ปฏิกิริยาออกซิเดชันแบบเลือกเกิดของ 1-โพรพานอล บนตัวเร่งปฏิกิริยา โลหะทรานซิชันออกไซด์ที่มีการเติมแมกนีเซียมออกไซด์ลงไป

นายวีรวัฒน์ มโนมัยวิบูลย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

SELECTIVE OXIDATION OF 1-PROPANOL OVER MAGNESIUM OXIDE PROMOTED TRANSITION METAL OXIDE CATALYSTS

Mr. Veerawat Manomaiviboon

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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จุฬาลงกรณ์มหาวิทยาลัย

วีรวัฒน์ มโนมัยวิบูลย์ : ปฏิกิริยาออกซิเดชันแบบเลือกเกิดของ 1-โพรพานอล บนตัวเร่งปฏิกิริยาโลหะทรานซิชันออกไซด์ที่มีการเติมแมกนีเซียมออกไซด์ลงไป (SELECTIVE OXIDATION OF 1-PROPANOL OVER MAGNESIUM OXIDE PROMOTED TRANSITION METAL OXIDE CATALYSTS)
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ศึกษาปฏิกิริยาออกซิเดชันแบบเลือกเกิดของ 1-โพรพานอล โดยสภาวะขาเข้า มีออกซิเจนร้อยละ 5โดยปริมาตร และ 1-โพรพานอลร้อยละ 8โดยปริมาตร ทำปฏิกิริยาในช่วงอุณหภูมิ 200 ถึง 500 องศาเซลเซียส ตัวเร่งปฏิกิริยาที่ใช้คือ โลหะทรานซิชันออกไซด์ (วานาเดียม โครเมียม แมงกานีส เหล็ก โคบอลต์ นิกเกิล ทองแดง สังกะสี โมลิบดินัมและทังสเตน) บนตัวรองรับอะลูมินาที่สนับสนุนด้วยแมกนีเซียมออกไซด์ การดูดซับโดยใช้ไพริดีนและเทคนิคโปรแกรมอุณหภูมิรีดักชันถูกนำมาใช้เพื่อศึกษาคุณสมบัติกรด-เบสและคุณสมบัติรีดอกซ์ตามลำดับ เพื่อหาความสัมพันธ์ระหว่างพฤติกรรมในการเกิดปฏิกิริยาและคุณสมบัติของตัวเร่งปฏิกิริยา(คุณสมบัติกรด-เบสและคุณสมบัติรีดอกซ์) ผลการทดลองแสดงให้เห็นว่าปฏิกิริยาออกซิเดชันของตัวเร่งปฏิกิริยา วานาเดียม เหล็ก โคบอลต์และสังกะสี-ออกไซด์จะให้ค่ายีลด์ของโพรพิโอนาลดีไฮด์ที่สูง เมื่อเทียบกับตัวเร่งปฏิกิริยาตัวอื่น การเติมแมกนีเซียมออกไซด์ลงในตัวเร่งปฏิกิริยาส่งผลถึงค่าการเปลี่ยนของ 1-โพรพานอล และค่าการเลือกเกิดของคาร์บอนออกไซด์และผลิตภัณฑ์ C1 และC2 เพียงเล็กน้อย แต่ส่งผลชัดเจนต่อค่าการเลือกเกิดของโพรพิลีนที่ลดลง และค่ายีลด์ของโพรพิโอนาลดีไฮด์ ที่เพิ่มขึ้น นอกจากนี้ค่ายีลด์ของโพรพิโอนาลดีไฮด์ไม่ได้เพิ่มขึ้นเป็นสัดส่วนกับปริมาณแมกนีเซียมออกไซด์ที่เติมลงไป ดังนั้นสัดส่วนปริมาณตำแหน่งกรด และตำแหน่งเบส ควรมีสัดส่วนที่เหมาะสม เพื่อทำให้ความว่องไวและค่าการเลือกเกิดในการเกิดปฏิกิริยาดีขึ้น

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VEERAWAT MANOMAIVIBOON : SELECTIVE OXIDATION OF 1-PROPANOL OVER MAGNESIUM OXIDE PROMOTED TRANSITION METAL OXIDE CATALYSTS.
THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D.
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The selective oxidation of 1-propanol to propionaldehyde under inlets conditions of 5 vol% of O_2 and 8 vol% of 1-propanol is studied in the reaction temperature range 200-500 ^oC. The transition metal oxide catalysts, promoted with MgO, used include V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo and W all supported on Al_2O_3. Pyridine adsorption and TPR technique are used to determine the acid-base property and redox property, respectively, to find the relationship between catalytic behavior and catalyst properties (acid-base and redox properties). From the catalytic reaction, it can be indicated that the catalytic oxidation over un-promoted catalysts, 8VOAl, 8FeOAl, 8CoOAl and 8ZnOAl catalysts yielded propionaldehyde more than other unpromoted catalysts. The addition of MgO to the catalysts slightly affects the over all conversion of 1-propanol and the selectivities to COx and C1-C2 products. But, significant decreases of the selectivity of propylene and increase in propionaldehyde yield were observed. Nevertheless, there is no direct proportion between the content of MgO addition and propionaldehyde yield. In addition, an appropriate combination between acid and basic sites should exist to improve the catalytic activity and selectivity.

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Department …Chemical Engineering… Student's signature.......................................

Field of study... Chemical Engineering ... Advisor's signature.......................................

Academic year............2002...................

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Finally, he would like to dedicate the achievement of this work to his parents, who have always been the source of his support and encouragement.

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CHAPTER I

INTRODUCTION

Selective oxidation processes using air or oxygen are use to manufacture a variety of chemicals, and complete catalytic oxidation is a practicable method for elimination of organic pollutants in gaseous streams. In the manufacture of organic chemicals, oxygen may be incorporated into the final product, as in the oxidation of propylene to acrolein or *o*-xylene to phthalic anhydride; or the reaction may be an oxidative dehydrogenation in which the oxygen does not appear in the desired product, as in the conversion of butylene to butadiene. The desired reaction may or may not involve C-C bond scission.

Among all reactions used to convert organic reactant into more useful and valuable products, selective oxidation is the most widely used, especially for the production of bulk organic chemicals. Most of catalysts used for the selective oxidation are supported transition metal oxides.

Transition metal oxides are technologically important materials that have found many applications. For example, in the chemical industry, these oxides are the functional components in the catalyst used in a large number of processes to convert hydrocarbons to other chemicals. They are also used as electrode materials in electrochemical processes. Some of the chemical processes that make use of transition metal oxides are list in Table 1.1

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Previous studied discovered that supported vanadium oxide and cobalt oxide catalysts can selectively oxidize alcohols to aldehydes [Youngwanishsate (1998), Pimanmas (1999)]. During the oxidation, the hydroxyl group of the alcohol is oxidized to from an aldehyde group. In this work the other transition metal oxides (oxide of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W) are investigated using the selective oxidation of 1-propanol reaction.

MgO is a basic support ever used as the support of V_2O_5 in the oxidative dehydrogenation reactions. There is a formation of complex metal oxides between V_2O_5 and MgO (V-Mg-O) and then the oxidation ability of V_2O_5 is changed.

Table 1.1 Examples of chemical processes that make use of transition metal oxides.

Process	Example
Oxidation	Production of SO_3 from SO_2 CO oxidation in emission control
Oxidative dehydrogenation	Production of formaldehyde from methanol and butadiene from butenes
Selective oxidation	Production of acrolein from propene, and maleic anhydride from benzene or butane
Selective reduction	Reduction of NO, selective hydrogenation of unsaturated ketones
Water-gas shift	Production of hydrogen

It has been reported that loading of Co_3O_4 on MgO, Co-Mg-O, could decrease the oxidative ability of Co_3O_4. It was found that Co-Mg-O is the new catalyst applied to use in the oxidative coupling of methane, the catalytic decomposition of N_2O, the oxidation of methane to synthesis gas, the oxidative dehydrogenation of propane, propylene, 1-propanol, and CO [Youngwanishsate (1998)], and the selective oxidation of alcohols [Kittikerdkulchai (1999)]. Therefore, this idea have been brought to the loading of MgO on the other transition metal oxide catalysts to study the effect of magnesium loading.

In this study, some transition metal oxide catalysts promoted (around 4%wt and 10%wt) and un-promoted with magnesium have been used to investigated:

1. The oxidation properties of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo and W catalysts for 1-propanol oxidation.
2. The effect of the magnesium loading on the catalysts for the oxidation of 1-propanol by co-impregnation method.

This present work is organized as follows:

Chapter II contains literature reviews of transition metal oxide catalysts on oxidation reactions.

The theory of this research, studies about the oxidation reaction and its possible mechanism, reaction of alcohols are presented in Chapter III.

Description of experimental systems and operational procedures are described in chapter IV.

Chapter V reveals the experimental results of the characterization of the catalysts and the oxidation reaction of 1-propanol over these catalysts.

Chapter VI contains the overall conclusion emerged from this research.

Finally, the sample of calculation of catalyst preparation, calibration curve from area to mole of 1-propanol, formaldehyde, acetaldehyde, propionaldehyde, methane, ethylene, propylene, CO and CO_2, and data of this experiment which has emerged from this study are included in appendices at the end of this thesis.

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CHAPTER II

LITERATURE REVIEWS

Selective oxidation processes using air or oxygen are used to manufacture a variety of chemicals, and complete catalytic oxidation is a widely used method for elimination of organic pollutants in gaseous streams. Effective catalysts for oxidation reactions fall into two categories, transition metal oxides and metals.

The heterogeneous catalytic oxidation on transition metal oxides is extensively used in catalysis for selective and total oxidation process. Selective oxidation of organic compounds, in particular of hydrocarbons, are the basis of numerous industrial process yielding organic oxides, aldehydes, organic acids and their anhydrides. Transition metal oxide catalysts have been known for many decades as active in many reactions such as oxidative dehydrogenation of light parrafins, complete oxidation of organic compound and selective oxidation of alcohols.

This chapter reviews the works about transition metal oxide catalysts in various reactions. In addition, the effect of support, metal concentration, reaction condition (oxygen/hydrocarbon ratio) and various transition metals in the first row is also demonstrated in this section.

2.1 Literature reviews

Yao (1984) studied the catalytic oxidation of ethanol at low concentrations. The catalysts used included Pt, Pd, Rh, Ag and the first row transition metal oxide supported on Al_2O_3. The results showed that $CuO/\gamma\text{-}Al_2O_3$ and $Mn_2O_3/\gamma\text{-}Al_2O_3$ gave the highest activity for total oxidation to CO_2. C_2H_4 was the only product found over $\gamma\text{-}Al_2O_3$. The amount of acetaldehyde formed was generally higher with the base metal oxide catalysts than with Pt or Pd. In case of $NiO/\gamma\text{-}Al_2O_3$ dehydration to C_2H_4 was predominant.

Ozkan *et al*. (1990) studied the methanol oxidation over transition metal oxide catalysts (oxide of Cr, Mn, Fe, Co, Ni, Cu) which supported on γ-Al_2O_3. The results showed that all the catalysts exhibited similar activities for methanol conversion but Cu catalyst was found to be considerably more selective to CO_2.

Kang and Wan (1994) studied the effects of acid or base additives on the catalytic combustion activity of chromium and cobalt oxides. It was found that the base additive could enhance the catalytic activity of Cr, Co/Al_2O_3 for carbon monoxide oxidation, but the acid additive reduces the activity. For ethane combustion, the addition of a base additive to the catalyst could reduce the ethane conversion. The selectivity of carbon dioxide, however, was increased to 100% because the rate of carbon monoxide oxidation was enhanced. On the other hand, the addition of acid additive to the catalyst gave an increase in ethane conversion, but the selectivity to carbon dioxide was reduced.

Yoon *et al*. (1995) investigated magnesium molybdate catalysts for the oxidative dehydrogenation of propane. The results showed that the catalytic activities of the magnesium molybdate catalysts were very high in oxidative dehydrogenation of propane. The catalyst with excess molybdenum, the ratio of Mg/Mo = 0.9-1.0 presented the highest activity in the reaction. The acidic properties caused by excess molybdenum ions on the surface of the magnesium molybdate catalysts affected the catalytic activities in the oxidative dehydrogenation of propane.

Abello *et al.* (1998) investigated the selective oxidation of propane over potassium and samarium promoted molybdenum supported on MgO/γ-Al_2O_3 catalyst in the oxidative dehydrogenation of propane. The modifications observed in the acid-base properties of the promoted catalysts were used to explain the different behavior found. Additional of Sm did not change the whole acidity, but promoted a slight redistribution of acid sites, whereas the addition of K markedly decreased moderate acidity and it correspondingly increases weak acidity. The total activity decreased in the sequence non-promoted catalyst > promoted with Sm catalyst > promoted with K catalyst. The selectivities to propylene at propane isoconversion increase in the same order. The higher the strength and the number of the acid sites on the surface, the lower the selectivity to alkene.

Baldi *et al.* (1998) investigated the catalytic combustion of 1-propanol and propanal over Mn_3O_4 catalyst. The results showed that Mn_3O_4 catalyst gave the good activity for the combustion catalysis. The conversion of the catalytic combustion of 1-propanol approached 100% at 280^{o}C. At low 1-propanol conversions the main product was propanal, whose selectivity progressively decreases. An increase in the formation of CO_2 and acetaldehyde (maximum selectivity 15%) was observed at 250^{o}C. The conversion of 1-propanol combustion became appreciable at 200^{o}C, with production of acetaldehyde and CO_2. At temperature more than 327^{o}C, total combustion occurred, with only CO_2 as a detectable product. It seems quite evident that propanal and acetaldehyde were intermediates in the 1-propanol combustion pathway.

Youngwanishsate (1998) studied the oxidation property of the Co-Mg-O catalyst in the oxidation reaction of propane, propylene, 1-propanol, and CO. It was found that the oxidation property of Co-Mg-O catalysts depends upon the type of reactants. For 1-propanol oxidation, at low reaction temperature and low 1-propanol conversion Co-Mg-O catalyst behaves as a selective catalyst. While at high reaction temperature it played role as a combustion catalyst. The cobalt composition in Co-Mg-O catalyst affected the catalytic activity and selectivity for propane oxidation. Co-Mg-O (8wt%Co) catalyst was the suitable catalyst for propane oxidation because it was active and selective for olefin production.

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Kittikerdkulchai (1999) studied oxidation property of the Co-Mg-O (8wt%Co) catalyst by using the oxidation reaction of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol as test reactions. The oxidation property of 8Co/MgO catalyst depends upon the type of reactant. For the oxidation of methanol and 1-butanol, 8Co/MgO catalyst played a role as a combustion catalyst at all the reaction temperature range. In case of ethanol, 1-propanol, and 2-propanol oxidation reaction, it was found that 8Co/MgO catalyst was an active and selective catalyst. It provided the maximum acetaldehyde and propionaldehyde yield ca. 58% and 53%, respectively, at 400^{o}C. In addition, it was also shown that the type of support affected the catalytic activity and selectivity of supported cobalt oxide catalyst.

Pimanmas (1999) investigated the application of V-Mg-O/TiO_2 catalyst on the selective oxidation of methanol, ethanol, 1-propanol and 2-propanol. In this research, the various conditions had been performed to determine the suitable conversion for each reaction. The amounts of oxygen and alcohols were varied in the range of 5-20% and 4-12%, respectively. The main products from ethanol and 1-propanol oxidation were acetaldehyde and propionaldehyde, respectively and CO_2. From investigating the effect of amounts of oxygen and alcohols, it was found that the CO_2 selectivity had the lowest value at 5% oxygen and the highest aldehyde yield obtained at 8% alcohols. Thus, it could be concluded that on of the best alcohol/oxygen ratio was to 8/5 given the best results. Then, the effect of WHSV was studied by changing from 60,000 to 20,000 ml/hr.g of catalyst or increasing the catalyst content from 0.1 to 0.3 g. The results showed that an increase in the amount of the catalyst or a decrease in the WHSV values given the higher aldehyde yield. After that, the methanol oxidation was examined by using the methanol/oxygen ratio equals to 8/5. CO_2 is the main product while CO was detected at high temperature. Due to CO formed, a further experiment was carried out by increasing the oxygen content to 20%, the result showed that no CO was obtained. Therefore, it could be conclude that at 5% oxygen used, the reaction was not complete combustion. For the oxidation of 2-propanol, propylene and CO_2 were the major products, which was different from the case of 1-propanol.

Chaiyasit (2000) investigated the selective oxidation reaction of 1-propanol and 2-propanol over Co-Mg-O/TiO_2 (8wt%Co, 1wt%Mg) catalyst. It was found that the oxidation property of Co-Mg-O/TiO_2 catalyst depends on type of the reactants. Propionaldehyde was the main product for selective oxidation of 1-propanol. In case of 2-propanol oxidation reaction, it was found that Co-Mg-O/TiO_2 catalyst was an active catalyst for selective oxidation reaction. The main product at low reaction temperature was propylene while at high reaction temperature the main reaction products are propylene and propionaldehyde. From the result of propylene oxidation, it could be indicated that propionaldehyde was produced directly from propylene. In addition, the sequence of cobalt and magnesium loading has no effect on the structure and catalytic performance of this catalyst. While the type of support affected the selectivity of supported cobalt catalyst.

Larsson and Andersson (2000) studied the oxides of copper, ceria promoted copper, manganese and copper manganese on Al_2O_3 for the combustion of CO, ethyl acetate and ethanol. The $CuMn_2O_4/Al_2O_3$ catalyst was more active than the CuO_x/Al_2O_3 and Mn_2O_3/Al_2O_3 catalyst for the complete oxidation of CO, ethyl acetate and ethanol. The characterization with XRD indicated that the copper oxide was presented as a copper aluminate surface phase on alumina with low copper oxide loading. At high loading, bulk CuO crystalites was presented as well. The active metal oxides in the alumina supported copper manganese oxide and manganese oxide catalysts were mainly presented as crystalline $CuMn_2O_4$ and Mn_2O_3, respectively.

Lemonidou *et al.* (2000) investigated the oxidative dehydrogenation of propane using vanadia type catalysts supported on Al_2O_3, TiO_2, ZrO_2 and MgO. The promotion of V_2O_5/Al_2O_3 catalyst with alkali metals (Li, Na, K) was also attempted. Evaluation of temperature programmed reduction patterns showed that the reducibility of V species is affected by the support acid-base character. The catalytic activity is favored by the V reducibility of the catalyst as it was confirmed from runs conducted at 450-550^{o}C. V_2O_5/TiO_2 catalyst exhibits the highest activity in oxydehydrogenation of propane. The support's nature also affects the selectivity to propylene. V_2O_5 supported on Al_2O_3 catalyst exhibits the highest selectivity. Reaction studies showed that addition of alkali metals decreases the catalytic activity in the order non-doped > Li > Na > K. Propylene selectivity significantly increases in the presence of doped catalysts.

Mongkhonsi *et al.* (2000) investigated the selective oxidation reaction of ethanol and 1-propanol over V-Mg-O/TiO_2 catalyst. Ethanol and 1-propanol could be selectivity oxidized to ethanal and propanal, respectively. Aldehyde yield up to 73% and 66% for ethanal and propanal, respectively, were achieved in the temperature range 200-250^{o}C. The catalyst was rather inactive for the further oxidation of aldehyde products to carboxylic acid.

Machli *et al*. (2002) studied the effect of magnesia addition to the vanadia catalysts supported on titania and alumina. The results were correlated with the catalytic performance in oxidative dehydrogenation of propane. The concentration of the acid sites was measured by FT-IR after pyridine sorption at 75°C. It was found that the catalysts studied possess only Lewis acid sites except the vanadia on titania catalyst, where a few Bronsted acid sites were identified. The concentration of acid sites was affected by both catalyst support and modifier added. The adsorption of propylene at 100°C followed by TPD was examined. The amount of propylene adsorbed strongly depended on the presence of Mg while the extent of deep oxidation of adsorbed propylene was related to the nature of the support and/or the surface concentration of active species. Testing of catalysts using 1/1 ratio of C_3H_8/O_2 as a function of temperature and W/F, showed that the vanadia on titania catalyst exhibits much higher surface activity than the alumina supported and magnesia modified catalysts. The sequence in surface activity parallels the concentration of acid sites. A significant increase in selectivity was obtained with the Mg modified catalysts, especially with the vanadia supported on titania catalyst. The primary dehydrogenation reaction for propylene formation was favored by the presence of Mg on the catalyst surface.

Kulkarni (2002) studied the number of active surface sites and turnover frequencies of isopropanol oxidation by metal oxide catalysts (MgO, CaO, SrO, BaO, Y_2O_3, CeO_2, TiO_2, ZrO_2, V_2O_5, Ta_2O_5, Cr_2O_3, MoO_3, WO_3, Mn_2O_3, Fe_2O_3, Co_3O_4, NiO, PdO, CuO, Ag_2O, Au_2O_3, ZnO, Ga_2O_3, SiO_2 and Bi_2O_3). On average, the number of active surface sites for isopropanol dissociative adsorption on these catalysts was 2-4 μmol/m^2. The number of active surface sites enabled quantification of the turnover frequency (TOF) for these catalysts. The TOF values for the various pure metal oxides were normalized at 200°C. The TOFs of catalysts showing redox activity varied by over six-orders of magnitude (10^2 to 10^{-4} s^{-1}). For catalyst showing acidic activity, the TOFs varied by over eight-orders of magnitude (10^1 to 10^{-7}s^{-1}). The reaction products from isopropanol oxidation at low conversions reflected the nature of the active surface sites, redox or acidic, on these catalysts. Redox surface sites yielded acetone and acidic surface sites yield propylene. Small amounts of isopropyl ether formation were sometimes also observed via bimolecular recombination of surface isopropoxide species on acidic surface sites. All catalysts with the exception of Fe_2O_3 and TiO_2 exhibited extremely high selectivity to either redox or acidic products.

Cherian *et al*. (2002) studied the oxidative dehydrogenation of propane over Cr_2O_3/Al_2O_3 and Cr_2O_3. The results showed that supported chromium oxide samples were active for the oxidative dehydrogenation reaction and that propylene was the major product. Bulk Cr_2O_3 was also studied for the oxidative dehydrogenation reaction and found to behave differently from the Cr_2O_3/Al_2O_3 catalysts. The bulk Cr_2O_3 was active for the complete oxidation reaction and CO_2 was the major product.

