ปฏิกิริยาออกซิเดชันด้วยอากาศในสภาวะที่มีตัวเร่งปฏิกิริยาของน้ำเสียจากระบบกำจัดกรด

นายวิทรรศ จึงวัฒนกิจ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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CATALYTIC WET AIR OXIDATION OF WASTEWATER FROM ACID REMOVAL SYSTEM

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
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Thesis Title	CATALYTIC WET AIR OXIDATION OF WASTEWATER FROM ACID REMOVAL SYSTEM
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วิทรรศ จึงวัฒนกิจ : ปฏิกิริยาออกซิเดชันด้วยอากาศในสภาวะที่มีตัวเร่งปฏิกิริยาของน้ำเสียจากระบบกำจัดกรด (CATALYTIC WET AIR OXIDATION OF WASTEWATER FROM ACID REMOVAL SYSTEM) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.บรรเจิด จงสมจิตร, หน้า.

วิทยานิพนธ์ฉบับนี้ได้ทำการศึกษาเกี่ยวกับการเร่งปฏิกิริยาในการบำบัดน้ำเสียที่ออกมาจากระบบกำจัดกรด โดยศึกษาถึงประสิทธิภาพในการเร่งปฏิกิริยาของกระบวนการออกซิเดชัน ซึ่งขั้นตอนแรกทำการศึกษาถึงแบบจำลองของอัตราการออกซิเดชันของน้ำเสียในกรณีที่ไม่มีตัวเร่งปฏิกิริยา โดยพบว่าอัตราการเกิดปฏิกิริยาขึ้นกับความเข้มข้นของโซเดียมซัลไฟด์ซึ่งเป็นสารปนเปื้อนหลักในน้ำเสีย และออกซิเจนยกกำลัง 2.10 และ 0.87 ตามลำดับ ส่วนค่าพลังงานก่อกัมมันต์ของปฏิกิริยาอยู่ที่ 16.24 กิโลจูลต่อโมล หลังจากนั้นนำตัวเร่งปฏิกิริยาที่ประกอบไปด้วยโลหะจำพวก คอปเปอร์, แมงกานีส, ลูธิเนียม หรือ วานาเดียม บนตัวรองรับ ซิลิกา, อะลูมินา, ซีเลีย หรือ ไททาเนีย เพื่อมาทดสอบประสิทธิภาพในการเร่งปฏิกิริยาของกระบวนการออกซิเดชันในน้ำเสีย โดยพบว่าตัวเร่งปฏิกิริยาคอปเปอร์บนไททาเนียมีประสิทธิภาพในการเร่งอัตราการเกิดปฏิกิริยาได้สูงสุดเมื่อเทียบกับตัวเร่งปฏิกิริยาชนิดอื่นที่ระดับราคาของโลหะที่เติมเท่ากัน ขั้นตอนต่อมาจึงทำการศึกษาถึงแบบจำลองของอัตราการออกซิเดชันของน้ำเสียในกรณีที่มีตัวเร่งปฏิกิริยา โดยพบว่าอัตราการเกิดปฏิกิริยาจะขึ้นกับความเข้มข้นของโซเดียมซัลไฟด์และออกซิเจนยกกำลัง 1.50 และ 1.13 ตามลำดับ ส่วนค่าพลังงานก่อกัมมันต์ของปฏิกิริยาในกรณีที่มีตัวเร่งปฏิกิริยามีค่าเท่ากับ 11.09 กิโลจูลต่อโมล ขั้นสุดท้ายเป็นการศึกษาความคุ้มทุนพบว่าการออกซิเดชันของน้ำเสียในกรณีที่ตัวเร่งปฏิกิริยาสามารถช่วยลดเงินลงทุนในการก่อสร้างจาก 1,117,400 บาท เหลือ 53,744 บาท แต่อย่างไรก็ตามควรมีการศึกษารายละเอียดเพิ่มเติมในส่วนของอายุการใช้งานของตัวเร่งปฏิกิริยาคอปเปอร์บนไททาเนียประกอบการพิจารณาต่อไป

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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WITAT JUENGWATANAKIJ: CATALYTIC WET AIR OXIDATION OF WASTEWATER FROM ACID REMOVAL SYSTEM. ADVISOR: ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., pp.

In this study, wet air oxidation of spent caustic waste water, generated from acid removal unit, was used for this study. The rate of reaction in oxidation was enhanced by catalyst. First, the kinetic model of non-catalytic wet air oxidation was investigated. From the reaction, the kinetic model was function of concentration of sodium sulfide, which is a main pollutant, at order of 2.10 and was function of oxygen at order of 0.87. The activation energy was 16.24 kJ/mol. Then, metals such as copper, manganese, ruthenium or vanadium on silica, alumina, ceria or titania were used as catalysts for determining the oxidation activity in the waste water. The weights of metal loading were based on the same cost of metals. From the reaction, copper metal on titania support was the most active catalyst among the others catalysts. After that, kinetic model of catalytic wet air oxidation was investigated. From the reaction, the kinetic model was function of concentration of sodium sulfide at order of 1.50 and was function of oxygen at order of 1.13. The activation energy in case of catalytic wet air oxidation was decreased to 11.09 kJ/mol. Finally, feasibility of the project was studied. Catalytic wet air oxidation can reduced the investment cost from 1,117,400 baht to 53,744 baht. However, more detail to determine life time of the copper on titania catalyst should be considered.

Department: Chemical Engineering Student's Signature ....
Field of Study: Chemical Engineering Advisor's Signature ....
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CHAPTER I

INTRODUCTION

Wastewater, which is generated during production, is a challenge issue for every plant. More ecological and cost effectiveness techniques are studied and selected for each type of wastewater. Spent caustic wastewater is one of the most difficult sources of wastewater in olefins plant. Normally, in economic scale of olefins plant generates spent caustic wastewater around 100-150 m^3/day. The wastewater is generated from acid gas removal unit, which carbon dioxide and hydrogen sulfide contained in process gas are removed by scrubbing with caustic soda solution. Therefore, the spent caustic wastewater is comprised of sodium sulfide salt and sodium bicarbonate salt from the reaction, remaining caustic soda and miscible oil, which is condensed when process gas is cooled down. With the compositions, the spent caustic wastewater is strong base and high chemical oxygen demand (COD), having pH at 14 and COD at 20,000 mg O_2/l. As a consequence of high concentration of pollutants, special technique is required for treating spent caustic wastewater before sending to biological treatment system.

Wet air oxidation unit (WAO) is typical equipment for olefins plant in order to handle with spent caustic wastewater. The technique is usually selected because concentration of pollutants in the wastewater is too low for incineration. A lot of energy is consumed for incinerating the large amount of spent caustic wastewater. Thus, the operating cost for the unit is not an economically feasible method. Conversely, biological treatment is the most widely used technique to treat wastewater, because being at near atmospheric pressure and ambient temperature. In addition, the operating cost and investment cost is lower when it is compared with other techniques. However, concentration of pollutants in term of COD loading per day in the spent caustic wastewater is too high for only biological treatment system for instance activated sludge unit. Because reaction rate of the technique is relatively slow compared with other techniques, hence massive size and large amount of land spacing for biological treatment system are required. Furthermore the spent caustic wastewater contains sodium sulfide, which is toxic to the bacteria at high concentration as in the spent caustic wastewater. Therefore, a primary treating unit is required to lessen the concentration. Typically, the sodium sulfide will be oxidized to sodium sulfate, which is less toxic form before sending to biological treatment system. Therefore, in economic point of view the wet air oxidation unit with biological treatment system is a choice of economically feasible method for spent caustic wastewater handling.

In normal practice, the main equipment for wet air oxidation unit in olefins plant is consisted of a reactor and a scrubber. The spent caustic wastewater and compressed air are introduced to bottom of the reactor. The temperature and pressure in reactor are controlled around 170-200^{o}C and 3-4 MPa, respectively. The wastewater and bubbled air have residence time in the reactor for 0.5 – 1 hour in oxidation. In the condition, the spent caustic wastewater can be achieved 80-90% of COD reduction. Organic and inorganic compounds in wastewater are oxidized to carbon dioxide, water and simpler biodegradable form. After that, treated spent caustic wastewater, generating gas and remaining gases leave from overhead of the reactor and charge to the scrubber. The effluents are degassed and cooled down in scrubber before sending to biological treatment system. The simplified block flow diagram of wet air oxidation unit is demonstrated as shown in Figure 1.1.

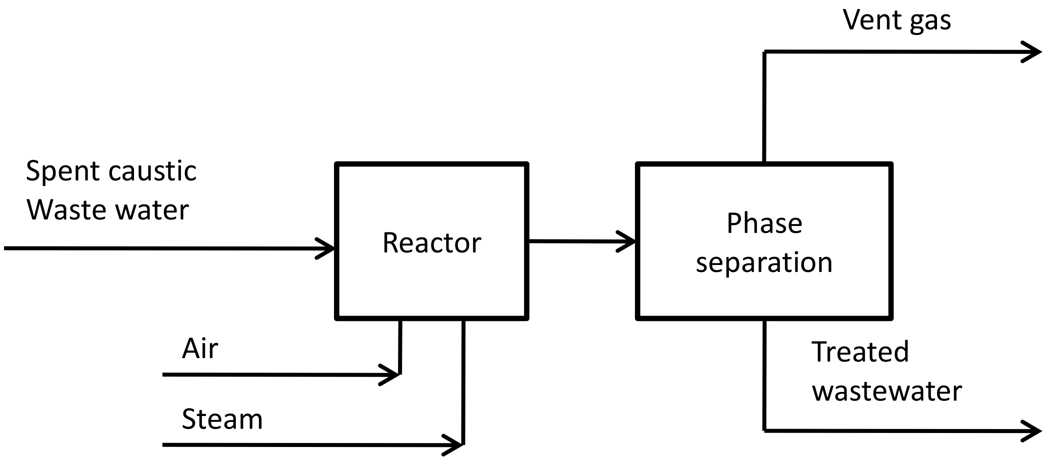


Figure 1.1 Simplified block flow diagram of wet air oxidation unit

There are many reasons that wet air oxidation unit is widely used. The technique is a clean technology compared with incineration due to no NOx, SOx, HCl, dioxine, furan and fly ash emission. The unit is a simple technique and low investment cost because it consists of only a few columns. Only high pressure steam, compressed air and pumping power are required as utilities. Nevertheless, low molecular weight oxygenated compound for instance acetic acid, propionic acid, methanol, ethanol, acetaldehyde and ammonia are by-products generated from side reaction. Deep oxidation of those refractory intermediates to relatively low COD level as discharged wastewater regulation required can be achieved, but more severe operating condition is required [1].

As refractory species were difficult to treat by the conventional wet air oxidation, supercritical water oxidation (SCWO) technique was developed to deal with the issue. From the advantage that water enters a special condition when temperature and pressure are above 374^{o}C and 221 bar. In this region, the density and viscosity of gas and liquid are closed together. Therefore, mass transfer between gas and liquid phase is improved. The reaction rate is controlled by intrinsic kinetic rate. Consequently, with the high temperature and high pressure condition, the COD removal can be achieved a 99.99 percent destruction of the organic contaminant[2]. However, size of supercritical water oxidation unit, which has enough capacity for high wastewater flow rate is not typically available. In addition, the investment and operating cost for supercritical water oxidation technique is not an economically feasible choice. Therefore, the wet air oxidation unit with biological treatment system is the typical solution for olefins plant to handle with spent caustic wastewater.

After wet air oxidation unit was commercialized, further studied for improvement of the efficiency for wet air oxidation was developed. Catalytic wet air oxidation has been studied and developed and the first patent was filed by DuPont since 1950 [1]. Base or noble metal was selected properly as catalyst for each pollutant in wastewater. Various benefits from catalytic wet air oxidation were observed. First, the energy consumption was decreased by lower the temperature and pressure of the oxidation reaction. Second, the pollutants and refractory compound in wastewater were oxidized more completely. Third, the reaction rate was higher than non-catalytic wet air oxidation by catalytic capability. Thus, size of reactor is reduced by lower the required residence time in reactor. Fourth, the material selection such as grade of metal and reactor wall thickness is lower by less severe operating condition. Consequently, the investment cost and operating cost are reduced by advantages of catalyst usage.

1.1 Objectives

As before-mentioned the catalytic wet air oxidation has benefits in various aspects. For instance, oxidizing is more complete, higher reaction rate, decreasing pressure and temperature in oxidation and reducing energy consumption. Therefore, not only size of reactor is reduced by lower the required residence time in reactor, but the material class such as grade of the metal and wall thickness of the reactor is also lower by less severe operating condition. Researcher hopes that this study will optimize investment cost and improve operating cost for commercial wet air oxidation unit.

1.2 Research scopes

The scopes of this research are to study the appropriate catalyst, which has capability to improve activity in oxidation of spent caustic wastewater. The scopes are summarized in the detail as follows:

- The catalyst of interested metal oxide such as ruthenium, vanadium, copper and manganese supported on silica, alumina, ceria and titania are determined based on the same cost of metal.
- Order of each reactant, rate constant, activation energy of both non-catalytic and catalytic wet air oxidation are determined in order to develop kinetic model of the reaction.
- Feasibility study is conducted to determine possibility for implementing the catalytic wet air oxidation.

1.3 Research methodology

The methodology of this research is shown in Figure 1.2.

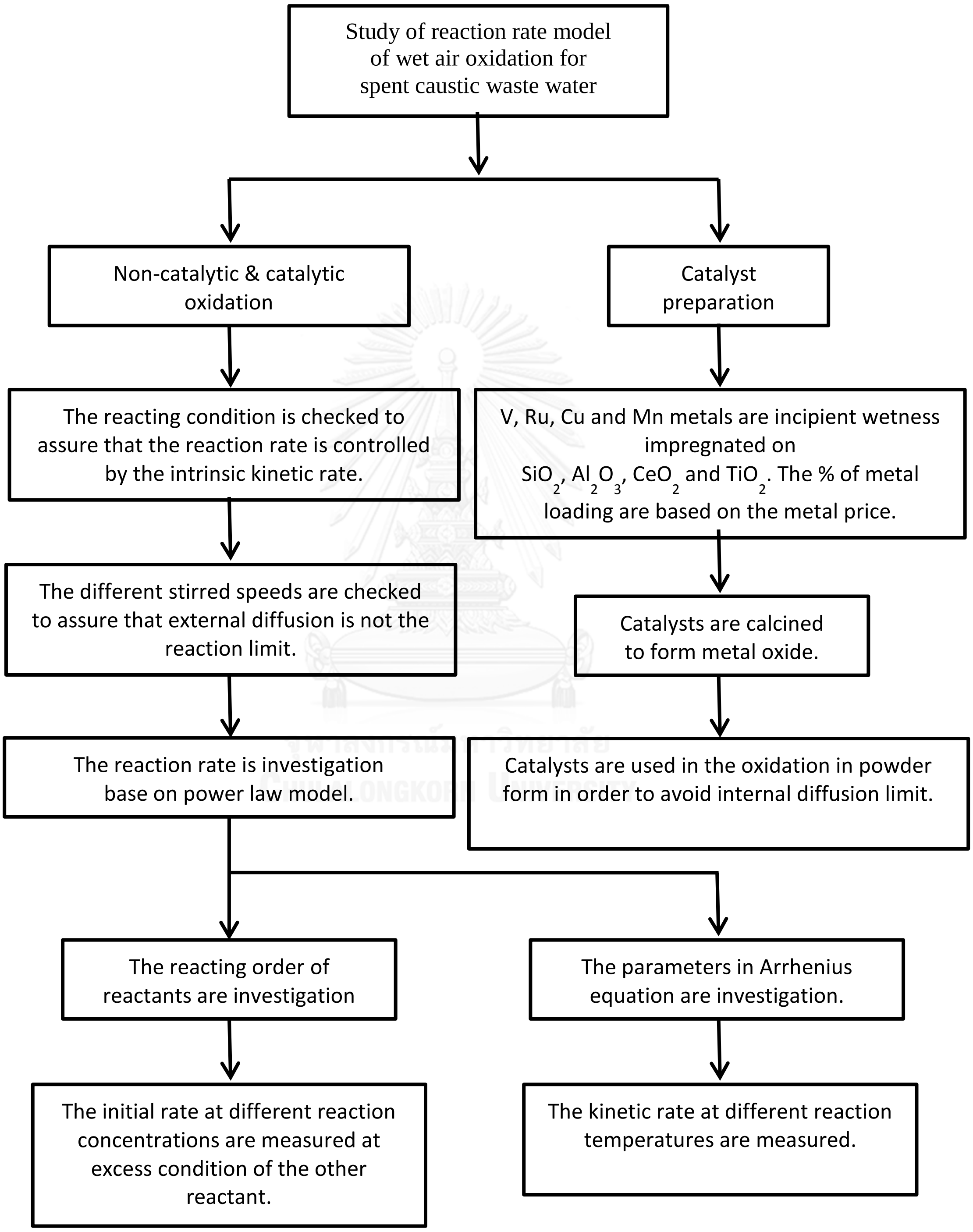


Figure 1.2 Flow diagram of research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Kinetic model

Rate law is an equation demonstrate characteristic of chemical reaction. The equation is function of the concentration of reactants and the reaction temperature. Normally rate law is demonstrated in form of power law which is the simplest form of rate law as shown in equation 2.1. The power law is correlated with the concentration of reactants by a constant value called specific reaction rate. The disappearing rate of the limiting reactant is often chosen to be demonstrated. The relative reaction rates for the other involved species are also obtained from ratio of the stoichiometric coefficient as shown in equation 2.2. The concentration of individual reactant is squared with a constant number. For instance a reaction has two reactants A and B. The reactants A and B are squared with a constant number Alpha (α) and Beta (ß) called order of reactant A and B respectively. The overall order of reaction is equal the summarized value of α and ß value.

$$-r_A = k_A C_A^{\alpha} C_B^{\beta} \tag{2.1}$$

$$aA + bB \rightarrow cC + dD$$

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{-r_C}{c} = \frac{-r_D}{d} \tag{2.2}$$

r_A : Rate of A disappearance
k_A : Specific reaction rate of A
C_A and C_B : Concentration of reactant A and B

In reaction involving single or multiple steps, the reaction follows elementary rate law when the order of reaction agrees with the stoichiometric coefficients. On the other hands, when the order of reaction disagrees with the stoichiometric coefficients, the reaction follows non-elementary rate law. Typical cases that the rate raw often follows non-elementary rate law are homogeneous reaction that the reaction is consisted of multiple steps, the intermediates are generated during the reaction, the reaction is driven by free radical mechanism and the reaction is reversible reaction. Heterogeneous reaction is another case that usually follows non-elementary rate law because the reaction steps involve reversible reaction such as adsorption, surface reaction and desorption step. Therefore, for more accuracy, the other type of model such as Langmuir-Hinshelwood model is usually developed for heterogeneous reaction. The model takes all adsorption, surface reaction and desorption step into account. The derived rate of reaction will be represented in term of reaction rate per unit weight of catalyst instead of reaction rate per volume.

Actually, specific reaction rate or reaction rate constant is not exactly constant. The value is varied with total pressure, ionic strength and choice of solvent. However it is most affected by temperature. Consequently, the Swedish chemistry Arrhenius proposed the correlation of specific reaction rate with temperature as shown in equation 2.3.

$$\mathrm{k_A} = \mathrm{A}e^{-\mathrm{E}/\mathrm{RT}} \qquad (2.3)$$

A : Pre-exponential factor or frequency factor
E : Activation energy, j/mol
R : Gas constant, 8.314 j/mol.K
T : Absolute temperature, K

For proceeding chemical reaction, atom and molecule need energy to distort or stretch their bonds. After that bonds of reactant atom and molecule are break up and formed with the others. The activation energy is a concept of energy barrier for describing chemical reacting criteria. Reactant will be converted to product when energy of reacting molecules is affordable to overcome the barrier as shown in Figure 2.1.

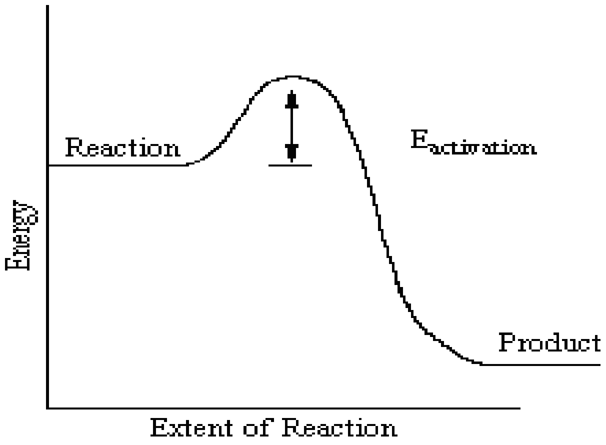


Figure 2.1 Level of energy in chemical reaction

2.2 Mechanism of wet air oxidation

The reaction in wet air oxidation is predominated by mechanism of free radical chain reaction. Chain reaction is a sequence of reactions where a reactive product or by-product causes additional reactions to take place. Reactive product is a way that energy is released or entropy is increased in order to reach a state of lower energy or higher entropy. The chemical reaction is occurred by high reactivity of active intermediate (R*). An active intermediate is a high energy molecule that formed by collision or interaction with other molecules. The activation occurs when translational kinetic energy is transferred into energy stored in internal degrees of freedom. The energy is transferred when the energy is absorbed into the chemical bonds. The result is bond of the absorbed molecule is ruptured, rearranged and decomposed [3].

The free radical chain reaction is comprised of three different steps. Initiation step, active intermediate is formed by collision or interaction with other molecules. The active intermediate is unpaired electron which is called free radicals. Normally free radicals are electron deficient and strongly electrophilic. Therefore free radicals have high potential to initiate chemical reaction. Propagation or chain transfer step is series of reactions. Reactant is interacted with the active intermediate to produce products or another active intermediate. The chain reaction is still continuously propagated by the regenerated active intermediate. Termination step, this step is found after series of reactions. The energy of free radical is continuously decreased after products formed. Finally, deactivation of the active intermediate is occurred and the chain reaction is terminated. The sequences of initiation, propagation and termination step are demonstrated as shown in equation 2.4 - 2.6.

Initiation : $A - B \rightarrow A^{*} + B^{*}$ (2.4)

Propagation : $A^{*} + C - D \rightarrow A - C + D^{*}$ (2.5)

$D^{*} + E - F \rightarrow D - E + F^{*}$

Termination : $F^{*} + D^{*} \rightarrow F - D$ (2.7)

2.3 Mechanism of heterogeneous catalyst in wet air oxidation

Catalytic wet air oxidation with heterogeneous catalyst is three phases, gas-liquid-solid reaction. The reaction is more complicated than homogeneous which is related only two phases, liquid-solid reaction. The mechanism begins with a group of external and internal mass transfer which is physical stage. In this step, Oxygen molecules from gas phase are transferred to liquid phase. The mass transfer is dominated by concentration difference as driving force. For oxygen which is only slightly soluble in water, well-designed condition for instance pressure, temperature and also enough gas-liquid interfacial area are significant factors to promote the mass transfer.

Second, the oxygen and pollutant molecules are diffused from bulk liquid to external surface of solid catalyst. In this step, the mass transfer is controlled by liquid resistance film as shown in equation 2.7. Superficial velocity is an important adjustable parameter for designer to minimize the liquid film resistance and boost the mass transfer because liquid film thickness is functioned with power two of superficial velocity.

$$W_{Ar} = k_{c}(C_{Ab} - C_{As}) \quad (2.7)$$

$$k_c = \frac{D_{AB}}{\delta}$$

W_{Ar} : Average molar flux
K_c : Mass transfer coefficient
C_{Ab} , C_{As} : Concentration of A in bulk fluid and at catalyst surface
D_{AB} : Diffusivity
δ : Film thickness

Third, the mass transfer is sequentially passed to internal mass transfer. The oxygen and pollutant molecules are diffused from the pore mouth into the catalyst pore. This step, suitable pore diameter selection of solid catalyst must be studied for individual type of pollutant molecule. Generally, pore diameter is categorized to three types by sizing of pore. Macropore has average size diameter > 50 nm, mesopore has average size diameter 3- 50 nm and micropore has average size diameter < 3 nm. Rate of reaction will be decreased, if pollutant molecule is larger than pore diameter of catalyst. Therefore the reaction will be limited only at the surface of catalyst.

After the oxygen and pollutant molecule are transferred to pore of catalyst. Next mechanisms are adsorption, surface reaction and desorption which are related with chemical stage. Forth step is the step that the oxygen and pollutant molecule are adsorbed to active site of catalyst. Adsorption is reversible reaction and slightly exothermic which is divided by type of interaction to physical and chemical adsorption. Physical adsorption is an interaction by van der waal force. Nevertheless the interaction is too weak to initiate further reaction. Thus oxidation reaction is not influenced with physical adsorption. The adsorption leading to reaction must be a stronger interaction than just physical adsorption. Therefore the reaction is mainly influenced by chemical adsorption. The adsorption has stronger molecule attraction because the attraction is boned by valence force. The bonding between substrate and active site of catalyst is further categorized by atomic interacting mechanism to dissociative and non-dissociated adsorption as shown in equation 2.8 – 2.9.

Dissociative adsorption : $O_2 + S \leftrightarrow O_2.S$ (2.8)

Non-dissociated adsorption : $O_2 + 2S \leftrightarrow 2\,O.S$ (2.9)

Fifth step, after the oxygen and pollutant molecule are adsorbed on active site of catalyst. The oxygen and pollutant molecule are catalyzed their chemical reactions. The low energy surface of electronic state on catalyst surface contributes to donate or accept electrons leading to making or breaking bonds process. Carbon monoxide and water are generated as main products for total oxidation of hydrocarbon substance. Low molecular hydrocarbons such as acetic acid are also generated from partial oxidation as by-products. Sixth, seventh and eighth step, are reversed step of adsorption, pore diffusion and bulk diffusion. The products are desorbed from surface of the catalyst, diffused though pore of the catalyst and finally transferred to bulk fluid.

2.4 Identification of kinetic model

Collection and analysis of experimental data are important steps for determining of reaction rate. Thoroughly understanding the method to set up reactor, collect data and analyze result are crucial points because the wrong methodology will lead to wrong result of reaction rate. Typically, method to determine rate of reaction is divided to two types of reactor: batch reactor and differential reactor. In batch reactor, data such as concentration of substrates, pressure and volume are measured in transient condition at different times during reaction. Whereas differential reactor, data such as feed flow rate, concentration of substrates are measured in steady state condition. In both cases, the reaction data is collected at various concentrations of reactants, operating pressure and operating temperature conditions in order to be raw data for analyzing the reaction model. In general, methodology which is widely used in analyzing reaction rate is comprised of four methods: differential method, integral method, non-linear regression method and initial method.

