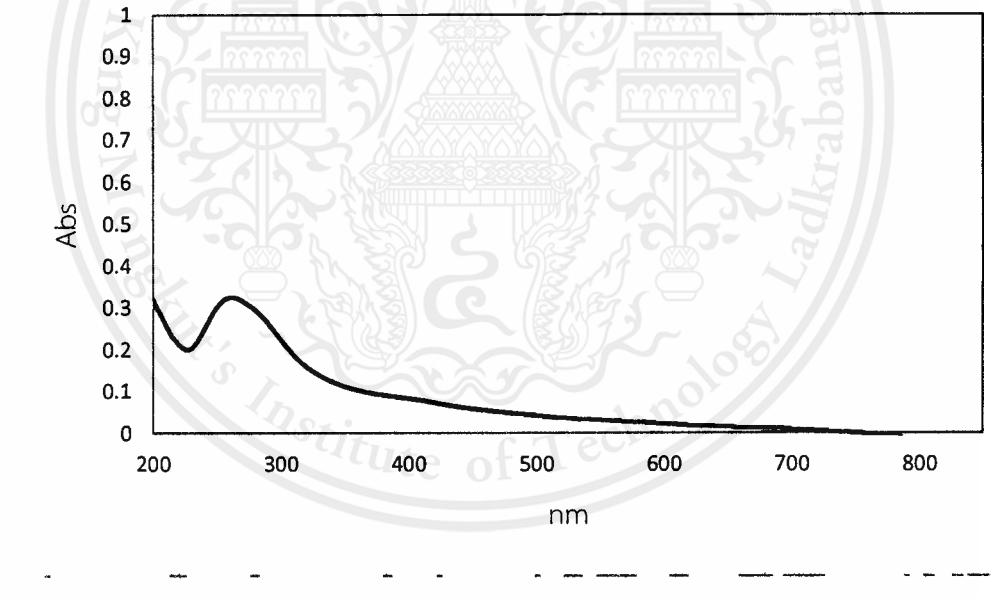

Figure C14 0.85%Mo/SiO_2 (IM) after run

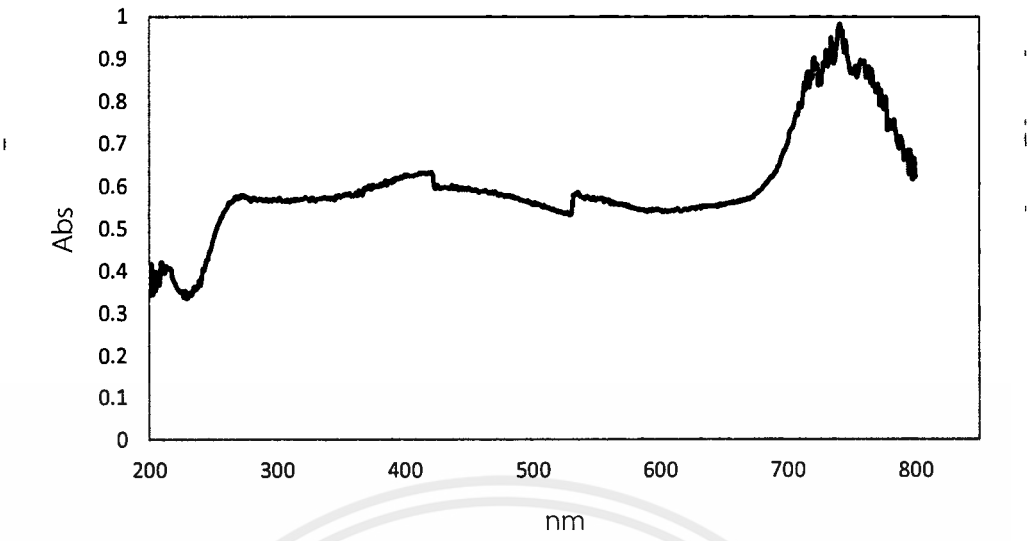

Figure C15 0.80%Co/SiO_2 (IM) before run