2.2 Comment on previous works

From the previous studies, there are many researches about catalytic properties of the first row transition metal oxides for the methanol and ethanol oxidation and also in oxidative dehydrogenation of light parrafins, such as ethane and propylene.

However there are some researches about selective oxidation of 1-propanol, only vanadium oxides and cobalt oxides. Thus, in this study will be expanded to other transition elements for selective oxidation of 1-propanol to studied the catalytic properties.

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CHAPTER III

THEORY

A large segment of the modern chemical industry is based on catalytic selective oxidation processes. Indeed, more than 60% of the chemicals and intermediates synthesized via catalytic processes are products of oxidation. Total catalytic oxidation is also becoming increasingly important as a method for destroying trace pollutants and contaminants in gaseous streams. One of the most important applications of selective oxidation catalysis is the functionalization of hydrocarbons. Today, catalytic oxidation is the basis for the synthesis of a large percentage of the monomers or modifiers used for the production of fibers and plastic [Centi (2001)].

Catalytic oxidation reactions involving free oxygen can be divided into complete oxidation and selective oxidation. Complete oxidation is the combustion of organic compound to the combustion products, CO_2 and H_2O. While selective oxidation is the reaction between hydrocarbon, the most used reactant, and oxygen to produce oxygenates or unsaturated hydrocarbons.

Selective oxidation of organic compounds, in particular of hydrocarbons, using air or oxygen on oxide catalysts are the basis of numerous industrial process yielding organic oxides, aldehydes, organic acids and their anhydrides. In the manufacture of organic chemicals, oxygen may be incorporated into the final product, as in the oxidation of methane to formaldehyde, or the reaction may be an oxidative dehydrogenation in which the oxygen does not appear in the desire product, as in the conversion of propane to propylene. The desire reaction may or may not involve C-C bond scission.

It has been reported that maximum selectivity is associated with an optimum degree of oxygen mobility. For an optimum selectivity combination of activity and selectivity there should be matching between the difficulty of oxidizing the reactant and the ease of removal oxygen from the catalyst. High mobile oxygen should result in a high activity catalyst, but one that is nonselective [Satterfield (1991)].

Selective oxidation of small-saturated hydrocarbons such as ethane and propane is a key challenge of current catalysis research. However, low yields in the desire product were frequently observed and, in almost all cases, the productivity of these processes was far from that of industrial interest. The main reasons are the free-radical nature of these processes, the high exothermicity, and the fact that oxygen attacks partially oxidized products more easily than the starting hydrocarbon, resulting in overoxidation [Sun *et al*. (1997)]. Therefore, there is an idea to use other chemicals such as alcohols as reactants for selective oxidation reaction.

3.1 Reactions of alcohols

Reactions of an alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the -OH group; or the O-H bond, with removal of -H bond. Either kind of reaction can involve substitution, in which a group replaces the -OH or -H, or elimination, in which a double bond is formed.

3.1.1 Oxidation

The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of product that is formed depends upon how many of this α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde,

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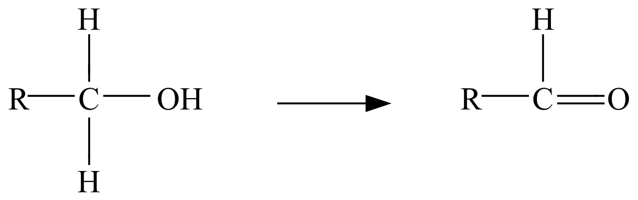
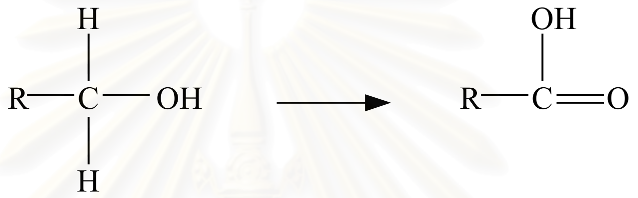


$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}OH \longrightarrow R{-}\overset{H}{C}{=}O}$$

A 1°alcohol An aldehyde

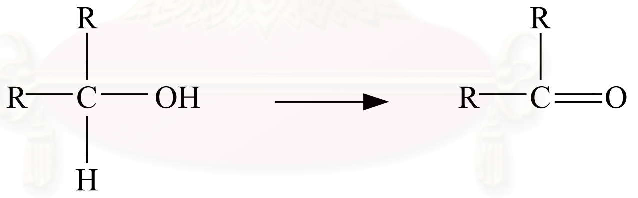
or both of them to form a carboxylic acid.



$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}OH \longrightarrow R{-}\overset{OH}{C}{=}O}$$

A 1° alcohol A carboxylic acid

A secondary alcohol can lose its only α-hydrogen to form a ketone.



$$\mathrm{R{-}\overset{R}{\underset{H}{C}}{-}OH \longrightarrow R{-}\overset{R}{C}{=}O}$$

A 2° alcohol A ketone

A tertiary alcohol contains no α-hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).

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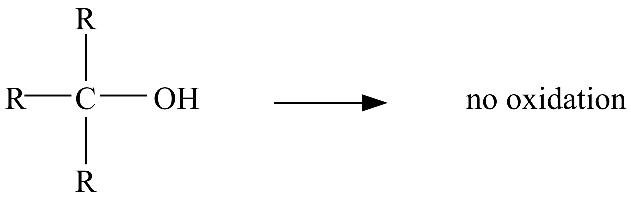
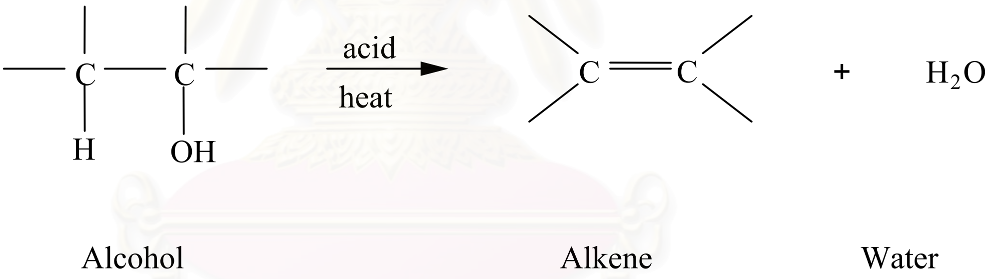


A 3° alcohol

3.1.2 Dehydration

Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulfuric or phosphoric acid; or (b) by passing the alcohol vapor over a catalyst, commonly alumina (Al_2O_3), at high temperature. An alcohol is converted into an alkene by dehydration (elimination of a molecule of water).



The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

Ease of dehydration of alcohol $3^{o} > 2^{o} > 1^{o}$

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3.2 Redox mechanism

The behavior of most oxidation catalysts can be interpreted within the framework of a redox mechanism. This postulates that the catalytic reaction comprises two steps [Mars van Krevelen (1954)]:

1. Reaction between catalyst in an oxidized form, Cat-O, and the hydrocarbon, R, in which the oxide becomes reduced:

$$\text{Cat-O} + \text{R} \longrightarrow \text{RO} + \text{Cat}$$

2. The reduced catalyst, Cat, becomes oxidized again by oxygen from the gas phase:

$$2\text{Cat} + \text{O}_2 \longrightarrow 2\text{Cat-O}$$

Under steady-state conditions the rates of the two steps must be the same.

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CHAPTER IV

EXPERIMENTAL

The experimental systems and procedures used in this work are divided into three parts:

1. The preparation of catalysts.
2. The characterization of catalysts.
3. The catalytic activity measurements.

The details of the experiments are described as the following.

The scope of this study.

The reaction conditions are chosen as follows:

Catalysts* : 8VOAl, 8V4MgOAl, 8V10MgOAl
8CrOAl, 8Cr4MgOAl, 8Cr10MgOAl
8MnOAl, 8Mn4MgOAl, 8Mn10MgOAl
8FeOAl, 8Fe4MgOAl, 8Fe10MgOAl
8CoOAl, 8Co4MgOAl, 8Co10MgOAl
8NiOAl, 8Ni4MgOAl, 8Ni10MgOAl
8CuOAl, 8Cu4MgOAl, 8Cu10MgOAl
8ZnOAl, 8Zn4MgOAl, 8Zn10MgOAl
8MoOAl, 8Mo4MgOAl, 8Mo10MgOAl
8WOAl, 8W4MgOAl, 8W10MgOAl
Reactant : 1-propanol
Feed composition : 1-propanol 8 vol%, oxygen 5 vol%, nitrogen balance
Flow rate of reactant : 100 ml/min
Reaction temperature : 200-500°C
Space velocity : 60 000 ml $g^{-1}h^{-1}$

* The number indicates approximated weight % of metal

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4.1 Preparation of catalysts

4.1.1 Chemicals

The details of chemicals used in this experiment are shown in table 4.1.

Table 4.1 The chemicals used in this experiment

Chemical	**Grade**	**Supplier**
Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$)	Analytical	Univar, Australia
Ammonium paratungstate ($H_{40}N_{10}O_{41}W_{12}\cdot 7H_2O$)	Analytical	Univar, Australia
Cobaltous acetate tetrahydrate ($Co(CH_3COO)_2\cdot 4H_2O$)	Analytical	Fluka, Switzerland
Chromium nitrate nonahydrate ($CrN_3O_9\cdot 9H_2O$)	Analytical	Fluka, Switzerland
Cupric nitrate trihydrate ($CuN_2O_6\cdot 3H_2O$)	Analytical	Fluka, Switzerland
Ferric nitrate nonahydrate ($FeN_3O_9\cdot 9H_2O$)	Analytical	Fluka, Switzerland
Manganese nitrate tetrahydrate ($Mn(NO_3)_2\cdot 4H_2O$)	Analytical	Riedel-deHaen, Germany
Nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$)	Analytical	Riedel-deHaen, Germany
Zinc nitrate hexahydrate ($ZnN_2O_6\cdot 6H_2O$)	Analytical	Fluka, Switzerland
Magnesium nitrate ($Mg(NO_3)_2$)	Analytical	Fluka, Switzerland
Alumina (Al_2O_3) JRC ALO2 (γ-phase)	Japan reference catalyst	Department of Material Science, Shimane University Catalysts and Chemicals Ind. Co., Ltd.

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4.1.2 Preparation of catalyst

The catalysts were prepared by impregnating powdered alumina support material with an aqueous solution of a salt of the desired element. The metal loadings on the catalysts were calculated from the weight of the support and the concentration of the salt solution used. The suspension was evaporated at 80^{o}C. After impregnation, the catalysts were heat-treated in the following: drying in the oven at 110^{o}C in air over night, calcination in air for 6 hours at 550^{o}C.

4.2 The characterization of catalyst

4.2.1 Determination of composition content of catalyst

The actual composition contents of all catalysts were determined by atomic absorption spectroscopy (AAS) at the Department of science service Ministry of science technology and environment. The calculation of the sample preparation is shown in Appendix A.

4.2.2 BET Surface area measurement

4.2.2.1 Apparatus

The apparatus consisted of two gas feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of a fine-metering valve. The sample cell was made from pyrex glass. The operation conditions of the gas chromatograph (GOW-MAC) is shown in Table 4.2

4.2.2.2 Procedure

The mixture of helium and nitrogen gas flowed through the system at the nitrogen gauge pressure of 0.3. The sample was placed in the sample cell, which was then heated up to 150°C and held at this temperature for 2 h. The sample was cooled down to room temperature and ready to measure the surface area. There were three steps to measure the surface area.

Table 4.2 Operation conditions of gas chromatograph (GOW-MAC)

Model	**GOW-MAC**
Detector	TCD
Helium flow rate	30 ml/min
Detector temperature	80°C
Detector current	80 mA

(1) Adsorption step

The sample cell was dipped into the liquid nitrogen. Nitrogen was adsorbed on the surface of the sample until an equilibrium was reached.

(2) Desorption step

The nitrogen-adsorbed sample was dipped into the water at room temperature. The adsorbed nitrogen was desorbed from the surface of the sample. This step was completed when the recorder line return back to the base line.

(3) Calibration step

1 ml of nitrogen gas at atmospheric pressure was injected at the calibration port and the area was measure. The area was the calibration peak.

(4) Then BET surface area is calculated using procedures described in Appendix C.

4.2.3 X-ray diffraction (XRD)

The phase structures of the samples were determined by X-ray diffraction, Siemens D 5000 X-ray diffractometer using CuKα radiation with Ni filter in the 2θ range of 20-80°. The sample is placed into XRD plate before placing on the measured position of XRD diffractometer.

4.2.4 Temperature Programmed Reduction (TPR)

The reducible site was determines by measuring the amount of H_2, which reduced oxide species on the surface. The product of this reaction was water vapor, which was trapped by liquid nitrogen. The thermal conductivity detector (TCD) measured the amount of H_2. The operating condition of the TCD is shown in Table 4.3.

Table 4.3 Operating condition of TCD for temperature programmed reduction

Detector	**TCD**
Carrier gas	5%H_2 / 95%Ar
Carrier gas flow	30 ml./min.
Detector temperature	80°C
Detector current	80 mA

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Catalyst sample 0.2 g was placed in a sample tube. The TPR runs were started at 50°C, by allowing the temperature to increase to 500°C at a rate of 10°C/min.

4.2.5 Pyridine Adsorption

The acid site of samples was determined by the pyridine adsorption. The apparatus consisted of the tube connected to the gas chromatograph (GC 9A). The condition of the gas chromatograph is shown in Table 4.4.

0.02 g of sample was placed in the tube. Then 0.01 μl of pyridine was injected to the gas chromatograph and peak area was measured. The pyridine was injected until the sample was saturated. The amount of acid sites of the sample was calculated from the total area of the pyridine adsorption.

Table 4.4 Operation condition of gas chromatograph (GC 9A)

Model	**GC 9A**
Detector	FID
Nitrogen flow rate	30 ml/min
Column temperature	150^{o}C
Detector temperature	180^{o}C
Injector temperature	180^{o}C

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4.3 The catalytic activity measurements

4.3.1 Equipment

Flow diagram of the reaction system is shown in Figure 4.1. The system consists of a saturator, a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system. The liquid phase reactant was filled in the saturator. N_2 is passed through the evaporator to evaporate the reactant and carried to the microreactor.

The reactor is made from a stainless steel tube. Two sampling points are provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

The gas supplying system consists of cylinders of ultra high purity nitrogen and air, each equipped with pressure regulators (0-120 psig), on-off valves and needle valves used for adjusting the flow rate of these gases.

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The composition of hydrocarbons in the product stream was analyzed by a Shimadzu GC14B gas chromatograph equipped with a flame ionization detector.

The composition of oxygenate compounds in the feed and product streams were measured by a Shimadzu GC14B gas chromatograph equipped with flame ionization detector.

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve to separate oxygen and carbon monoxide and a Porapak-Q column to separate CO_2 and water were operated in parallel. The operating conditions are shown in the Table 4.5.

Table 4.5 Operating condition for gas chromatograph

Gas chromatograph	Shimadzu GC8A	Shimadzu GC14A	Shimadzu GC14B
Detector	TCD	FID	FID
Column	MS-5A, Porapak-Q	Capillary	VZ10
Carrier gas	He (99.999%)	N_2 (99.999%)	N_2 (99.999%)
Carrier gas flow	25 ml/min	25 ml/min	25 ml/min
Column temperature			
- Initial	100	40	70
- Final	100	140	70
Detector temperature	130	150	150
Injector temperature	130	100	100
Analyzed gas	CO, CO_2, H_2O	Oxygenates	Hydrocarbon C_1-C_4

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4.3.2 Oxidation procedure

The oxidation procedures are described in the detail below.

1. 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in the electrical furnace.

2. The total flow rate was 100 ml/min. Flow rate of 1-propanol, nitrogen and air were adjusted to the required values. The gas mixtures for 1-propanol oxidation were 8 vol% 1-propanol, 5 vol% oxygen and balance with nitrogen.

3. The reaction temperature was between 200-500^{o}C. The effluent gases were analyzed by using the FID and TCD gas chromatographs. The chromatograph data were changed into mole of methane, ethylene, propane, propylene, 1-propanol, formaldehyde, acetaldehyde, propionaldehyde, and CO_2 by calibration curves in Appendix C.

4. The result of catalytic test was calculated in the term of

$$\%\text{A conversion (C)} = \frac{\text{mole of A converted}}{\text{mole of A in feed}}$$

$$\%\text{selectivity (S) to B} = \frac{\text{mole of B formed}}{\text{mole of A converted}} \times \frac{\text{no. of C atom of B}}{\text{no. of C atom of A}} \times 100$$

$$\%\text{yield (Y) to B} = \frac{\%\text{A conversion} \times \%\text{selectivity to B}}{100\%}$$

where A is reactant

B is product

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CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into three sections. In the first section, the catalyst characterization using XRD, BET and AAS are described. Next, effect of transition metal oxide, loading on alumina support, on the catalytic activity for selective oxidation of 1-propanol to propionaldehyde are discussed. Effects of Mg promoted on the catalyst are presented in the last section.

5.1 Catalyst characterization

5.1.1 Determination of composition content and BET surface area of catalyst

The results of metal composition and BET surface area of all catalysts, which are analyzed by Atomic Absorption Spectroscopy (AAS) and BET surface area are summarized in Table 5.1.

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Table 5.1 The composition of catalyst and BET surface area

Catalyst*	wt% Transition metal	wt% Mg	BET surface area (m^2/g)
Al_2O_3	-	-	130.5
8VOAl	7.6	-	123.3
8V4MgOAl	7.3	3.4	119.5
8V10MgOAl	7.4	9.3	114.1
8CrOAl	7.9	-	126.9
8Cr4MgOAl	7.8	3.9	100.9
8Cr10MgOAl	8.0	9.5	92.3
8MnOAl	8.0	-	136.3
8Mn4MgOAl	7.6	3.4	114.5
8Mn10MgOAl	7.8	9.8	93.3
8FeOAl	7.8	-	100.5
8Fe4MgOAl	7.4	3.5	89.7
8Fe10MgOAl	8.2	9.7	100.9
8CoOAl	8.1	-	128.5
8Co4MgOAl	7.8	4.1	122.7
8Co10MgOAl	7.6	9.4	114.2
8NiOAl	7.8	-	98.4
8Ni4MgOAl	7.7	3.6	97.7
8Ni10MgOAl	7.8	10	97
8CuOAl	7.9	-	111.98
8Cu4MgOAl	7.8	4.1	94.6
8Cu10MgOAl	7.6	9.8	105.9
8ZnOAl	7.9	-	132.8
8Zn4MgOAl	7.8	3.7	106.9
8Zn10MgOAl	7.7	9.5	97.3
8MoOAl	7.7	-	93.5
8Mo4MgOAl	7.9	3.5	90.3
8Mo10MgOAl	8.1	9.8	94.7

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Table 5.1 The composition of catalyst and BET surface area (continue)

Catalyst*	**wt% Transition metal**	**wt% Mg**	**BET surface area (m^2/g)**
8WOAl	7.6	-	112.7
8W4MgOAl	7.4	3.9	121.9
8W10MgOAl	7.9	9.7	128.6

[*] The number in the catalysts symbol denotes the approximate weight percentage of the catalysts composition.

The above data in Table 5.1 show that the metal and magnesium content in all catalysts are close to the calculated value. The correlation between the transition metal oxide and magnesium amounts and the surface area could not be defined.

5.1.2 X-ray Diffraction (XRD)

The first three strongest XRD peaks of transition metal oxides from the reference [The JCPDS (1980)] using CuKα radiation are listed in Table 5.2.

Table 5.2 The reference XRD patterns for transition metal oxides

Oxides	**Position (2θ)**
CrO_3	14.2°, 25.8°, 26.2°
Cr_2O_3	33.6°, 36.2°, 54.6°
CrO	34.6°, 44.4°, 48°
MnO	20.2°, 21.6°, 36.4°
MnO_2	21.8°, 35.8°, 55°
Mn_3O_4	18.2°, 35.4°, 62°
Mn_2O_3	32.2°, 35.6°, 53°
MoO_3	9.6°, 25.8°, 29.4°
MoO_2	26°, 36.8°, 53.4°
WO_3	24°, 33°, 55°
WO_2	25.8°, 36.8°, 37°
Fe_2O_3	29.8°, 32.8°, 67.5°
FeO	61°, 61.4°, 73°
ZnO	33.6°, 58.4°, 62.6°
ZnO_2	31.8°, 37°, 63°
CuO	35.4°, 35.6°, 38.8°
Cu_2O	37°, 40.4°, 42.4°
Ni_2O_3	32°, 44.8°, 51.6°
NiO	37.2°, 43.2°, 62.6°
MgO	37°, 43°, 62.8°

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If the catalysts studied contained a transition metal oxide form, some of the peaks shown in Table 5.2 should appear in the XRD spectra. But from the Figures 5.1 to 5.10, all of the catalysts investigated did not show any peak of those transition metal oxides. All of the catalysts showed the XRD patterns in the same position as Al_2O_3 support that showed 4 peaks at 37°, 45°, 46°, and 65.5°. The peaks of these transition metal oxides were not detected possibly because the XRD patterns of these transition metal oxides were hidden by the XRD patterns of Al_2O_3 support, the oxides did not form a crystal with significant size or it did not form a crystal.