2.4.1 Differential method

The differential method in batch reactor is one of the simplest techniques to determine rate data of homogenous reactor. There are several assumptions for using the method. The reaction must be irreversible reaction. The reaction must be carried out at isothermal condition and also in constant volume condition. Differential method is most applicable with reaction with one reactant. However the method still can be applied for reaction with two reactants by excess one reactant. Concentration of the excess reactant is assumed a constant value and combined in specific reaction rate value as shown in equation 2.10. From the condition, the concentration of the limiting reactant is measured at different times. The reaction order of limiting reactant can be calculated from slope of the natural logarithm plot between reaction rate and the concentration as shown in equation 2.11. Reaction order of another reactant also can be determined in the same step by excess the concentration of the first reactant instead. Finally, the remaining unknown parameter, specific reaction rate, can be determined. A condition of reacting concentration and the corresponding rate of reaction are chosen. After that the specific reaction rate can be calculated from substitute the values to the rate raw.

$$-r_A = k_A C_A^{\alpha} C_B^{\beta}$$

$$-r_A = k_A C_{B0}^{\beta}\, C_A^{\alpha}$$

$$-r_A = k' C_A^{\alpha} \tag{2.10}$$

Mole balance

$$\begin{bmatrix}\text{Flow}\\ \text{rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Flow}\\ \text{rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\end{bmatrix}$$

$$0 - 0 - r_A V = \frac{dN_A}{dt}$$

Constant volume

$$r_A = -\frac{dC_A}{dt}$$

Substitute with equation (2.10)

$$-\frac{\mathrm{dC_A}}{\mathrm{dt}} = \mathrm{k'C_A^{\alpha}}$$

Take natural logarithm

$$ln\left[\frac{-(dC_A)}{dt}\right] = \ln k' + \alpha \ln C_A \qquad (2.11)$$

2.4.2 Integral method

Integral method holds the same assumption with differential method. Only the form of equation is converted from differential to integrated form. The steps are started with guessing the reaction order. The assumed reaction order is collect, if the plot of concentration term and reaction time is a linear graph. From the difficulty in guessing the reaction order, the method is most often used when the reaction order is known. The method is applicable to find the specific reaction rate. The value can be directly determined from slope of correlation graph between concentration term and reaction time as shown in equation 2.12.

From equation (2.10) assumed first order reaction

$$-\frac{\mathrm{dC_A}}{\mathrm{dt}} = \mathrm{k'C_A}$$

Integrate the equation with the limit $C_A = C_{A0}$ at t = 0 gives

$$\ln\frac{\mathrm{C_{A0}}}{\mathrm{C_A}} = \mathrm{kt} \qquad (2.12)$$

2.4.3 Non-linear regression method

Non-linear regression method is a technique that applying nonlinear least-squares analysis in finding the reaction order and specific reaction rate. All reaction rate data from various reacting condition are compared with reaction rate from calculation. The correct reaction order and specific reaction rate value are the values that minimize the summarized squares of the differences between the measured values and the calculated values as shown in equation 2.13. This method is not only used to determine reaction order and specific reaction rate, but Non-linear regression method is also widely used to discriminate different rate law model, such as Langmuir-Hinshelwood model for heterogeneous reaction.

$$\sigma^2 = \sum_{i=1}^{N} \frac{(r_{im}-r_{ic})^2}{N-K} \tag{2.13}$$

N : Number of runs
K : Number of parameters to be determined
r_{im} : Measured reaction rate of run i
r_{ic} : Calculated reaction rate of run i

2.4.4 Initial method

Differential method is the simplest method to analyze rate data because only one experiment is required in analysis. Nevertheless, the method takes only forward reaction into account. Therefore other suitable methodology is required for significant reverse reaction. A solution such as Initial rate method is proposed. Series of experiments are carried out at different initial concentrations of substance. The concentrations of substance data are differentiated and extrapolated to time zero for determining the initial rate of reaction as shown in equation 2.14. After that reaction order is obtained from slope of natural logarithm plot between initial rate of reaction and initial concentrations of substance as shown in equation 2.15.

$$-r_{A0} = k' C_{A0}^{\alpha} \tag{2.14}$$

r_{A0} : Rate of A appearance at time zero
C_{A0} : Initial concentration of reactant

Take natural logarithm

$$\ln[-r_{A0}] = \ln k' + \alpha \ln C_{A0} \tag{2.15}$$

As above-mentioned methods, experimental set up is applicable with batch reactor type. Differential reactor is another technique to determine rate data. The experiment is set up in plug flow reactor. Catalyst is packed as static bed in reacting column. Then reactants as various conditions is fed through the reactor for the measuring the conversion. The differential reactor also has criterions of assumption in the reaction. First, the conversion of reactants and the temperature gradient is should be small. The differential reactor should have no gradient along the reactor because the CSTR equation is used to be the design equation. The steady-state mole balance for differential reactor is demonstrated as shown in equation 2.16. After that reaction order is obtained from slope of natural logarithm plot between initial rate of reaction and initial concentrations of substance as shown in equation 2.17.

Mole balance

$$\begin{bmatrix}\text{Flow}\\ \text{rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Flow}\\ \text{rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\end{bmatrix}$$

$$F_{A0} - F_{Ae} - r'_A \Delta W = 0$$

$$r'_A = \frac{F_{A0} - F_{Ae}}{\Delta W}$$

$$r'_A = \frac{v_0 C_{A0} - v C_{Ae}}{\Delta W}$$

Constant volume

$$r'_A = \frac{v_0 (C_{A0} - C_{Ae})}{\Delta W} = \frac{v_0 C_P}{\Delta W} \qquad (2.16)$$

r'_A : rate of A disappearance per unit catalyst weight

ΔW : weight of catalyst

C_{A0} : initial concentration of reactant

C_{Ae} : equilibrium concentration of reactant

C_P : concentration of product

Substitute equation (2.16) to (2.10)

$$\frac{v_0 C_P}{\Delta W} = k' C_{A0}^{\alpha}$$

Take natural logarithm

$$\ln\left[\frac{v_0 C_P}{\Delta W}\right] = \ln k' + \alpha \ln C_{A0} \tag{2.17}$$

2.5 General information of wet air oxidation reaction

Typically, wet air oxidation is an oxidation a liquid aqueous reaction in high temperature 100-374 C and elevated pressure 5-18 MPa condition. The unit is called wet air oxidation since in most cases air is used as the oxidation agent. Organic carbon source in wastewater is converted to carbon dioxide and water in the main reaction. However carboxylic acids such as acetic acid and propionic acid are always generated in side reaction. For other sources such as organic nitrogen, sulfur, phosphorus and chlorine compound are converted to ammonia, sulfates, phosphates and hydrochloric acid respectively as material balance for general oxidation reaction as shown in equation 2.18. The oxidation is moderately fast reaction. Typically pollutants at COD load 10-80 kg O_2/m^3 can be converted by wet air oxidation in 1-3 h. The oxidation reactions are mildly exothermic. Typically, energy self-sufficiency is obtained when COD load is exceeded 12-15 kg O_2/m^3 [4].

$$\begin{aligned} &C_mH_nO_kCl_wN_xS_yP_z + \big(m + 0.25(n-3x) - 0.5k + 2(y+z)\big)O_2 \\ &\rightarrow mCO_2 + 0.5(n-3x)H_2O + xNH_3 + wCl^- + ySO_4^{2-} + zPO_4^{3-} + \Delta H_R \end{aligned} \tag{2.18}$$

Wet air oxidation reaction is also consequence of chain reaction. The first step initiation, active radical R^* is generated from reaction between pollutants and oxygen molecule as shown in equation 2.19. Hydrogen atom is abstracted from the weakest C-H bond of organic pollutants by oxygen molecule. The generated active radical R^* is very active and potentially further reacts with other molecules. The reaction series are propagated by the active radical R^* during a coupling with oxygen molecule, or from the reaction with the radical HO_2^*, or decomposing of hydrogen peroxide, or further react from carboxylic radical as shown in equation 2.20-2.23 respectively. In the series of reaction propagation step is usually rapid with the reaction constant around 107-109 $dm^3.mol^{-1}s^{-1}$. Thus, the rate limiting step is often controlled by the initiation step with the activation energy around 100-200 kJ/mol [4].

Initiation step : $\mathrm{RH + O_2 \rightarrow R^* + HO_2^*}$ (2.19)
Propagation step : $\mathrm{O - O + R^* \rightarrow ROO^*}$ (2.20)
$\mathrm{RH + HO_2^* \rightarrow R^* + H_2O_2}$ (2.21)
$\mathrm{H_2O_2 + M \rightarrow 2HO^* + M}$ (2.22)
$\mathrm{ROO^* + RH \rightarrow R^* + ROOH}$ (2.23)

2.6 General information of catalytic wet air oxidation reaction

In order to increase rate of oxidation reaction and achieve higher conversion, increasing of operating temperature in the reactor is an effective method. Since the rate constant is much impacted by the operating temperature as Arrhenius equation. Nevertheless, increasing temperature and pressure of reaction not only increase operating cost of wet air oxidation but also the material grade of reactor must be upgraded to special class because of operated at higher corrosive condition. Therefore, varieties of catalyst have been studied from researchers for catalytic wet air oxidation. Oxide of base metal and precious metal were found that they were very effective method as catalyst to promote the rate of oxidation reaction.

Metal-catalyzed oxidations can be divided to 2 groups, homogeneous catalyst and heterogeneous catalyst, by phases of catalyst and substrate. Homogeneous catalyst is typically soluble transition metals salts such as Co, Mn, Fe or Cu. Those metals involve in catalytic cycle through the reduction-oxidation of free radicals. The oxidation rate is stimulated because the free radical which is rate limiting step can be generated more rapidly.

Since 1980, several commercial homogeneous catalyzed processes were launched. Ciba-Geigy was developed soluble copper ion. The ion has capability to treat chemical and pharmaceutical wastes. The wastes were oxidized at relatively elevated temperature above 300°C. Thus, LOPROX was introduced Soluble Fe ion catalyst with an advantage of mild condition reaction. The ion has activity to treat various organic substances at 150°C but the resident time is required for 2 hours. Therefore WPO process was developed. The soluble Fe ion was combined with hydrogen peroxide for increasing the activity [5].

However homogeneous catalyst is not widely used due to difficulty in metal recovery process. The complexity of equipment and operating cost are considerable disadvantage of the technique. Precipitation by pH adjustment or chemical addition before unit of filtration are common steps of separation to recycle the metal for reused. Therefore heterogeneous catalyst is more interesting choice due to no added cost for separation.

Heterogeneous catalyst for wet air oxidation is more widely studied. The performance of base metals or noble metals as oxidation catalyst has been investigated on variety sources of wastewaters. The results showed the catalyst was selective for each source of wastewater. Oxidation of sodium sulfide is emphasized in this research because the COD value in spent caustic wastewater is most dominated with the demand for treating sodium sulfide. However few numbers of researches were published for the specie.

In 1999, Jagushte and Mahajani [6] studied the oxidation of thiosulfate, which is intermediate substance and is often the rate limiting step in sodium sulfide oxidation. Power law models of both non-catalytic and catalytic wet air oxidation were investigated in semi batch reactor. The result showed reaction rate of thiosulfate was depended on concentration of thiosulfate and oxygen partial pressure with order 1. The specific reaction rate was $8.53*10^{22}$ at temperature 120°C and activation energy was 183.31 $kJ.mol^{-1}$. For catalytic wet air oxidation, precipitated copper in hydroxide form was used in the experiment. The result showed reaction rate of thiosulfate was depended on concentration of thiosulfate and oxygen partial pressure with order 1 and 0.5 respectively. The specific reaction rate was $9.01*10^{12}$ at temperature 80°C and activation energy was 110.71 $kJ.mol^{-1}$

In 2007, Maugans and Kumfer [7] studied the oxidation industrial spent caustic wastewater from ethylene crackers and refineries. The pre-oxidized spent caustic was further reacted at temperature 280°C for 60 minutes in a batch reactor with Mn/Ce and Pt/TiO_2 catalyst. The result showed Mn/Ce catalyst performed higher activity in COD removal than Pt/TiO_2 catalyst. Besides, the conversion was enhanced when pH in the spent caustic wastewater was neutralized before oxidation.

In 2011 [8], Montante et al was compared the performance of catalytic oxidation for treating spent caustic waste generated from petroleum refining process. Copper and vanadium metal were impregnated on silica and clinoplolite support. Supported catalysts were performed oxidation at temperature 70°C for 50 minutes. The activity showed copper on silica was the most active catalyst. The researcher found that the catalytic activity was related with the number of liquid phase acid sites.

In 2013, Chen and Cheng [9] studied non-catalytic and catalytic wet air oxidation of refinery spent caustics wastewater. The COD degradation conversion was achieved 75% at temperature 200˚C and partial pressure 2MPa for 3 hours reaction without catalyst. For catalytic wet air oxidation, the composite catalyst MnO2-CeO2/γ on Al_2O_3 support had an effective catalytic activity. The COD degradation conversion was achieved 95% at the same condition. The kinetic model of the reaction rate was investigated. The reaction of pseudo-first order equations could be successfully applied for non-catalytic and catalytic wet air oxidation system and the activation energy was reduced from 45.5 to 27.2 kJ/mol.

For commercialized catalyst, several heterogeneous catalysts for wet air oxidation were launched since 1950. The first patent was filled by Dupont. Mn-Zr-Cr oxide was applied for treating organic nature industrial waste at reacting condition temperature 120-200°C. In 1980, Osaka process was developed precious metal supported catalyst TiO_2 and TiO_2-ZrO_2. The catalyst was used to treat acetic acid and ammonia in wastewater at reacting condition temperature 250°C. In NS-LC process bimetal Pt-Pd on TiO_2-ZrO_2 was introduced to be a choice for phenol oxidation.

Almost 99% of phenol was converted at temperature 220°C, pressure 4 MPa, space velocity 2 h^{-1} condition [5].

2.7 Reaction pathway of wet air oxidation

Simplified reaction pathway for general oxidation reaction is proposed as shown in Figure 2.2. The pathway of main reaction, organic compound molecule in wastewater is reacted with oxygen molecule. The molecules are converted to carbon dioxide and water with reaction rate constant k_1. Simultaneously, low organic compound molecule is generated from partial oxidation reaction with reaction rate constant k_2. Acetic acid is usually an intermediate product of the side reaction which is usually the rate limiting intermediate with reaction rate constant k_3.

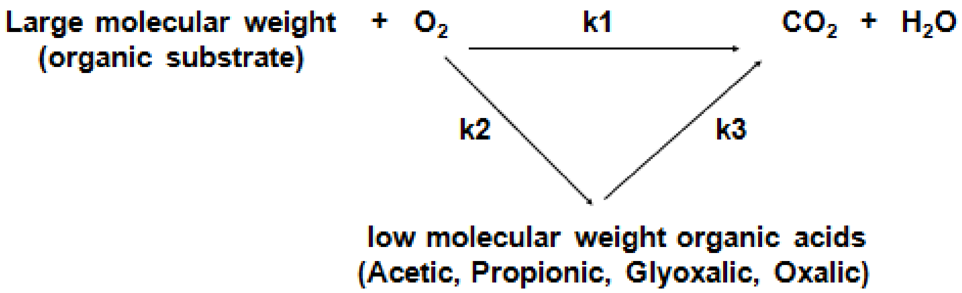


Figure 2.2 Simplified reaction pathways for general wet air oxidation

2.8 Kinetic model for wet air oxidation

As the real industrial wastewater is compound of varieties of organic and inorganic species. The concept of lumped kinetic model is a method to simplify the oxidation kinetic model. Consequently, represented parameters A and B were proposed. A is the pollutants molecule and B is the reacted intermediate molecule as shown in Figure 2.3 [10].

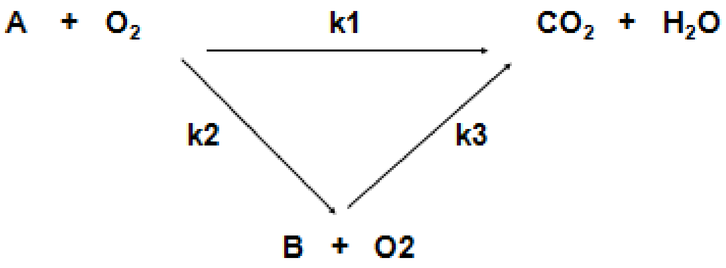


Figure 2.3 Reaction pathways of lumped kinetic model

The rate law of lumped kinetic model can be described as below equations. The concentration of pollutants (C_A) is decreased over reaction time as shown in equation 2.24. Conversely, the concentration of refractory compounds (C_B) is increased over reaction time as shown in equation 2.25. Effect of oxygen partial pressure is included in rate constant k_1, k_2 and k_3 which is followed Arrhenius equation due to excess oxygen assumption as shown in equation 2.26 – 2.28. Therefore, the conversion of pollutants is expressed as shown in equation 2.29 [4].

$$-\frac{dC_A}{dt} = k_1C_A + k_2C_A \tag{2.24}$$

$$-\frac{dC_B}{dt} = k_2C_A - k_3C_B \tag{2.25}$$

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right)[O_2]^{n_1} \tag{2.26}$$

$$k_2 = k_{0,2}\exp\left(\frac{-E_2}{RT}\right)[O_2]^{n_2} \tag{2.27}$$

$$k_3 = k_{0,3}\exp\left(\frac{-E_3}{RT}\right)[O_2]^{n_3} \tag{2.28}$$

$$[C_A + C_B]/[C_A + C_B]_0 = \frac{k_2}{[k_1+k_2-k_3]}\exp(-k_3t) + \frac{[k_1-k_3]}{[k_1+k_2-k_3]}\exp(-[k_1 + k_2]t) \tag{2.29}$$

However, the power law model was the most frequent model to demonstrate reaction rate of wet air oxidation by many researches such as [6], [9], [11]-[12]. Since the analysis methodology of power law is simpler than the lumped kinetic model. Besides, the parameters in power law are also less than the lumped kinetic model. Therefore less complicated model is used for sizing reactor. In the power law model, four impact factors for instance reaction temperature, concentration of pollutants, oxygen partial pressure and catalyst loading were included. The concentration of pollutants was substituted by represented parameter such as chemical oxygen demand (COD) or total organic compound (TOC) value as shown in equation 2.30.

$$\frac{d[COD]}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)[COD]^m[O_2]^n \tag{2.30}$$

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals and materials used in this research were specified, having details as following below:

1. Spent caustic wastewater was supplied from plant at PTT Global chemical Co., Ltd.
2. Air zero was purchased from Linde (Thailand) PLC.
3. Nitrogen gas was purchased from Linde (Thailand) PLC.
4. Vanadium(IV)-oxy acetylacetonate purum, ≥97.0% was purchased from Aldrich Co., Ltd., and used as received.
5. Ruthenium(III) nitrosyl nitrate solution in dilute nitric acid, Ru1.5% was purchased from Aldrich Co., Ltd., and used as received.
6. Copper(II) nitrate was purchased from Univar Co., Ltd., and used as received.
7. Manganese(II)acetate tetrahydrate 99+% was purchased from Aldrich Co., Ltd., and used as received.
8. Silica gel 0.063-0.200 mm was purchased from Merck Co., Ltd., and used as received.
9. Cerium(IV)oxide power < 5 micron 99.9% was purchased from Aldrich Co., Ltd., and used as received.
10. Aluminum oxide 0.05-0.15 mm was purchased from Fluka Co., Ltd., and used as received.
11. Titanium(IV) oxide powder < 5 micron 99.9% was purchased from Sigma-aldrich Co., Ltd., and used as received.
12. Potassium dichromate 99.5% was purchased from Carlo erba Co., Ltd., and used as received.

13. Potassium hydrogen phthalate > 99.5% was purchased from Merck Co., Ltd., and used as received.
14. Mercury sulfate > 99% was purchased from Fluka Co., Ltd., and used as received.
15. Silver sulfate > 99.5% was purchased from Sigma-aldrich Co., Ltd., and used as received.
16. Sulfuric acid 95-97% was purchased from Merck Co., Ltd., and used as received.

3.2 Characterization instruments

In order to determine the concentration of pollutant in wastewater, the samples of wastewater were tested according to the testing method of APHA 5220C. For catalyst determination, the physical and chemical properties were investigated by Nitrogen adsorption-desorption isotherm and X-ray diffraction as follows;

3.2.1 UV-visible spectroscopy

The chemical oxidation demand (COD) of wastewater was determined by digestion with oxygenated reagent. The digesting was conducted in acidic and high temperature condition. Strong chemical oxidizing agent such as potassium dichromate and silver sulfate as catalyst were added to the wastewater sample. In case the sample consists of chloride ion, which is an inhibitor for the oxidation, the mercury sulfate was added to minimize the effect. After digestion step, the dichromate (Cr^{6+}) is converted to chromate (Cr^{3+}) as shown in equation 3.1. The COD values were investigated from measuring amount of the transformed chromate by UV-visible spectroscopy at 600 nm. The COD value was evaluated from adsorption value by comparing with calibration graph of standard chemical.

$$2Cr_2O_7{}^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 3O_2 + 8H_2O \qquad (3.1)$$

The steps of COD testing are described as follow.

1. Digesting solution: 10.216 g of potassium dichromate, which was dried at 110°C for 2 hours was dissolved and filled with de-ionized water to 500 ml. Then, 167 ml and 33.3 g of concentrated sulfuric acid and mercury sulfate respectively were added. After that the solution was cooled down and diluted to 1000 ml.
2. Catalyzing reagent: 5.5 g of silver sulfate was dissolved in 1 kg of concentrated sulfuric acid.
3. Calibration graph: 0.425 g of potassium hydrogen phthalate (KHP) which was dried at 110°C for 1 hour was dissolved and filled with de-ionized water to 1000 ml. The standard COD value of KHP is 1.176 mg oxygen per mg KHP.
4. Digestion: The sample and reagents were charged into digestion vessel as shown in table 3.1 and heated at 150 °C for 2 hours.
5. Measurement: Chromate in the sample can be measured by UV-visible spectroscopy at wavelength 600 nm. The adsorption was zeroed by blank sample, which de-ionized water was also digested as the same steps with sample of wastewater.
6. Analyze the result: The absorption values were converted to COD value by comparing with the value in COD calibration graph.

Table 3.1 Mixing volume for COD test

Digest vessel	**Sample (ml)**	**Digestion solution (ml)**	**Catalyzing reagent (ml)**	**Total final (ml)**
16*100 mm	2.5	1.5	3.5	7.5

3.2.2 Nitrogen adsorption-desorption isotherm (BET method)

Surface area, pore size and pore volume were determined by Micromeritics ASAP 2000 instrument. The internal surface of the catalyst was implied by the adsorption-desorption values. N_2 was condensed at temperature 77 K using static vacuum procedures. The number of N_2 molecules adsorbed at monolayer coverage were measured and calculated to be the internal surface area.

3.2.3 X-ray diffraction (XRD)

X-rays diffraction is normally utilized in determining crystalline of material. The crystal structures of catalysts were provided by SIEMENS D5000. X-ray diffractometer, using CuK_α radiation with Ni filter in the 2θ range of 10-80 degrees resolution 0.04^o, was used in this project.

3.2.4 Temperature programmed reduction (TPR) and temperature programmed oxidation (TPO)

Behavior in reduction and oxidation of catalyst was determined by this technique. In temperature-programmed reduction (TPR), 0.1 gram of catalyst was dried at 250^oC by 25 milliliter per minute of nitrogen gas for 1 hour in order to remove moisture and oxygen. After cooled down to ambient, 20 milliliter per minute of 10% hydrogen in argon was feed in. The temperature ramp rate was set at 5^oC per minute until the temperature reached 250^oC, then the catalyst was purged and cooled down by nitrogen gas. After that temperature-programmed oxidation (TPO) technique was started by introduced 1% oxygen in helium. The temperature ramp rate was set at 5^oC per minute until the temperature reached 250^oC.

3.2.5 Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) Spectroscopy

SEM provides detailed high resolution images of the sample by injecting electron beam across the surface and detecting secondary or backscattered electron signal. An Energy Dispersive X-Ray Analyzer (EDX or EDA) is also used to provide elemental identification and quantitative compositional information.

3.3 Experimental steps

In this research, the experimental steps were separated to 2 main parts; study of reaction rate and catalyst screening. The detail methodology is elaborated as shown below.

The oxidation reaction was carried out in a 100 cm^3 SS316 reactor. The reactor has 2 ports. The inlet port was connected with air and nitrogen cylinders for reacting and purging. The gases were bubbled under the liquid phase for enhancing mass transfer between gas phase and liquid phase. The other port of the reactor was used for venting the remaining gas from reaction. For controlling the reacting condition, the temperature of high pressure reactor was monitored by measured temperature in the oil bath. The pressure was regulated from the air cylinder regulator. Flow rate of bubbled air was manipulated from the vent control valve at reactor outlet port. Mixing insight the reactor was adjusted by a variable speed magnetic stirrer. Diagram of the reactor is demonstrated as shown in Figure 3.1.

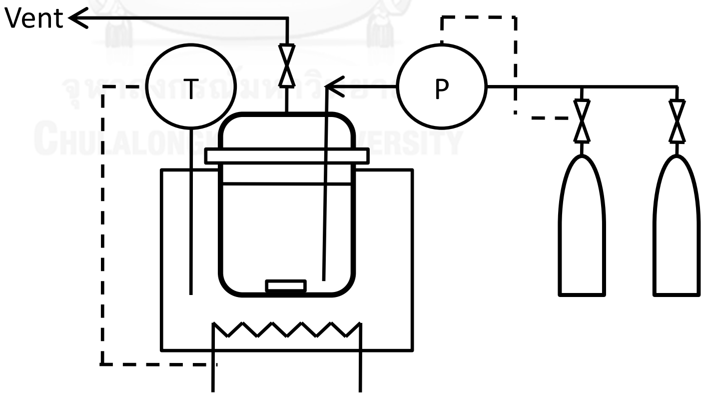


Figure 3.1 Equipment and controlling diagram of reactor

3.3.1 Study of reaction rate

Rate of reaction is the most important information, which is representing the characteristic of each chemical reaction. Before kinetic model development, several experiments were required to assure that the rate limiting step was truly controlled by intrinsic rate. Stirred speed was used to be the identification parameter. Since the oxygen in gas phase is diffused to liquid phase more effectively, when stirred speed is increased. Therefore, series of experiments at different stirred speeds were a method to identify that the diffusion was not limiting step of the reaction. Constant of the COD values are expected even the stirred speed is increased, when intrinsic rate is the rate limiting step.

First, 100 ml of spent caustic wastewater was charged into reactor. The liquid height per reactor diameter ratio was 1:1 as standard reactor criteria. The reactor was put in to an oil bath. 2 inch magnetic stirrer was aligned at center of the reactor. The reactor cover and inlet/outlet gas connecting tube were re-instated and tighten. After that the heating step was started. The temperature of reactor was measured at the oil bath. When the temperature was reached to targeted temperature, the reactor was kept at the condition at least 15 minutes. The oxidation was started, when air was fed in and the pressure was adjusted to desired pressure. The stirred speed and vent valve were adjusted to targeted condition that intrinsic rate was the rate limiting step and air flow rate was exceeded.

The reaction order of sodium sulfide (α) was investigated by differential method. The oxidation was conducted for 10 minutes. The wastewater was sampled every 2 minutes during the reaction. The order of sodium sulfide was calculated from slope of $\ln(\frac{\mathrm{dC}}{\mathrm{dt}})$ and $\ln(\mathrm{COD})$ graph.

Second, the reaction order of oxygen (β) was investigated by initial method. Series of different reaction pressure were conducted. Initial rate of the oxidations were measured at 2 and 4 minutes of the reaction. The order of oxygen was calculated from slope of $\ln(\frac{\mathrm{dC}}{\mathrm{dt}})$ and $\ln(\mathrm{Solubilty\ of\ O_2\ in\ liquid\ phase})$ graph.

Third, the specific reaction rate was investigated by initial method. Series of different reaction temperature were conducted. Initial rate of the oxidations were measured at 2 and 4 minutes of the reaction. The specific reaction rate (k') could be calculated since the order of reactants were already known from the previous steps. Then, the activation energy and pre-exponential factor were evaluated from slope and intercept point of $\ln(\mathrm{k})$ and $\ln(\frac{1}{\mathrm{T}})$ graph.