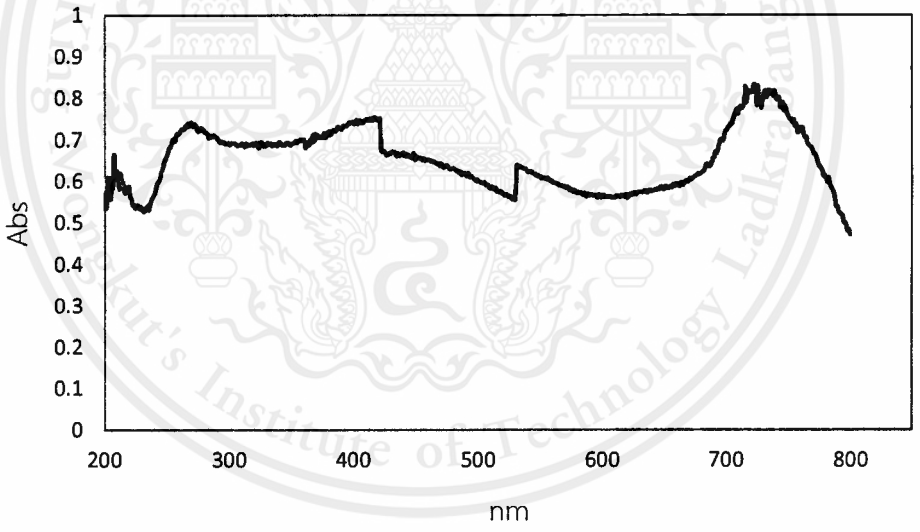

Figure C16 0.80%Co/SiO_2 (IM) after run

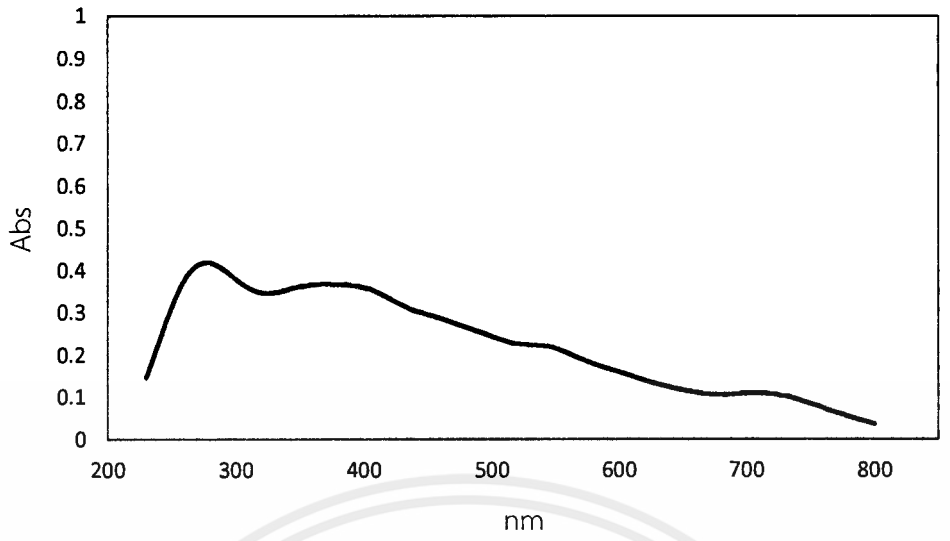

Figure C17 0.27%Cr/SiO_2 (SEA) before run

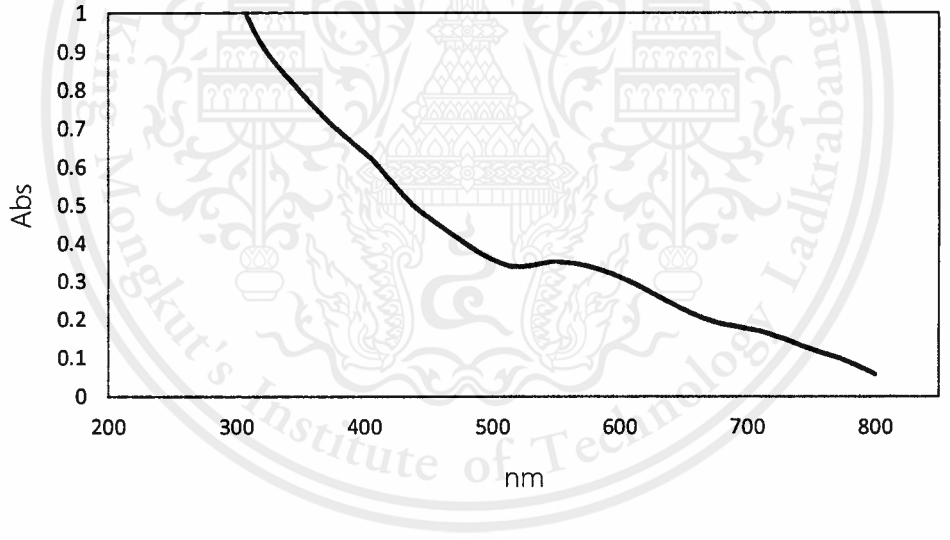