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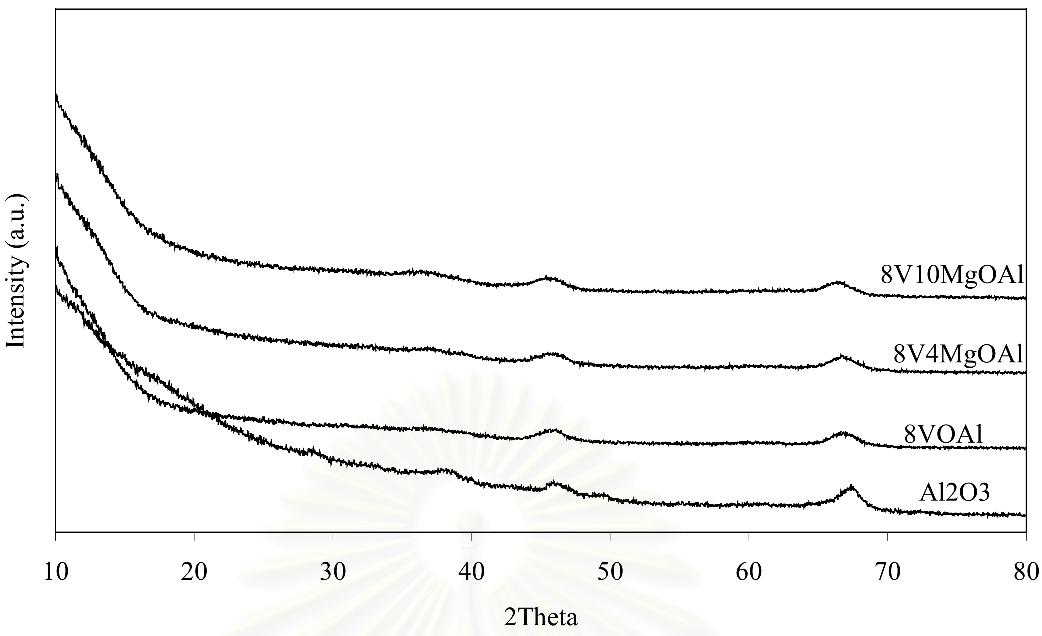

Figure 5.1 The XRD patterns of 8VOAl, 8V4MgOAl, 8V10MgOAl catalysts compare with Al_2O_3

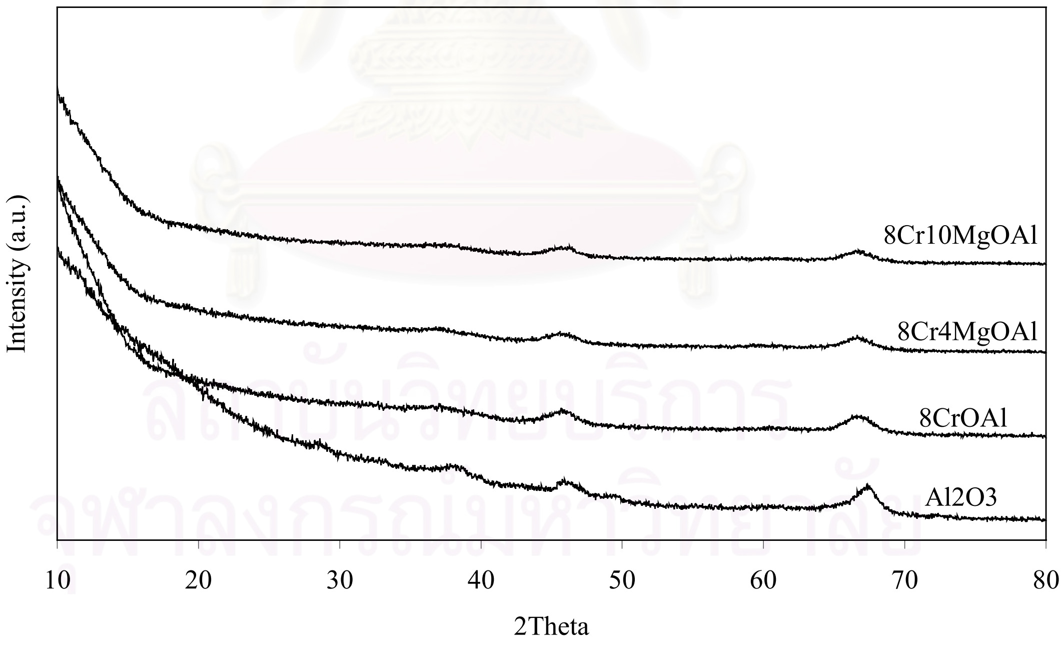

Figure 5.2 The XRD patterns of 8CrOAl, 8Cr4MgOAl, 8Cr10MgOAl catalysts compare with Al_2O_3

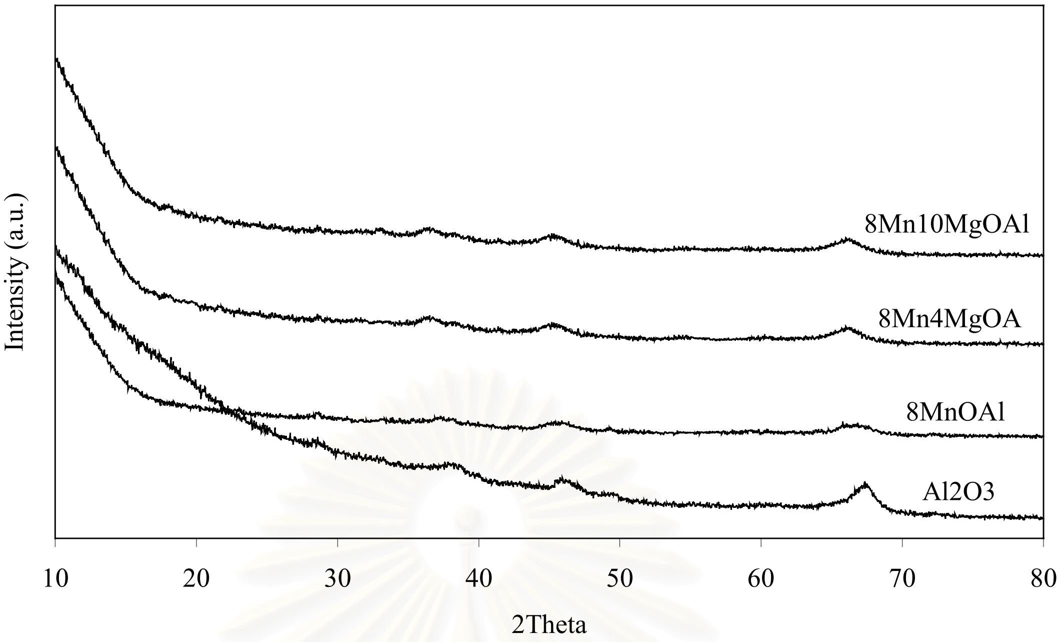

Figure 5.3 The XRD patterns of 8MnOAl, 8Mn4MgOAl, 8Mn10MgOAl catalysts compare with Al_2O_3

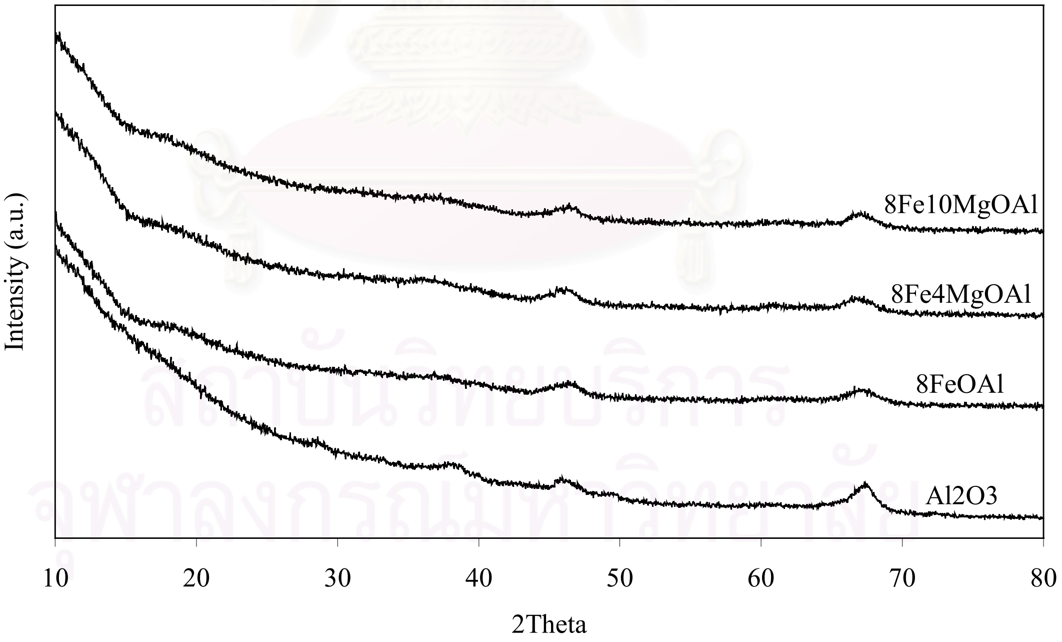

Figure 5.4 The XRD patterns of 8FeOAl, 8Fe4MgOAl, 8Fe10MgOAl catalysts compare with Al_2O_3

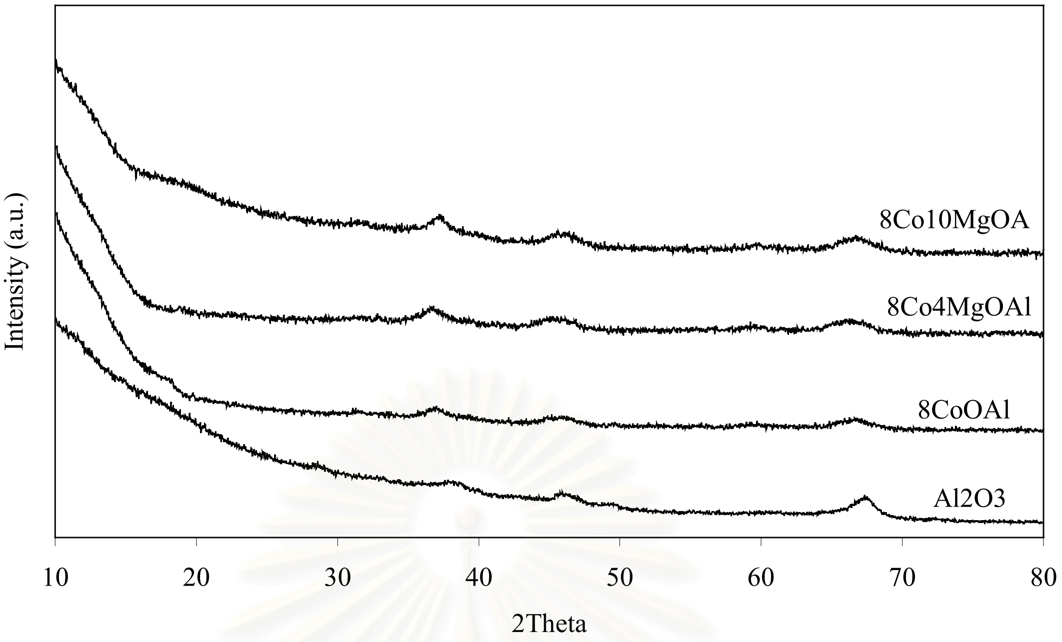

Figure 5.5 The XRD patterns of 8CoOAl, 8Co4MgOAl, 8Co10MgOAl catalysts compare with Al_2O_3

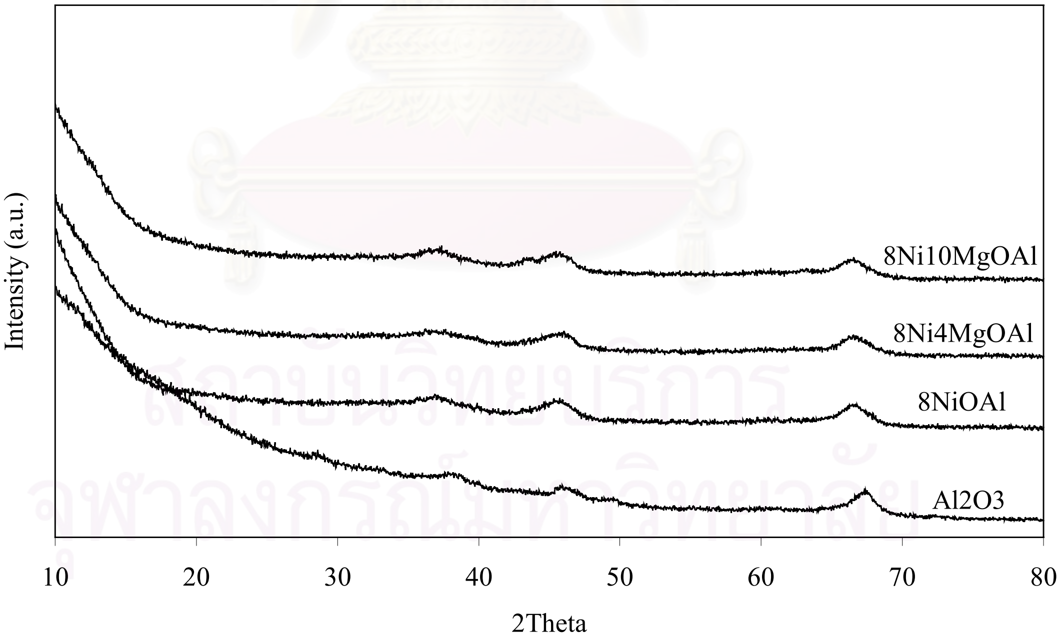

Figure 5.6 The XRD patterns of 8NiOAl, 8Ni4MgOAl, 8Ni10MgOAl catalysts compare with Al_2O_3

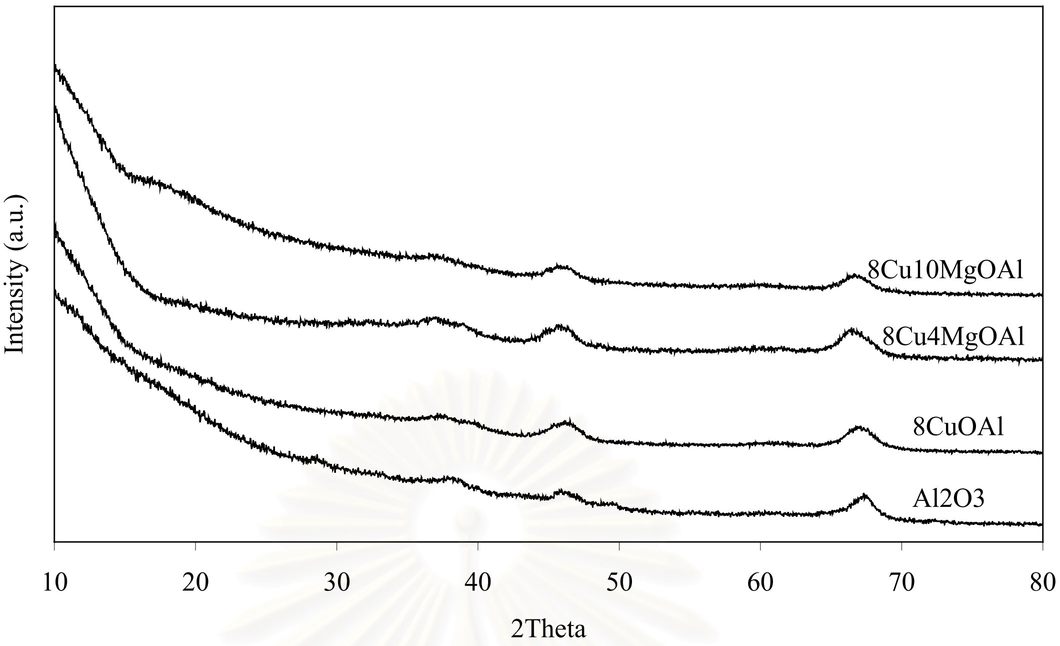

Figure 5.7 The XRD patterns of 8CuOAl, 8Cu4MgOAl, 8Cu10MgOAl catalysts compare with Al_2O_3

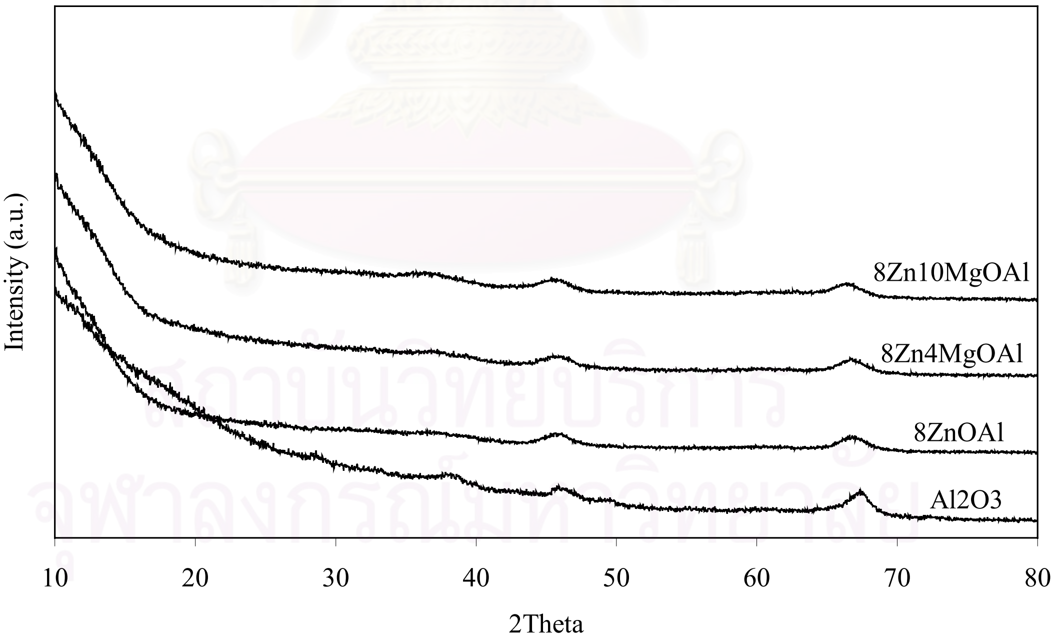

Figure 5.8 The XRD patterns of 8ZnOAl, 8Zn4MgOAl, 8Zn10MgOAl catalysts compare with Al_2O_3

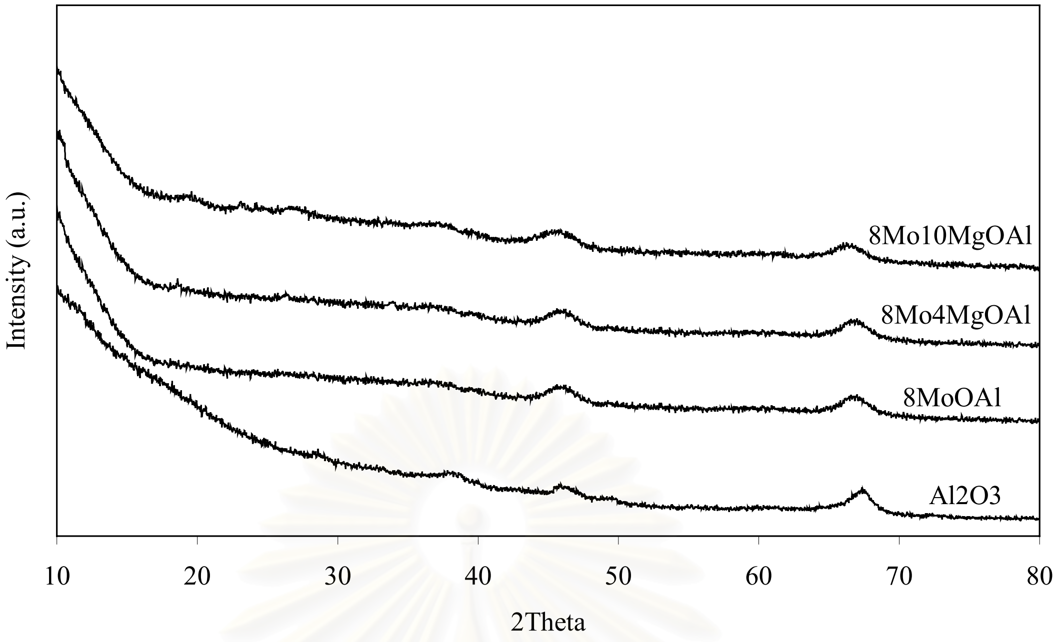

Figure 5.9 The XRD patterns of 8MoOAl, 8Mo4MgOAl, 8Mo10MgOAl catalysts compare with Al_2O_3

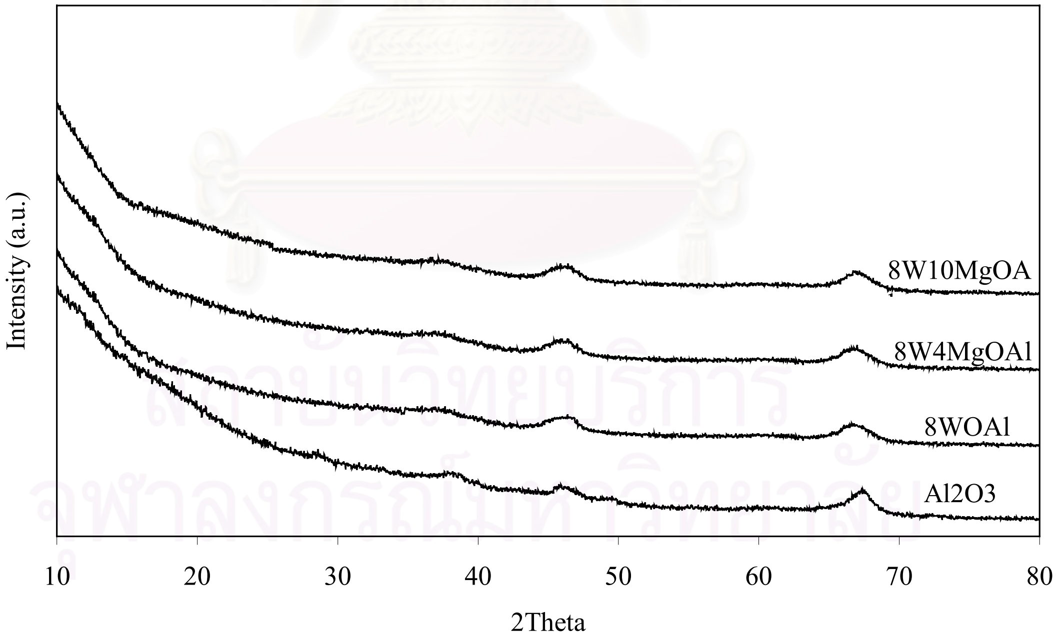

Figure 5.10 The XRD patterns of 8WOAl, 8W4MgOAl, 8W10MgOAl catalysts compare with Al_2O_3

5.2 Effect of types of transition metal oxide on catalyst activity for the selective oxidation of 1-propanol

a) 8VOAl

The catalytic property of 8VOAl catalyst on 1-propanol oxidation is illustrated in Figures 5.11a and 5.11b. The 1-propanol conversion increased from 9% to 88% at the temperature range of 200–400°C and steadily increased until the temperature reached 500°C, which the conversion was about 95%.