3.3.2 Catalyst screening

Various metals and supports were studied for the activity in oxidation. Ruthenium, vanadium, copper and manganese are frequently the most active metals for treating spent caustic wastewater, containing sodium sulfide. The activity is not only affected by the metal species but also affected by type of the support. Therefore, the metals were impregnated on several most common supports, for instance silica (SiO_2), alumina (Al_2O_3), ceria (CeO_2) and titania (TiO_2) by the incipient wetness impregnation method. For more realistic in economically compared, the percentage of metals loading was based on the pricing of each metal as shown in Table 3.2.

Table 3.2 Chemical for catalyst preparation

Precursor	**Metal/price g /100$**	**wt% metal loading (based on same $)**	**Total precursor g per 3 g support**
$Ru(NO)NO_3$	0.42	0.1	0.240
$Cu(NO_3)_2 . 2.5H_2O$	26.02	7.0	0.826
$Mn(C_2H_3O_2)_2$. 4H2O	27.78	7.4	1.075
$OV(C_5H_7O_2)_2$	9.42	2.7	0.425

Precise weight of metal was dissolved in water, which volume of prepared water was matched with pore volume of each support. Therefore, percentage of each metal loading which was filled into the supports was controlled. Then, the impregnated catalyst was dried in oven at 110°C for 1 day to remove the water. After that dried catalyst was calcined at 500°C in condition of air for 4 hours in order to form metal oxide.

In activity testing, catalyst 2 g catalyst per liter of wastewater was added to reactor. All other steps are conducted as same as the method for non-catalytic wet air oxidation. The performance in COD removal was used for comparing the efficiency of each catalyst.

3.4 Feasible study of catalytic wet air oxidation

As above section, the kinetic model of catalytic and non-catalytic wet air oxidation for spent caustic wastewater were developed. Those equations are important information for finding the optimum temperature and pressure. The minimum investment cost of the reactor was also calculated from the simulation.

Basis:

- Packed bed reactor
- Excess air (Oxygen concentration is constant)
- Isothermal condition (Constant temperature)
- No pressure drop
- No mass transfer limit

Decision variables:

1. T: the operating temperature of reactor (Celsius)
2. P: the operating pressure of reactor (bar)
3. D: the diameter of reactor (meter)
4. t: the minimum metal thickness of reactor (inch)

Known variables:

1. C0: concentration of sodium sulfide at inlet of reactor = 0.295 mole per liter
2. X: conversion of sodium sulfide at outlet of reactor = 0.9996

Equality constraints:

1. Mole balance of sodium sulfide

$$V = F_{Na_2S,in} \int_0^{X_{Na_2S}} \frac{dX_{Na_2S}}{-r}$$

$$\frac{\pi D^2}{4} * 20D = C_0 Q \int_0^{X_{Na_2S}} \frac{dX_{Na_2S}}{-k\left[C_{Na_2S}\right]^{\alpha}[O_2]^{\beta}}$$

$$\frac{\pi D^2}{4} * 20D = \frac{C_0 Q}{-Ae^{\frac{-E_a}{RT}} {C_0}^{\alpha} {O_2}^{\beta}} \int_0^{X_{Na_2S}} \frac{dX_{Na_2S}}{(1-X)^{\alpha}}$$

As dissolved oxygen concentration is estimated by experimental data [13].

Solubility of oxygen in water =

$$(-3 \times 10^{-7}T^3 + 0.0001T^2 - 0.0125T + 1.2182)0.21P$$

2. Minimum thickness require ASME BPVC I (2010), boiler & pressure vessel

$$t = \frac{PD}{2SE+2yP} + C$$

Symbols used in the formulas are defined as follows;

t = minimum metal thickness (inch)

C = minimum allowance for threading and structural stability

= 0.1 mm for threated pipe D > 3/4 inch

E = Weld strength reduction factors for Cr-Mo alloy longitudinal seam weld cylinder

= 1 for temperature is less than 427°C

S = maximum allowable stress value at the design temperature of the metal

= 12900 for temperature is less than 204°C

= -28.979 T + 18817 for temperature is more than 204°C

y = temperature coefficient

= 0.4 for temperature is less than 480°C

Inequality constraints:

1. D ≥ 0: the diameter of reactor is positive value.
2. t ≥ 0: the minimum metal thickness of reactor is positive value.
3. T ≥ 0: the operating temperature of reactor is positive value.
4. 204 ≤ T : the operating temperature of reactor is limited by saturated temperature of high pressure steam.
5. P ≥ 0: the operating pressure of reactor is positive value.
6. 33 ≤ P: the operating pressure of reactor is limited by pressure of air compressor.

Objective:

Minimizations for investment cost of non-catalytic and catalytic wet air oxidation reactor =

(reactor surface area x thickness) x metal density x metal price
+ weight of catalyst x catalyst price

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Study of catalyst characteristic

In order to understand and explain the correlation between activity and characteristic of catalysts, not only the physical catalyst properties such as surface area, pore size, pore volume and morphology were studied, but also the chemical properties of the catalyst such as crystal structure, reduction and oxidation behaviors were also determined.

4.1.1 Study of catalyst physical properties

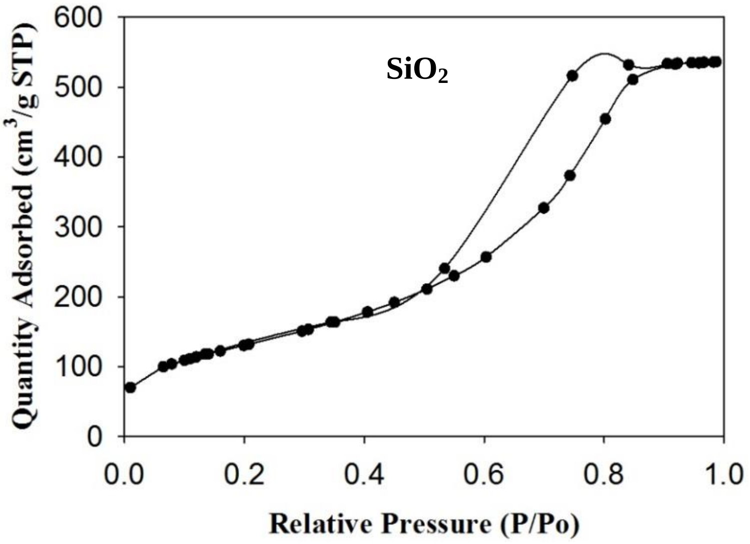
The surface area, pore diameter and pore volume of catalyst are important parameters, because the properties affect to the performance of metal dispersion and also the diffusivity of reactants to active site of catalyst. From nitrogen adsorption-desorption isotherm (BET), silica and alumina are identified that the supports are porous material. The value of surface area and pore volume are much higher than ceria and titania. After the silica support was impregnated by high metal loading such as copper, the value of surface area and pore volume are slightly decreased as shown in Table 4.1. It means pore of the silica and alumina supports was slightly blocked by metal. The diffusivity of catalyst might be slightly decreased, but did not significantly impact to overall mass transfer. For the other supports, Ceria and titania are non-porous material. The oxidation of substrates was occurred only at outside surface of the catalyst. Diffusion of substrates to pore of ceria and titania could be neglected.

Table 4.1 Surface area, pore size and pore volume of catalysts

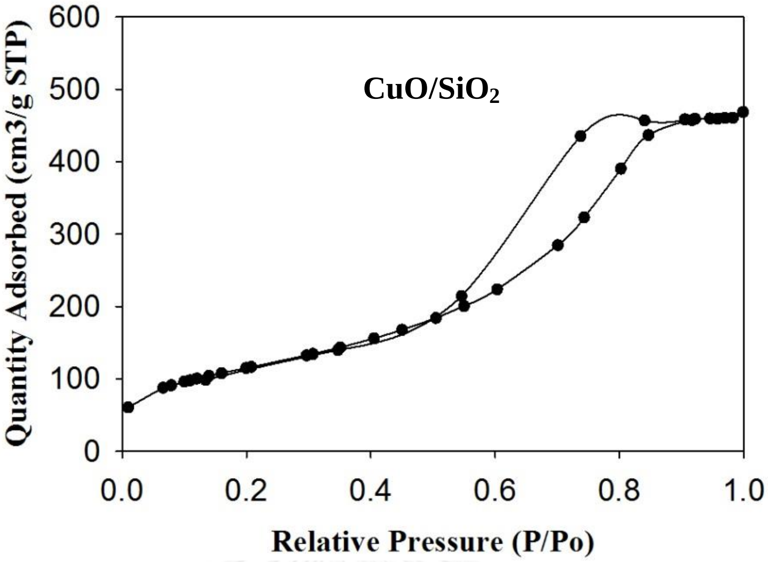
Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
SiO_2	476	0.85	4.51
CuO_2/SiO_2	421	0.74	4.56
Al_2O_3	151	0.23	3.88
CeO_2	7	0.01	3.48
TiO_2	12	0.01	8.69

The value of pore size indicated that silica and alumina supports are classified in range of mesoporous material. Furthermore, graph between quantity adsorbed and relative pressure showed the concurrently result. The graphs are clearly observed hysteresis loops (type IV) in silica, impregnated silica and alumina supports, which indicate that the supports are mesoporous material. For ceria and titania supports, the supports are non-porous material. Small size of hysteresis loop is observed, which represent non-porous material as shown in Figure 4.1.

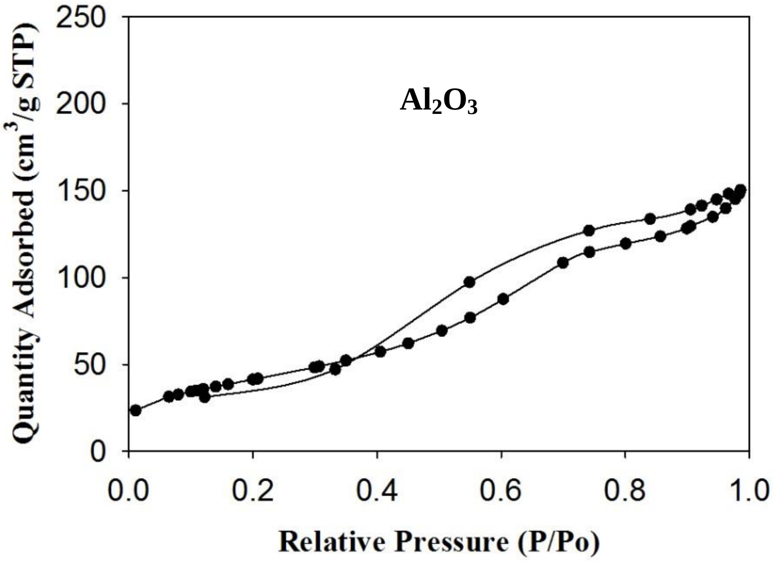
a)



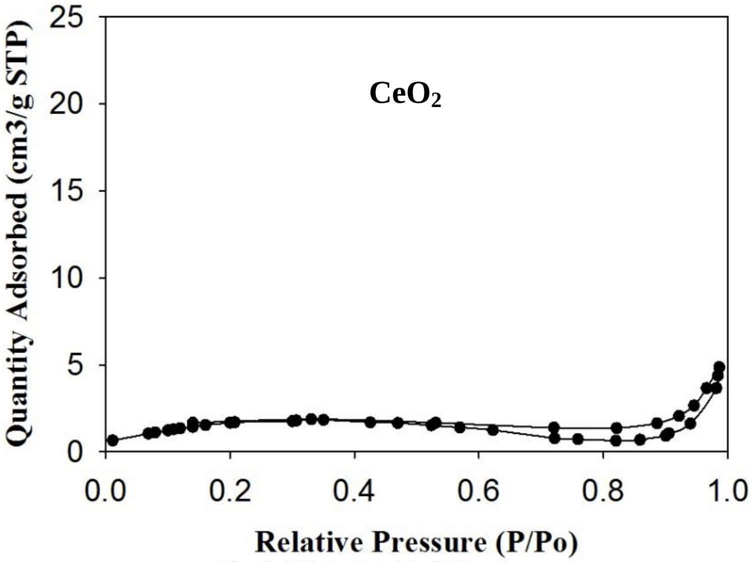
b)


CuO/SiO2
Quantity Adsorbed (cm3/g STP)
600
500
400
300
200
100
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)

c)


Al2O3
Quantity Adsorbed (cm3/g STP)
250
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)

d)



e)

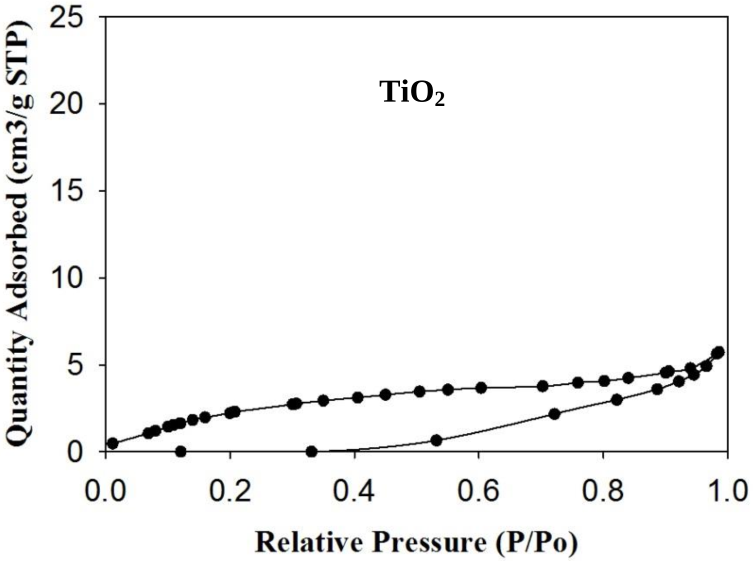


Figure 4.1 Effect of relative pressure through quantity adsorbed of supports: a) silica, b) copper oxide on silica, c) alumina, d) ceria and e) titania

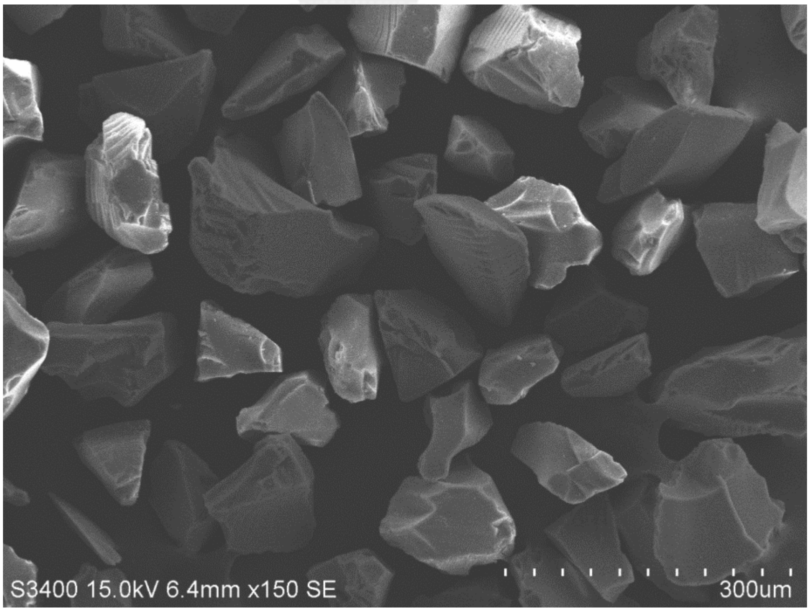
4.1.2 Study of catalyst morphology

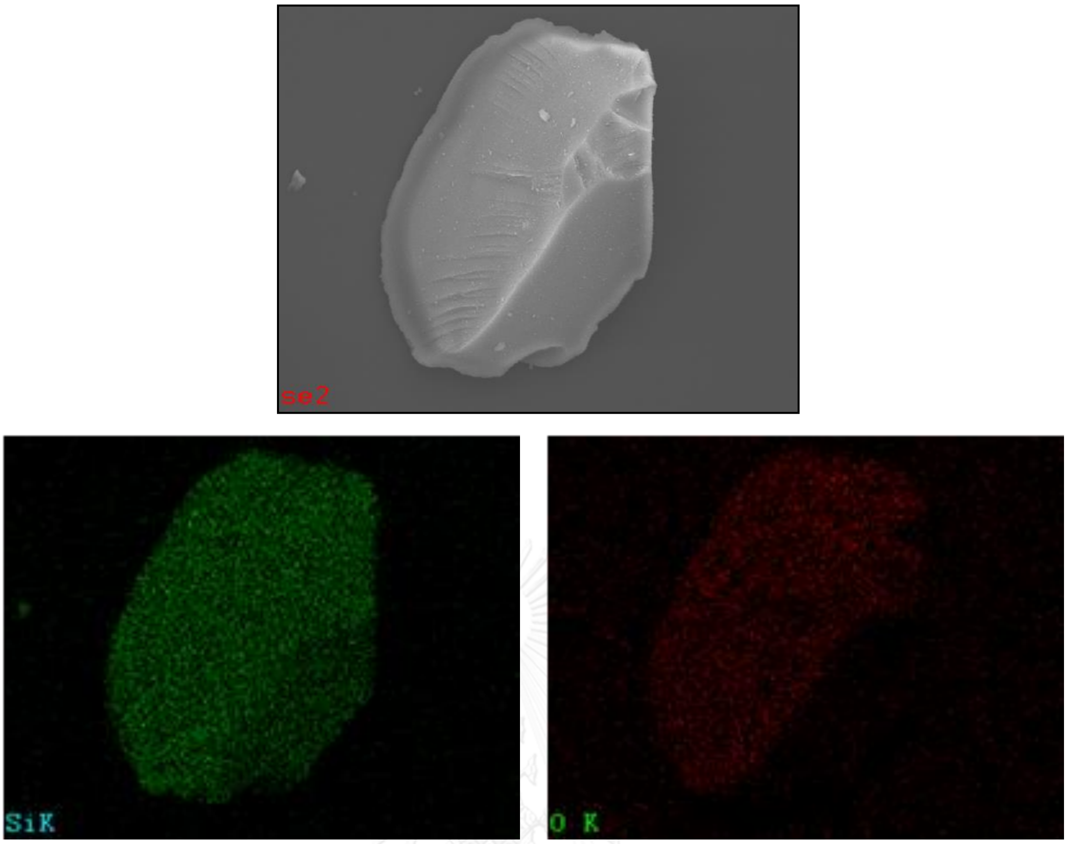
By performance of electron microscope, morphology such as surface, shape, particle size and agglomeration of catalyst were observed. Furthermore, metal dispersions on the catalyst surface also were mapped by EDX mode.

Morphology of silica is flake, sharp edge and smooth surface. The average particle diameter is 100 micron as shown in Figure 4.2 a). Some agglomerated metal oxides are observed on the surface of silica especially copper oxide as shown in Figure 4.2 b) to e).

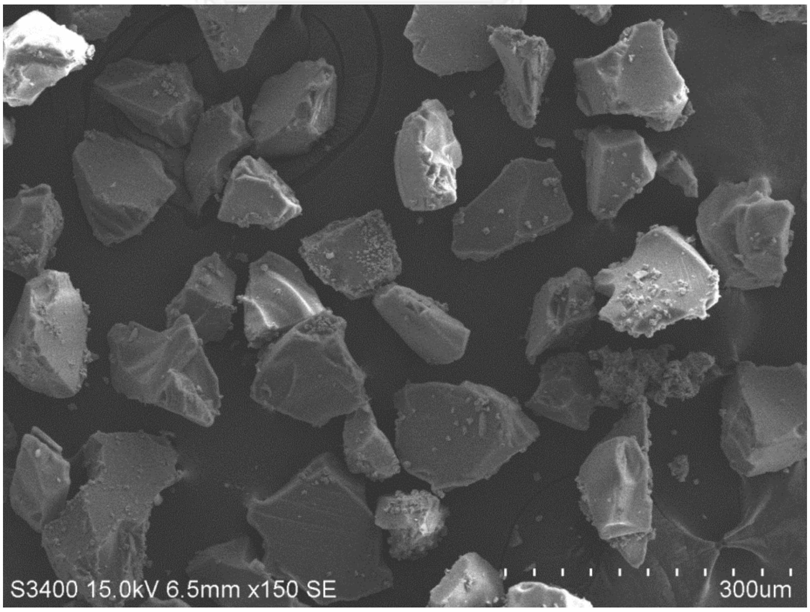
Dispersion of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were observed by SEM-EDX. The metals are well dispersed on the surface of silica as shown in Figure 4.2 b) to e).

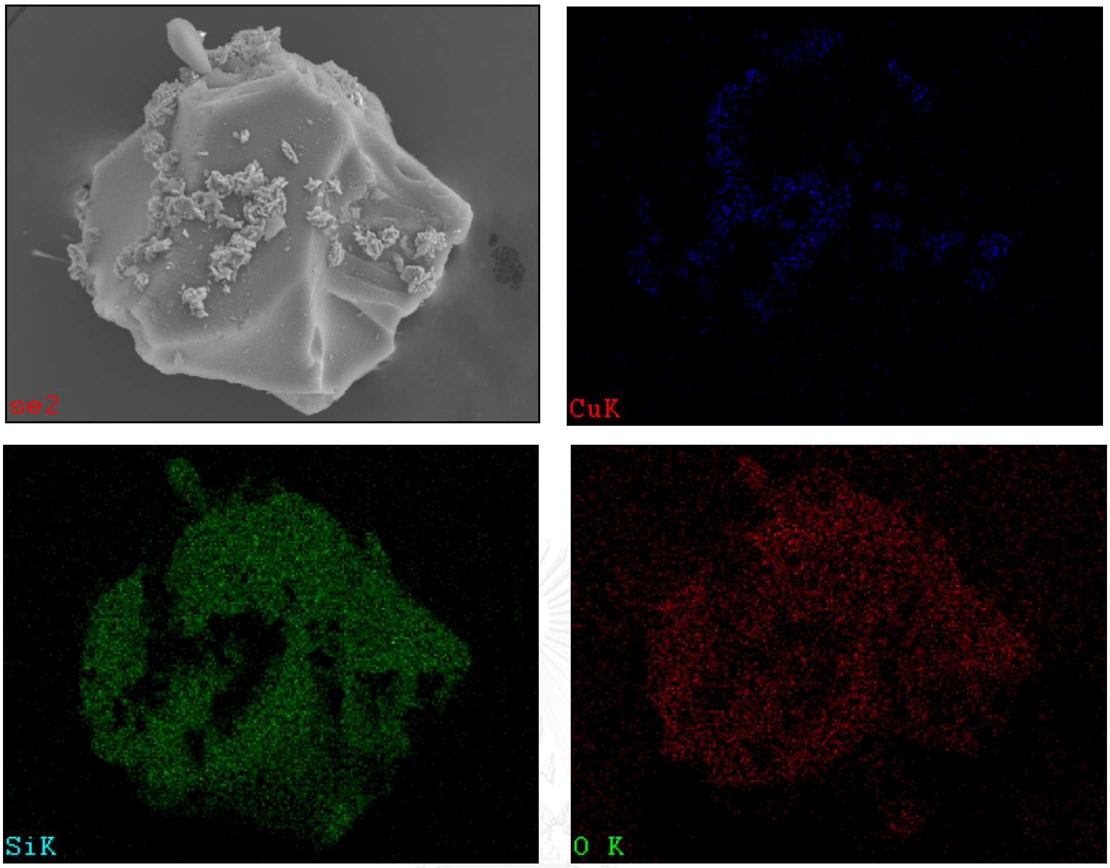
a)



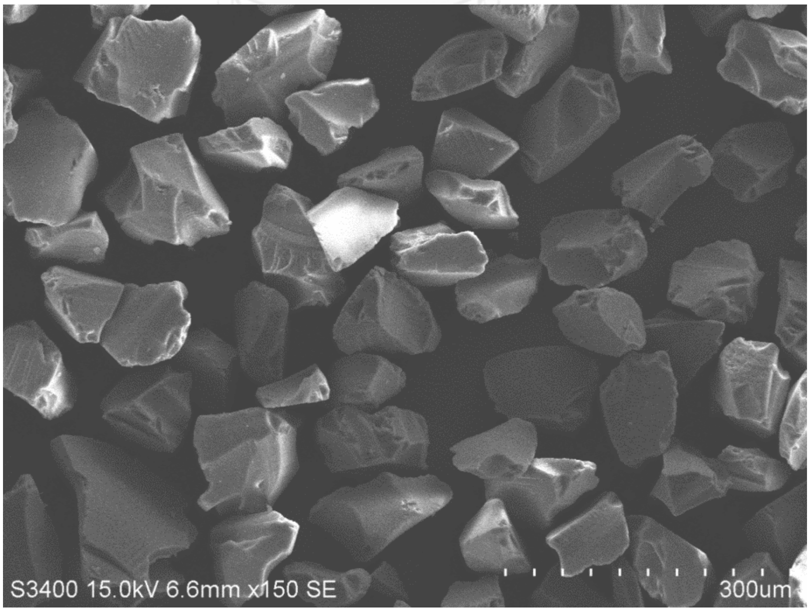


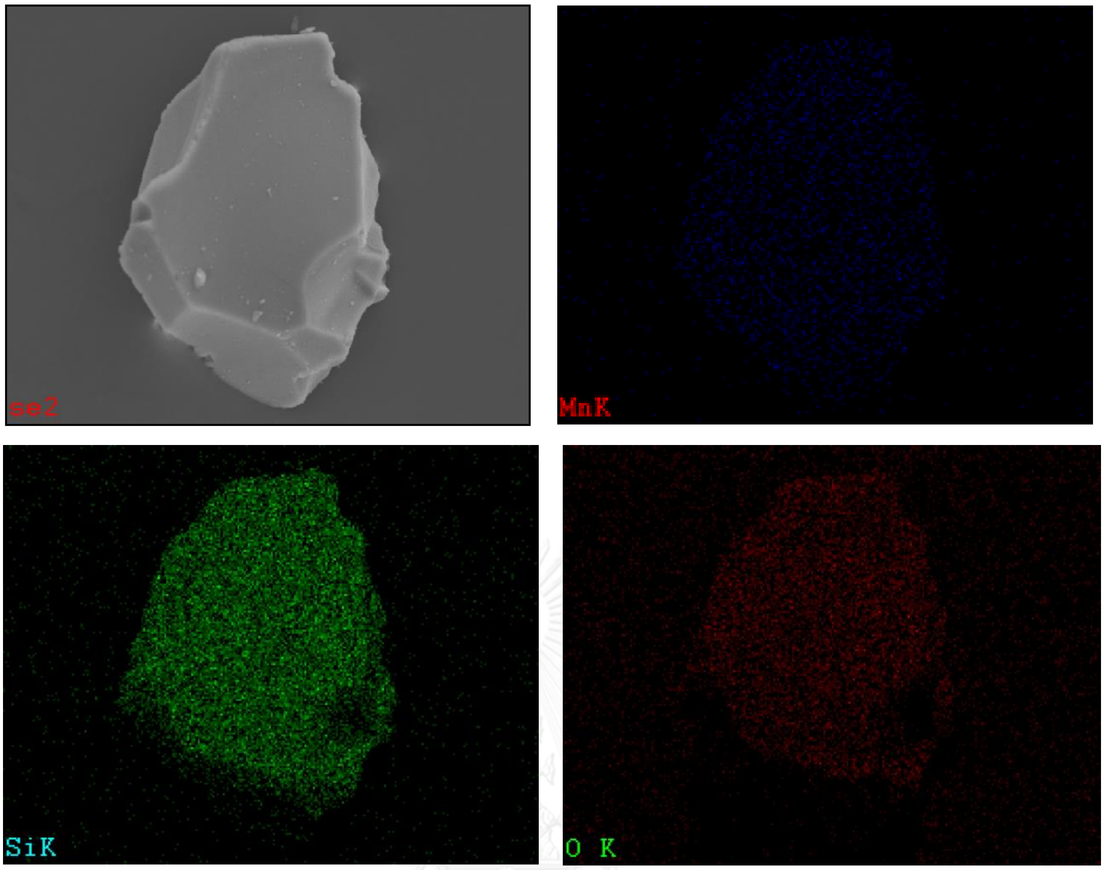
b)