Figure C18 0.27%Cr/SiO_2 (SEA) after run

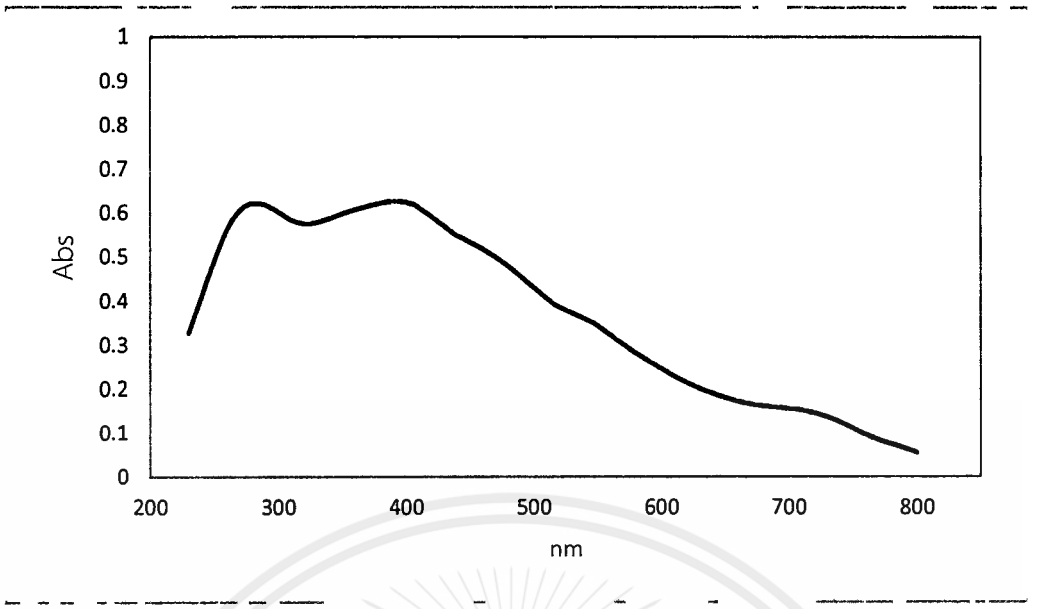

Figure C19 0.37%Cr/SiO_2 (SEA) before run

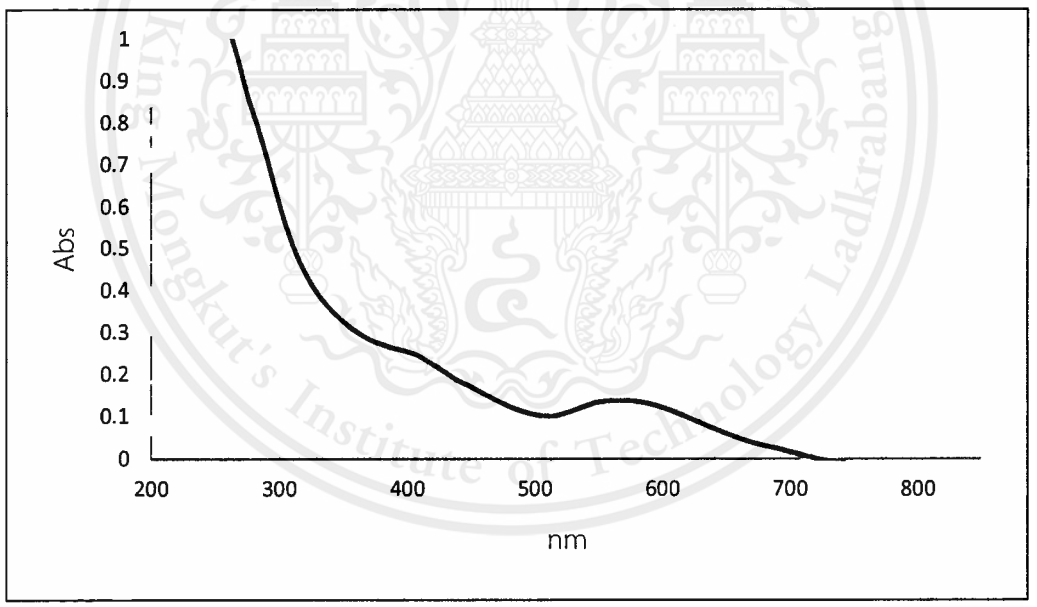