At low 1-propanol conversion (200-250°C) the major reaction product is propionaldehyde. Also, there are some formations of other reaction products i.e., formaldehyde, acetaldehyde, methane, ethylene, propylene, CO and CO_2. While at high 1-propanol conversion (300-500°C) the main products are propionaldehyde, propylene and CO_2 and with traces of formaldehyde, acetaldehyde, methane, ethylene and CO. Consequently, the selectivity of propionaldehyde moderately falls from 92% to 35% and the selectivities of CO_2 and propylene slightly rise from 0% to 20% and 3% to 23%, respectively, with increasing reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 43% at 350°C.

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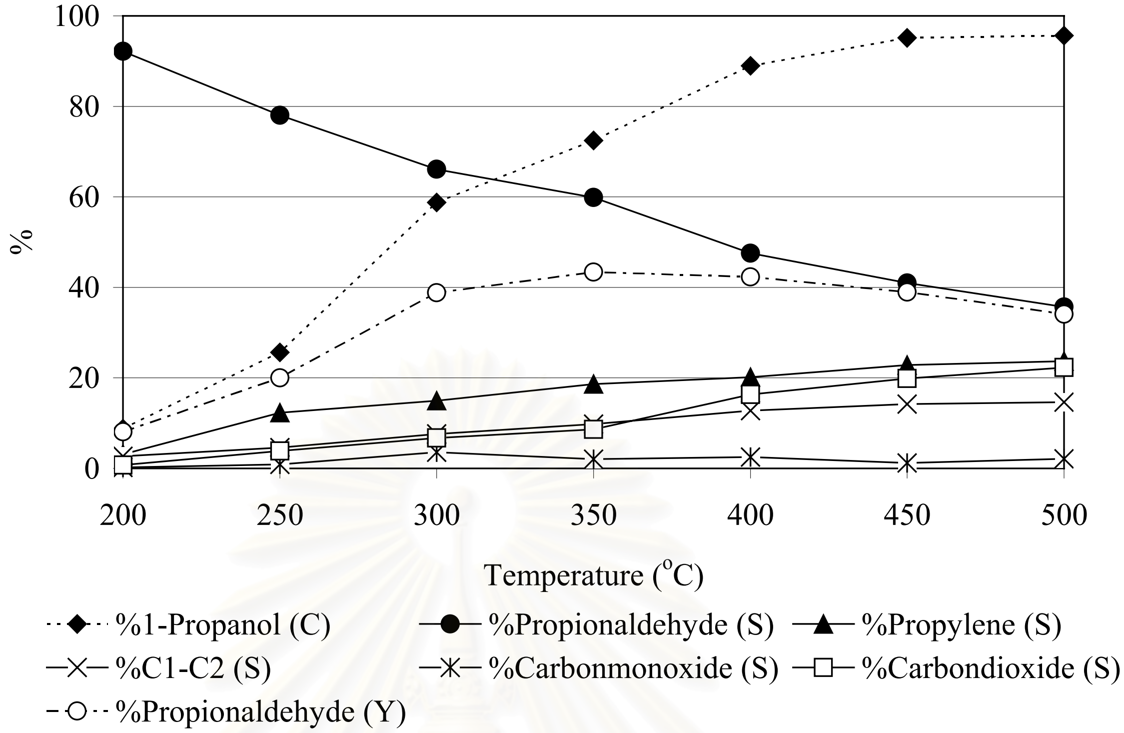

Figure 5.11a Catalytic property of 8VOAl catalyst in the 1-propanol oxidation

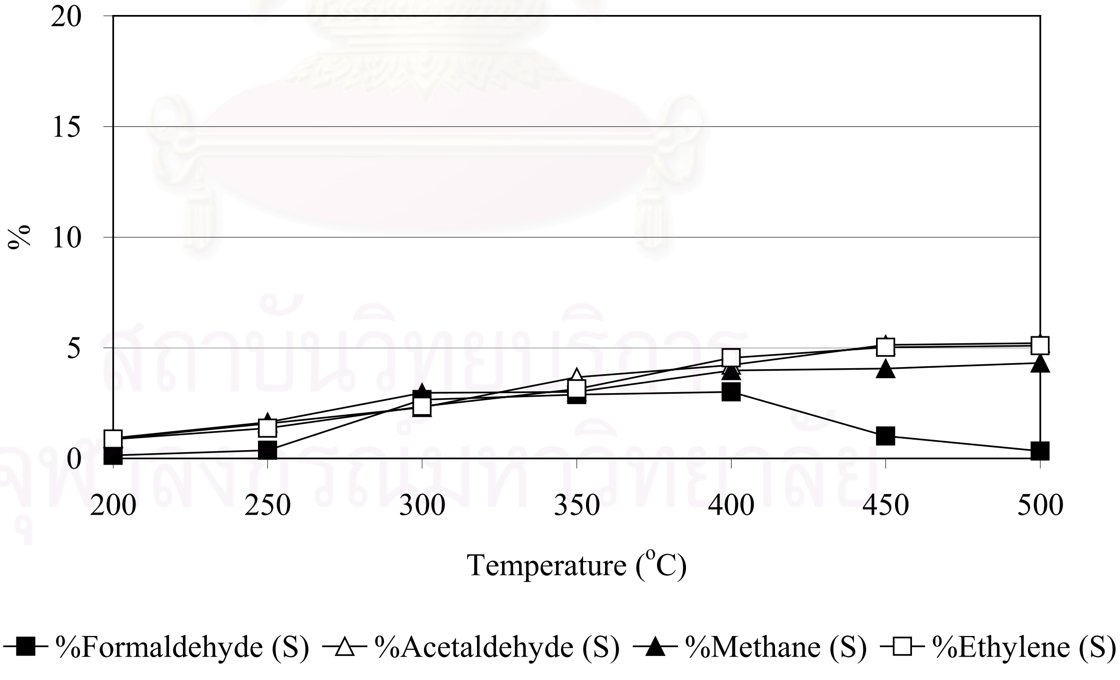

Figure 5.11b C1-C2 products of 8VOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

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b) 8CrOAl

The catalytic results, obtained in the oxidation of 1-propanol on 8CrOAl are illustrated in Figures 5.12a and 5.12b. The conversion of 1-propanol increases from 28% to 85% on the increase of reaction temperature from 200°C to 300°C and the slightly increases up to 97% at 500°C. At low 1-propanol conversions the main products are propionaldehyde, whose selectivity progressively decreases (85% to 7%) and propylene. An increase in the formation of CO_2 (10% to 48%) is observed between 250°C and 500°C, together with small amounts of methane, ethylene and acetaldehyde and traces of formaldehyde. The maximum yield of propionaldehyde is ca. 33% at 250°C

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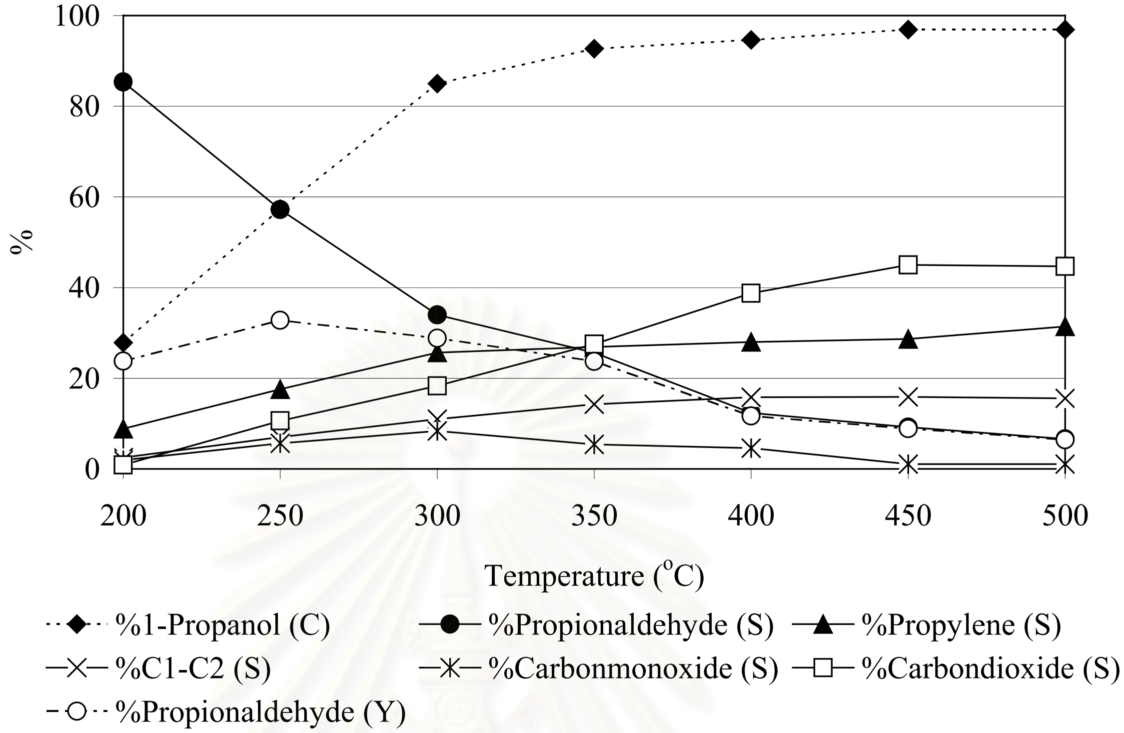

Figure 5.12a Catalytic property of 8CrOAl catalyst in the 1-propanol oxidation

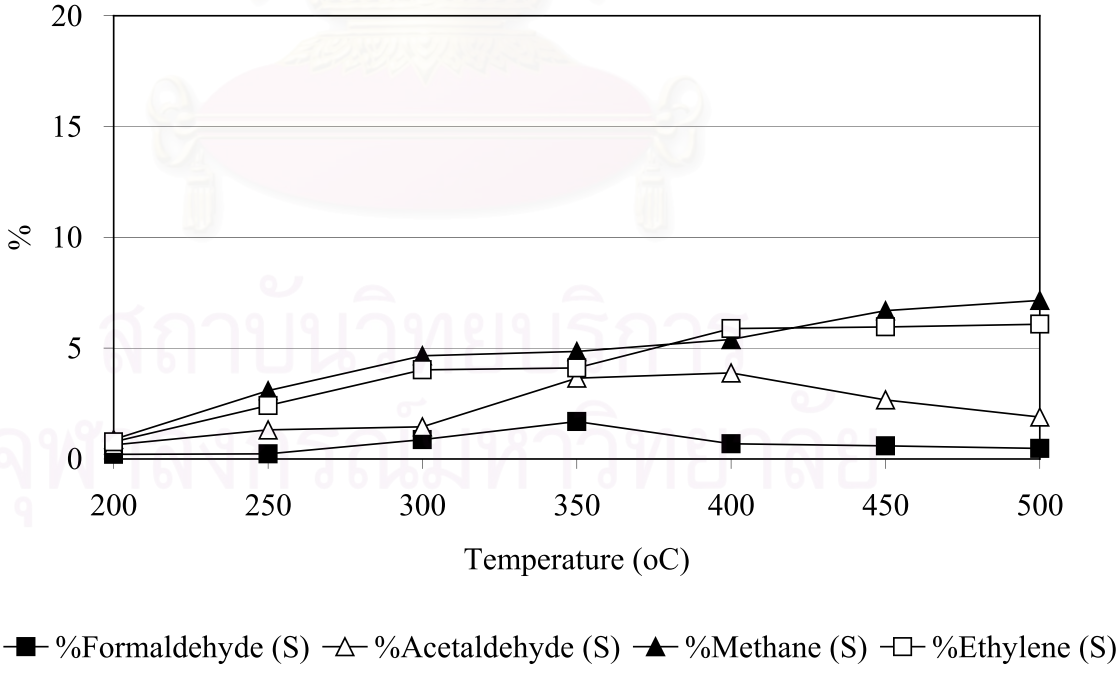

Figure 5.12b C1-C2 products of 8CrOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

c) 8MnOAl

Figures 5.13a and 5.13b demonstrate the catalytic property of 8MnOAl in the 1-propanol oxidation. The conversion of 1-propanol increases from 34% to 91% on the increase of reaction temperature from 200°C to 300°C and gradually rises from 91% to 99% at 500°C. At low 1-propanol conversion (200-350°C) the major reaction products are propylene and propionaldehyde. Also, there are some formations of CO_2 with traces of formaldehyde, acetaldehyde, methane, ethylene, and CO. While at high 1-propanol conversion (300-500°C) the main products are CO_2 and some formation of propylene, with traces of acetaldehyde, formaldehyde, propionaldehyde, methane and ethylene are detected. The maximum yield of propionaldehyde is ca. 36% at 250°C.

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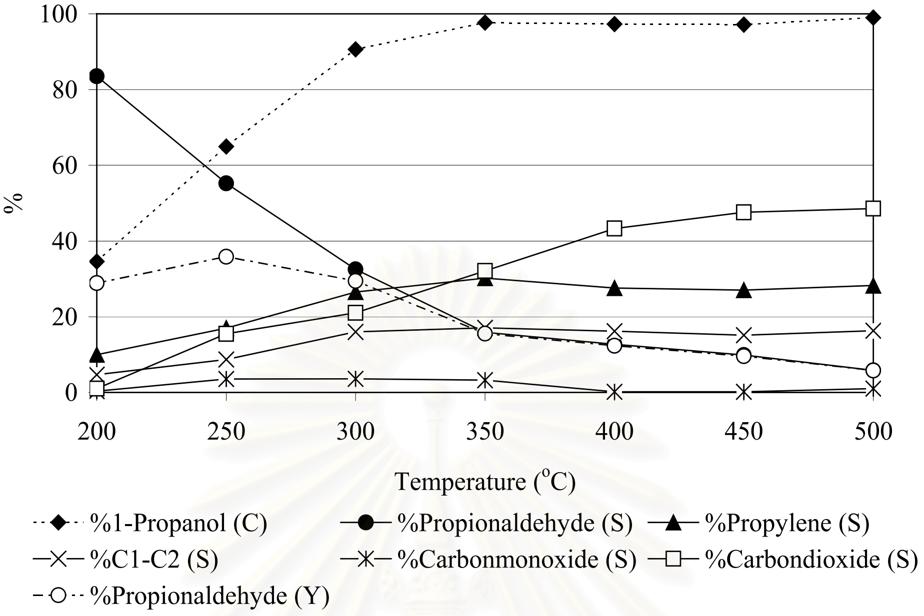

Figure 5.13a Catalytic property of 8MnOAl catalyst in the 1-propanol oxidation

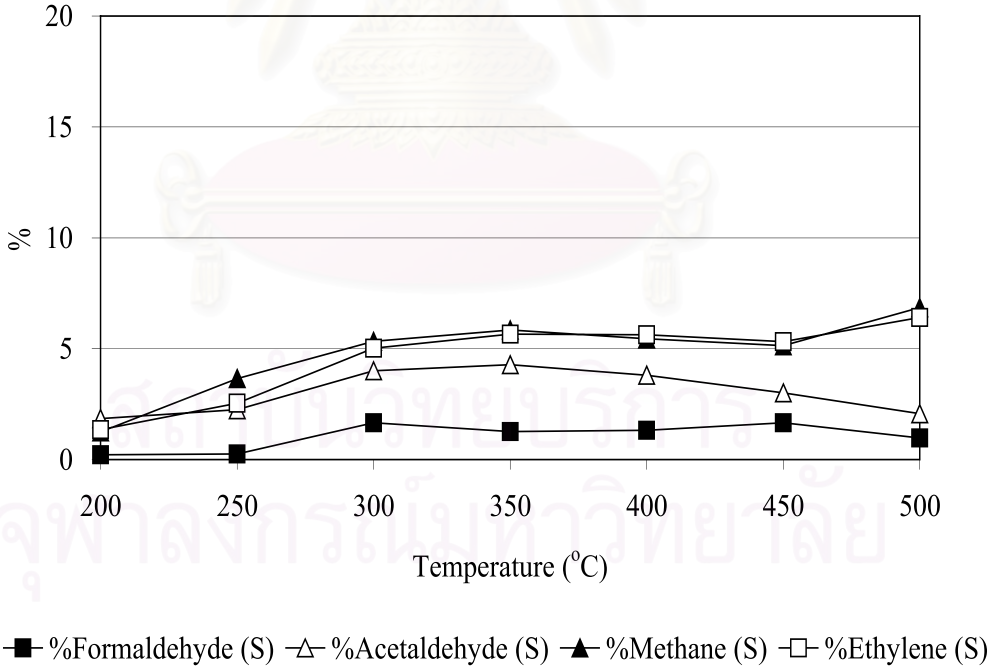

Figure 5.13b C1-C2 products of 8MnOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

d) 8FeOAl

The results of catalytic oxidation of 1-propanol are summarized in Figures 5.14a and 5.14b. Conversion of 1-propanol increases from 12% to 84% on the increase of reaction temperature from 200°C to 400°C and gradually increases up to 93% at 500°C. The increase of reaction temperature from 200°C to 500°C causes selectivity to propionaldehyde falls from 89% to 41% while propylene selectivity rises from 3% to 18% and the CO_2 selectivity rises from 1% to 17. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO are detected. The maximum yield of propionaldehyde is ca. 42% at 350°C.

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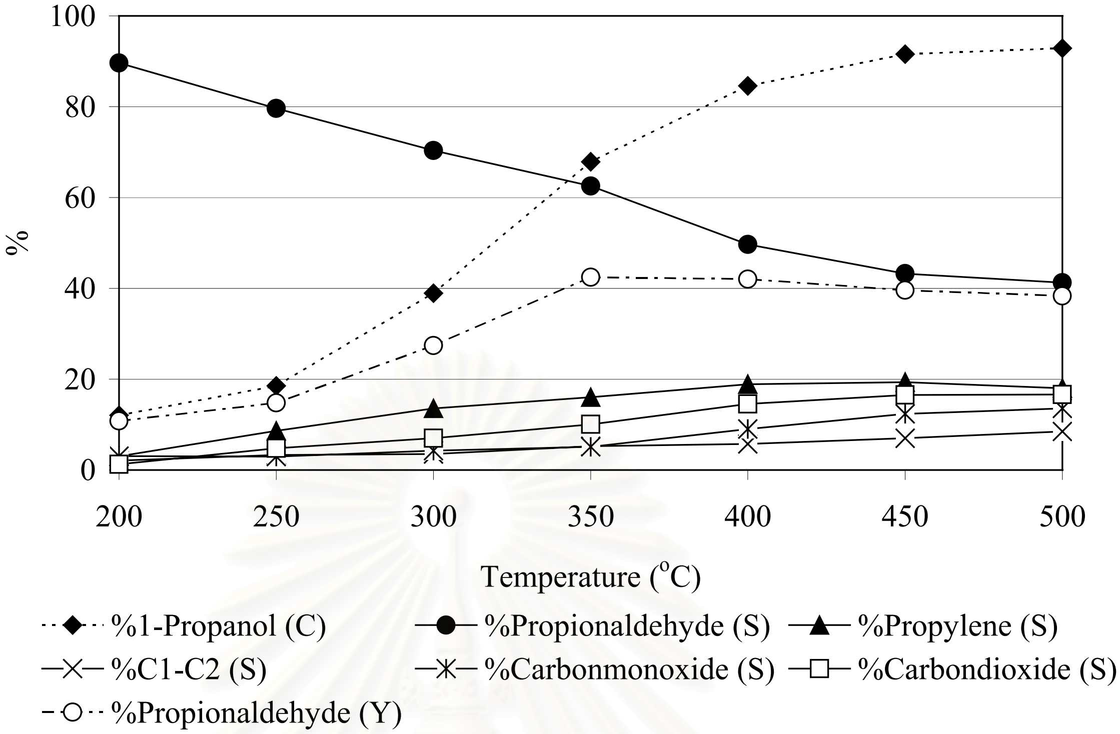

Figure 5.14a Catalytic property of 8FeOAl catalyst in the 1-propanol oxidation

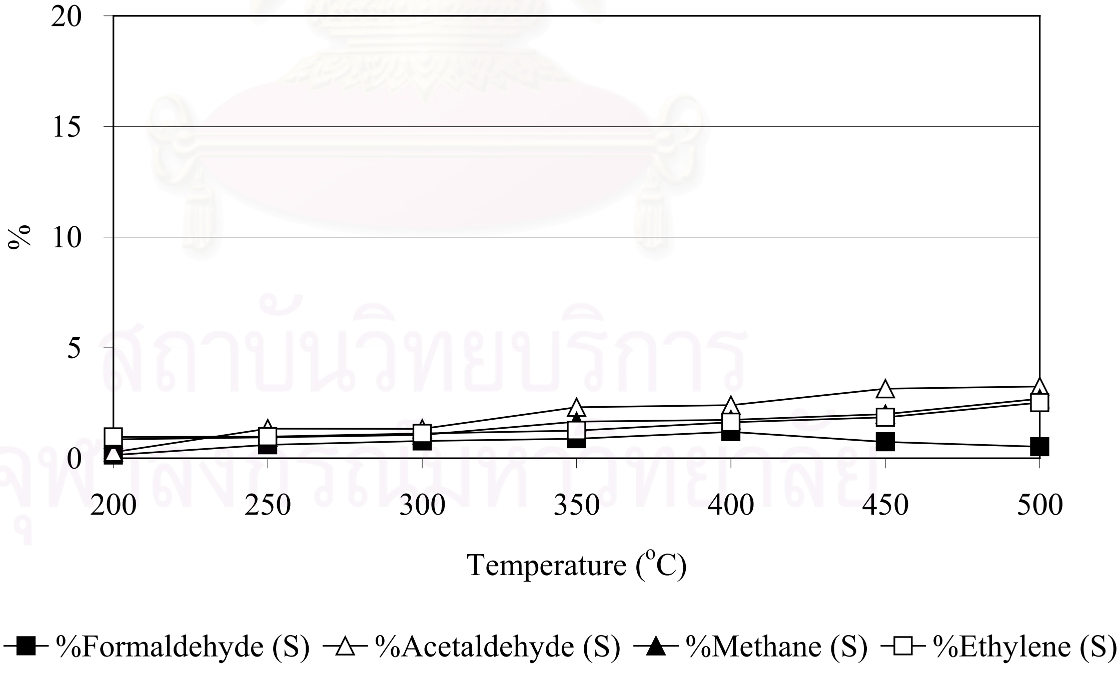

Figure 5.14b C1-C2 products of 8FeOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

e) 8CoOAl

The behavior of the 8CoOAl catalyst in 1-propanol oxidation is described in Figures 5.15a and 5.15b. Increasing the reaction temperature from 200^{o}C to 400^{o}C results in the increase in 1-propanol conversion from 7% to 88%. Further increasing temperature 95% conversion is obtained at reaction temperature 500^{o}C.