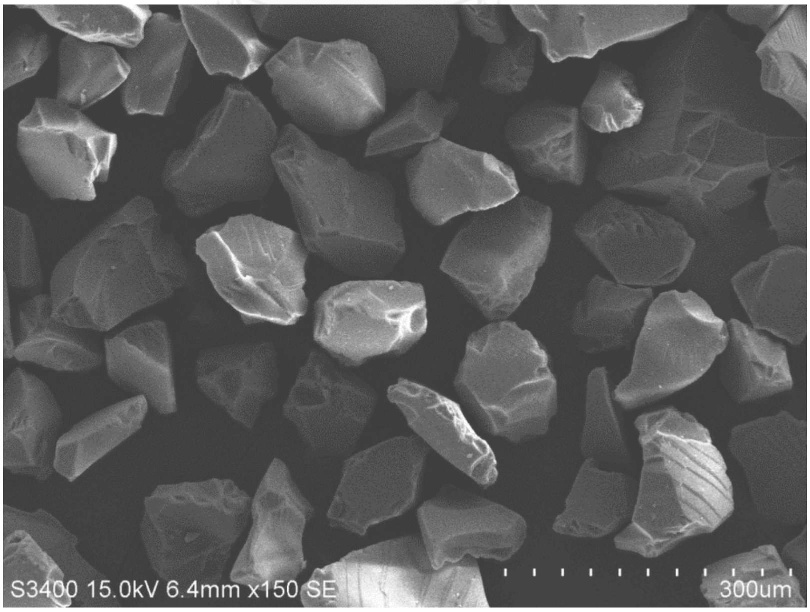


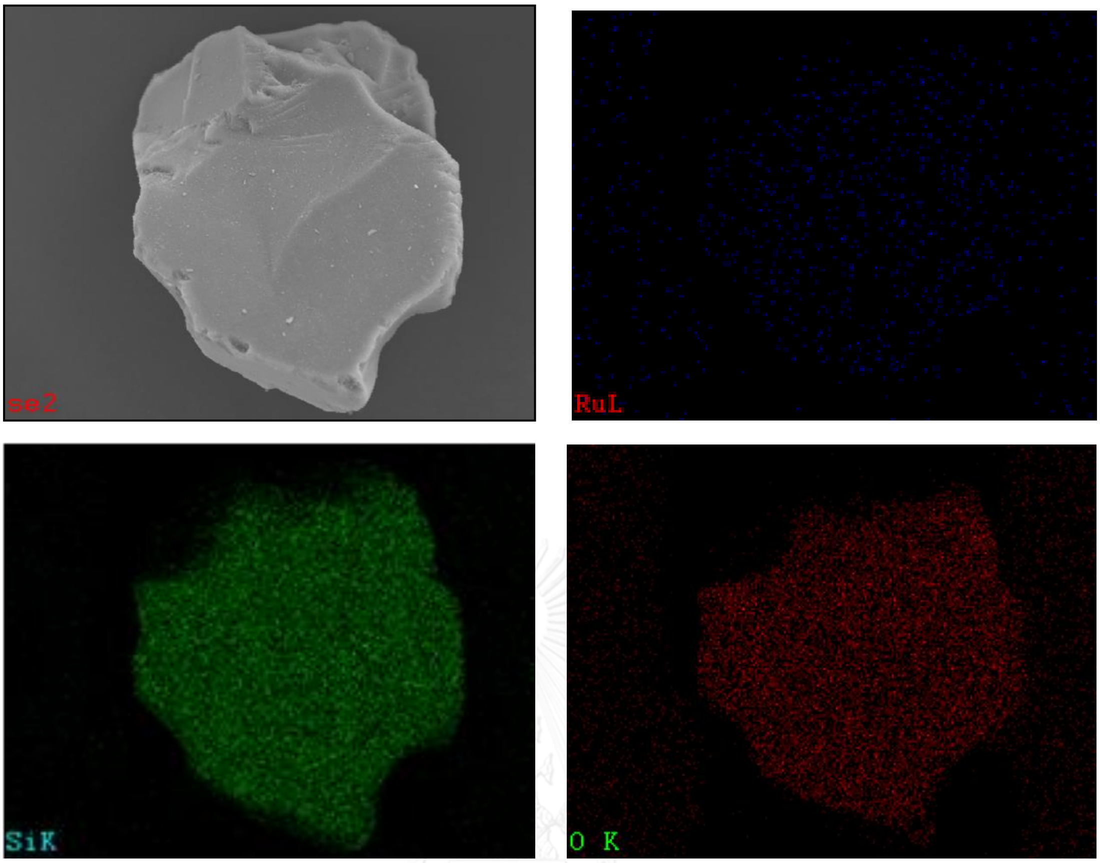
c)



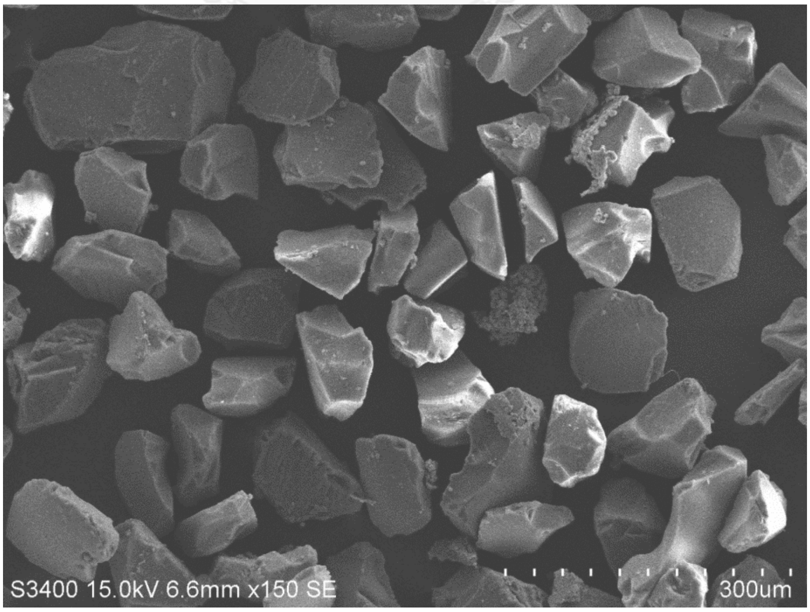


d)





e)



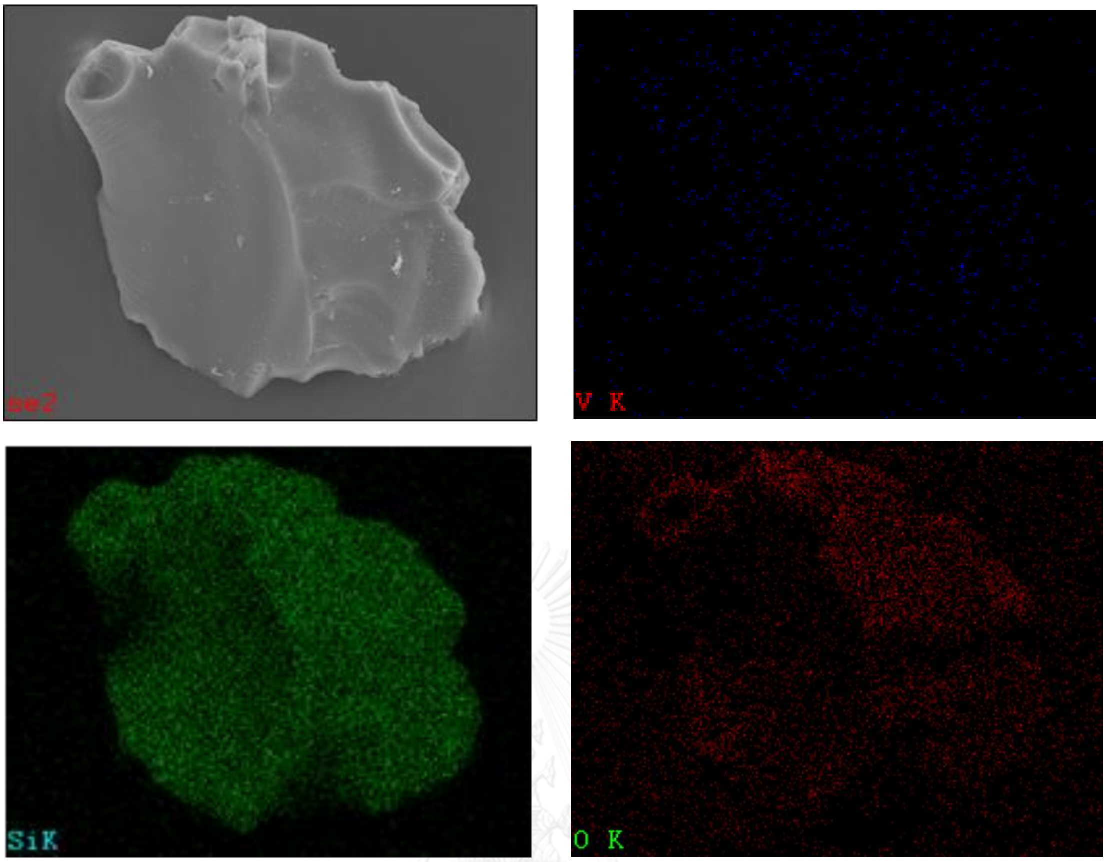
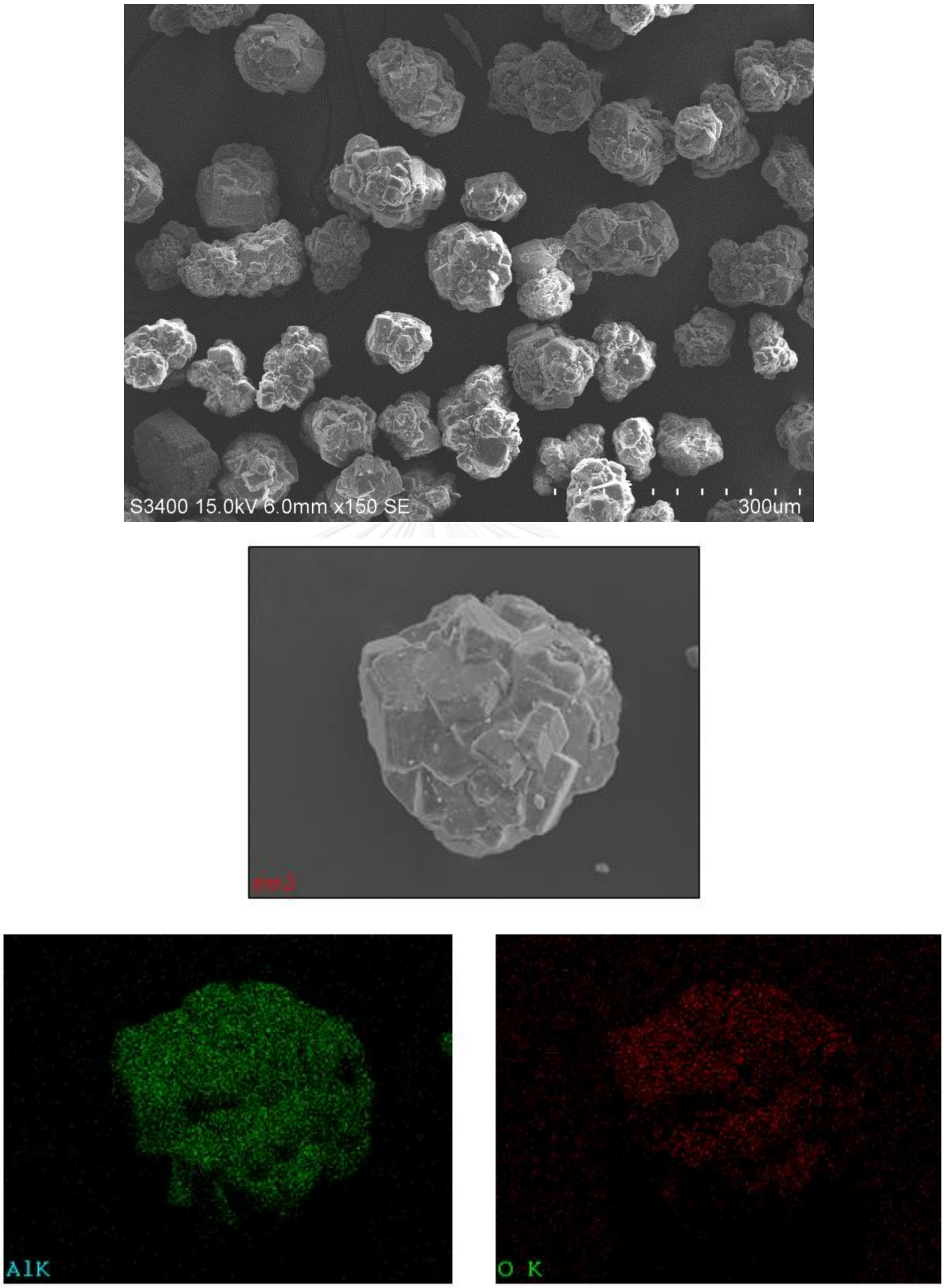


Figure 4.2 Surface morphology and metal mapping of catalysts: a) silica, b) copper oxide on silica, c) manganese oxide on silica, d) ruthenium oxide on silica and e) vanadium oxide on silica

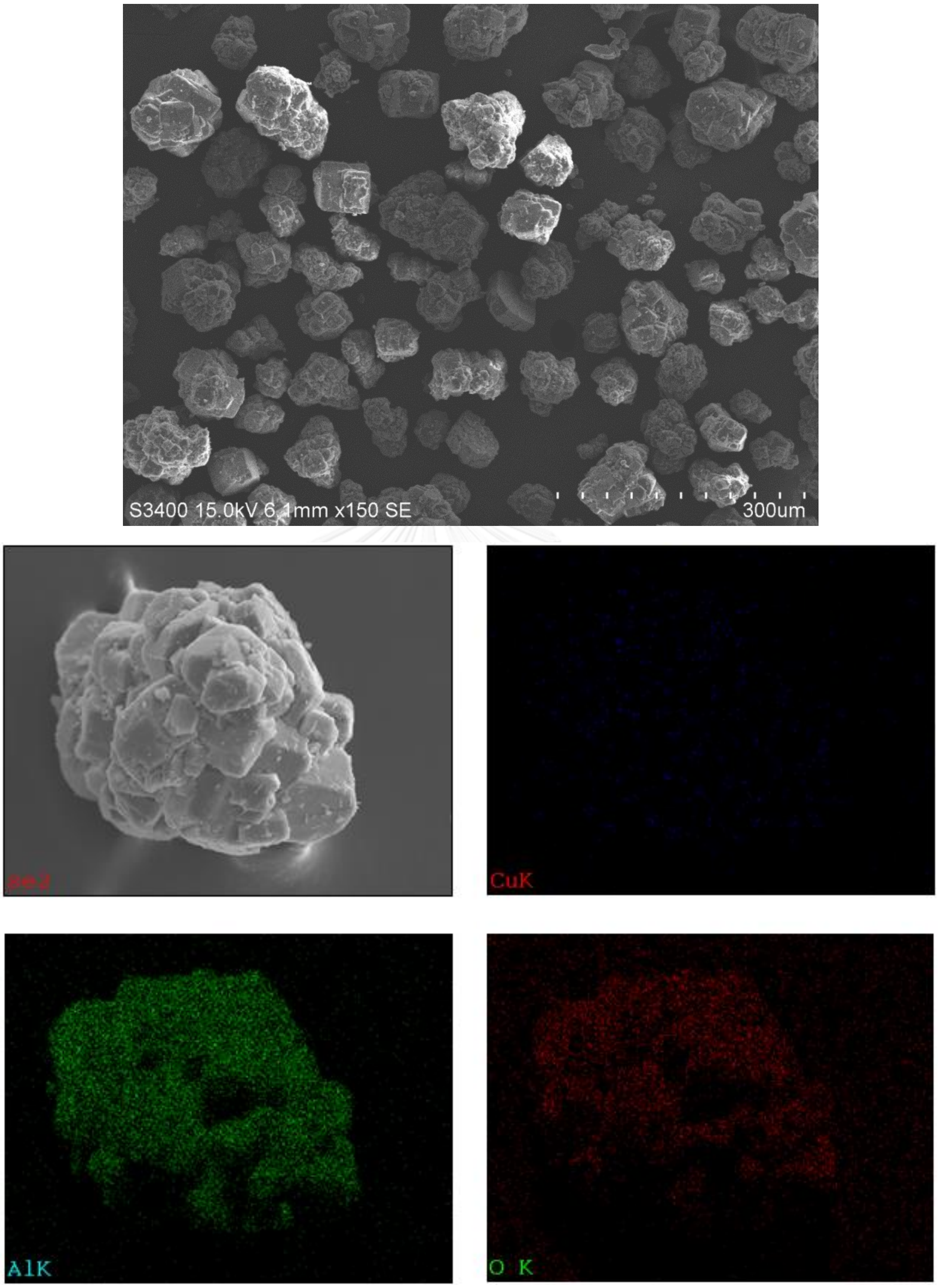
Morphology of alumina is spherical shape, but the surface is not smooth. The average particle diameter is 100 micron as shown in Figure 4.3 a). Some agglomerated metal oxides were observed on the surface of alumina as shown in Figure 4.3 b) to e).

Metal dispersion of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were observed by SEM-EDX. The metals are well dispersed on the surface of alumina as shown in Figure 4.3 b) to e).

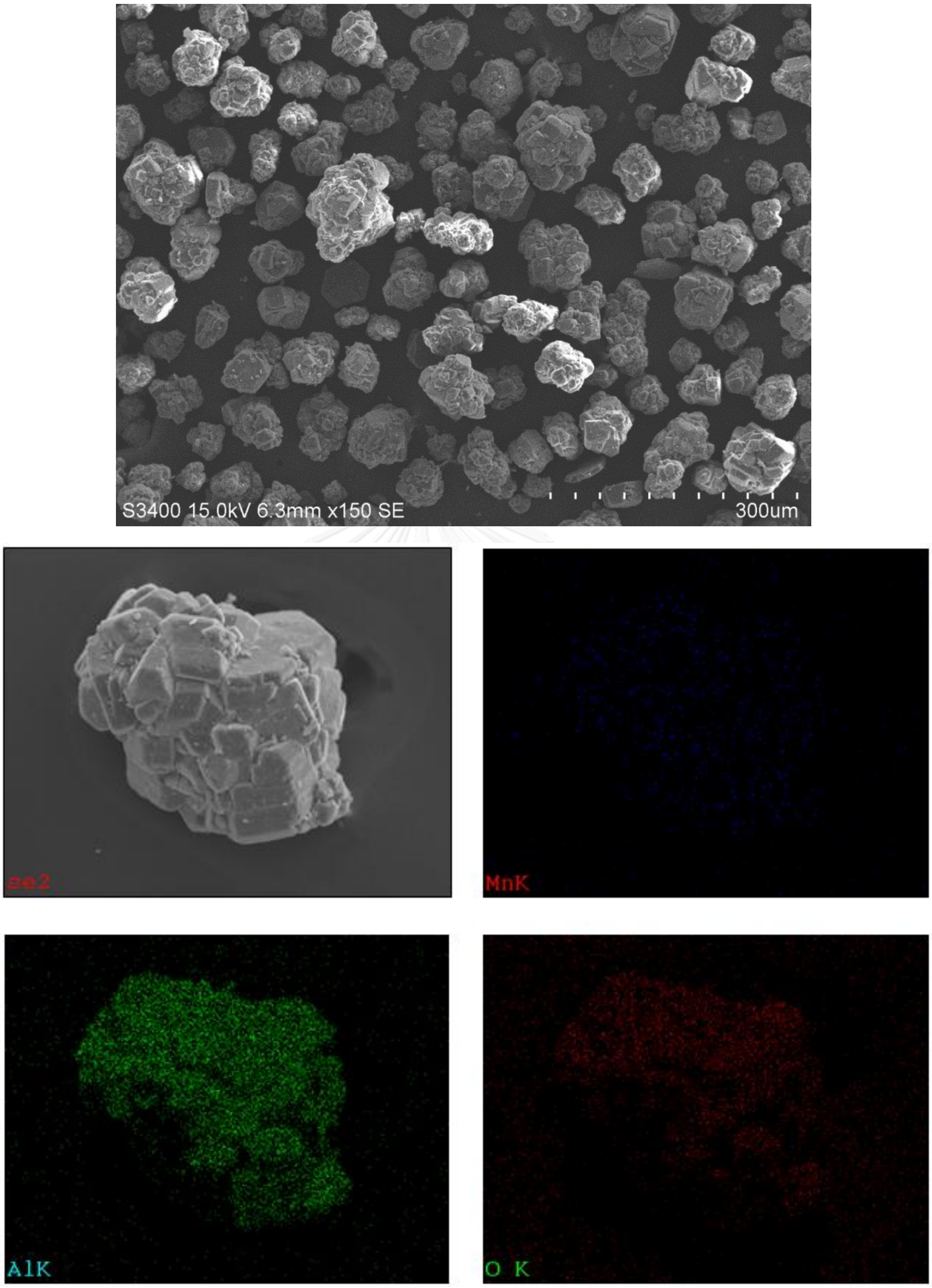
a)



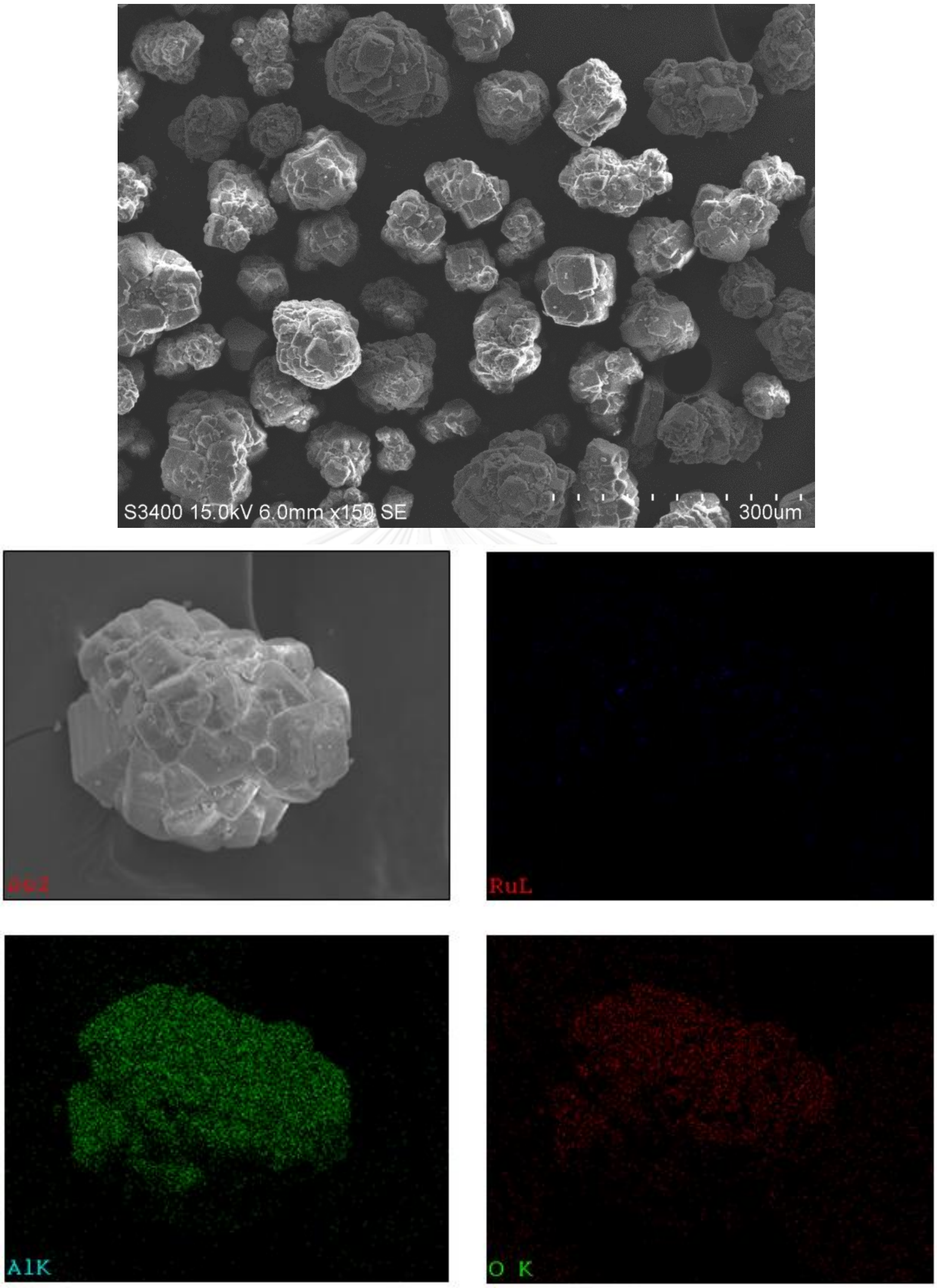
b)



c)



d)



e)