Figure C20 0.37%Cr/SiO_2 (SEA) after run

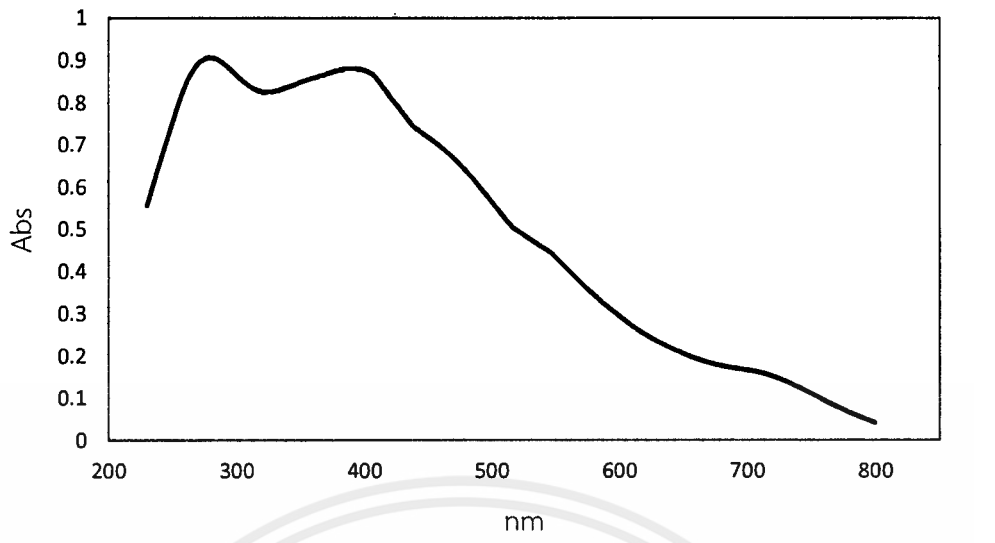

Figure C21 0.40%Cr/SiO_2 (SEA) before run

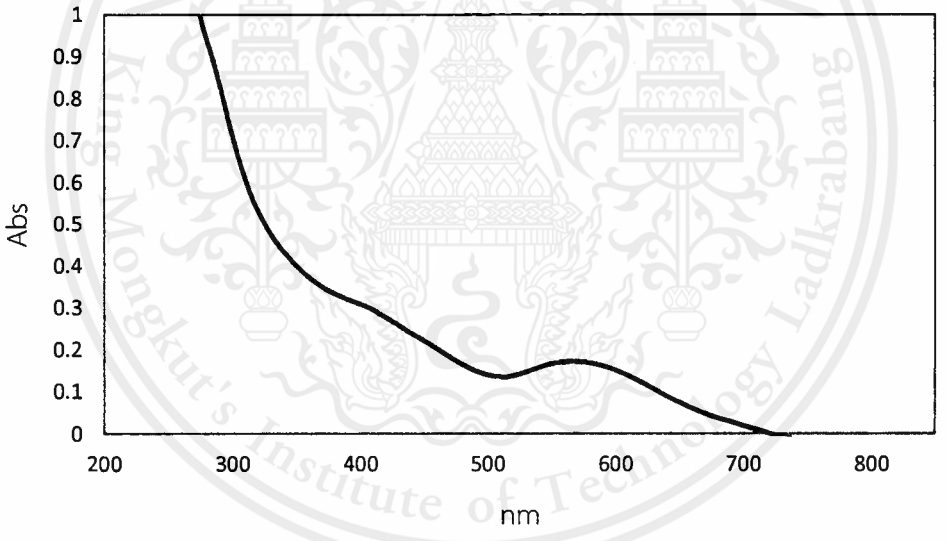