In the beginning (reaction temperature range 200-350^{o}C), the main reaction product is propionaldehyde with some formation of propylene and CO_2. At the reaction temperature higher than 350^{o}C propionaldehyde, propylene and CO_2 are the main products. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO_2 are detected. Consequently, the selectivity of propionaldehyde substantially falls from 92% to 30% with increasing reaction temperature from 200-500^{o}C. The maximum yield of propionaldehyde is ca. 42% at 350^{o}C.

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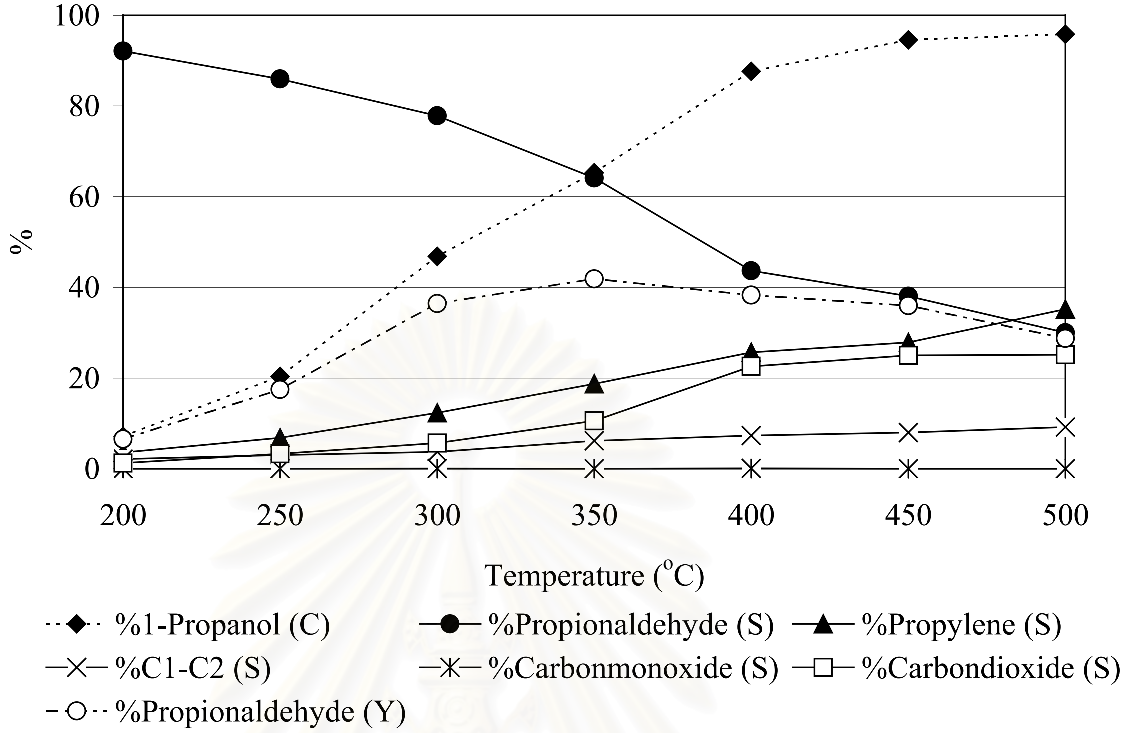

Figure 5.15a Catalytic property of 8CoOAl catalyst in the 1-propanol oxidation

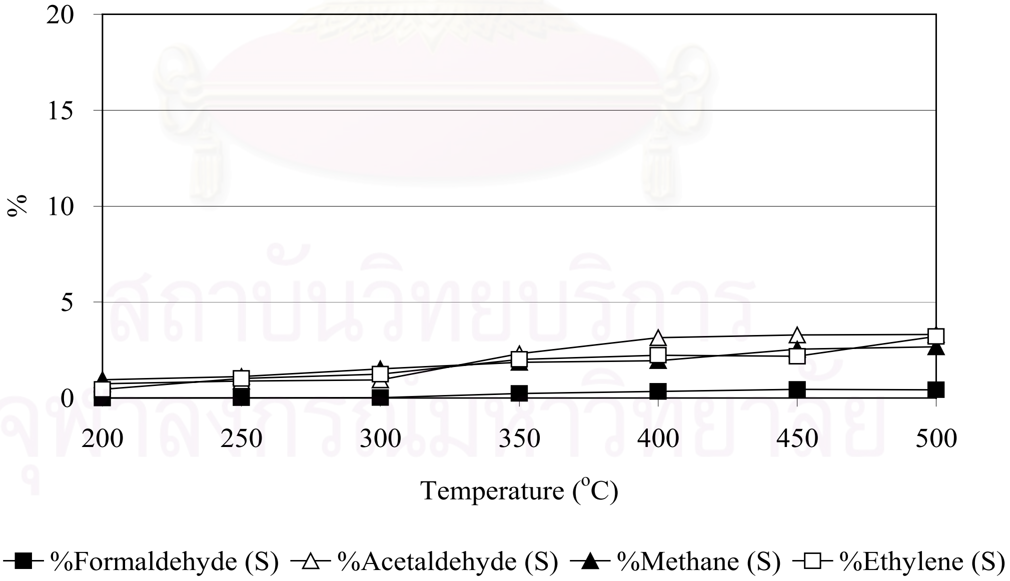

Figure 5.15b C1-C2 products of 8CoOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

f) 8NiOAl

Figures 5.16a and 5.16b demonstrate the catalytic property of 8NiOAl in the 1-propanol oxidation. The conversion of 1-propanol increases from 5% to 90% on the increase of reaction temperature from 200°C to 400°C and gradually rises from 90% to 95% at 500°C. An increase of reaction temperature from 200°C to 500°C causes the selectivity to propionaldehyde steadily falls from 87% to 22% while CO_2 and propylene selectivity rises from 1% to 45% and 5% to 23%, respectively. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO are detected. The maximum yield of propionaldehyde is ca. 28% at 300°C.

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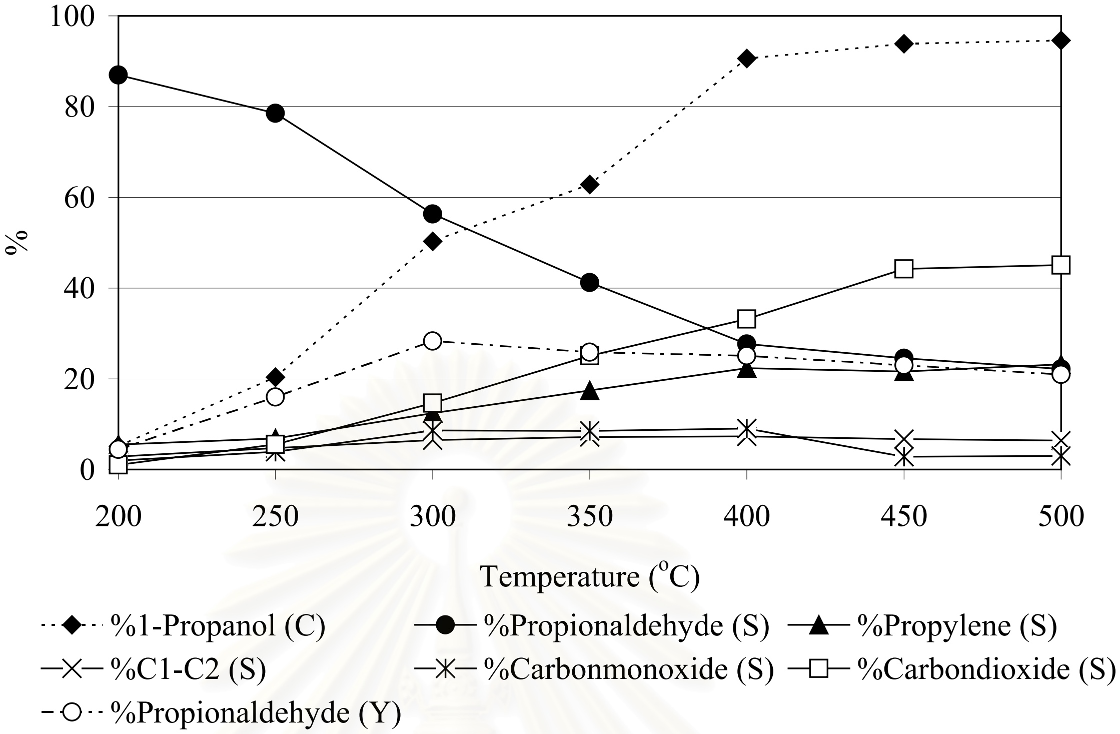

Figure 5.16a Catalytic property of 8NiOAl catalyst in the 1-propanol oxidation

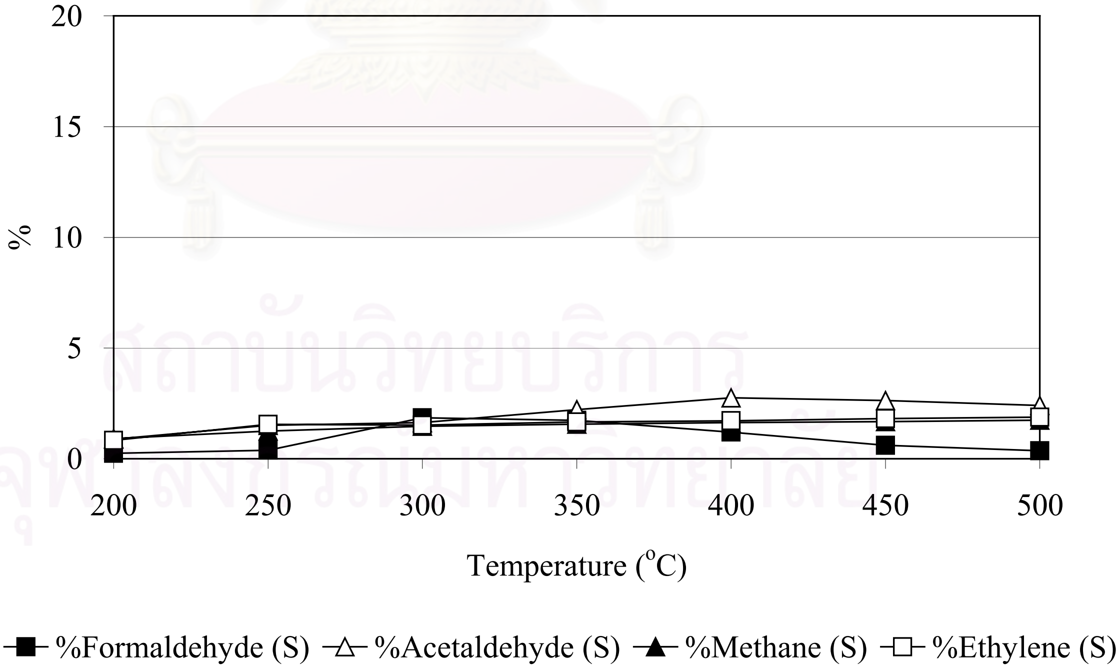

Figure 5.16b C1-C2 products of 8NiOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

g) 8CuOAl

Figures 5.17a and 5.17b demonstrate the catalytic property of 8CuOAl in the 1-propanol oxidation. The conversion of 1-propanol increases from 15% to 89% on the increase of reaction temperature from 200°C to 350°C and gradually rises from 89% to 96% at 500°C. At low 1-propanol conversion (200-350°C) the major reaction product is propionaldehyde. Also, there are some formations of propylene and CO_2 with traces of formaldehyde, acetaldehyde, methane, ethylene, and CO. While at high 1-propanol conversion (300-500°C) the main product is CO_2 and some formation of propylene, and propionaldehyde. Traces of acetaldehyde, formaldehyde, methane and ethylene are detected. The maximum yield of propionaldehyde is ca. 37% at 300°C.

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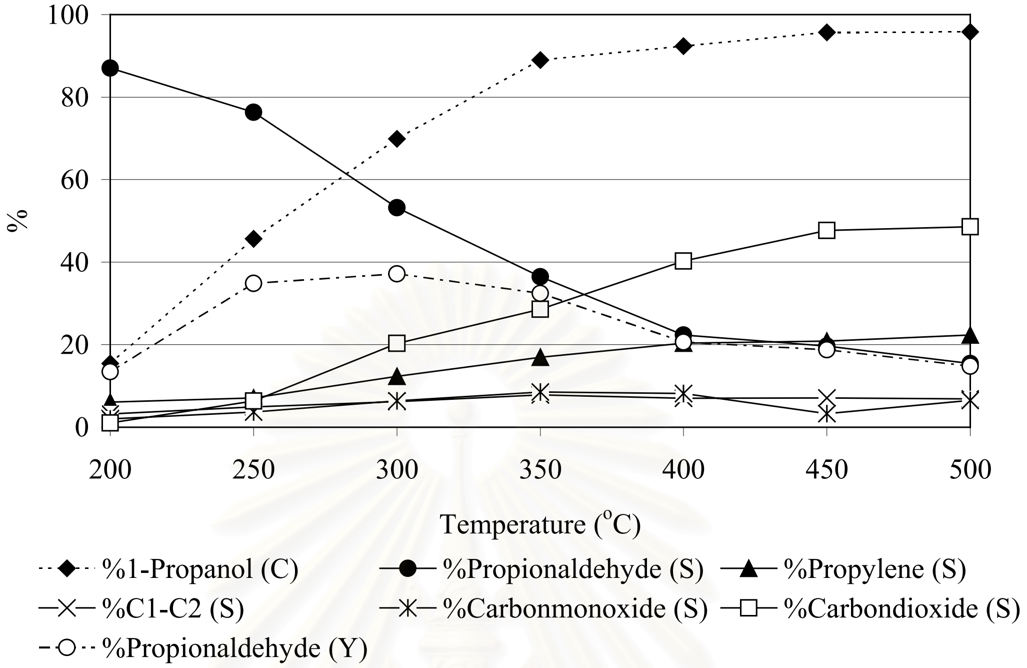

Figure 5.17a Catalytic property of 8CuOAl catalyst in the 1-propanol oxidation

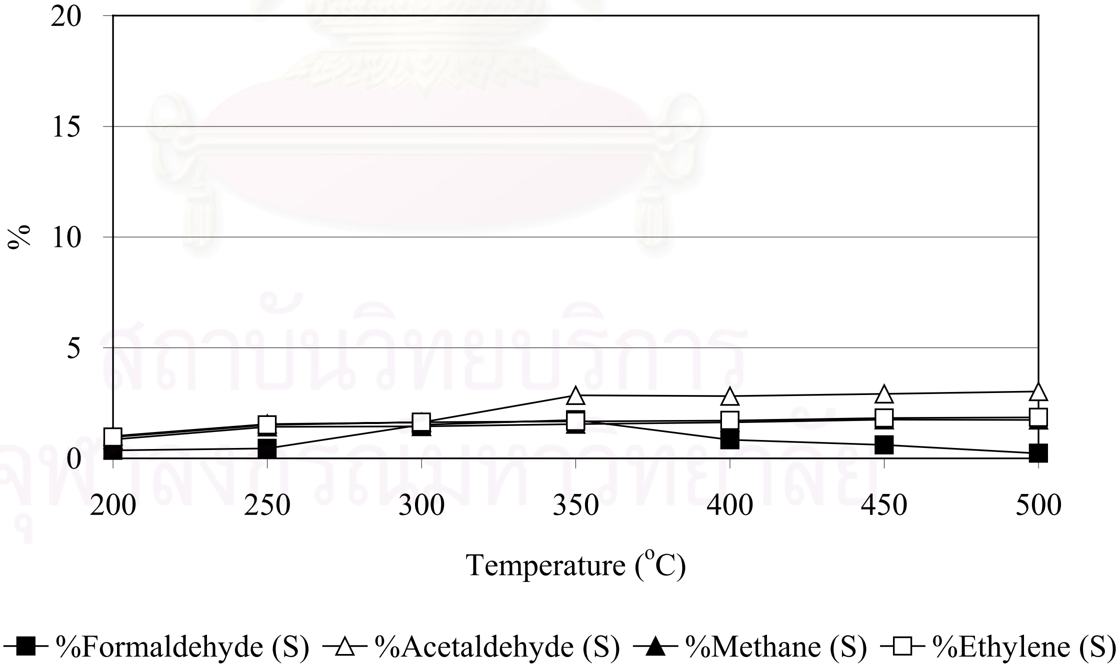

Figure 5.17b C1-C2 products of 8CuOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

h) 8ZnOAl

The catalyst property of 8ZnOAl catalyst on 1-propanol oxidation is illustrated in Figures 5.18a and 5.18b. The 1-propanol conversion increased from 4% to 85% at the temperature range of 200–400°C and steadily increased until the temperature reach 500°C, which the conversion was about 93%.

At low 1-propanol conversion (200-300°C) the major reaction product is propionaldehyde. Also, there are some formations of CO_2 and propylene with traces of formaldehyde, acetaldehyde, methane, ethylene, and CO. While at high 1-propanol conversion (300-500°C) the main products are propionaldehyde, propylene and CO_2 and with traces of formaldehyde, acetaldehyde, methane, ethylene and CO. Consequently, the selectivity of propionaldehyde moderately falls from 88% to 40% and the selectivities of CO_2 and propylene slightly rise from 1% to 20% and 6% to 20%, respectively, with increasing reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 41% at 400°C.

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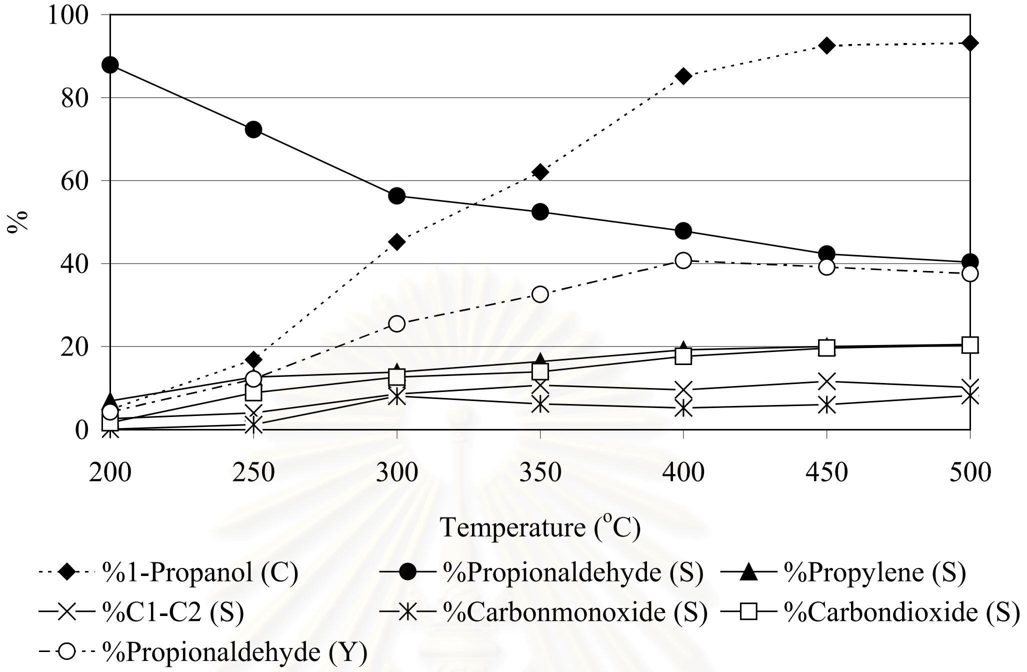

Figure 5.18a Catalytic property of 8ZnOAl catalyst in the 1-propanol oxidation

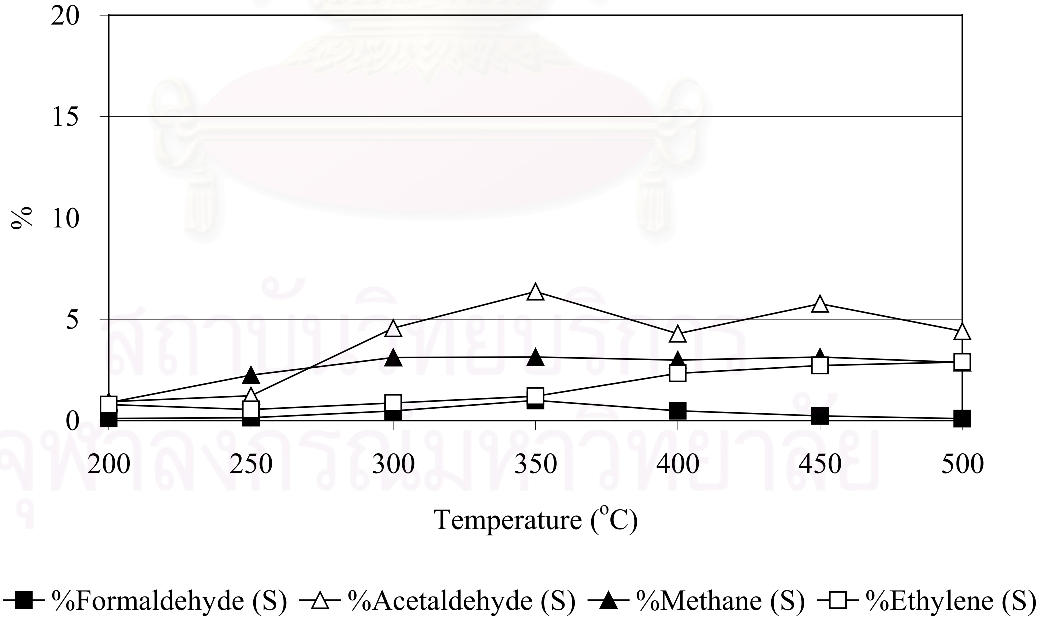

Figure 5.18b C1-C2 products of 8ZnOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

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i) 8MoOAl

The results of catalytic test on 8MoOAl catalyst are shown in Figures 5.19a and 5.19b. The conversion of 1-propanol increases from 3% to 90% on the increase of reaction temperature from 200°C to 400°C and the slightly increases up to 95% at 500°C. An increase of reaction temperature from 200°C to 500°C causes the selectivity to propionaldehyde steadily falls from 88% to 27% while CO_2 rises from 0% to 15%. The propylene selectivity rises from 5% to 23% on the increase of reaction temperature from 200°C to 500°C. The selectivity of C1-C2 products increase from 2% to 32%. The maximum yield of propionaldehyde is ca. 27% at 400°C.