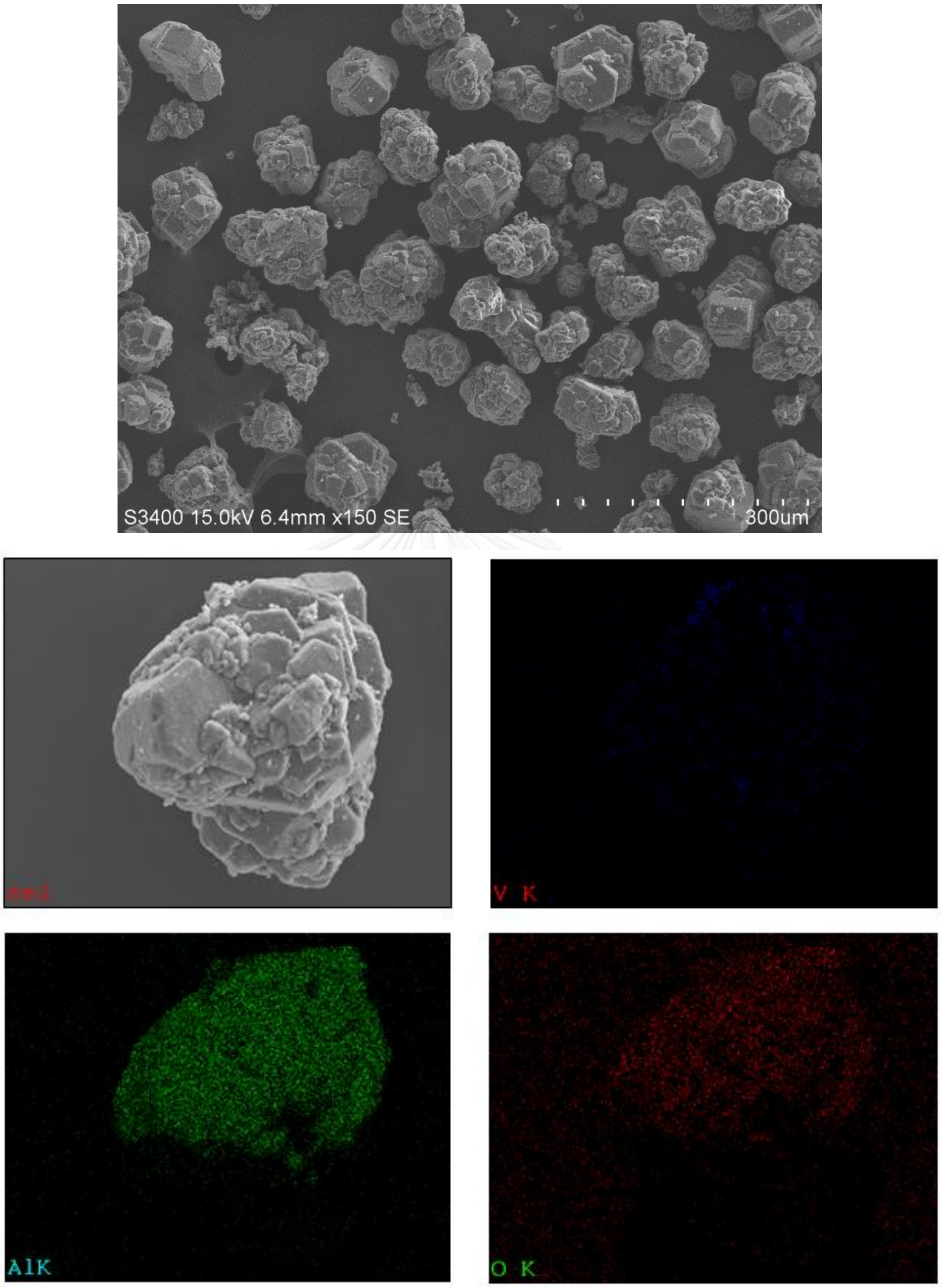
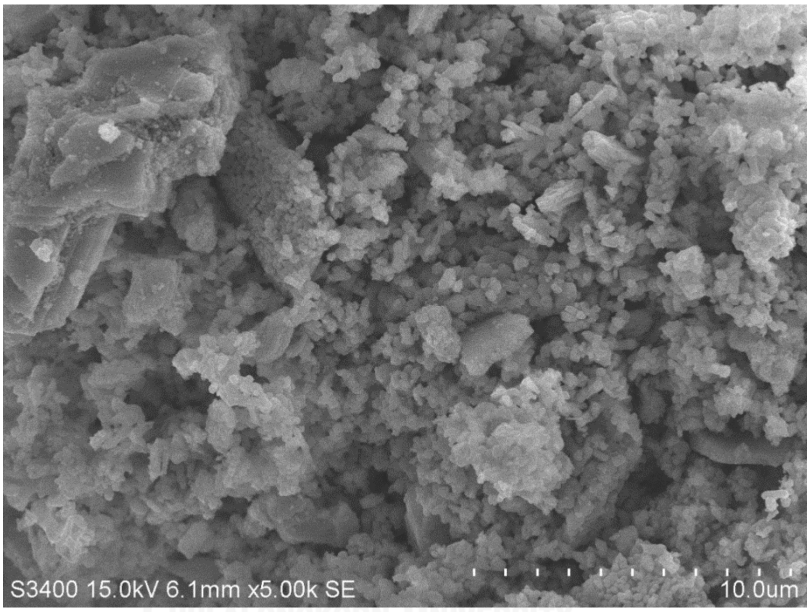


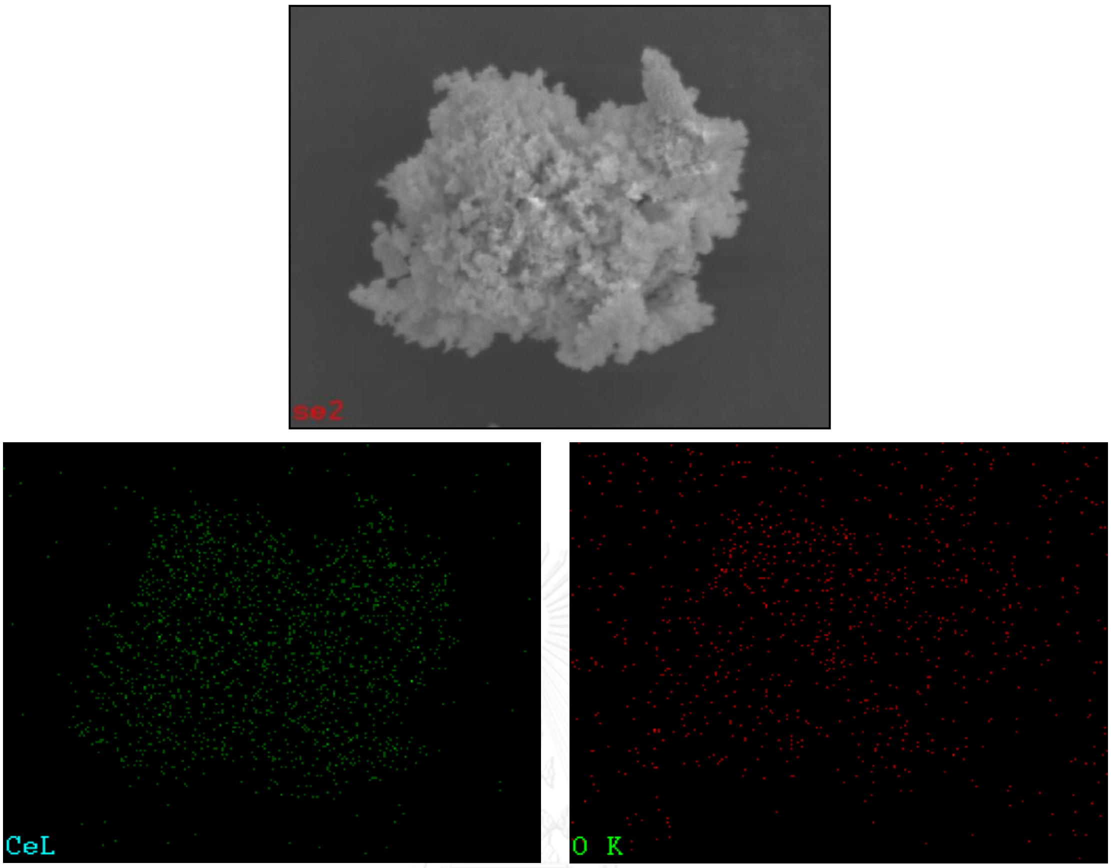
Figure 4.3 Surface morphology and metal mapping of catalysts: a) alumina, b) copper oxide on alumina, c) manganese oxide on alumina, d) ruthenium oxide on alumina and e) vanadium oxide on alumina

Morphology of ceria is fine powder. The average particle diameter is less than 1 micron as shown in Figure 4.4 a). The metal oxides are not clearly observed because the particle diameter of ceria is small as shown in Figure 4.4 b) to e).

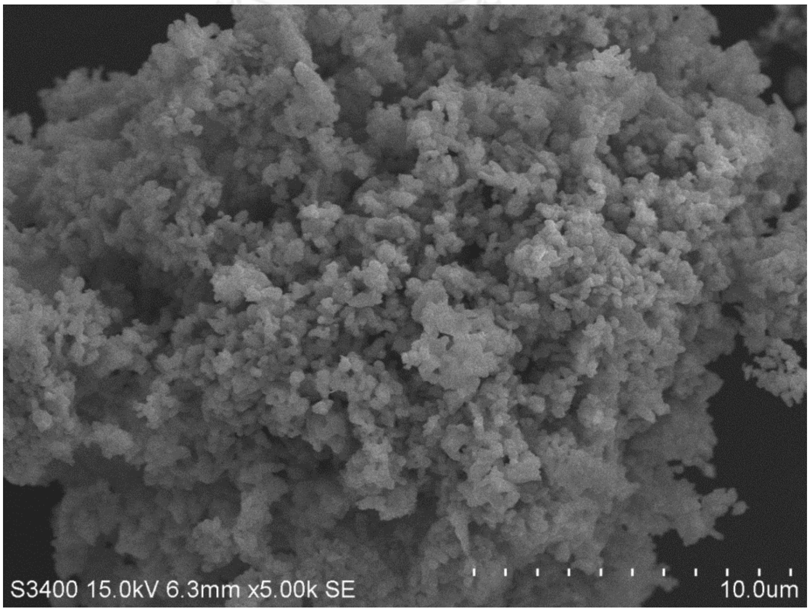
However the metal dispersion of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were observed by SEM-EDX. The metals are well dispersed on the surface of ceria as shown in Figure 4.4 b) to e).

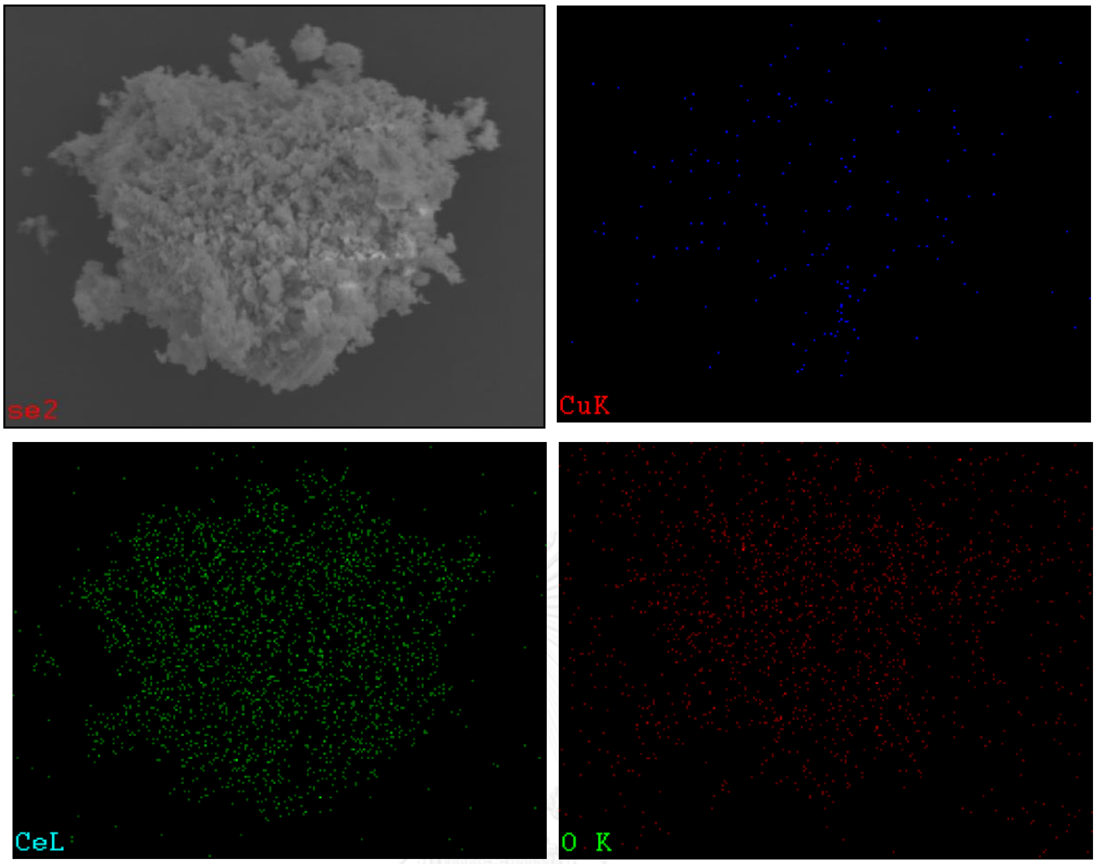
a)



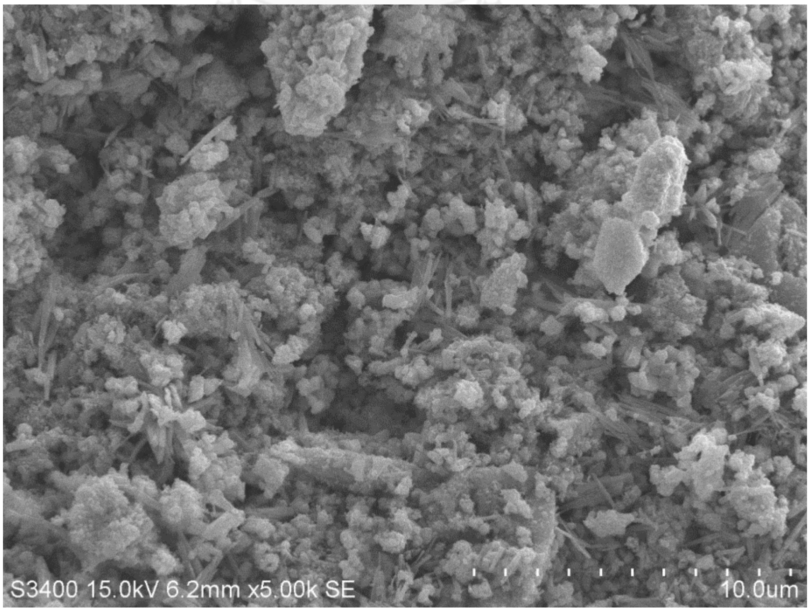


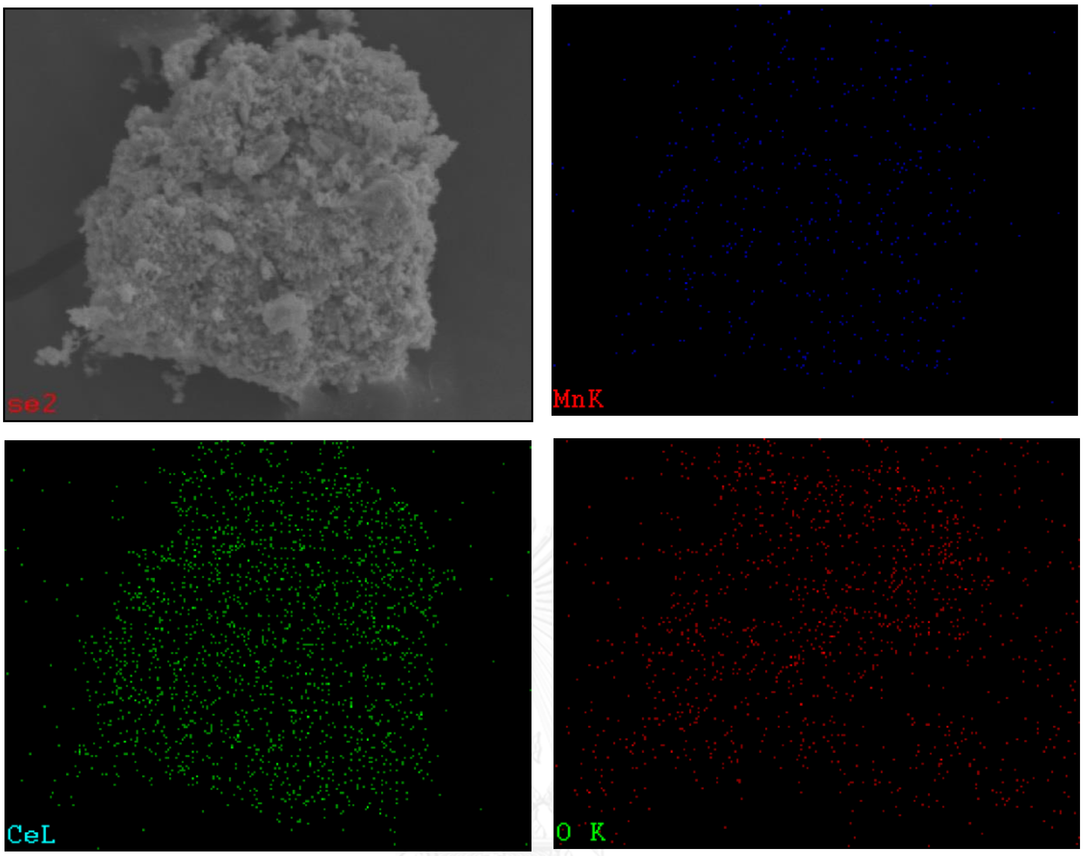
b)



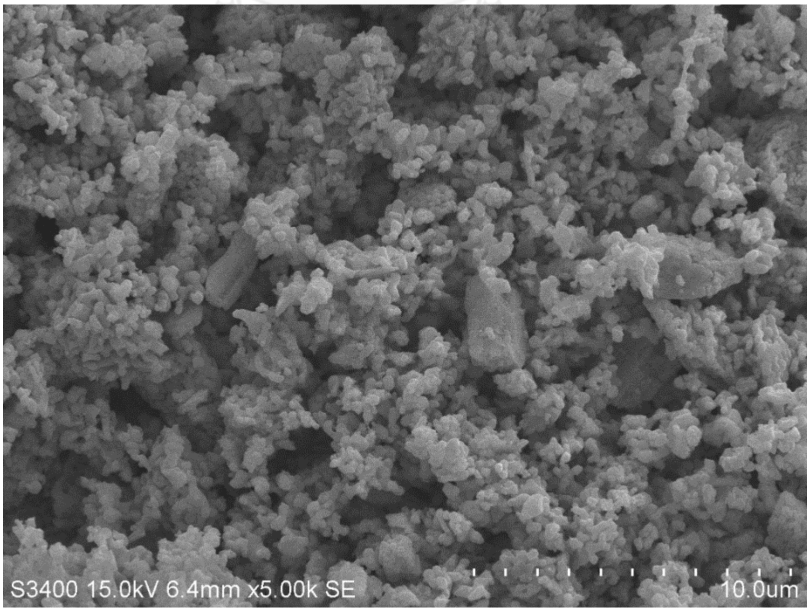


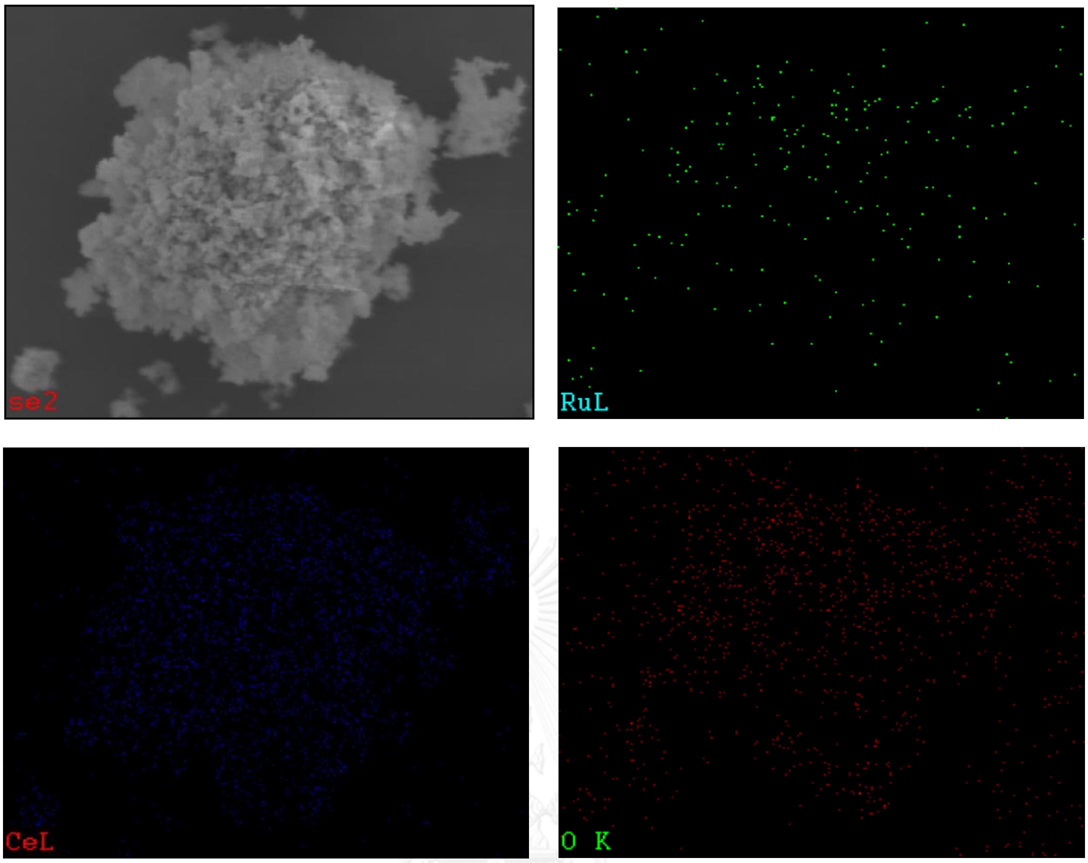
c)



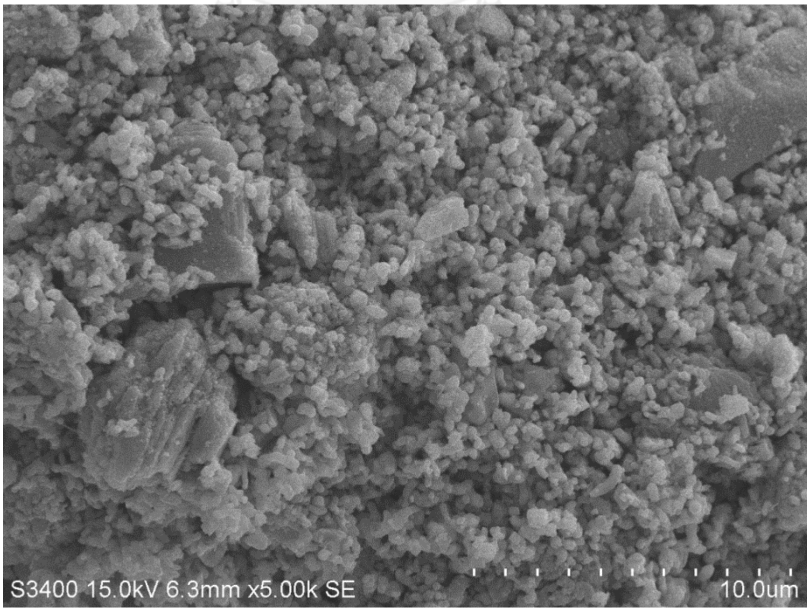


d)





e)



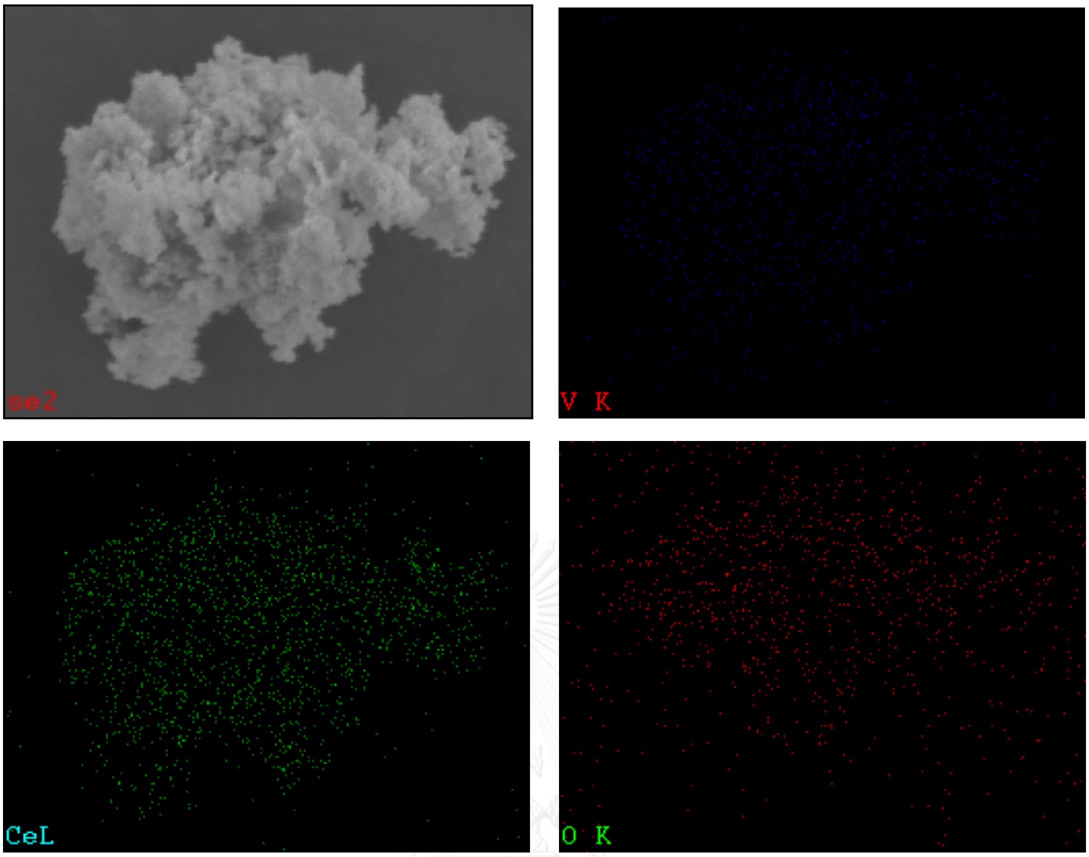
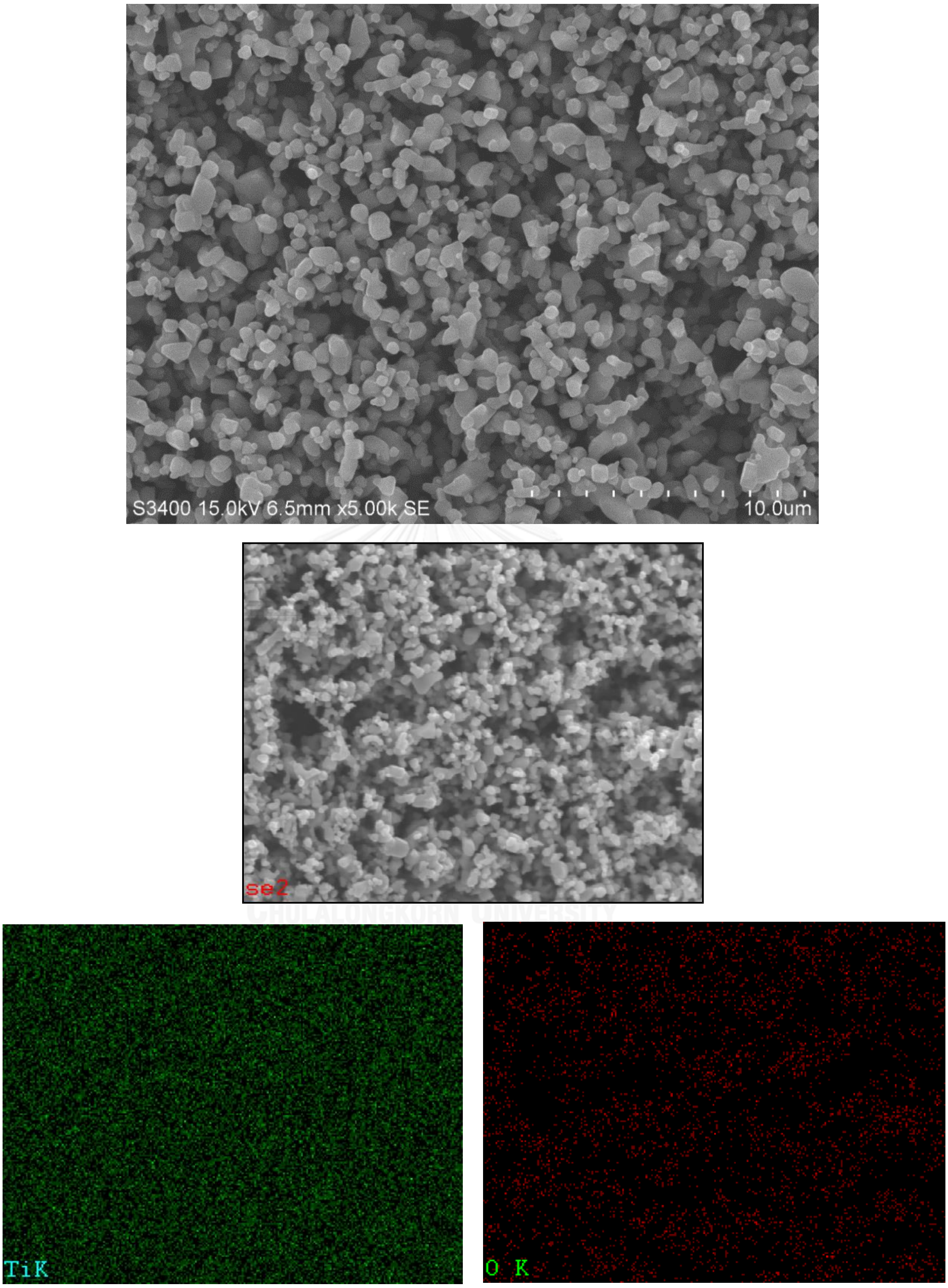