Figure C22 0.40%Cr/SiO_2 (SEA) after run

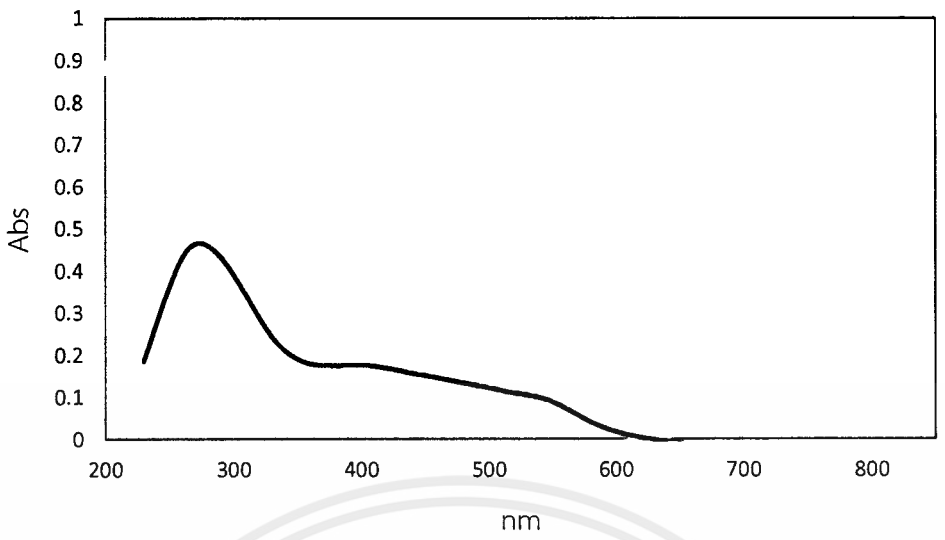

Figure C23 0.17%Fe/SiO_2 (SEA) before run

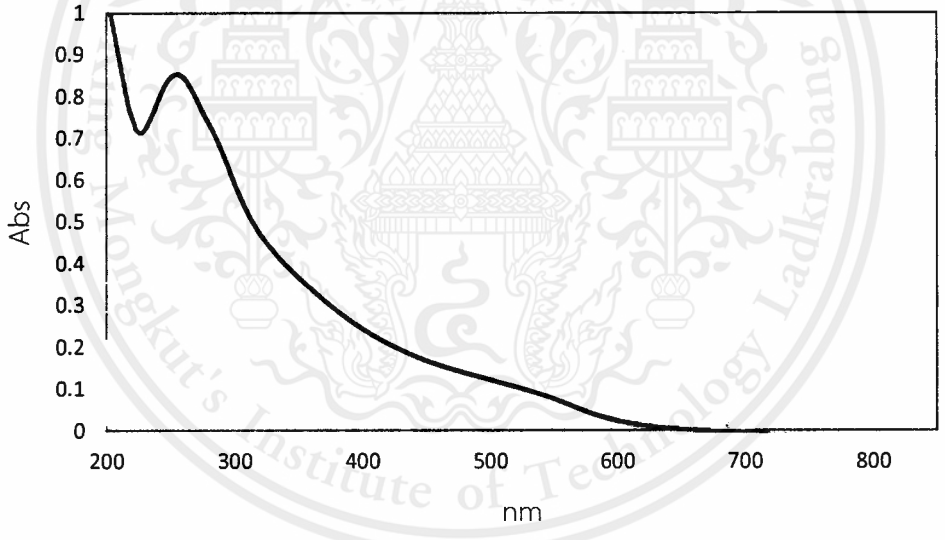