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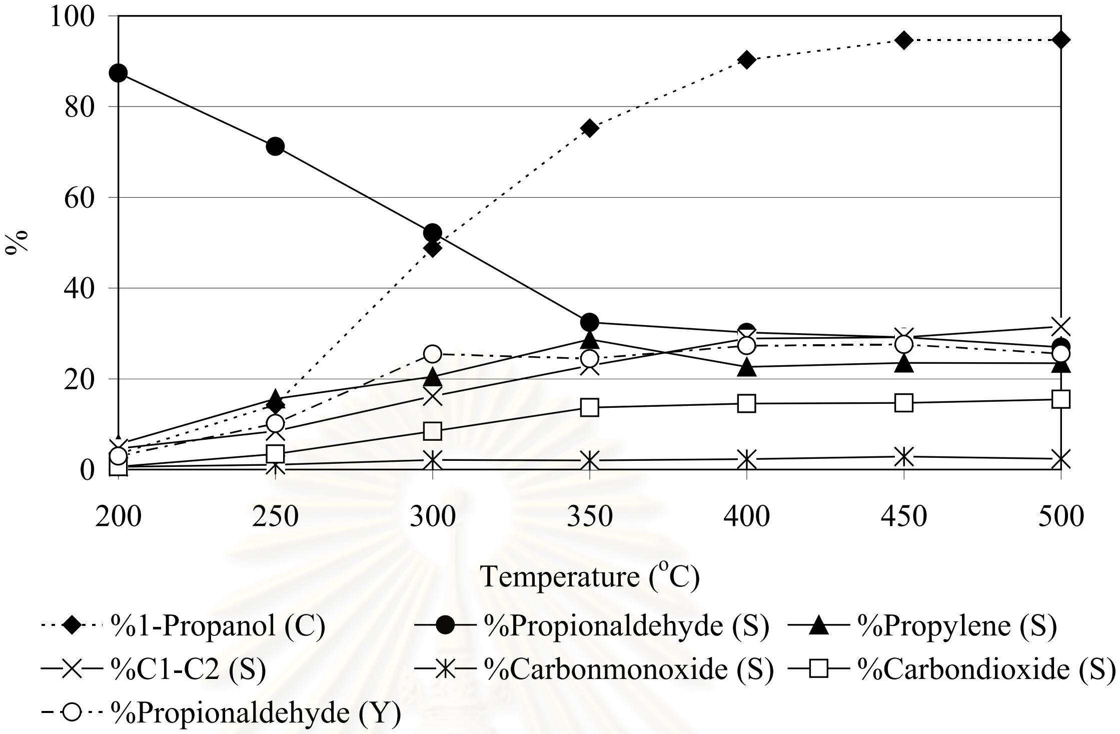

Figure 5.19a Catalytic property of 8MoOAl catalyst in the 1-propanol oxidation

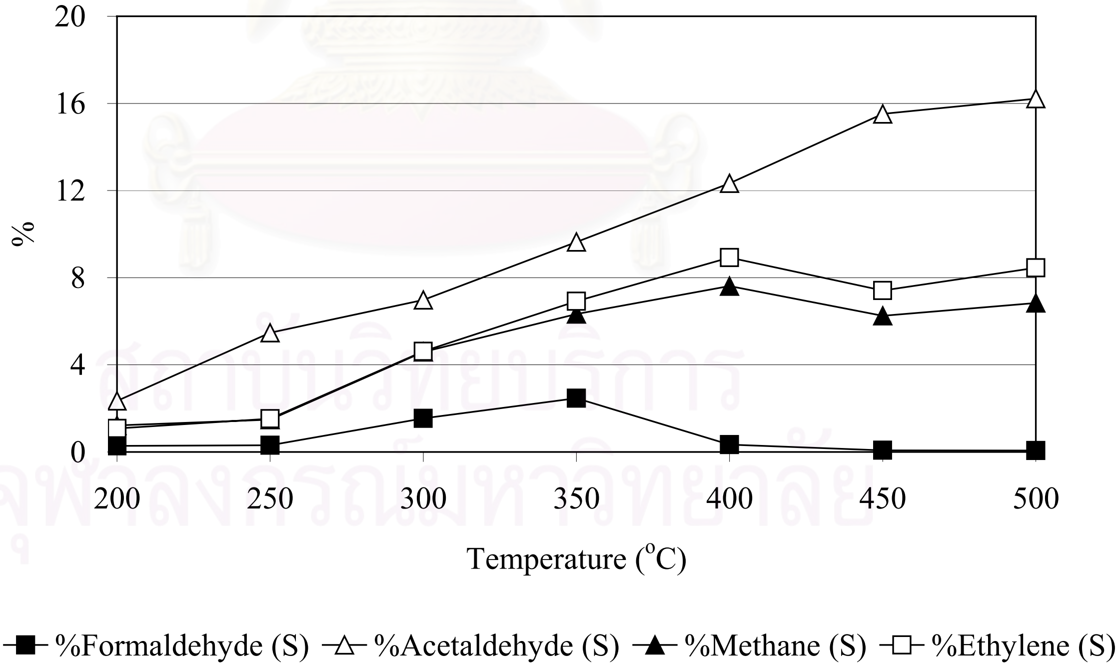

Figure 5.19b C1-C2 products of 8MoOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

j) 8WOAl

The catalyst property of 8WOAl catalyst on 1-propanol oxidation is illustrated in Figures 5.20a and 5.20b. The 1-propanol conversion increased from 8% to 89% at the temperature range of 200–400°C and steadily increased until the temperature reach 500°C, which the conversion was about 93%.

At low 1-propanol conversion (200-300°C) the major reaction products are propionaldehyde, propylene and C1-C2 products. Also, there are some formations of CO_2 and CO. While at high 1-propanol conversion (300-500°C) the main products are propylene and C1-C2 products. There are some formation of CO_2 and propionaldehyde. Consequently, the selectivity of propionaldehyde moderately falls from 76% to 10% and the selectivities of CO_2 slightly rise from 1% to 16% with increasing reaction temperature from 200-500°C. However the propylene and C1-C2 selectivity rises form 5% to 30% and 8% to 42%, respectively, in the temperature range 200-500°C. The maximum yield of propionaldehyde is ca. 21% at 400°C.

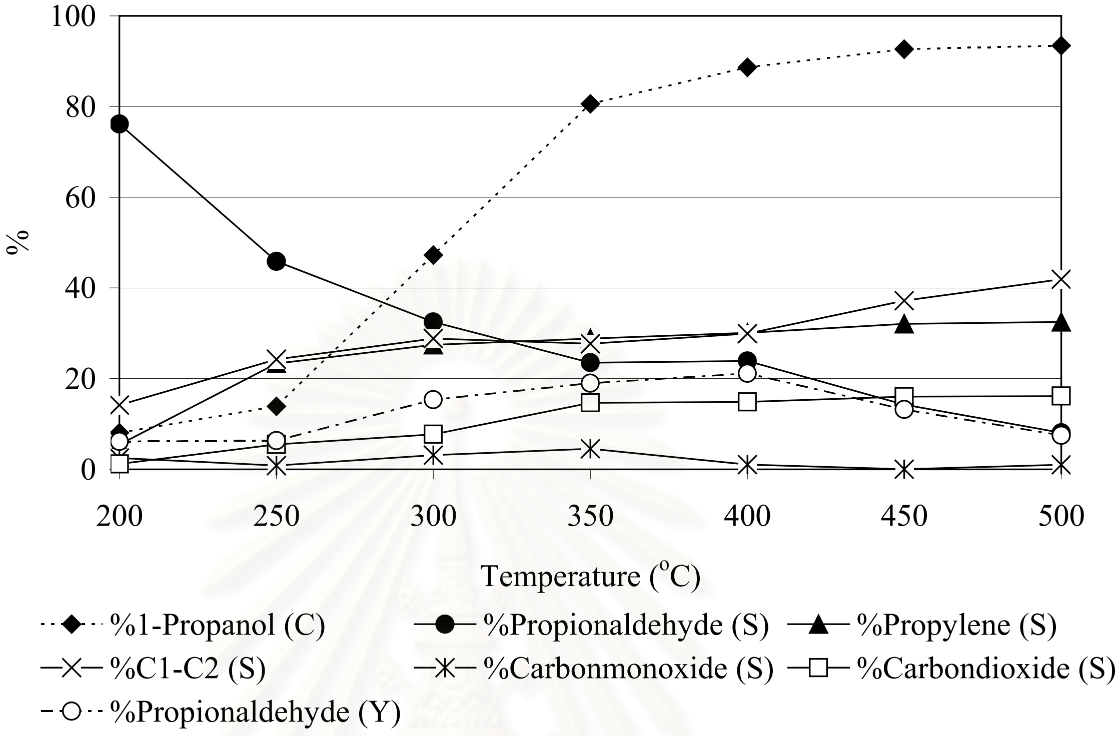

Figure 5.20a Catalytic property of 8WOAl catalyst in the 1-propanol oxidation

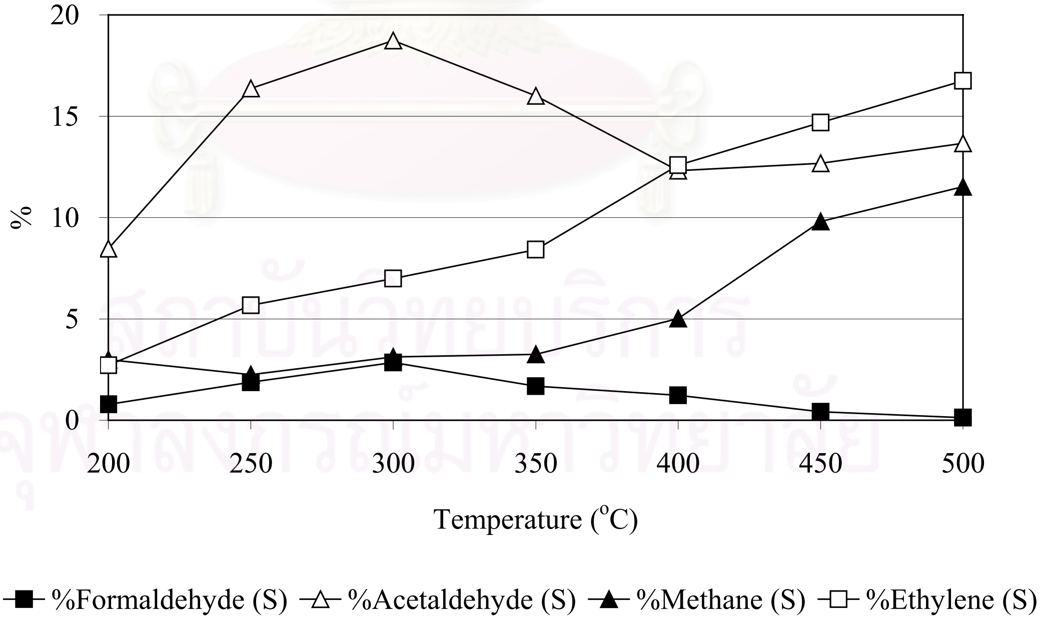

Figure 5.20b C1-C2 products of 8WOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

To accommodate for consideration and discussion in details, overall images of catalyst activity behavior are carefully collected. From all the reaction tests described above, there are two main groups of products formed in the 1-propanol conversion. The former group is the so-called redox products consisting of aldehydes (propionaldehyde, acetaldehyde and formaldehyde) and CO_x (CO and CO_2) while the latter one, acid products, is comprised of propylene, ethylene and methane. In this work, the activity behavior of the catalysts can be evaluated in terms of product yield, especially emphasizing yield of propionaldehyde, which is the desired product as shown in Figure 5.21. When similarity in patterns of catalytic behavior are remarkably focused, three groups of the catalysts can be distinguished and will be denoted as Group A, B and C hereafter.

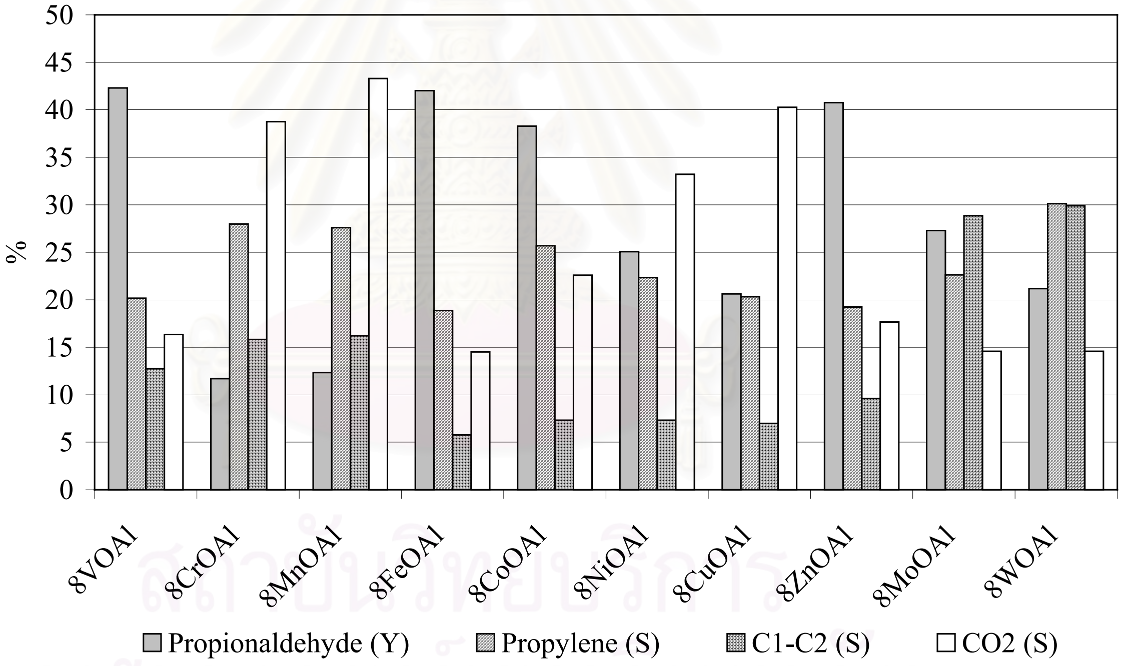

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Figure 5.21 Catalytic property of transition metal oxide catalyst in the 1-propanol oxidation at 400°C

Group A catalysts consisting of 8CrOAl, 8MnOAl, 8NiOAl and 8CuOAl reveal low propionaldehyde yield and high selectivity to CO_2. 8VOAl, 8CoOAl, 8FeOAl and 8ZnOAl (Group B catalysts) show high propionaldehyde. Additionally, CO_2 selectivity is less than that observed from Group A catalysts. Group C catalysts (Mo and W) give low propionaldehyde yield and high selectivity to propylene and C1-C2 products.

Basically, the presence of acid-base sites can play a significant role in oxidation reactions [Centi (2001)]. Different behaviors observed on the catalytic activity over various types of catalysts may be presumably due to the difference of acid-base properties of such catalysts. Many attempts have been made to find correlation between acid-base characteristics and catalytic activity employing various characterization techniques, e.g. pyridine adsorption or NH_3-TPD. In this study, the technique of pyridine adsorption is used to quantitatively determine the acidity of the catalysts. Details of experiment are presented previously in experimental section (Chapter 4). Table 5.2 lists the relative amount of pyridine adsorption of the alumina-supported transition metal oxide catalysts.

Table 5.3 The relative amount of pyridine adsorption compare with Al_2O_3 for transition metal oxide catalysts (Al_2O_3 = 1.00)

Catalyst	**Relative amount of pyridine absorbed per unit surface**	**Catalyst**	**Relative amount of pyridine absorbed per unit surface**
8VOAl	1.03	8NiOAl	0.60
8CrOAl	1.30	8CuOAl	0.61
8MnOAl	1.96	8ZnOAl	0.75
8FeOAl	0.65	8MoOAl	2.13
8CoOAl	1.02	8WOAl	1.89

Assuming that adsorption of pyridine on alumina support is unity, the values less than 1.00 represent the lower acidity whereas the values above 1.00 correspond to higher acidity compared to the acidity of alumina support. As seen, there is no simple correlation between the amount of acid sites (acidity) and the catalyst activity observed. For example, according to the activity behavior; 8NiOAl, 8CuOAl, 8CrOAl and 8MnOAl are in the same group, therefore their acidity should be in the similar region values if acidity is the key role to explain activity behavior. However, the amount of acidity observed is 0.60, 0.61, 1.30 and 1.96 for 8NiOAl, 8CuOAl, 8CrOAl and 8MnOAl catalysts, respectively. Obviously, the explanation of acidic sites can explain the catalytic behavior of 8NiOAl and 8CuOAl, but fails to explain the rest. Or, in another case, 8MnOAl and 8WOAl give approximately the same acidity values, however, their catalytic behavior is totally different (belongs in group A and group C, respectively). Therefore, it is likely that the catalytic behavior depends on other influencing parameters.

There is general agreement that the electrophilic oxygen species, is associated with nonselective total oxidation of the hydrocarbon, while the nucleophilic oxygen is involved in selective insertion of oxygen into the hydrocarbon molecule to form partial oxygen products (aldehydes, acids, e.g., from the corresponding alkenes) [Centi (2001)]. Considering the nature of such oxygen species, adsorption strength of electrophilic species on the surface is lower than that of nucleophilic species. Although the distinction between electrophilic and nucleophilic species cannot be directly measured, attempts to indirectly envisage the interaction of oxygen species on the surface are made by employing temperature programmed reduction technique. It is noted that the identification of TPR profiles is not attempted here, but the oxygen activation by considering the reduction temperature. Additionally, the quantity of reduced species is also considered by measuring the integral area underneath the TPR profiles as shown in Figure 5.22. It is noted that the analysis of TPR profiles is based on the patterns of catalytic activity previously mentioned.

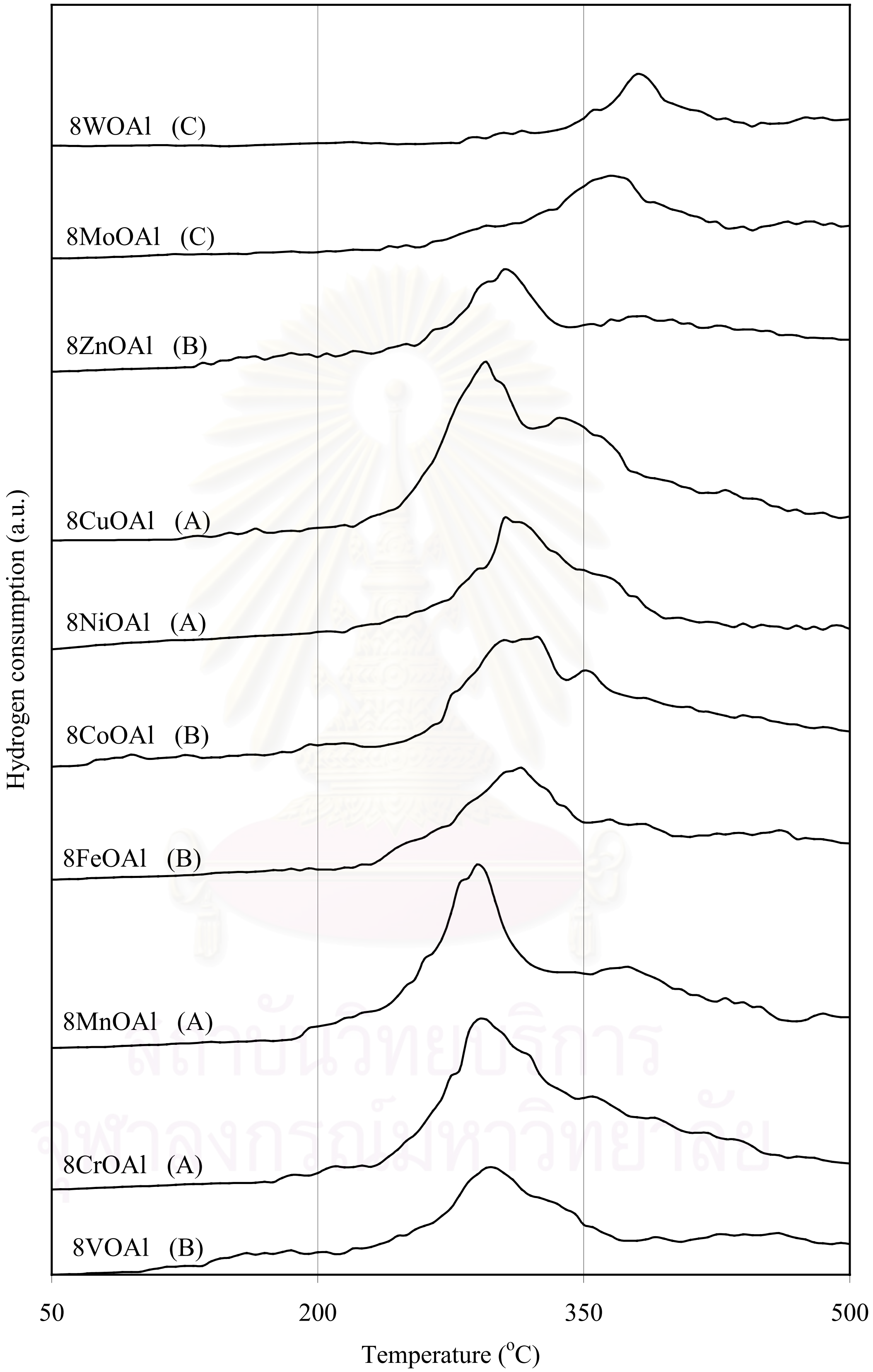

Figure 5.22 Temperature programmed reduction profiles of transition metal oxide catalysts

Group A catalysts (8CrOAl, 8MnOAl, and 8CuOAl) show the also the same TPR patterns, i.e., (1) maxima at low temperature region (290-295°C) and (2) high amount of reduced species. It is remarkable that the TPR profile observed from 8NiOAl catalyst is different from other catalysts in this group, although the similarity in catalytic pattern is registered. Group B (8VOAl, 8FeOAl, 8CoOAl and 8ZnOAl) gives lower amount of reduced species compared to Group A catalysts. The TPR maxima observed from Group B catalysts also shift to higher temperature (300-315°C). Group C catalysts (8MoOAl and 8WOAl) show the distinguishable behavior; i.e., the peak maxima shift to very higher temperature (360°C for 8MoOAl and 380°C for 8WOAl) and a very small amount of reduced species is seen.