Figure 4.4 Surface morphology and metal mapping of catalysts: a) ceria, b) copper oxide on ceria, c) manganese oxide on ceria, d) ruthenium oxide on ceria and e) vanadium oxide on ceria

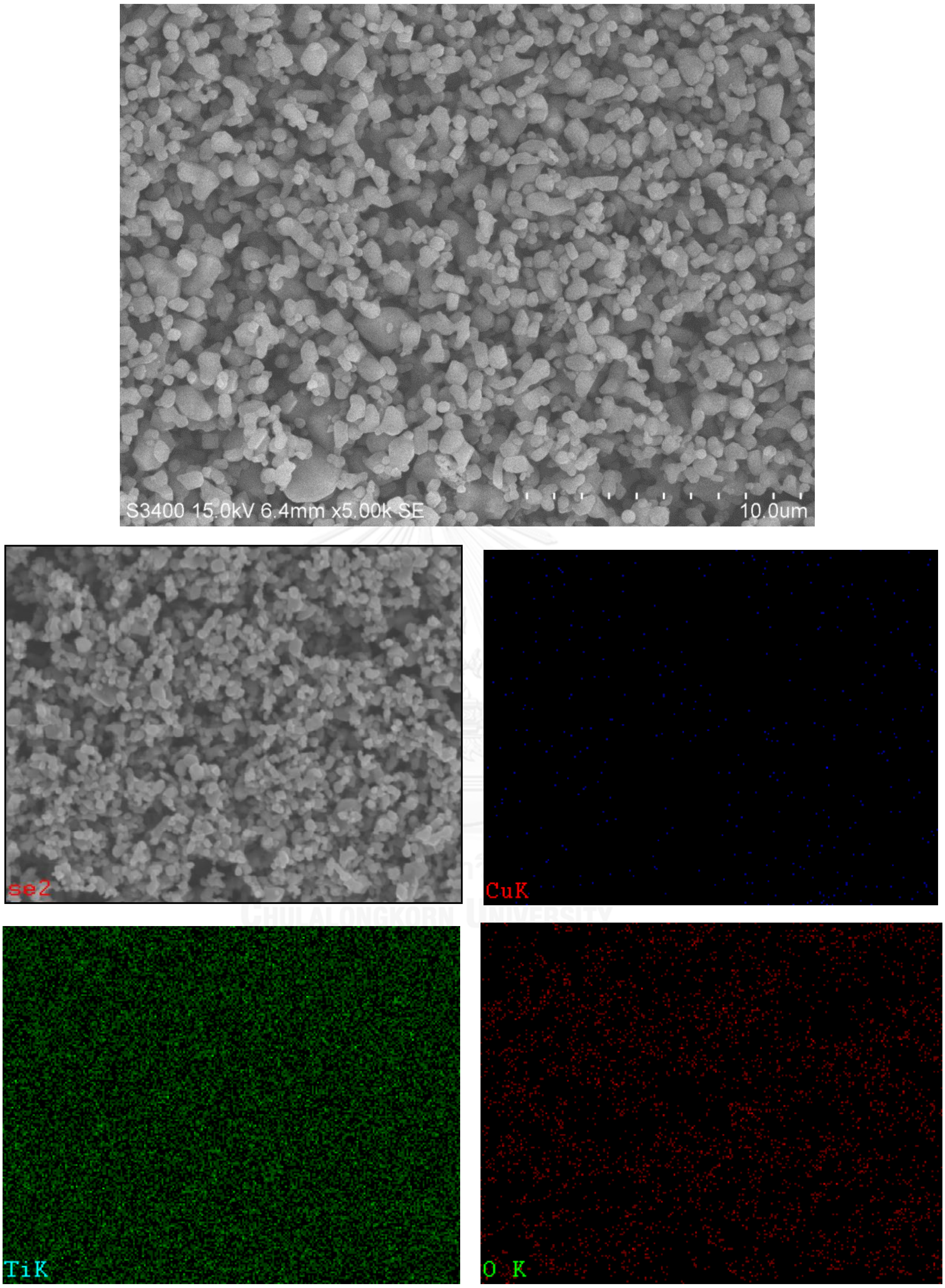
Morphology of titania is fine powder. The average particle diameter is less than 1 micron as shown in Figure 4.5 a). The metal oxides are not clearly observed because the particle diameter of titania small as shown in Figure 4.5 b) to e).

However the metal dispersion of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were observed by SEM-EDX. The metals are well dispersed on the surface of titania as shown in Figure 4.5 b) to e).

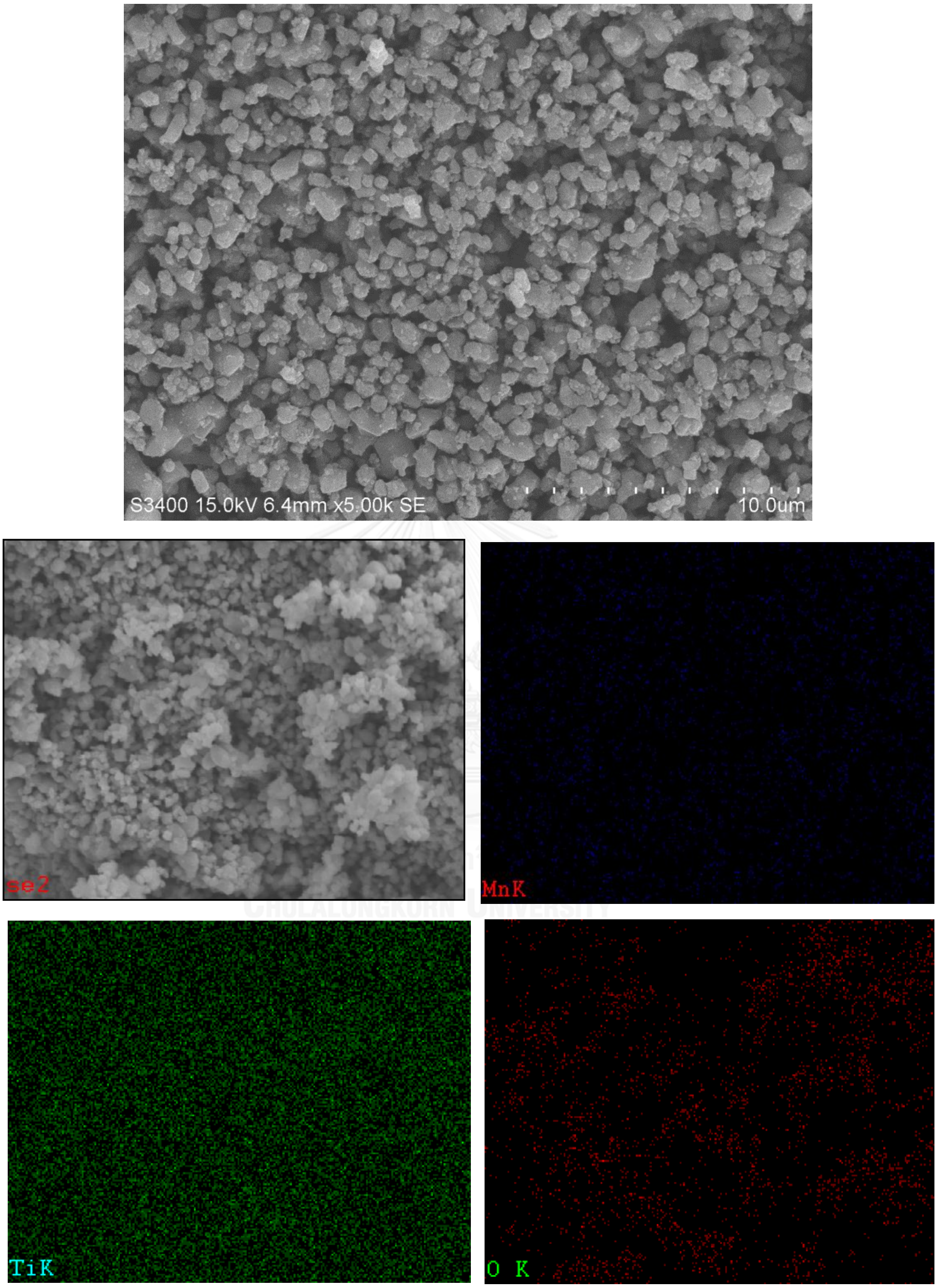
a)



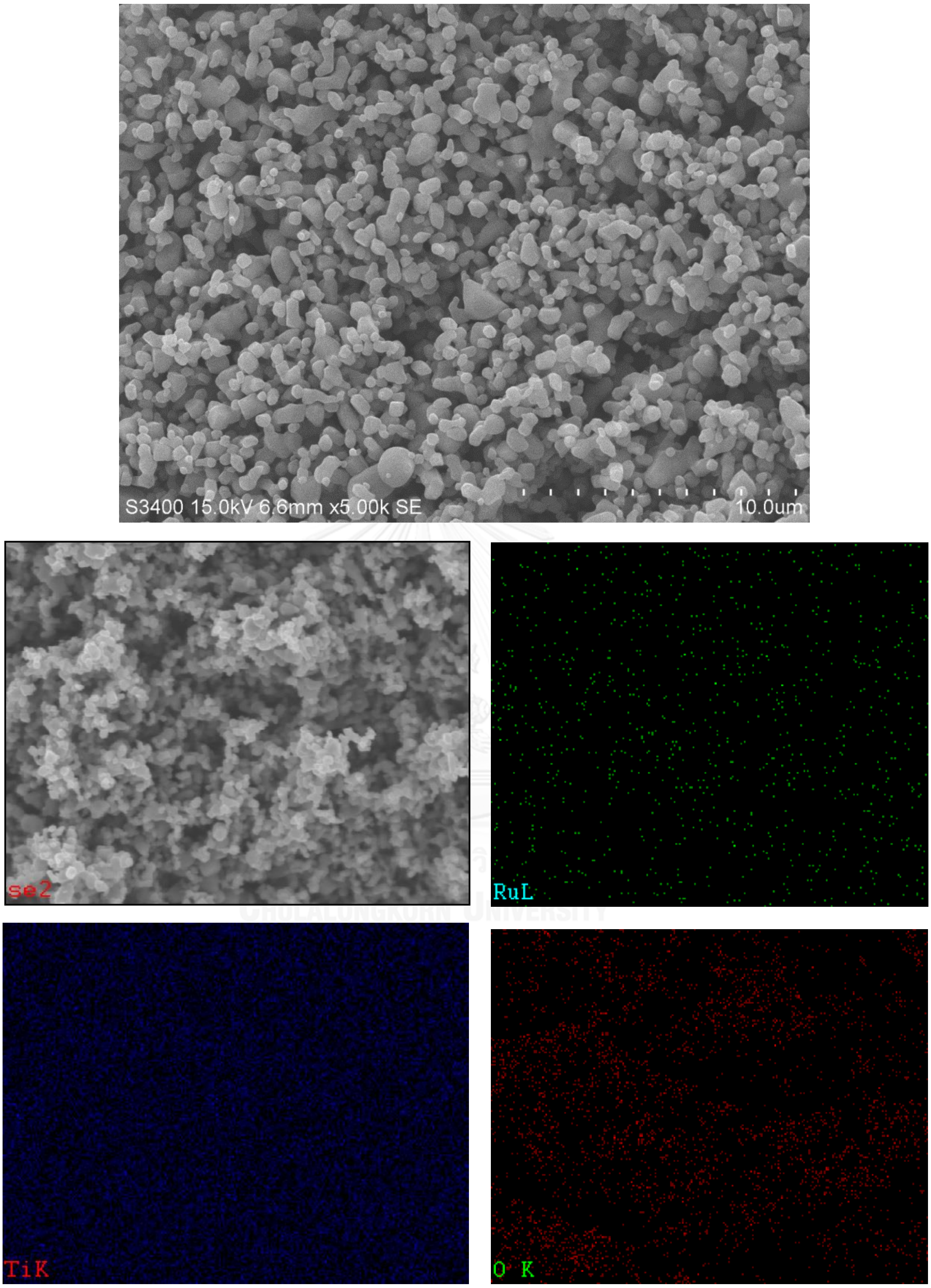
b)



c)



d)



e)

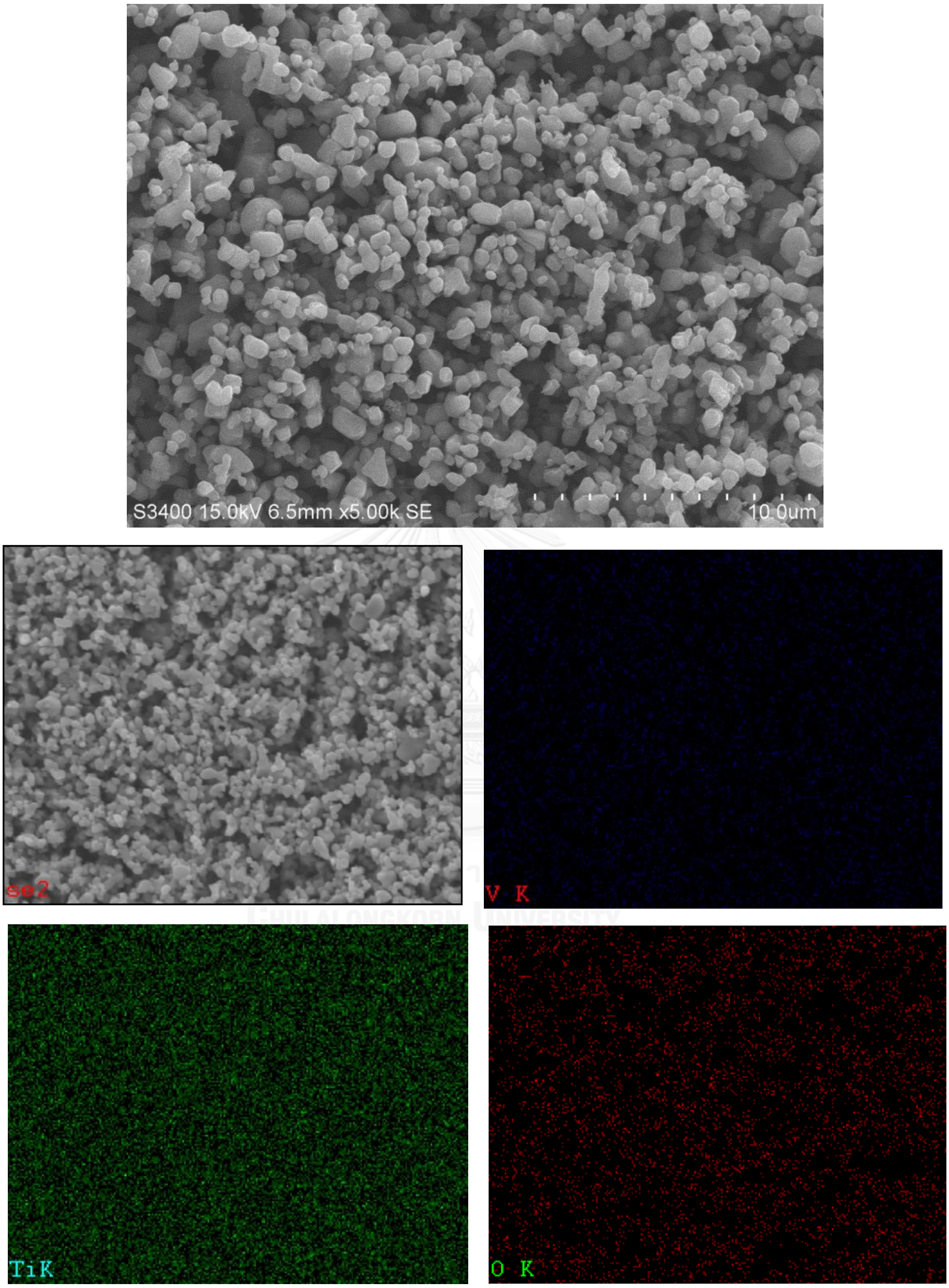


Figure 4.5 Surface morphology and metal mapping of catalysts: a) titania, b) copper oxide on titania, c) manganese oxide on titania, d) ruthenium oxide on titania and e) vanadium oxide on titania

4.1.3 Study of catalyst crystal structure

In order to identify the crystal structure of catalysts after calcination, X-ray diffraction data of each catalyst were collected. The peak pattern of X-ray diffraction is own characteristic for individual crystal structure.

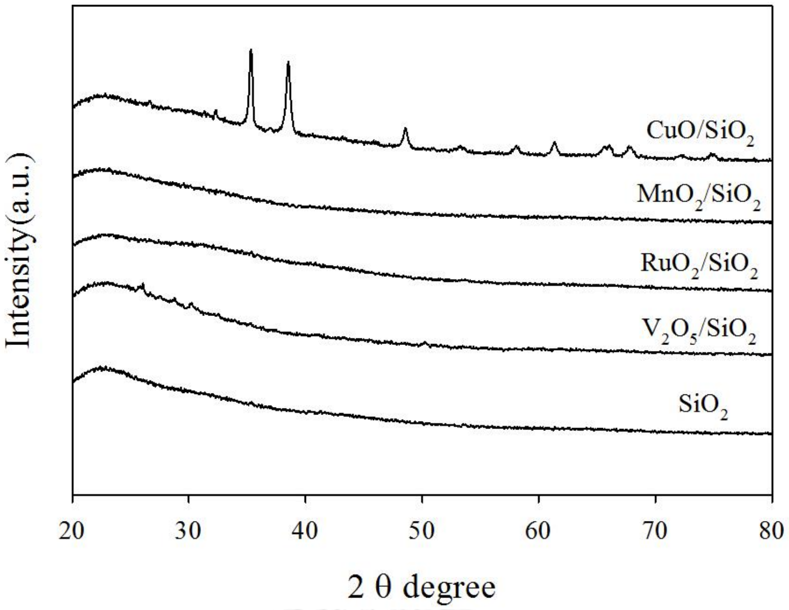
In series of impregnated silica, blank silica showed a broad peak, representing amorphous phase. Shape peaks were observed at 35.5, 38.7and 48.8, representing crystalline phase of copper oxide (CuO) [14]. However, peaks of manganese oxide, ruthenium oxide and vanadium oxide were not observed as shown in Figure 4.6 a).

In series of impregnated alumina, blank alumina showed peaks at 36.9, 45.3 and 66.7, representing structure of gamma-alumina [15]. However, peaks of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were not observed as shown in Figure 4.6 b) due to their highly dispersed form.

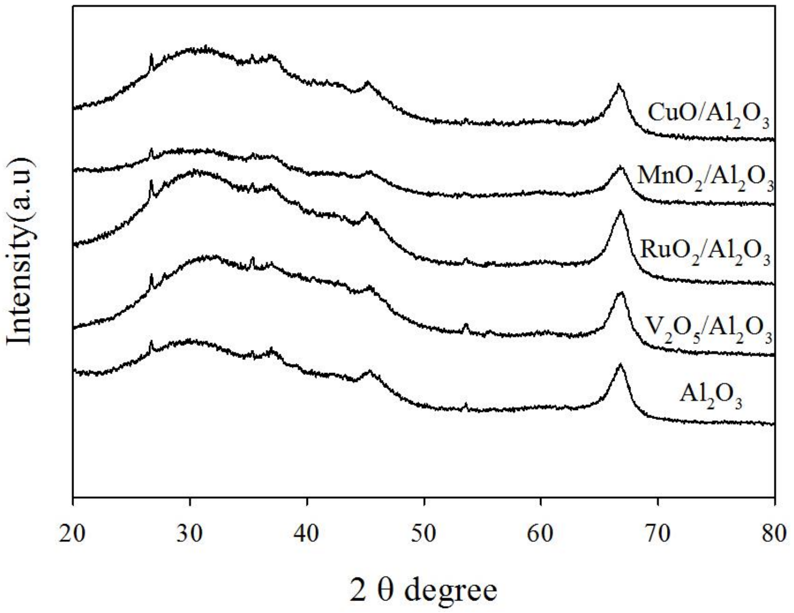
In series of impregnated ceria, blank ceria showed peaks at 28.2, 32.8, 47.3 and 56.1, representing crystalline structure [16]. However, peaks of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were not observed as shown in Figure 4.6 c) due to their highly dispersed form.

In series of impregnated titania, blank titania showed peaks at 25.1, 39.1, 54.1, 56.5, 68.8, 69.6 and 27.3, 35.8, 41.1, 43.8, 62.6, 63.8 representing structure of mixed anatase and rutile structure respectively [17]. However, peaks of copper oxide, manganese oxide, ruthenium oxide and vanadium oxide were not observed as shown in Figure 4.6 d) due to their highly dispersed form.

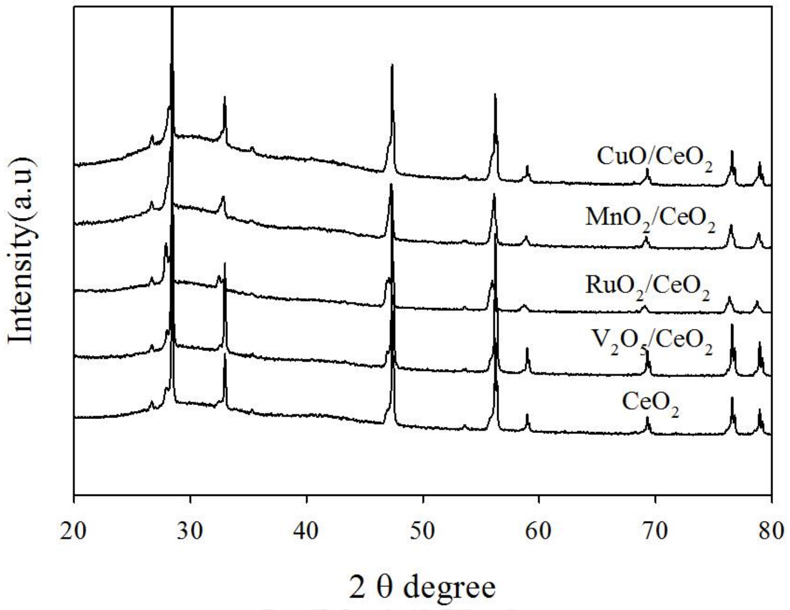
a)


CuO/SiO2
MnO2/SiO2
RuO2/SiO2
V2O5/SiO2
SiO2
Intensity(a.u.)
20
30
40
50
60
70
80
2 θ degree

b)


CuO/Al2O3
MnO2/Al2O3
RuO2/Al2O3
V2O5/Al2O3
Al2O3
Intensity(a.u)
20
30
40
50
60
70
80
2 θ degree

c)



d)

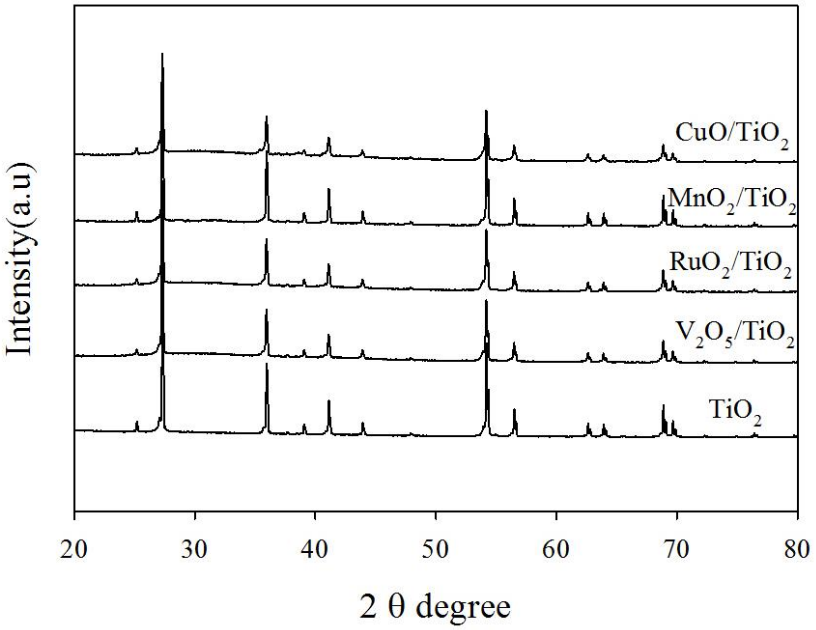


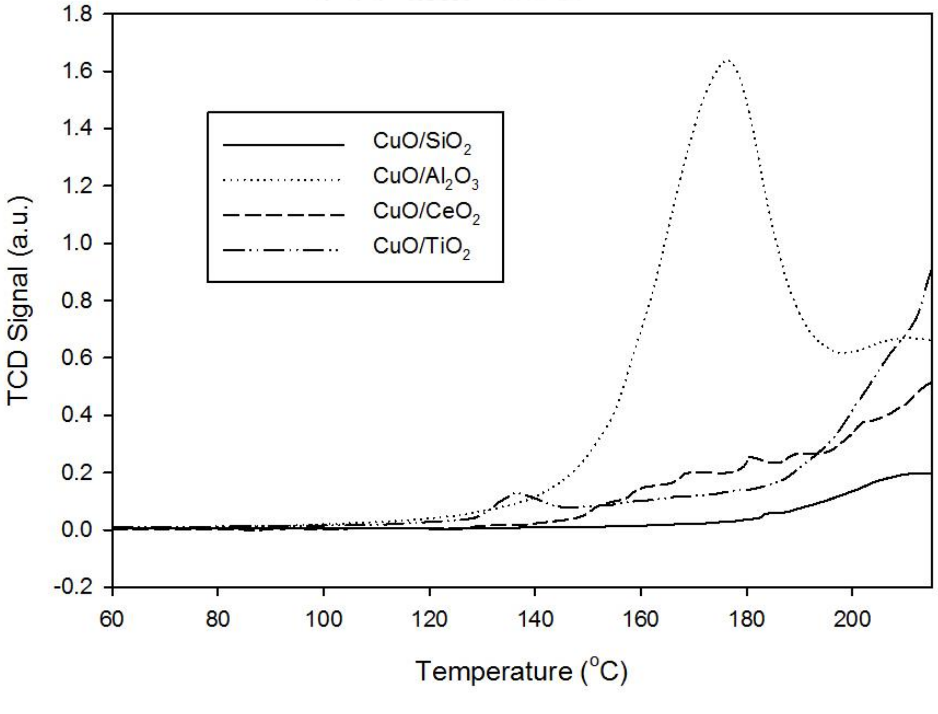
Figure 4.6 Crystal structure of catalysts a) silica support, b) alumina support, c) ceria support and d) titania support

4.1.4 Study of catalyst reduction and oxidation behaviors

Series of copper oxide on various supports such as silica, alumina, ceria and titania and series of various metals such as copper oxide, manganese oxide, ruthenium oxide and vanadium oxide on titania support were selected for comparing the effect of support type and metal oxide type on activity in reduction and oxidation.