Figure C24 0.17%Fe/SiO_2 (SEA) after run

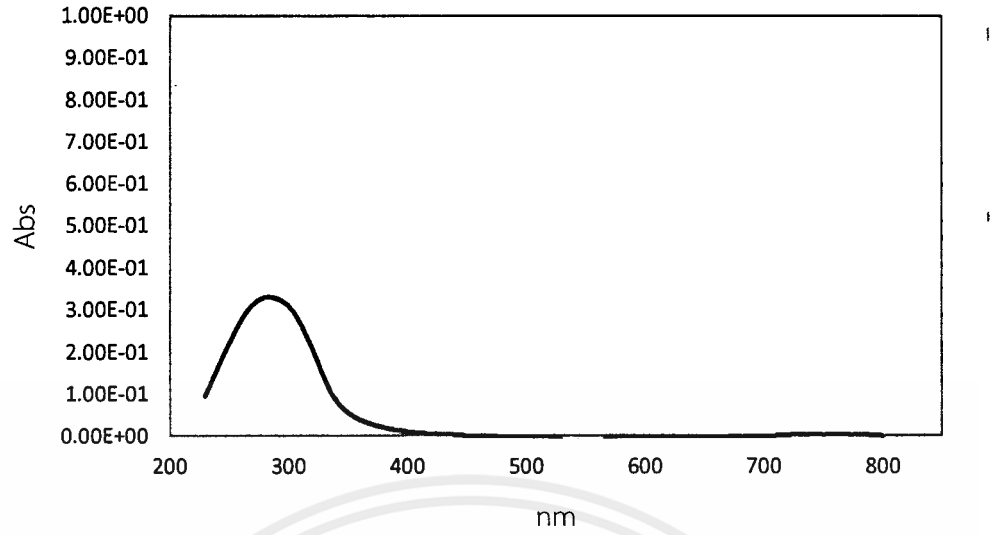

Figure C25 0.16%Mo/SiO_2 (SEA) before run

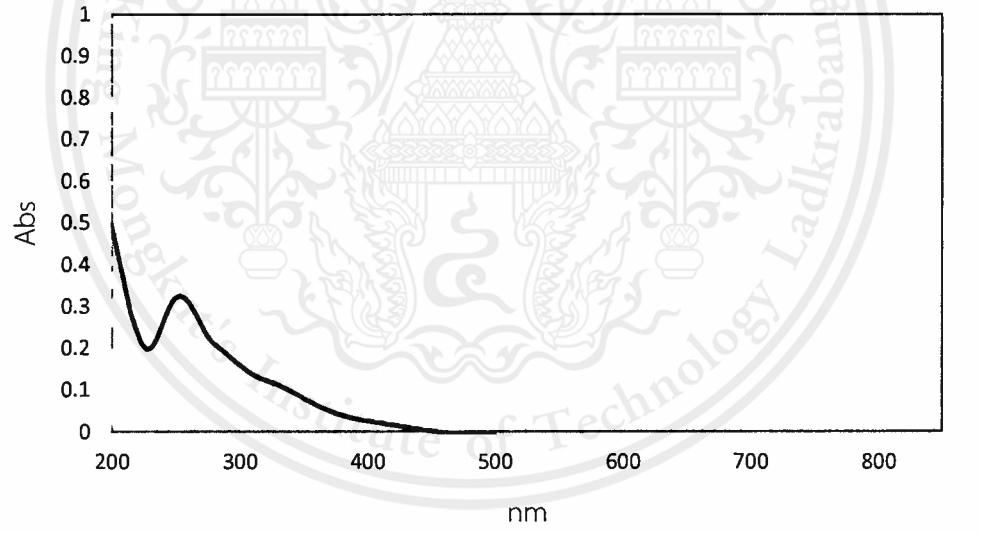

Figure C26 0.16%Mo/SiO_2 (SEA) after run