Generally, the TPR maxima refer to the oxygen activation of the sample, i.e., the shift of the TPR maxima to higher temperature means the stronger oxygen activation. Therefore, the oxygen activation of the catalysts drawn from lower to higher is as follows:

Group A < Group B < Group C

Taking the integral area underneath the TPR profiles observed from the catalyst samples in Figure 5.21 into account, it is suggested that the three groups of catalysts previously mentioned (Group A, B and C) also have approximately the same amount of reduced species. Group A catalysts show high integral area, implying that these catalysts contained high level of reduced lattice oxygen whereas Group B and C give lower amount of reduced species.

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Observation of similarity between the catalytic pattern and the pattern of TPR profiles suggests that the redox property of the catalysts can explain the catalytic behavior. Group A catalysts, whose lattice oxygen can be reduced easily, indicating from low temperature TPR maxima (290-295°C), and also high level of reduced species, show high selectivity to CO_2. It is likely that the catalysts in this group contain high level of lattice oxygen which may readily react with 1-propanol to form propionaldehyde. High conversion of 1-propanol is also revealed. The propionaldehyde produced may react further with excess oxygen to form CO_x products. On the other hand, TPR maxima observed from the catalysts in group B shift to higher temperature, suggesting the lower oxygen activation with respect to group A catalysts. Additionally, the lower amount of reduced species is found from catalysts in this group. This suggests a lower concentration of lattice oxygen to react with 1-propanol. Propionaldehyde product is therefore observed at higher temperature region and is more difficult to further react to form CO_x products. For group C catalysts where TPR maxima are located at very high temperature with a small quantity of reduced species suggest that the reaction of 1-propanol with lattice oxygen preferably takes place at very high temperature. Consecutive reactions of propionaldehyde are also limited as a consequence.

According to the study of acidic and redox properties mentioned above, attempts to explain the catalytic behaviour observed from all catalysts will be made as follows:

Group A catalysts (8CrOAl, 8MnOAl, 8NiOAl and 8CuOAl) yield high level of CO_2 products because of their high redox properties. Consideration of the products observed suggests that acidity property also have significant effect on the product selectivity. High amount of propylene, C1-C2 and CO_2 is exhibited from 8CrOAl and 8MnOAl catalysts as they contain more acidic sites compared to those of 8NiOAl and 8CuOAl catalysts.

In contrast with group A catalysts, 8MoOAl and 8WOAl catalysts (group C) show a more dominant acidic property than redox property. Dehydration which favors acidic sites is therefore preferable, giving high level of propylene and C1-C2 products.

Group B catalysts (8VOAl, 8FeOAl, 8CoOAl and 8ZnOAl) give highest desired propionaldehyde product compared to other two groups. The amount of reduced species observed from the catalysts in this group is smaller than group A, but higher than group C catalysts. The proper proportion of lattice oxygen is expected to provide for the reaction with 1-propanol without further reaction of propionaldehyde product. A higher propylene and C1-C2 products is expected from 8VOAl and 8CoOAl catalysts compared to 8FeOAl and 8ZnOAl catalysts as a result of higher acidic sites.

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5.3 Effect of MgO on the activity of alumina-supported transition metal oxide catalysts for the selective oxidation of 1-propanol

Regarding the previous work by Chaiyasit, 2000, the MgO promoted Co/Al_2O_3 catalyst has given a high activity for the selective oxidation of 1-propanol to propionaldehyde. It is also interesting to see how MgO addition affects other transition metal oxide catalysts for this reaction. In this section, MgO was introduced into the transition metal oxide catalysts studied in section 5.2 and the reaction test at the identical conditions was performed.

It is well known that MgO has a strong basicity characteristic which is different from other catalysts previously mentioned. Therefore, before studying the effect of MgO on the catalytic behavior of alumina-supported transition metal oxide catalysts for the selective oxidation of 1-propanol, the effect of MgO on alumina support will be investigated first. Figures 5.22 to 5.24 depict catalyst activity for selective oxidation of 1-propanol over alumina support, 4 wt% of Mg (4MgOAl) and 10 wt% of Mg (10MgOAl), respectively. Addition of MgO, as shown in Figure 5.26, slightly affects overall conversion of 1-propanol and selectivity of C1-C2 and COx. However, a significant decrease in propylene product and an increase in propionaldehyde yield are observed. A remarkable decrease in selectivity of propylene can be explained by the reduction of acid sites where dehydration of 1-propanol proceeds [Thomasson (1999)] by promoting with MgO. On the other hand, the higher amount of propionaldehyde product observed is believed to be a result of the basic sites increased by MgO addition. This is in good agreement with reported by Rekoske (1996) and Kulkarni (2002) that both acid and basic sites promoted the activity for oxidative dehydrogenation (selective oxidation).

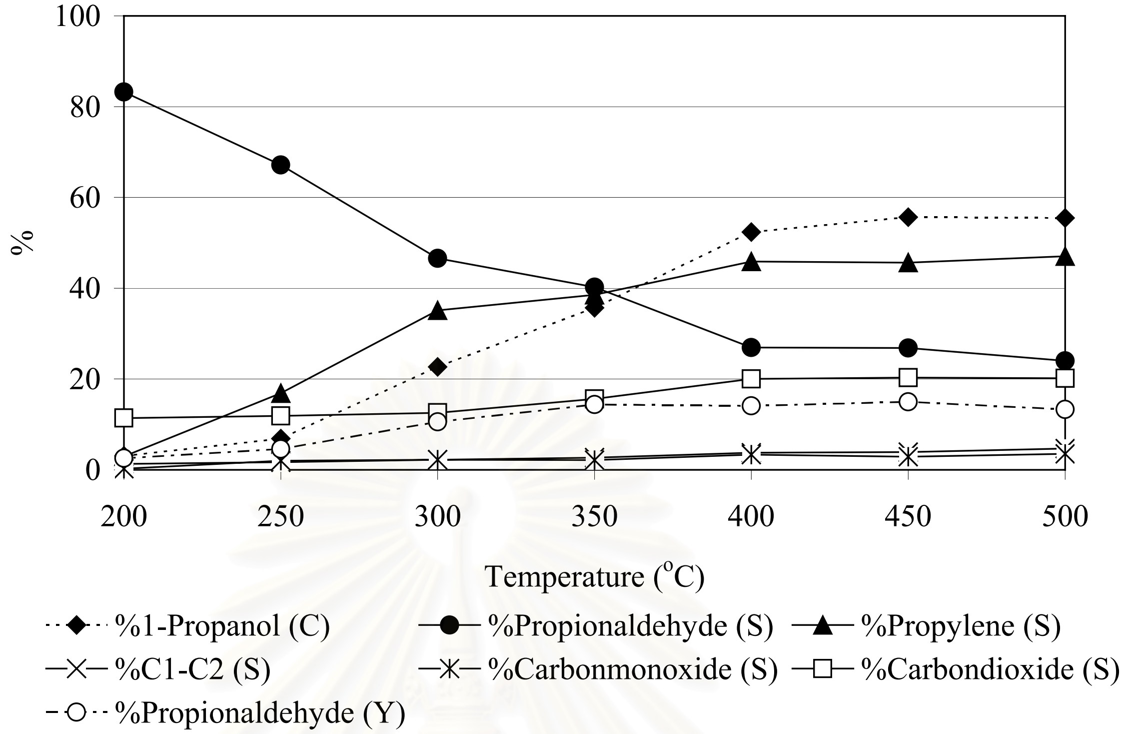

Figure 5.23a Catalytic property of Al_2O_3 support in the 1-propanol oxidation

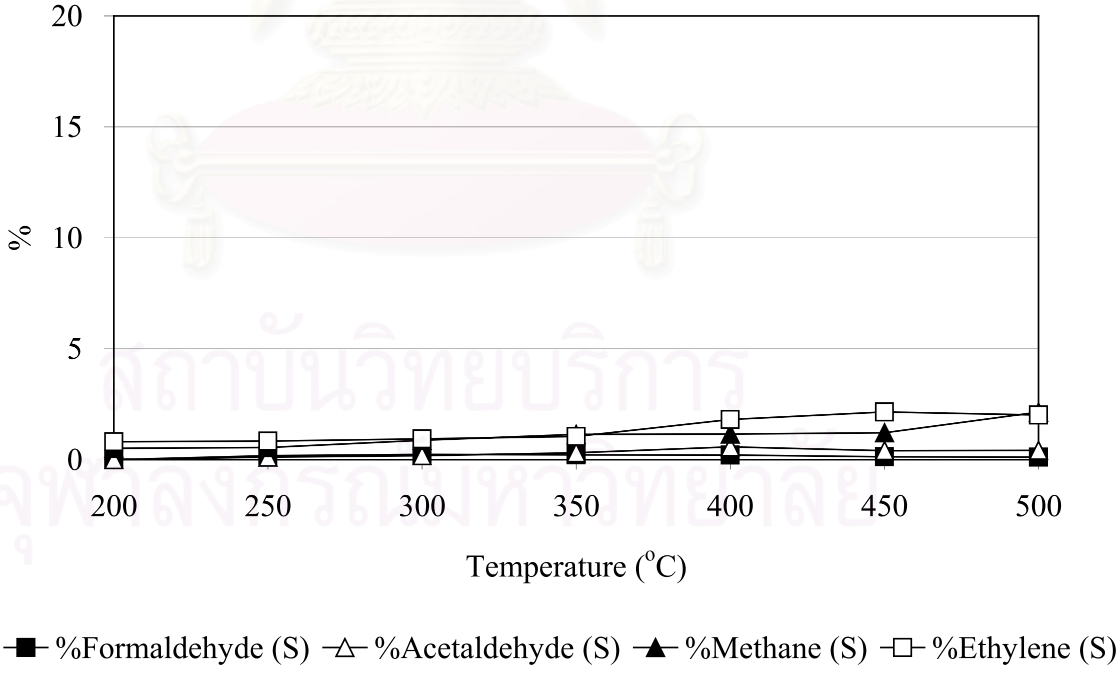

Figure 5.23b C1-C2 products of Al_2O_3 support in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

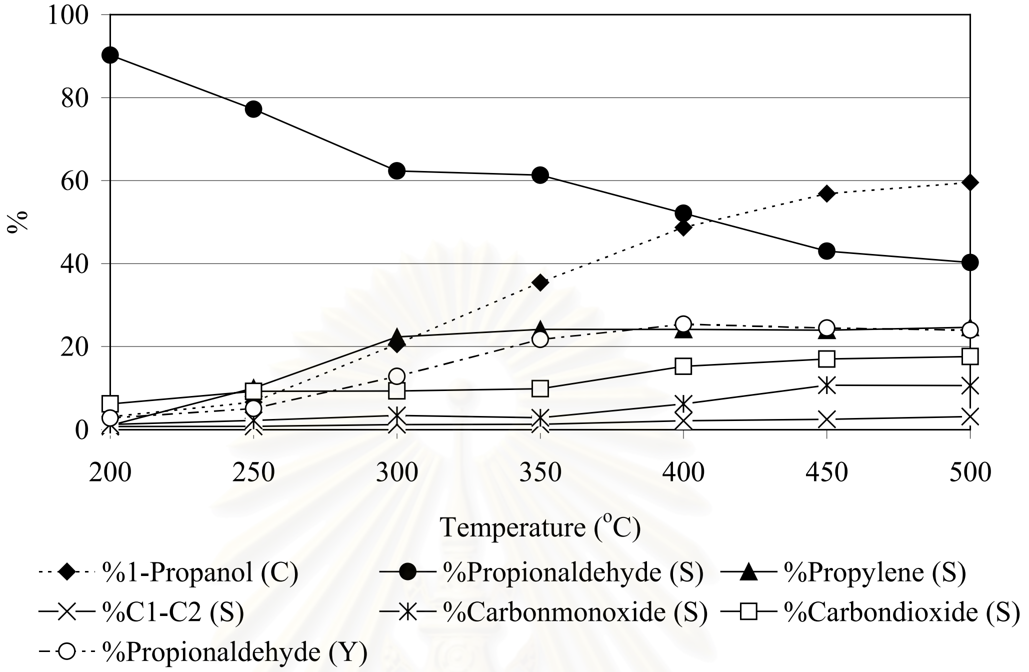

Figure 5.24a Catalytic property of 4MgOAl catalyst in the 1-propanol oxidation

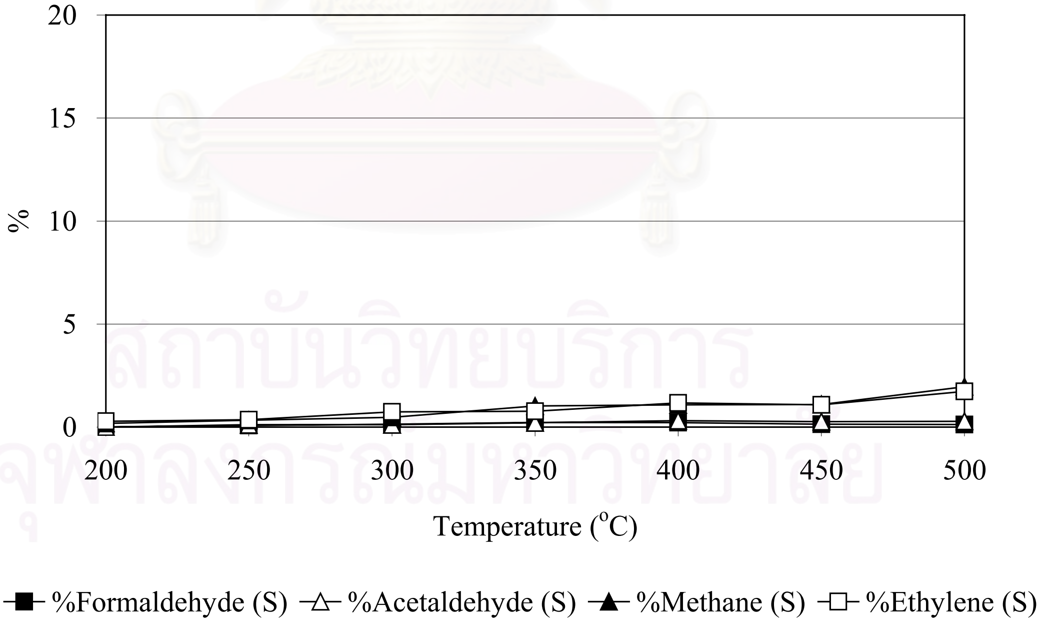

Figure 5.24b C1-C2 products of 4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

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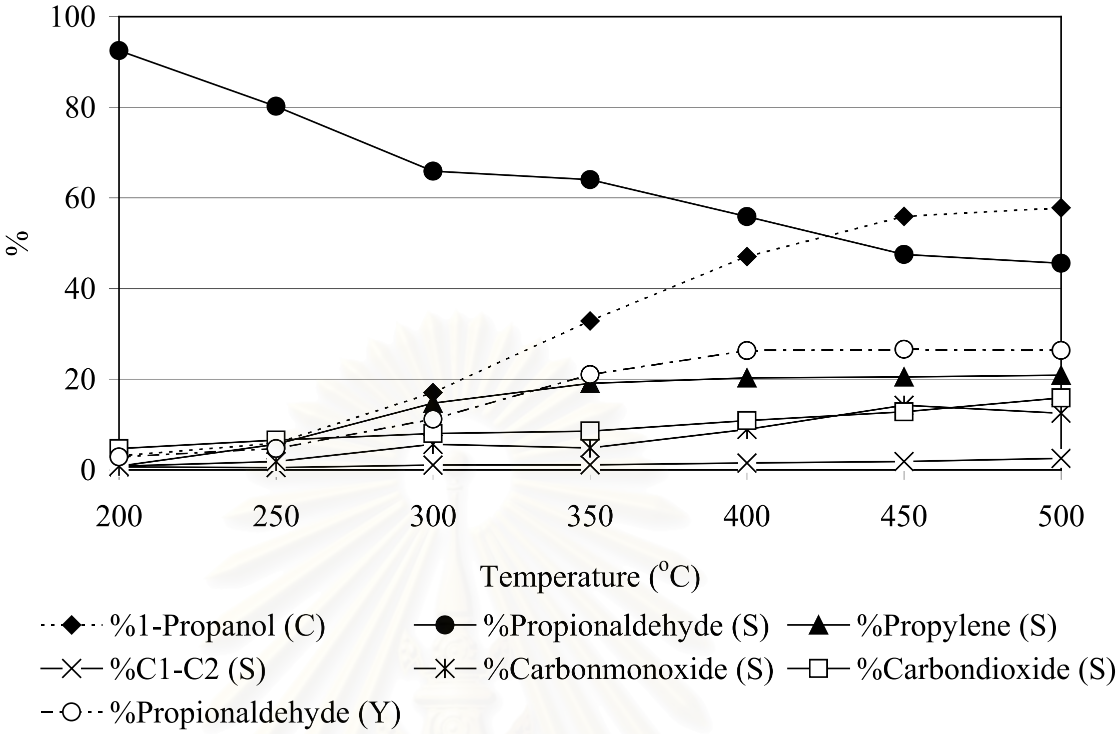

Figure 5.25a Catalytic property of 10MgOAl catalyst in the 1-propanol oxidation

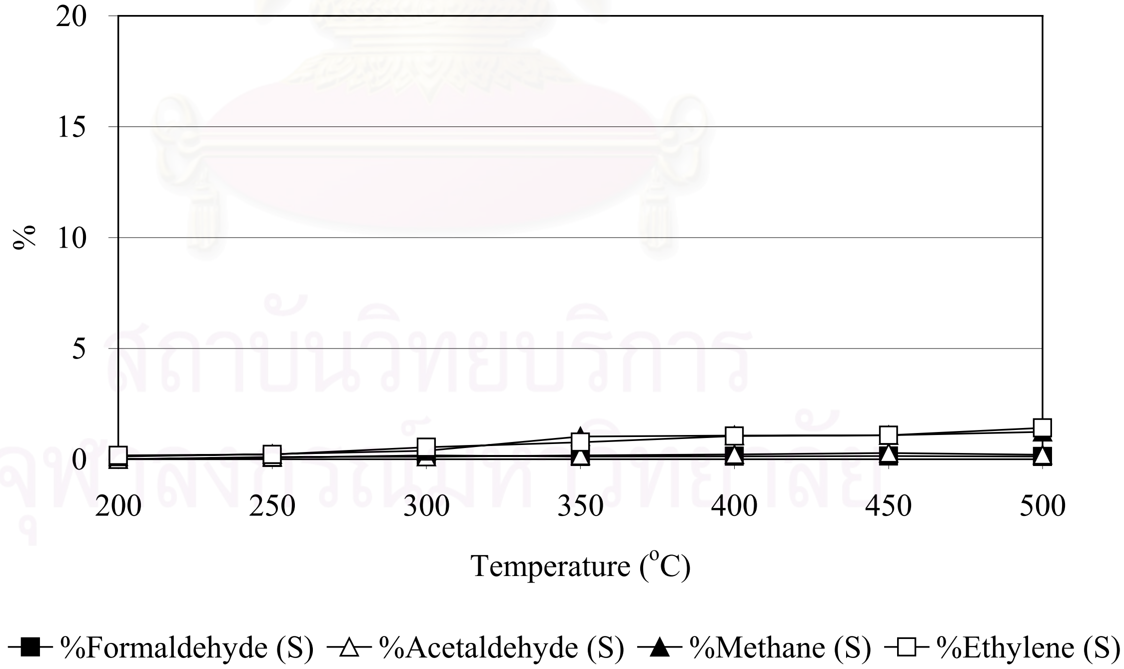

Figure 5.25b C1-C2 products of 10MgOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

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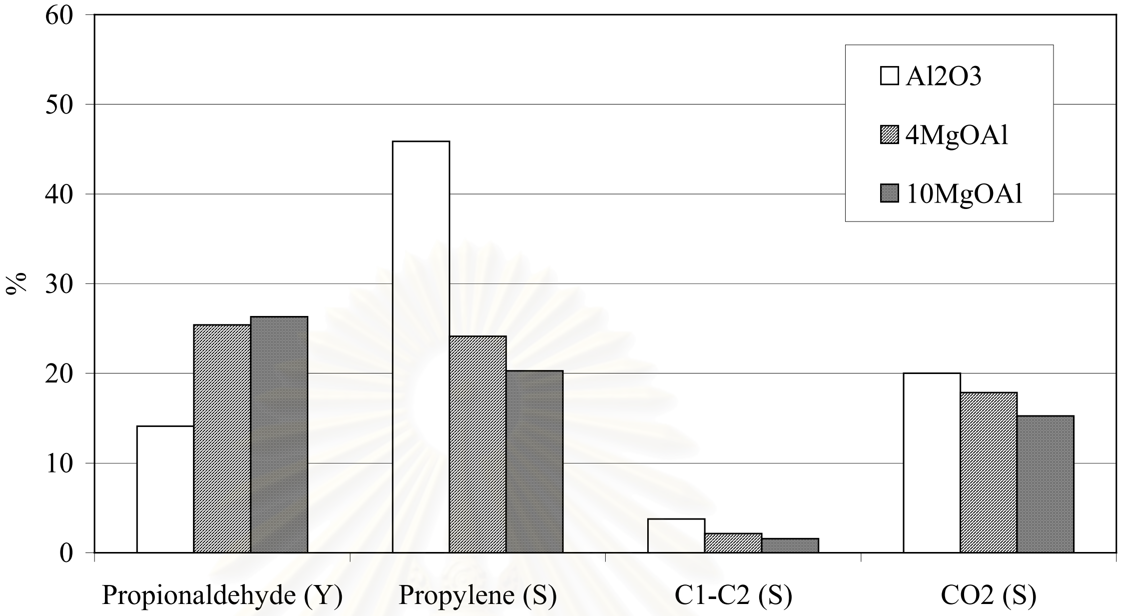

Figure 5.26 The effect of MgO loading on alumina support at 400°C

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Effect of MgO addition on the catalytic behaviour of alumina-supported transition metal oxides is described as below.

5.3.1 Vanadium oxide catalysts

a) 8V4MgOAl

Figures 5.27a and 5.27b show the catalytic activity of 8V4MgOAl catalyst for 1-propanol oxidation reaction. At low reaction temperature the 1-propanol conversion slightly increases from 7% to 26% on the increase of reaction temperature from 200 to 250°C. The conversion of 1-propanol significantly rises from 26% to 88% in the temperature range 250-400°C and then gradually increases up to 94% at 500°C.