Activity in reduction and oxidation of copper oxide on various supports were compared as shown in Figure 4.7 a) and b) respectively. The copper oxide on alumina oxide showed the highest activity in reduction and oxidation at low temperature 100 – 200 °C. However, at high temperature above 200 °C copper oxide on titania and copper oxide on ceria showed higher activity in reduction and oxidation, respectively.

a)



b)

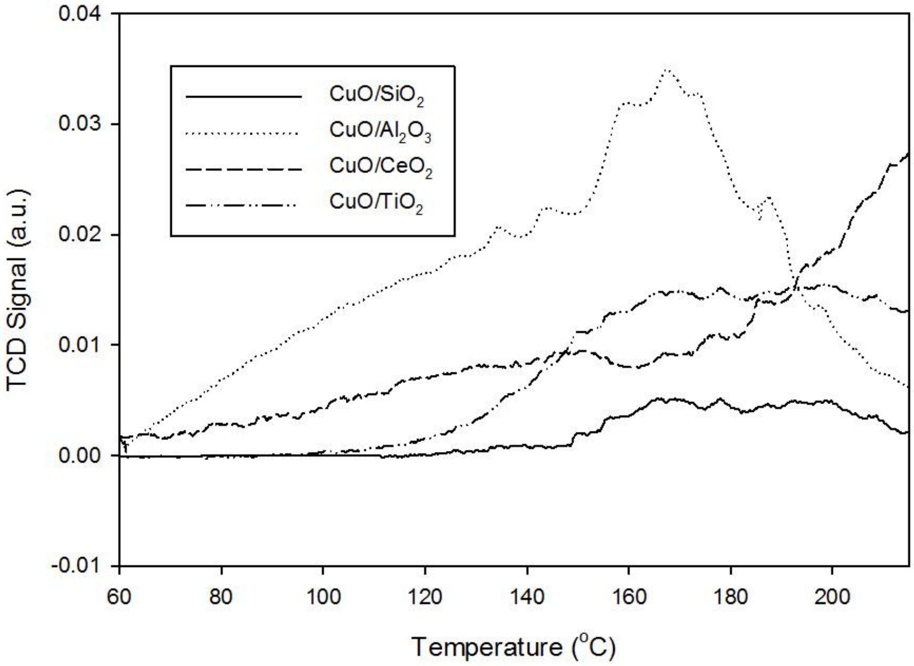


Figure 4.7 Temperature programmed a) reduction, b) oxidation of copper oxide on various supports

Activity in reduction and oxidation of various metals on titania support were compared as shown in Figure 4.8 a) and b), respectively. The copper oxide on titania showed the highest activity in reduction and oxidation at all range of the programed temperature.

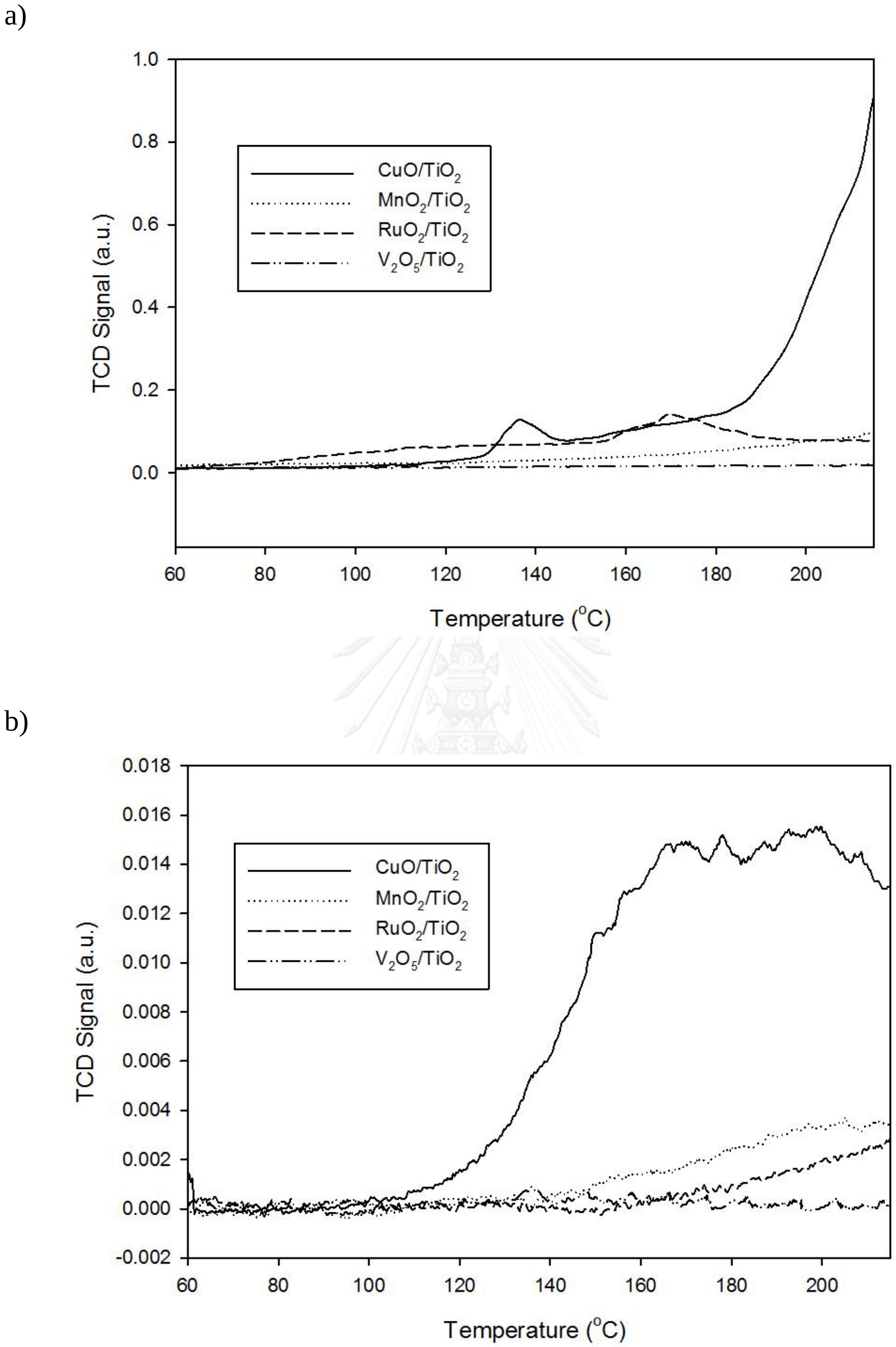


Figure 4.8 Temperature programmed a) reduction, b) oxidation of various metals on titania support

4.2 Kinetic study for non-catalytic wet air oxidation

Before kinetic model development, reaction condition must be verified that the rate of reaction is controlled by intrinsic rate. The rate of reaction might be controlled by rate of mass transfer at condition, for instance too low stirred speed, too high reactants concentration and too high reaction temperature. Therefore, the reaction condition, which is used in developing kinetic model, must be verified.

4.2.1 Effect of stirred speed through rate of oxidation

From series of stirred speed of 0, 150, 300, 450 and 600 rpm, the rate of oxidation was increased from 0.038 to 0.057 mole Na_2S/l.h, while stirred speed was increased from 0 to 450. After stirred speed 450 rpm, the rate of oxidation was stable as shown in Figure 4.9 representing that the rate of reaction was shifted from mass transfer limited to kinetic limited after stirred speed at 450 rpm.

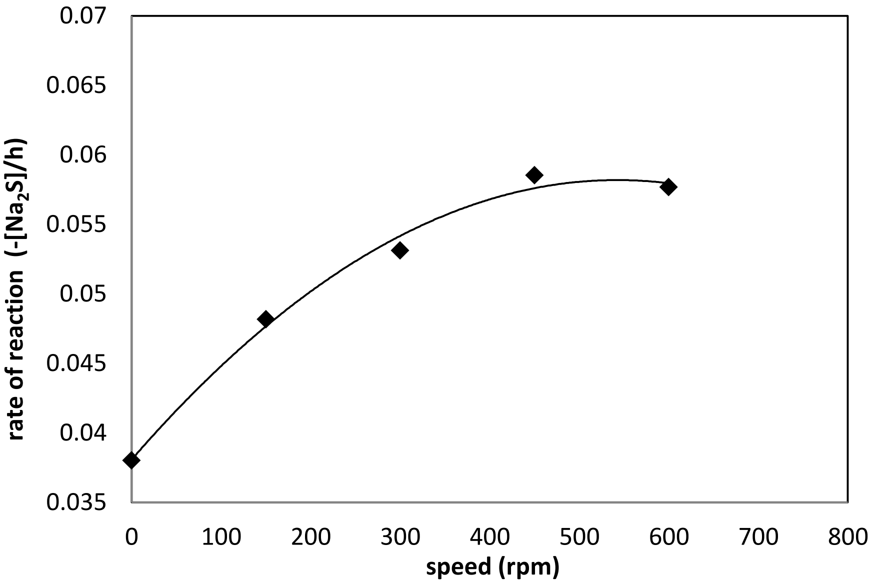


Figure 4.9 Effect of stirred speed through reaction rate of 20 times diluted spent caustic soda at 60°C, 10 bar and oxygen flow rate 300 ml/minute for 5 minutes

After verification, the kinetic model of non-catalytic wet air oxidation in term of power law was determined. Series of reacting time, oxygen partial pressure and temperature of reaction were corrected in order to analyze reaction order of sodium sulfide, oxygen and rate constant. As power law model, the kinetic model of wet air oxidation is function of both concentration of sodium sulfide and oxygen. In order to determine reaction order of each reactant, the concentration of the other reactant must be kept at constant value.

4.2.2 Effect of oxygen flow rate through rate of oxidation

Before determination of reaction order of sodium sulfide, reacting condition that excess oxygen must be verified. Series of reacting condition at oxygen flow rate of 214-375 ml/min were conducted. The rate of oxidation was increased from 0.051 to 0.057 mole Na_2S/l.h, while oxygen flow rate was increased from 214 to 250 ml/min. After oxygen flow rate 250 ml/min, the rate of oxidation was stable as shown in Figure 4.10. The values indicated that the concentration of oxygen was constant, when the oxygen flow rate was adjusted over 250 ml/min.

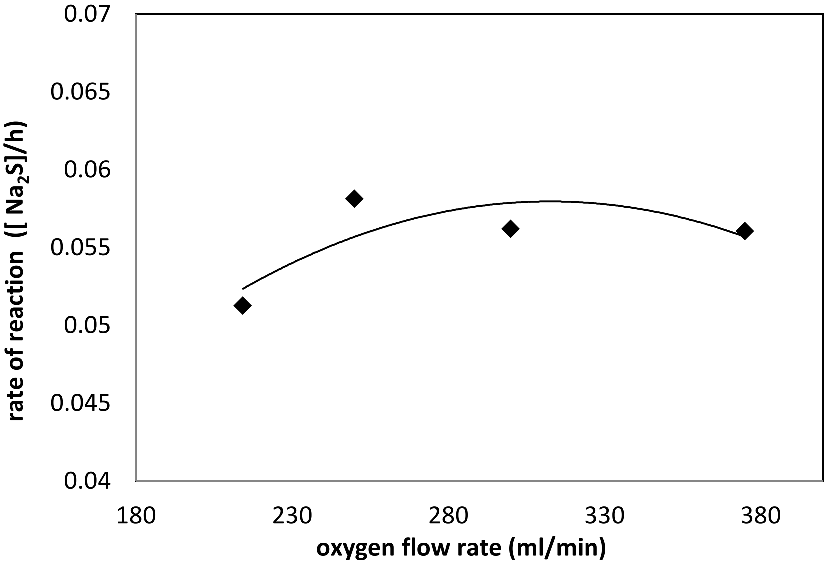


Figure 4.10 Effect of oxygen flow rate through reaction rate of 20 times diluted spent caustic soda at 60°C, 10 bar and oxygen flow rate 300 ml/minute for 5 minutes

4.2.3 Determination of reaction order of sodium sulfide

In order to determine reaction order of sodium sulfide, series of resident time 2, 4, 6, 8 and 10 minute in reaction were conducted. The rates of oxidation were gradually decreased from 0.134 to 0.023 mole Na_2S/l.h, according to lessen of the remaining sodium sulfide reactant. From experimental data, the reaction order of sodium sulfide was 2.10, which was calculated from the slope value of correlation graph between natural logarithm of reaction rate and sodium sulfide concentration as shown in Figure 4.11.

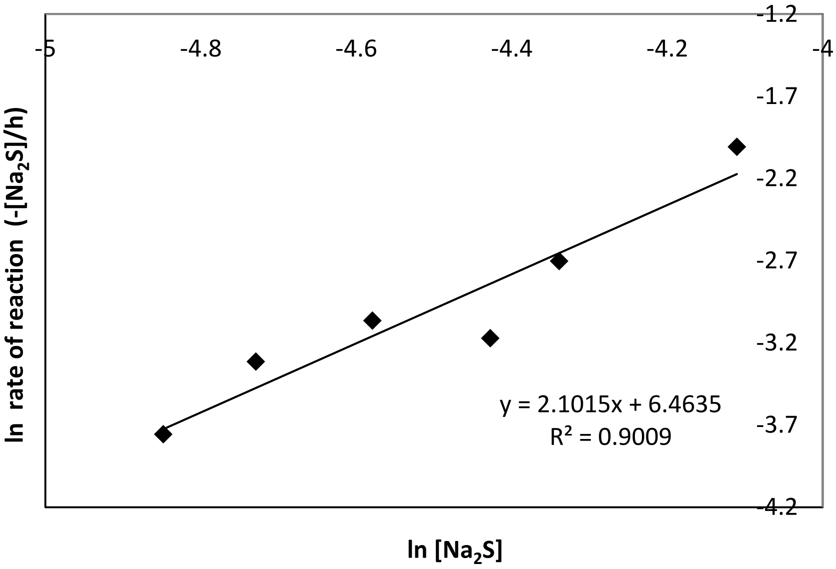


Figure 4.11 Effect of sodium sulfide concentration through reaction rate of 20 times diluted spent caustic soda at 60°C, 10 bar and oxygen flow rate 300 ml/minute

4.2.4 Determination of reaction order of oxygen

The reaction order of oxygen was investigated by initial method. Series of oxygen pressure of 3.3, 6.6 and 10 bar in reaction were conducted. The rates of oxidation were gradually increased from 0.06 to 0.134 mole Na_2S/l.h, according to increasing of the oxygen partial pressure. From experimental data, the reaction order of oxygen was 0.87, which was calculated from the slope value of correlation graph between natural logarithm of reaction rate and oxygen concentration as shown in Figure 4.12.

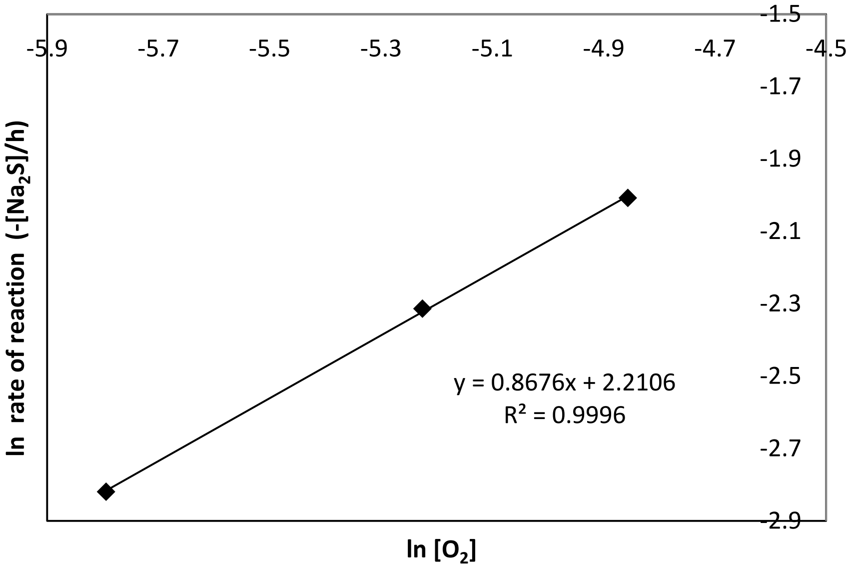


Figure 4.12 Effect of oxygen concentration through reaction rate of 20 times diluted spent caustic soda at 60^{o}C and oxygen flow rate 300 ml/minute

4.2.5 Determination of rate constant

The specific reaction rate was investigated by initial method. Series of reaction temperature between 60, 70 and 80°C were conducted. From analysis of the experimental data, the –Ea/R and pre-exponential factor were determined from slope and intercept value of correlation graph between natural logarithm of rate constant and reaction temperature as shown in Figure 4.13. Activation energy and pre-exponential factor were 16.24 kJ/mole and 2.28E+07, respectively.

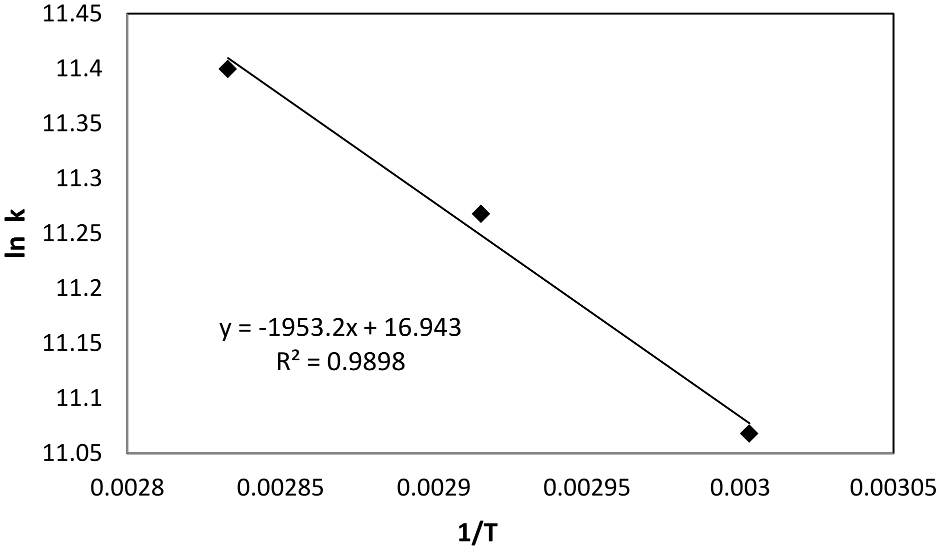


Figure 4.13 Effect of reaction temperature through reaction rate of 20 times diluted spent caustic soda at 10 bar and oxygen flow rate 300 ml/minute

From above data, the kinetic model for spent caustic wastewater can be demonstrated in term of power law as shown in equation 4.1. When compare the reaction order and the activation energy with other researches. Jagushte and Mahajani [6] reported that, the reaction rate of thiosulfate was depended on concentration of thiosulfate and oxygen partial pressure with order 1 and activation energy was 183.31 kJ.mol^{-1}. Chen and Cheng [9] reported that, the reaction rate of refinery spent caustics followed pseudo-first order equations and the activation energy was 45.5 kJ/mol. Reasons that the reaction order and activation energy in this study are not same with the other researches. Because the different in impurity substrate from Jagushte and Mahajani [6], which thiosulfate was used. From Chen and Cheng [9] research, the reaction rate was only functioned of COD value. However, effect of oxygen concentration to reaction rate was ignored.

$$\text{Rate of reaction} = 2.28\text{E} + 07\ \text{EXP}^{-\frac{16240}{\text{RT}}}[\text{Na}_2\text{S}]^{2.10}[\text{O}_2]^{0.87} \qquad (4.1)$$

4.3 Study of catalytic activity of wet air oxidation

As catalyst has various advantages, the potential use of catalytic WAO with catalysts such as copper oxide, manganese oxide, ruthenium oxide and vanadium oxide on silica, alumina, ceria and titania supports were further investigated for enhancing in oxidation reaction.

4.3.1 Activity of catalytic wet air oxidation

In activity testing, 2 grams of catalyst per liter of wastewater were charged to the reactor. Within 30-minute WAO reaction at 70°C and 10 bar of oxygen, the COD value was decreased 33.77%. From catalytic activity, the copper oxide on titania exhibited the highest catalytic activity toward the sodium sulfide oxidation. The conversion was enhanced to 56.13% (increased by 22.36%) as shown in Table 4.2. Series of impregnated ceria and titania showed higher activity than series of impregnated silica and alumina. It might affect from superior activity in reduction and oxidation of ceria and titania.

Table 4.2 Effect of catalytic activity on oxidation

Catalyst	% Conversion	Catalyst	% Conversion
non-catalyst	33.8		
SiO_2	46.5	CeO_2	47.9
CuO/SiO_2	49.9	CuO/CeO_2	55.5
MnO_2/SiO_2	44.3	MnO_2/CeO_2	48.0
RuO_2/SiO_2	47.1	RuO_2/CeO_2	43.1
Al_2O_3	44.1	TiO_2	47.9
CuO/Al_2O_3	46.9	CuO/TiO_2	56.1
MnO_2/Al_2O_3	43.5	MnO_2/TiO_2	49.6
RuO_2/Al_2O_3	43.3	RuO_2/TiO_2	46.2

4.4 Kinetic study for catalytic wet air oxidation

In this step, copper oxide on titania, which showed the highest activity in oxidation of spent caustic wastewater, was selected to study the kinetic model. Series of reacting time, oxygen partial pressure and temperature of reaction were conducted in order to analyze reaction order of sodium sulfide, oxygen and rate constant as same as the step in non-catalytic wet air oxidation.

4.4.1 Effect of catalyst dosage through rate of oxidation

Before developing the kinetic model, series of catalyst dosage of 0, 0.1, 0.2, 0.3, 0.4 and 0.5 gram of copper oxide on titania per liter of wastewater were conducted in order to find the proper weight of catalyst for modelling. From experimental, the rate of oxidation was increased from 0.057 to 0.092 mole Na_2S/l.h, while catalyst dosage was increased from 0 to 0.4 gram per liter of wastewater. After catalyst dosage 0.4 gram per liter of wastewater, the rate of oxidation was stable as shown in Figure 4.14. The values indicated that the reaction rate was limited by mass transfer.

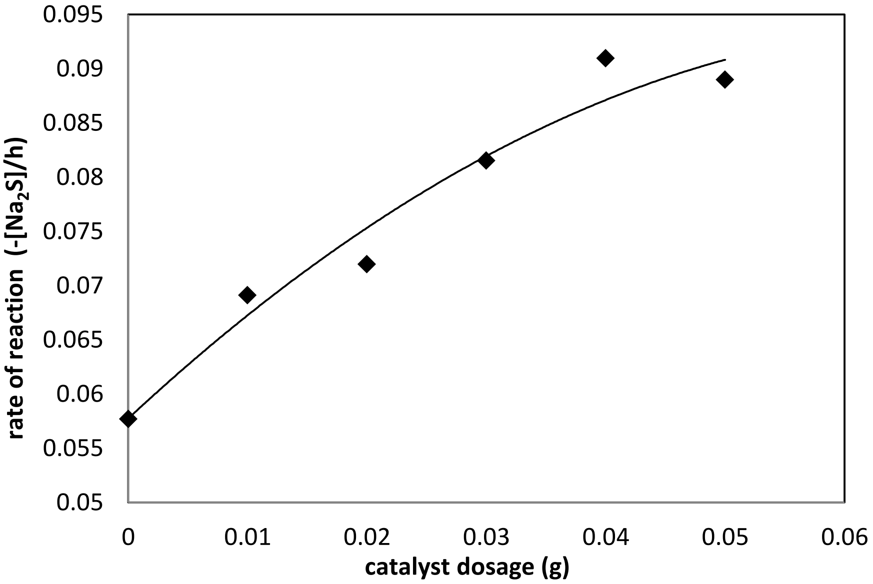


Figure 4.14 Effect of catalyst dosage through reaction rate of 20 times diluted spent caustic soda at 60°C, 10 bar and oxygen flow rate 300 ml/minute for 5 minutes

4.4.2 Determination of reaction order of sodium sulfide with catalytic effect

In order to determine reaction order of sodium sulfide, series of reacting time 2, 4, 6, 8 and 10 minutes in reaction were conducted. Rates of reaction from the experimental were subtracted with rate of reaction from non-catalytic wet air oxidation in order to get rate of reaction from catalyst. The results showed, the rates of reaction were decreased from 0.021 to 0.008 mole Na_2S/l.h, according to lessen of the remaining sodium sulfide reactant. From experimental data, the reaction order of sodium sulfide was 1.50, which was calculated from the slope value of correlation graph between natural logarithm of reaction rate and sodium sulfide concentration as shown in Figure 4.15.

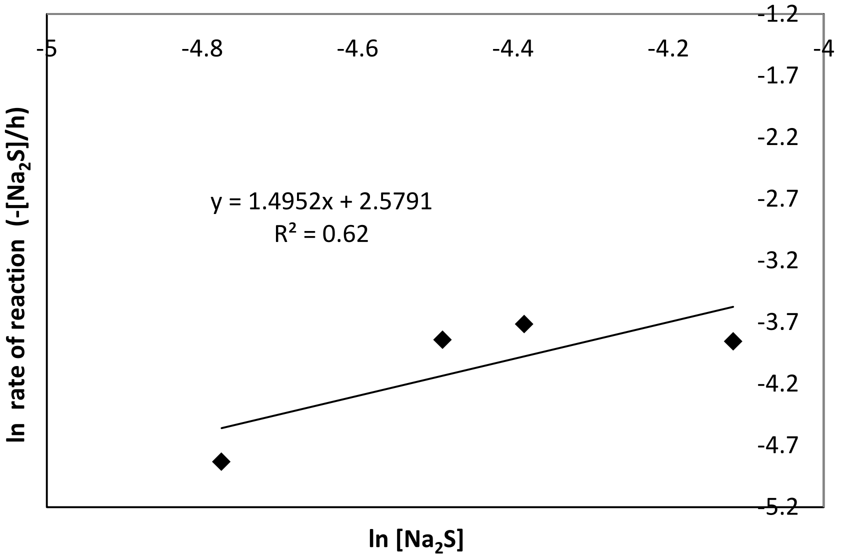


Figure 4.15 Effect of sodium sulfide concentration through reaction rate of 20 times diluted spent caustic soda with 0.2 g copper oxide on titania per liter of wastewater at 60^{o}C, 10 bar and flow oxygen 300 ml/minute

4.4.3 Determination of reaction order of oxygen with catalytic effect

Series of oxygen partial pressure of 3.3, 6.6 and 10 bar were conducted. Rates of reaction from the experimental were subtracted with rate of reaction from non-catalytic wet air oxidation in order to get rate of reaction from catalyst. The results showed, the rates of oxidation were gradually increased from 0.008 to 0.020 mole Na_2S/l.h, according to increasing of the oxygen partial pressure. From experimental data, the reaction order of oxygen was 1.13, which was calculated from the slope value of correlation graph between natural logarithm of reaction rate and oxygen concentration as shown in Figure 4.16.