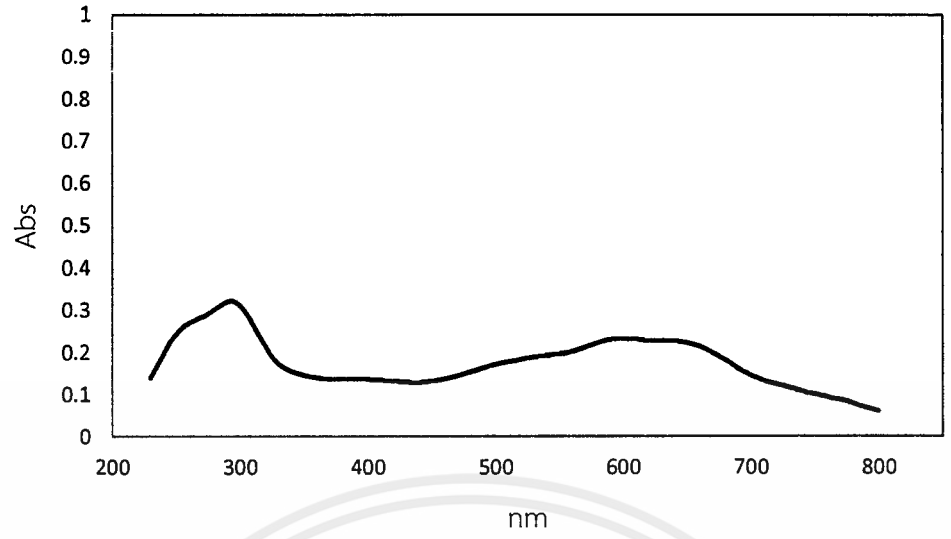

Figure C27 0.59%Co/SiO_2 (SEA) before run

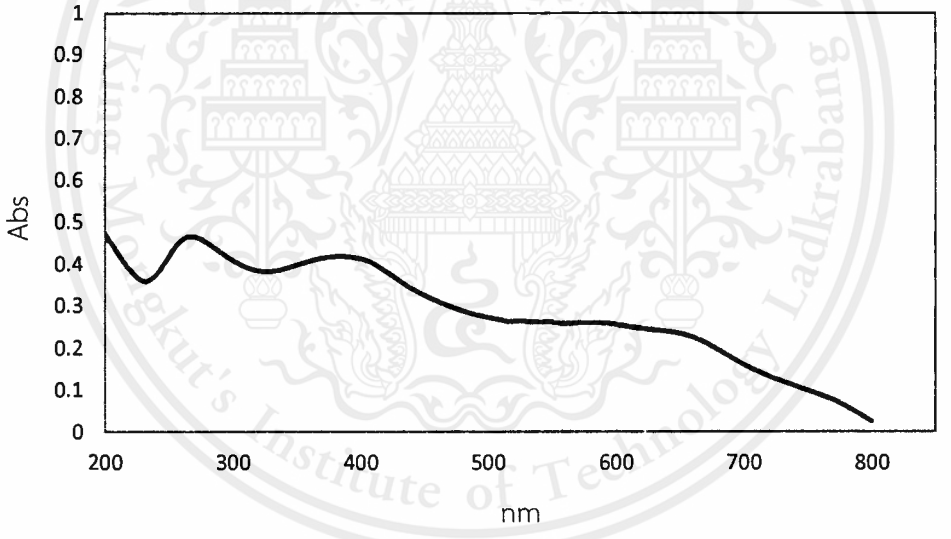

Figure C28 0.59%Co/SiO_2 (SEA) after run