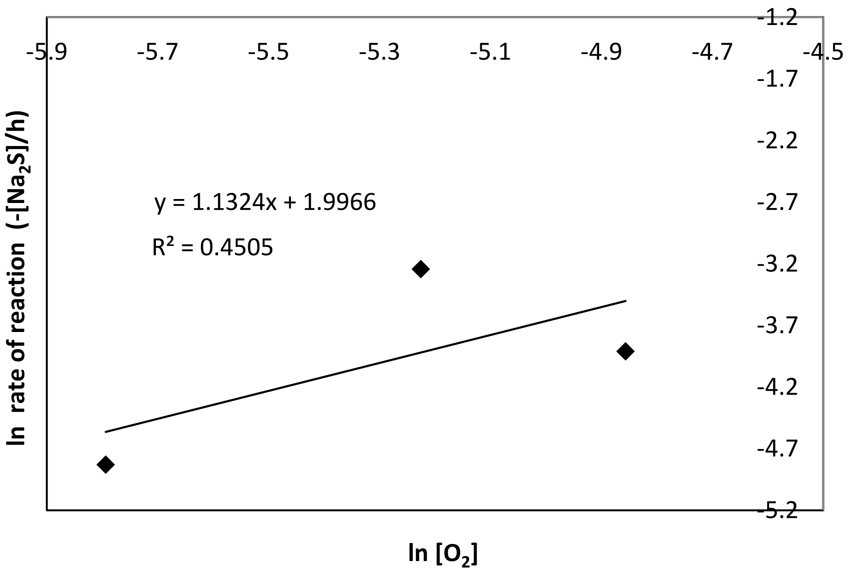


Figure 4.16 Effect of oxygen concentration through reaction rate of 20 times diluted spent caustic soda with 0.2 g copper oxide on titania per liter of wastewater at 60°C, 10 bar and flow oxygen 300 ml/minute

4.4.4 Determination of rate constant with catalytic effect

The specific reaction rate was investigated by initial method. Series of different reaction temperature between 60, 70 and 80°C were conducted. Rates of reaction from the experimental were subtracted with rate of reaction from non-catalytic wet air oxidation in order to get rate of reaction from catalyst. From analysis of the experimental data, the –Ea/R and pre-exponential factor were determined from slope and intercept value of correlation graph between natural logarithm of rate constant and reaction temperature as shown in Figure 4.17. Activation energy and pre-exponential factor were 11.09 kJ/mole and 6.75E+04, respectively.

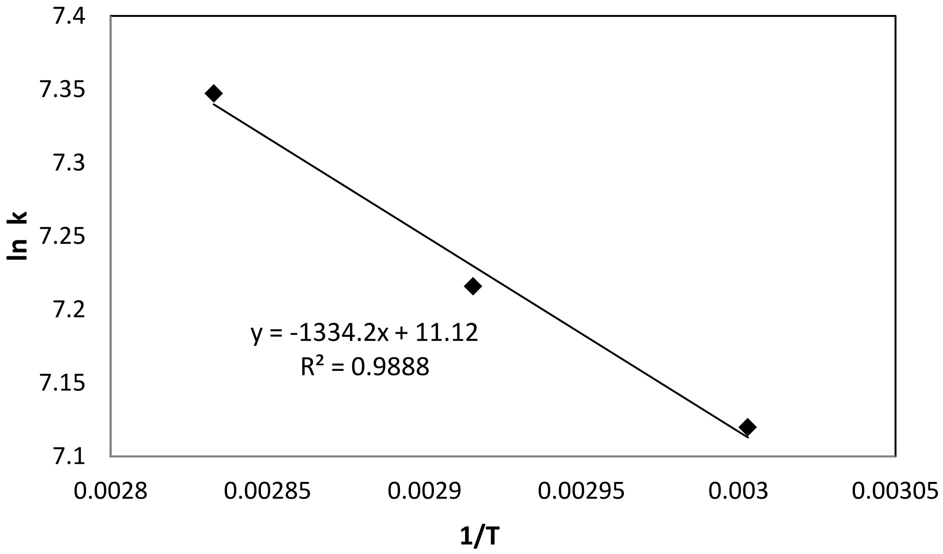


Figure 4.17 Effect of reaction temperature through reaction rate of 20 times diluted spent caustic soda with 0.2 g copper oxide on titania per liter of wastewater at 10 bar and flow oxygen 300 ml/minute

From above data, the kinetic model of catalytic wet air oxidation of spent caustic wastewater can be demonstrated in term of power law as shown in equation 4.2. When compare the reaction order and the activation energy with other researches, Jagushte and Mahajani [6] reported that, reaction rate of thiosulfate was depended on concentration of thiosulfate and oxygen partial pressure with order 1 and 0.5. The activation energy was 110.71 kJ.mol^{-1}. Chen and Cheng [9] reported that, the reaction rate of refinery spent caustics followed pseudo-first order equations and the activation energy was 27.2 kJ/mol. Reasons that the reaction order and activation energy in this study are not same with the other researches. Because the different in impurity substrate from Jagushte and Mahajani [6], which thiosulfate was used. From Chen and

Cheng [9] research, the reaction rate was only functioned of COD value. However, effect of oxygen concentration to reaction rate was ignored.

$$\text{Rate of reaction}\left(\frac{mol/dm^3}{h\,.\,g\,cat}\right) = 6.75\text{E}+04\ \text{EXP}^{-\frac{11090}{\text{RT}}}[\text{Na}_2\text{S}]^{1.50}[\text{O}_2]^{1.13} \times \frac{0.1}{0.02} \quad (4.2)$$

4.5 Feasible study of catalytic wet air oxidation

From above kinetic model, list of equations were input to MATHLAB program in order to find the optimum condition for minimum investment cost of the wet air oxidation reactor.

4.5.1 Non-catalytic wet air oxidation optimization

Basis, decision variables, known variable, equality constraints, inequality constraints and objective as shown below were formulated from experimental data and typical value of materials. Results of the operating condition and reactor size were simulated as follow;

Basis:

- Packed bed reactor
- Excess air (Oxygen concentration is constant)
- Isothermal condition (Constant temperature)
- No pressure drop
- No mass transfer limit

Decision variables:

1. T: the operating temperature of reactor (Celsius)
2. P: the operating pressure of reactor (bar)
3. D: the diameter of reactor (mater)
4. t: the minimum metal thickness of reactor (inch)

Known variables:

1. C0: concentration of sodium sulfide at inlet of reactor = 0.295 mole per liter
2. X: conversion of sodium sulfide at outlet of reactor = 0.9996
3. Q: Volumetric flow rate of the wastewater = 3.5 m^3/h
4. α: reaction order of sodium sulfide = 2 for WAO and 1.5 for CWAO
5. β: reaction order of oxygen = 1

Equality constraints:

1.

$$D = \left[\frac{3.5}{(k_{\mathrm{Non\ cat}})(0.295)[O_2]^1}\left(\left(\frac{1}{1-0.9996}\right)-1\right)\frac{4}{20\pi}\right]^{0.33}$$

As

$$k_{\mathrm{Non\ cat}} = 2.28E+07e^{\frac{-16.24*1000}{8.314T}}$$

$$[O_2] = (-3\times10^{-7}T^3 + 0.0001T^2 - 0.0125T + 1.2182)0.21P$$

2.

$$t = \frac{PD}{2(-28.979\,T + 18817) + 0.8P} + 0.1$$

Inequality constraints:

1. $D \geq 0$
2. $t \geq 0$
3. $T \geq 0$
4. $204 \leq T$
5. $P \geq 0$
6. $33 \leq P$

Objective:

From assumptions, the designed reactor is cylindrical shape. The height is 20 times of its diameter. Density of iron is approximately 8030 kg/m^3. Price per weight of 304 stainless steel plate is approximately 2000 $/metric ton with 10% additional cost for fabrication. The objective function of the simulation is.

$$\text{Minimization of investment cost} = (\pi D \times 20D \times t) \times 8.03 \times 2200 \times 35$$

Result:

Operating temperature = 173^{o}C
Operating pressure = 33 bar
Reactor diameter = 1.1 m
Minimum thickness requires = 0.91 inch
Cost of reactor = 1,119,100 Baht

4.5.2 Catalytic wet air oxidation optimization

The investment cost of catalytic wet air oxidation reactor was calculated from the same assumption of the non-catalytic wet air oxidation. Operating condition of the non-catalytic wet air oxidation reactor was used to calculate weight of required catalyst. Bulk density of catalyst is approximately 800 kg/m^3. Price per weight of catalyst is approximately 3318 Baht/kg and processing cost is 100% of the raw material price.

$$\text{Weight of catalyst (kg)}$$
$$= \frac{3.5/1000}{(\mathrm{k_{Cat}})(0.295)^{0.5}[\mathrm{O_2}]^{1} \times (\frac{0.1}{0.02}) \times 0.5}\left(\left(\frac{1}{(1-0.9996)^{0.5}}\right) - 1\right)$$

As

$$\mathrm{k_{Cat}} = 6.75\mathrm{E}+04\mathrm{e}^{\frac{-11.09*1000}{8.314\mathrm{T}}}$$
$$[\mathrm{O_2}] = (-3\times10^{-7}\mathrm{T}^3 + 0.0001\mathrm{T}^2 - 0.0125\mathrm{T} + 1.2182)0.21\mathrm{P}$$

Objective:

$$\text{investment cost} = \left((\pi \mathrm{D} \times 20\mathrm{D} \times \mathrm{t}) \times 8.03 \times 2200 \times 35\right) + (6636 \times \mathrm{W})$$

Result:

Operating temperature = 163^{o}C

Operating pressure = 33 bar

Catalyst weight = 8 kg

Minimum thickness requires = 0.16 inch

Cost of reactor = 53,744 Baht

From catalytic activity, the investment cost of reactor for treating spent caustic wastewater can be reduced from 1,117,400 to 53,744 baht. However, only investment cost is not enough to decision that catalytic wet air oxidation is a reasonable choice. The life time of catalyst, cost of catalyst regeneration and cost of catalyst replacement should be taken into account.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research was focused on the oxidation catalyst in the heterogeneous catalyst system for treating spent caustic wastewater. Various metals such as copper, manganese, vanadium and ruthenium were impregnated on commercial supports such as silica, alumina, ceria and titania. The catalysts were characterized upon physical and chemical properties by BET, SEM&EDX, XRD, TPR and TPO analysis technique. The silica and alumina catalysts are mesoporous material (type IV). The average particle sizes are 100 micron. The metals are well dispersed on surface of supports. From XRD results, the catalysts are identified as amorphous silica and gamma-alumina. Only peak of copper oxide on silica was detected. The ceria and titania catalysts are non-porous material. The average particle sizes are less than 1 micron. The metals are well dispersed on surface of supports. From XRD results, the catalysts are identified as crystalline ceria and mixed rutile-anatase titania.

The potential catalysts were further investigated in oxidation at 70°C, 10 bar of oxygen and reaction time of 30-minute. At non-catalytic condition, the COD value was decreased by 34%. From catalytic activity, the copper oxide on titania exhibited the highest catalytic activity toward the sodium sulfide oxidation. The conversion of sodium sulfide was enhanced to 56% (increased by 22%). The series of ceria and titania catalyst showed higher activity than series of silica and alumina catalysts. It might affect from superior behavior in reduction and oxidation of ceria and titania.

Series of experiments were conducted for developing the kinetic model of non-catalytic and catalytic wet air oxidation. Empirical kinetic model in form of power law was evaluated by collecting batch data. The result showed that the reaction order of sodium sulfide and oxygen followed 2.10 and 0.87, respectively. The activation energy was 16.24 kJ per mole for non-catalytic wet air oxidation. The reaction order of sodium sulfide and oxygen followed 1.50 and 1.13, respectively. The activation energy was 11.09 kJ per mole for catalytic wet air oxidation.

The kinetic models were used in optimization simulation for feasible study. The operating pressure and temperature were driven to upper boundary of the input constraints in order to minimize the reactor investment cost. From catalytic activity, the reactor diameter was decreased. The estimated investment cost of reactor and catalyst of catalytic wet air oxidation is 53,744 baht, reduced from 1,117,400 baht of the conventional reactor. However, only investment cost is not enough to decision that catalytic wet air oxidation is a reasonable choice. The life time of catalyst, cost of catalyst regeneration and cost of catalyst replacement should be taken into account.

5.2 Recommendations

As many catalysts were determined the activity in oxidation, stirred reactor is the simplest type of reactor for the reaction. Because this reactor type is easy for system setup and small amount of catalyst required. Moreover, the method in order to analyze the result is less complicated than packed bed reactor. However, in actual plant, packed bed reactor is more widely used because catalyst separation unit is not required. Therefore, experiments of the catalytic activity in packed bed reactor should be studied in more detail. Especially copper oxide on alumina, which showed superior behaviors to reduction and oxidation at low temperature, might perform good activity in packed bed reactor.

Not only catalytic activity is important factor in reaction, but stability of the catalyst is also significant. In actual plant, practical catalyst must have reasonable life time in reaction, because plant is always continuously operated. Frequently unit shutdown and a lot of maintenance work in catalyst replacement are needed for catalyst, which has rapidly deactivation. Moreover, more energy is consumed during operating reactor. Increasing the operating temperature is unavoidable in order to keep the conversion. Thus, more detail to determine stability of the catalyst should be considered.

Catalytic wet air oxidation is three phases reaction. Mass transfer of reactants, for instance oxygen from gas phase to liquid phase and reactants from bulk liquid into active site in pore of catalyst, are a complicated topic to design. Even rate of reaction is promoted by catalyst, but the rate of reaction might be limited by rate of mass transfer. More detail in reactor design and pilot scale testing are worth to pay attention.

The wet air oxidation is mildly exothermic reaction. In actual condition, the reaction rate along the bed is usually different due to the heat of reaction. Temperature gradient is found especially in packed bed reactor. Therefore, Non-isothermal reaction is recommended for basis of calculation before commercialized. More complicated in reactor design is required

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APPENDIX

APPENDIX A

UV-VISIBLE SPECTOSCOPY

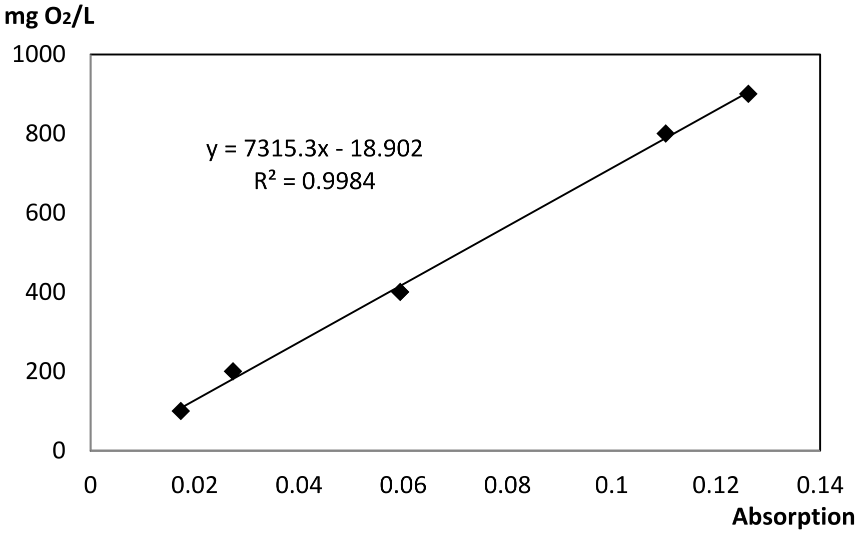

Figure A.1 Calibration curve of standard solution for COD

Table A.1 Calibration curve of standard solution for COD

COD	
mgO_2/l	**Absorption**
100	0.0174
200	0.0274
400	0.0595
800	0.1104
900	0.1263

Table A.2 Effect of stirred speed through reaction rate of 20 times diluted spent caustic soda at 60°C, 10 bar and oxygen flow rate 300 ml/minute for 5 minutes

		COD	**conc.**	**rate**
Parameter	**Absorption**	**mgO2/l**	**mol Na_2S/l**	**mol $Na_2S/l.h$**
pure 50%	0.0739	1043.35	0.0163	
speed 0	0.1175	840.68	0.0131	0.038
speed 150	0.1101	786.58	0.0123	0.048
speed 300	0.1065	760.17	0.0119	0.053
speed 450	0.1025	731.21	0.0114	0.059
speed 600	0.1032	735.78	0.0115	0.058

Table A.3 Effect of oxygen flow rate through reaction rate of 20 times diluted spent caustic soda at 60^{o}C, 10 bar and oxygen flow rate 300 ml/minute for 5 minutes

		COD	**conc.**	**rate**
Parameter	**Absorption**	**mgO$_2$/l**	**mol Na$_2$S/l**	**mol Na$_2$S/l.h**
pure	0.0642	958.00	0.0150	
214	0.0962	684.80	0.0107	0.0512
250	0.0912	648.23	0.0101	0.0581
300	0.0926	658.47	0.0103	0.0562
375	0.0927	659.20	0.0103	0.0560

Table A.4 Effect of sodium sulfide concentration through reaction rate of 20 times diluted spent caustic soda at 60^{o}C, 10 bar and oxygen flow rate 300 ml/minute

		COD	**conc.**	**Rate**	**ln -dC/dt**	**ln Ca**
Parameter	**Absorption**	**mgO$_2$/l**	**mole Na$_2$S/l**	**mole Na$_2$S/l.h**	**mole Na$_2$S/l.h**	**mole Na$_2$S/l**
pure 50%	0.074	1050	0.0164	0.1341	-2.008	-4.110
2 min	0.1168	835	0.0131	0.0669	-2.704	-4.339
4 min	0.1071	765	0.0119	0.0418	-3.174	-4.427
6 min	0.0924	657	0.0103	0.0466	-3.065	-4.579
8 min	0.0799	566	0.0088	0.0363	-3.315	-4.729
10 min	0.0712	502	0.0078	0.0233	-3.759	-4.848

Table A.5 Effect of oxygen concentration through reaction rate of 20 times diluted spent caustic soda at 60°C and oxygen flow rate 300 ml/minute

Parameter	Abs.	COD	Conc.	Rate	ln -dC/dt	ln Ca
		mgO$_2$/l	mole Na$_2$S/l	mole Na$_2$S/l.h	mole Na$_2$S/l.h	mole Na$_2$S/l
pure 50%	0.074	1050	0.0164	0.1342	-2.008	-4.856
10bar2min	0.117	835	0.0131			
10bar4min	0.107	765	0.0119			
pure 50%	0.074	1050	0.0164	0.0989	-2.314	-5.225
6.6bar2min	0.123	880	0.0138			
6.6bar4min	0.111	792	0.0124			
pure 50%	0.074	1050	0.0164	0.0596	-2.820	-5.794
3.3bar2min	0.131	941	0.0147			
3.3bar4min	0.121	868	0.0136			

Table A.6 Effect of reaction temperature through reaction rate of 20 times diluted spent caustic soda at 10 bar and oxygen flow rate 300 ml/minute

Parameter	Abs.	COD	Conc.	Rate	a	[O$_2$]	b
		mgO$_2$/l	mole Na$_2$S/l	mole Na$_2$S/l.h		mgO$_2$/l	
Pure 50%	0.074	1050	0.0164	0.134	2	0.0078	1
2 min	0.117	835	0.0131				
4 min	0.107	765	0.0119				
pure 50%	0.074	1050	0.0164	0.141	2	0.0067	1
70 C 2 min	0.115	822	0.0128				
70 C 4 min	0.104	742	0.0116				
pure 50%	0.074	1050	0.0164	0.140	2	0.0058	1
80 C 2 min	0.115	819	0.0128				
80 C 4 min	0.101	722	0.0113				

Parameter	k	lnk	1/T	Ea	A
				kJ/mol	
60 C	64081	11.068	0.003	16.24	2.28E7
70 C	78261	11.268	0.003		
80 C	89292	11.400	0.003		

Table A.7 Effect of catalyst dosage through reaction rate of 20 times diluted spent caustic soda at 60^{o}C, 10 bar and oxygen flow rate 300 ml/minute for 5 minutes

		COD	**Conc.**	**Rate**
Parameter	**Absorption**	**mgO$_2$/l**	**mole Na$_2$S/l**	**mole Na$_2$S/l.h**
pure 50%	0.0696	999	0.0156	
0 g	0.0971	691	0.0108	0.0577
0.01 g	0.0888	631	0.0099	0.0691
0.02 g	0.0867	615	0.0096	0.0720
0.03 g	0.0797	564	0.0088	0.0815
0.04 g	0.0729	514	0.0080	0.0910
0.05 g	0.0743	525	0.0082	0.0890

Table A.8 Effect of sodium sulfide concentration through reaction rate of 20 times diluted spent caustic soda with 0.2 g copper oxide on titania per liter of wastewater at 60^{o}C, 10 bar and flow oxygen 300 ml/minute

		COD	**conc.**	**Rate**	**ln -dC/dt**	**ln Ca**
Parameter	**Absorption**	**mgO$_2$/l**	**mole Na$_2$S/l**	**mole Na$_2$S/l.h**	**mole Na$_2$S/l.h**	**mole Na$_2$S/l**
pure 50%	0.0739	1043	0.0163	0.154	-1.869	-4.116
2 min	0.1116	797	0.0125	0.076	-2.573	-4.385
4 min	0.1007	718	0.0112	0.060	-2.808	-4.491
6 min	0.0838	540	0.0084	0.058	-2.846	-4.775
8 min	0.0651	470	0.0073	0.028	-3.577	-4.914
10 min	0.0601	421	0.0066	0.018	-4.004	-5.025

Table A.9 Effect of oxygen concentration through reaction rate of 20 times diluted spent caustic soda with 0.2 g copper oxide on titania per liter of wastewater at 60^{o}C, 10 bar and flow oxygen 300 ml/minute

Parameter	**Abs.**	**COD**	**Conc.**	**Rate**	**ln -dC/dt**	**ln Ca**
		mgO_2/l	**mole Na_2S/l**	**mole Na_2S/l.h**	**mole Na_2S/l.h**	**mole Na_2S/l**
pure 50%	0.074	1043	0.0163	0.1542	-1.869	-4.856
2 min	0.112	797	0.0125			
4 min	0.101	718	0.0112			
pure 50%	0.074	1043	0.0163	0.1379	-1.981	-5.225
6.6bar2min	0.114	816	0.0127			
6.6bar4min	0.101	721	0.0113			
pure 50%	0.074	1043	0.0163	0.0676	-2.694	-5.794
3.3bar2min	0.128	918	0.0143			
3.3bar4min	0.116	831	0.0130			

Table A.10 Effect of reaction temperature through reaction rate of 20 times diluted spent caustic soda with 0.2 g copper oxide on titania per liter of wastewater at 10 bar and flow oxygen 300 ml/minute

Parameter	**Abs.**	**COD**	**Conc.**	**Rate**	**a**	**[O2]**	**B**
		mg O_2/l	**mole Na_2S/l**	**mole Na_2S/l.h**		**mg O_2/l**	
pure 50%	0.074	1043	0.0163	0.154	2	0.0078	1
2 min	0.112	797	0.0125				
4 min	0.101	718	0.0112				
pure 50%	0.074	1043	0.0163	0.160	2	0.0067	1
70 C 2 min	0.110	787	0.0123				
70 C 4 min	0.099	702	0.0110				
pure 50%	0.074	1043	0.0163	0.159	2	0.0058	1
80 C 2 min	0.109	781	0.0122				
80 C 4 min	0.094	670	0.0105				

Parameter	**k**	**lnk**	**1/T**	**Ea**	**A**
				kJ/mole	
60C	74581	11.220	0.0030	15.60	2.10E7
70C	89917	11.407	0.0029		
80C	102586	11.538	0.0028		

APPENDIX B

MATHLAB SIMULATION

Optimization simulation of non-catalytic wet air oxidation reactor is shown as follow:

Objective:

```
function [ f ] = obj( x )
f=(3.14*x(1)*20*x(1)*x(2)*2.54/100*8.03*2000*35);

end
```

Constraints:

```
function [ c,ceq ] = cons( x )
%Nonlinear inequality constraints
c = [-x(1);-x(2);-x(3);-x(4);x(3)-204;x(4)-33];
%Nonlinear equality constraints
ceq = [x(1)-(((3.5*1000)/(2.28E+07*exp(-16.24*1000/8.314/(x(3)+273)))/0.295/((-
3E-07*x(3)^3+0.0001*x(3)^2-
0.0125*x(3)+1.2182)/22.4*0.21/34*x(4))^1/1000*((1/(1-0.999577922077922))-
1))/5/3.14)^0.33;x(2)-(x(4)*14.7*x(1)*100/2.54/((2*12900)+(0.8*x(4)*14.7)))-0.1];

end
```

Command window:

```
x0=[100 1 200 30]; % Starting guess
f=obj(x0) %The values at starting point
[c,ceq]=cons(x0)
options=optimoptions('fmincon','Algorithm','interior-point');
[x,fval]=fmincon(@obj,x0,[],[],[],[],[],[],@cons,options)
value(x)
```

Optimization simulation of non-catalytic wet air oxidation reactor is shown as follow:

Objective:

```
function [f] = objj(x)
f=(3.14*((x(1)/800/3.14*4/20)^0.3333)*20*((x(1)/800/3.14*4/20)^0.3333)*x(2)*2.54
/100*8.03*2000*35)+(x(1)*3318);


end
```

Constraints:

```
function [ c,ceq ] = conss( x )
%Nonlinear inequality constraints
c = [-x(1);-x(2);-x(3);-x(4);x(3)-204;x(4)-33];
%Nonlinear equality constraints
ceq = [x(1)-((3.5*1000)/0.295^0.5/((-3E-07*x(3)^3+0.0001*x(3)^2-
0.0125*x(3)+1.2182)/22.4*0.21/34*x(4))^1*((1/(1-0.999577922077922)^0.5)-
1)/0.5/0.1*0.02/(6.75E+04*exp(-11.09*1000/8.314/(x(3)+273)))/1000);x(2)-
(x(4)*14.7*((x(1)/800/3.14*4/20)^0.3333)*100/2.54/((2*12900)+(0.8*x(4)*14.7)))-
0.1];

end
```

Command window:

```
x0=[100 1 200 30]; % Starting guess
f=objj(x0) %The values at starting point
[c,ceq]=conss(x0)
options=optimoptions('fmincon','Algorithm','interior-point');
[x,fval]=fmincon(@objj,x0,[],[],[],[],[],[],@conss,options)
value(x)
```

VITA

Mr. Witat Juengwatanakij was born on June 28, 1987 in Chonburi, Thailand. After graduated from Trium udom suksa pattanakarn College in 2004, he spent his 4 years for study in a Bachelor of Chemical engineering at Chulalongkorn University. After graduated, he worked at PTT global chemical company for 5 years. Afterward, he continued his Master's degree at Department of Chemical Engineering at Chulalongkorn University and joined the Center of Excellence on Catalysis and Catalytic Reaction Engineering in 2015.