At the initial reaction temperature (200-300°C) the main product is propionaldehyde and there are some formations of propylene, CO_2 and with traces amount of formaldehyde, acetaldehyde, methane, ethylene and CO. When increasing reaction temperature (350-500°C), the main products are propionaldehyde, propylene and CO_2 and with traces of formaldehyde, acetaldehyde, methane, and ethylene. Consequently, the selectivity of propionaldehyde moderately falls from 93% to 40% and the selectivities of CO_2 and propylene slightly rise from 0% to 19% and 2% to19%, respectively, with increasing reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 49% at 350°C

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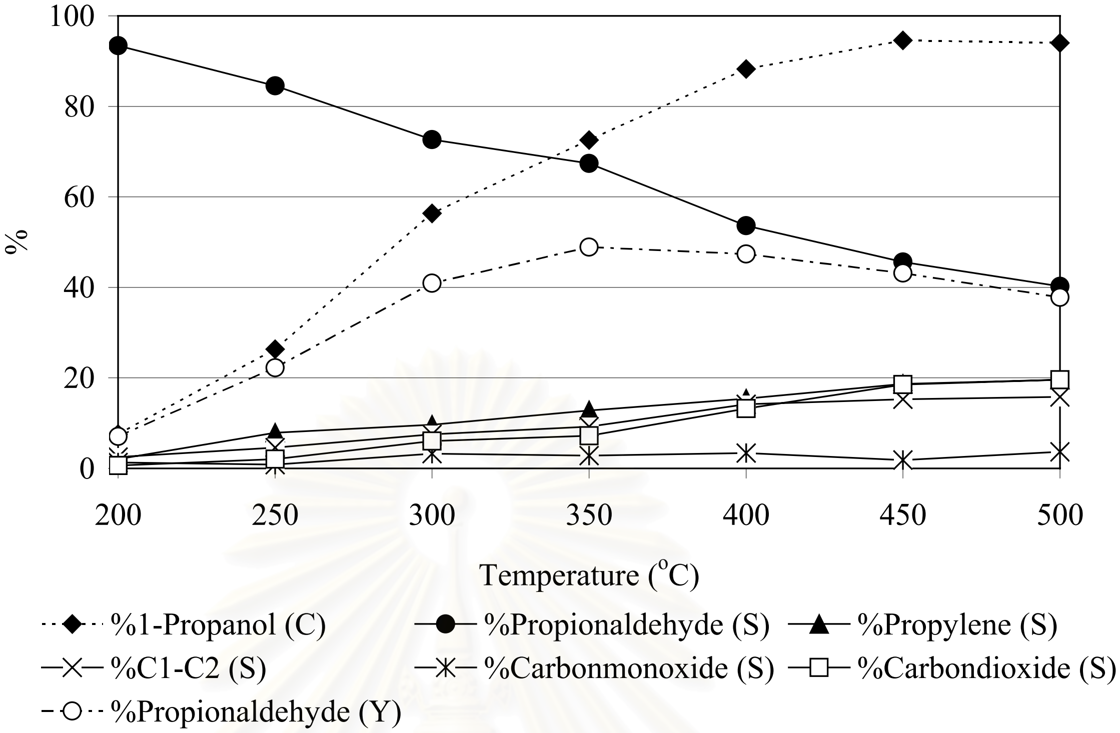

Figure 5.27a Catalytic property of 8V4MgOAl catalyst in the 1-propanol oxidation

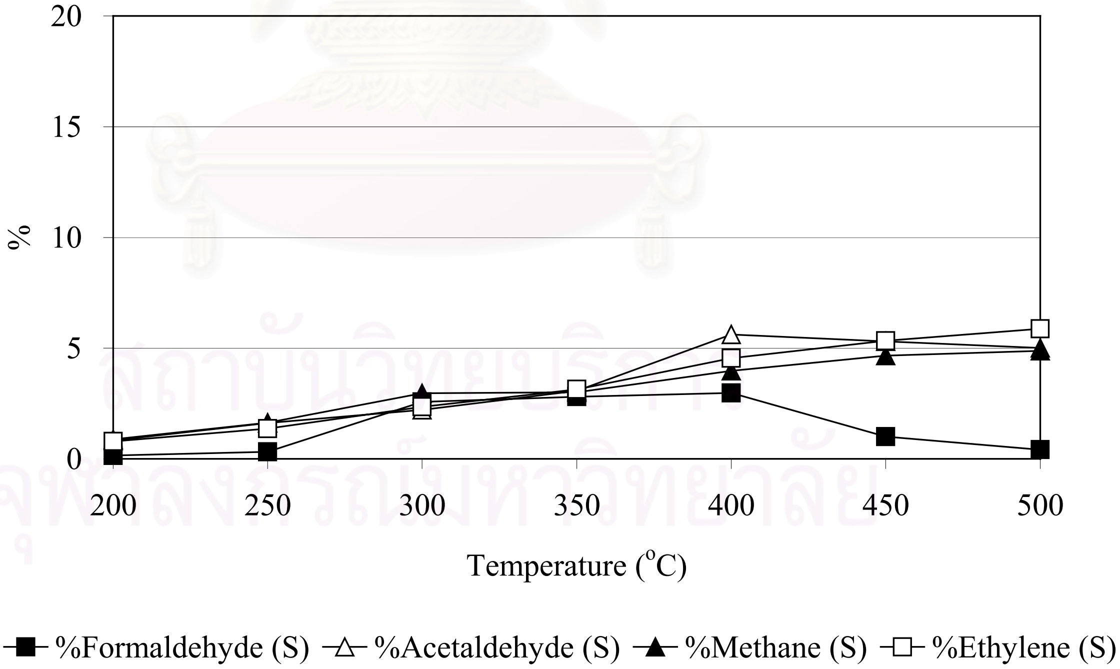

Figure 5.27b C1-C2 products of 8V4MgOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

b) 8V10MgOAl

The behavior of 8V10MgOAl catalyst for 1-propanol oxidation is illustrated in Figures 5.28a and 5.28b. In the initial reaction temperature, the conversion of 1-propanol gradually increases from 3% to 14% on the increase reaction temperature from 200 to 250°C. When the reaction temperature is higher than 250°C the 1-propanol conversion of this catalyst rapidly rises to 90% at 400°C and slightly increases up to 91% at 500°C.

At low 1-propanol conversion the main oxidation product is propionaldehyde with small amount of propylene and CO_2. At high 1-propanol conversion (above 350°C) propionaldehyde selectivity rapidly decreases while CO_2 and propylene selectivities quickly increase. The selectivity to propylene is lower than 8VOAl and 8V4MgOAl catalysts at all reaction temperature. The maximum selectivities to CO_2 and propylene are about 20% and 17% at 500°C, respectively. The maximum yield of propionaldehyde is ca. 45% at 400°C.

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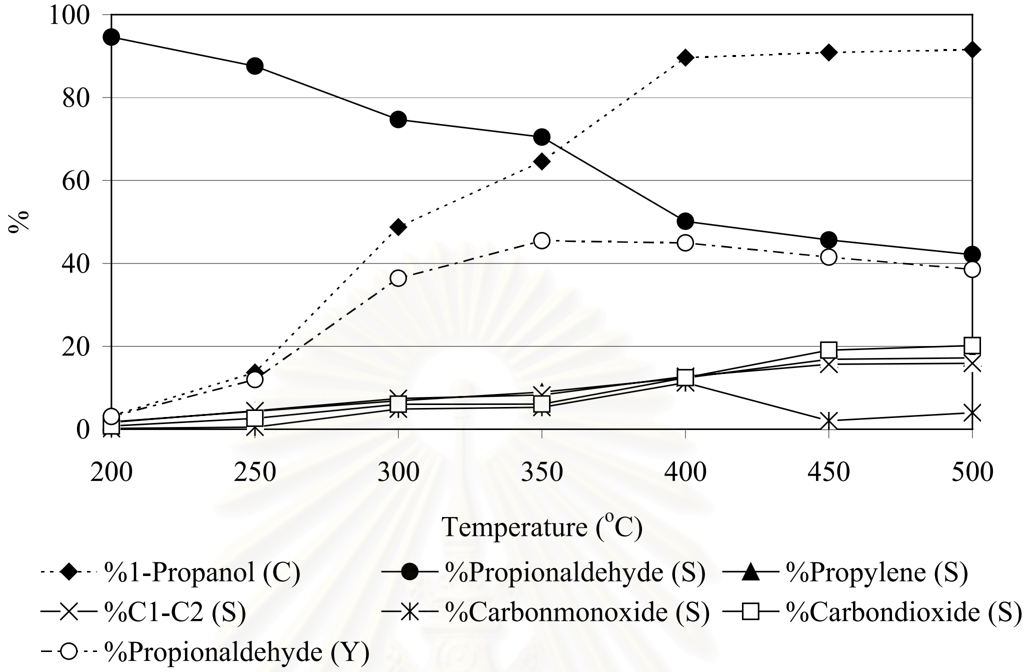

Figure 5.28a Catalytic property of 8V10MgOAl catalyst in the 1-propanol oxidation

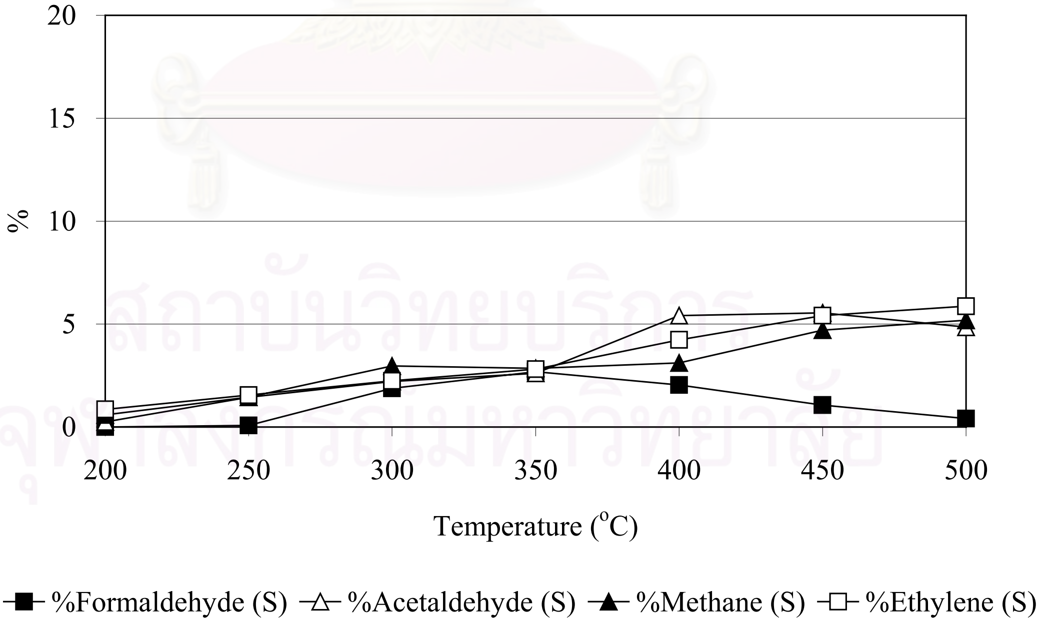

Figure 5.28b C1-C2 products of 8V10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

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Figure 5.29 showed the summary of the effect of MgO loading for the V-oxide catalysts at the reaction temperature of 400°C.

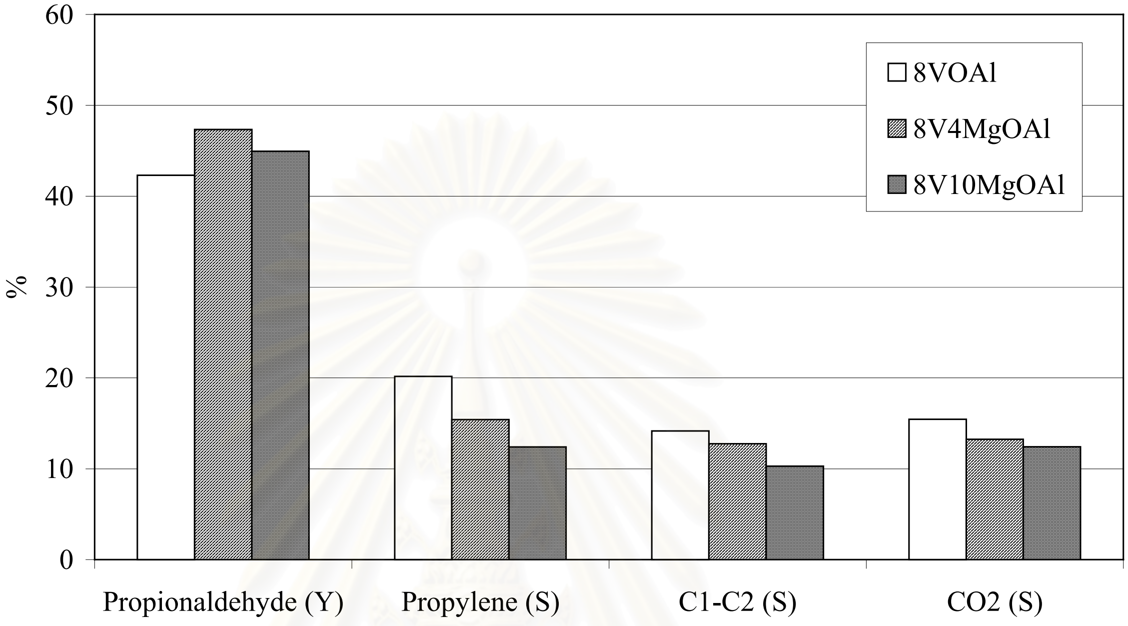

Figure 5.29 The catalytic properties of 1-propanol oxidation for V-oxide catalysts at 400°C

5.3.2 Chromium oxide catalyst

a) 8Cr4MgOAl

The catalytic results, obtained in the oxidation of 1-propanol on 8Cr4MgOAl are illustrated in Figures 5.30a and 5.30b. The conversion of 1-propanol increases from 23% to 81% on the increase of reaction temperature from 200°C to 300°C and the slightly increases up to 96% at 500°C. At low 1-propanol conversions the main products are propionaldehyde, whose selectivity progressively decreases (85% to 7%) and propylene. An increase in the formation of CO_2 (1% to 44%) is observed between 250°C and 500°C, together with small amounts of methane, ethylene and acetaldehyde and traces of formaldehyde. The maximum yield of propionaldehyde is ca. 35% at 250°C.

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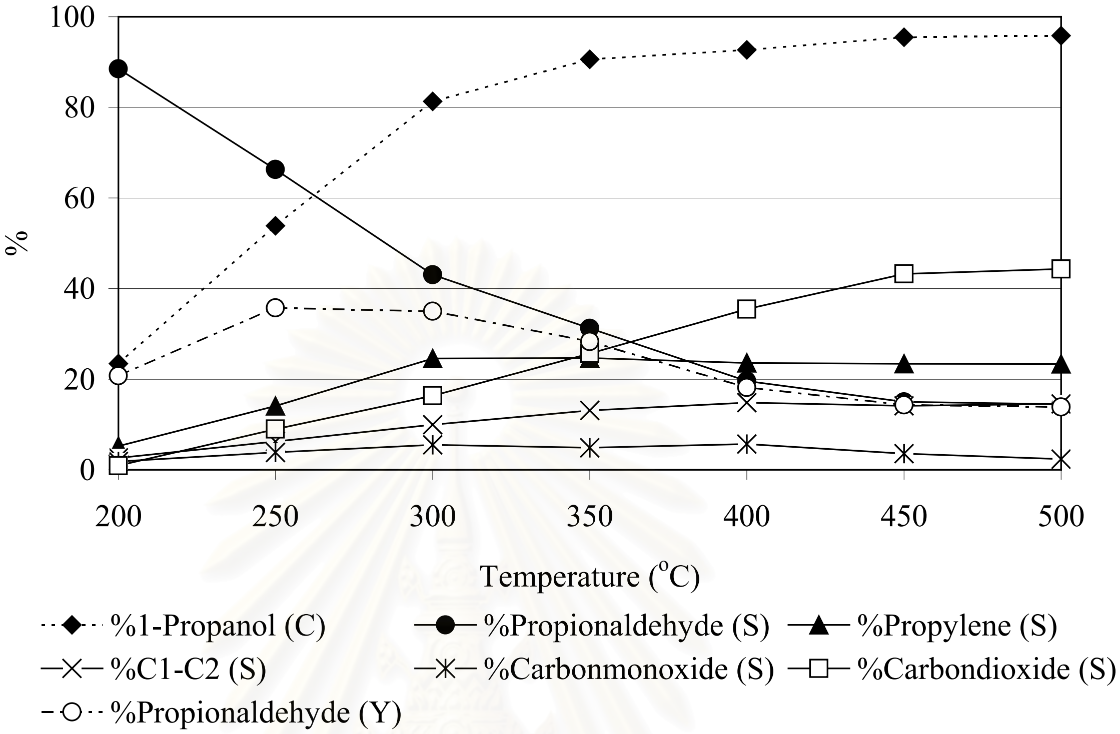

Figure 5.30a Catalytic property of 8Cr4MgOAl catalyst in the 1-propanol oxidation

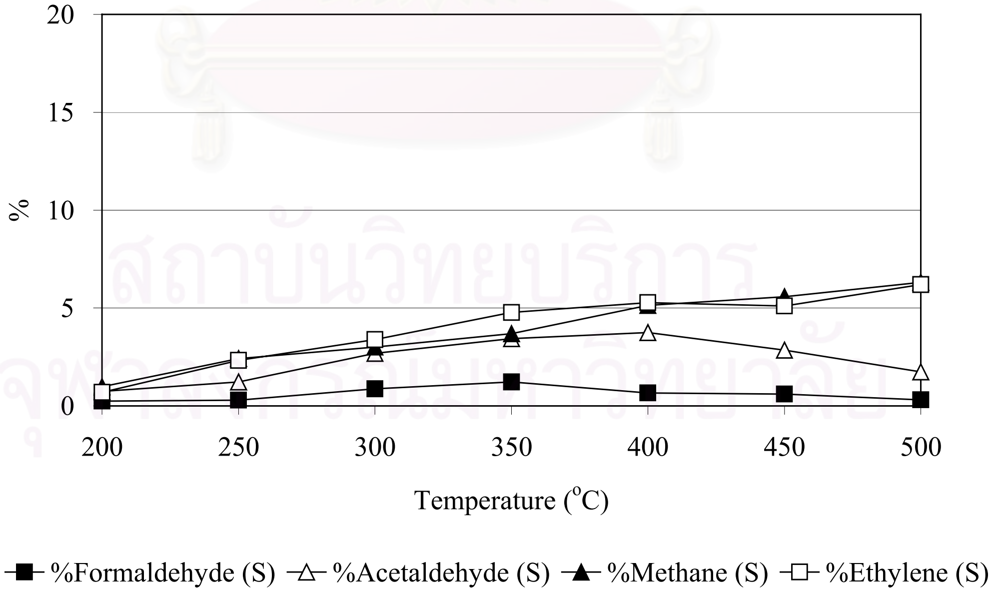

Figure 5.30b C1-C2 products of 8Cr4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Cr10MgOAl

The behavior of the 8Cr10MgOAl catalyst in 1-propanol oxidation is described in Figures 5.31a and 5.31b. Increasing the reaction temperature from 200^{o}C to 400^{o}C results in the increase in 1-propanol conversion from 21% to 92%. Further increasing temperature 94% conversion is obtained at reaction temperature 500^{o}C.

In the beginning (reaction temperature 200-350^{o}C), the main reaction products are propionaldehyde and propylene, some formation of CO_2. At the reaction temperature higher than 350^{o}C CO_2 is the main product. Some products of propionaldehyde, propylene, methane and ethylene are detected. Consequently, the selectivity of propionaldehyde substantially falls from 90% to 19% with increasing reaction temperature from 200-500^{o}C. The maximum yield of propionaldehyde is ca. 37% at 300^{o}C.

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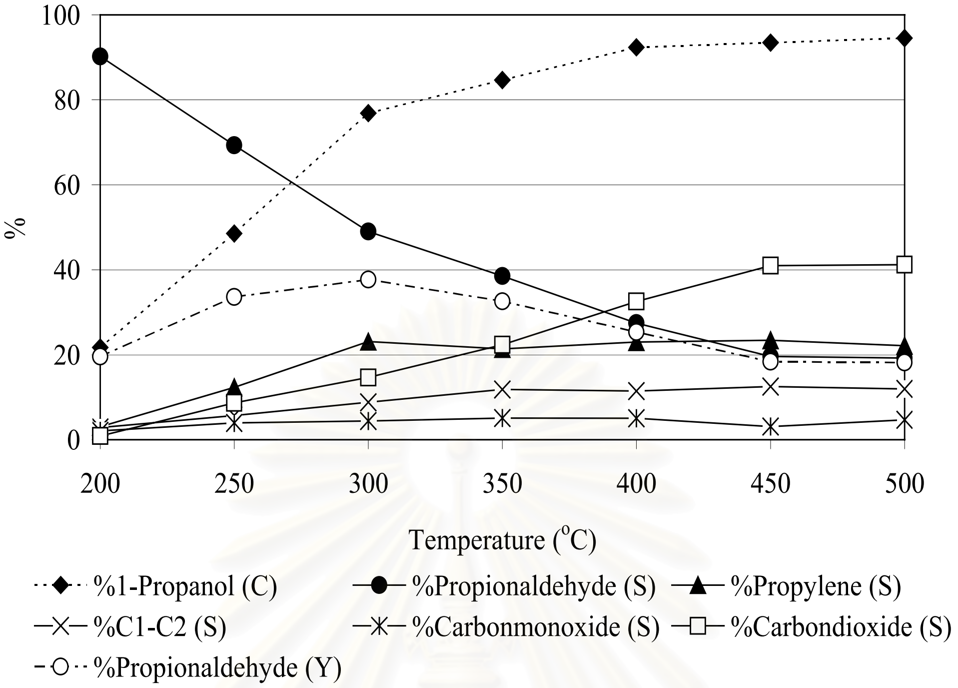

Figure 5.31a Catalytic property of 8Cr10MgOAl catalyst in the 1-propanol oxidation

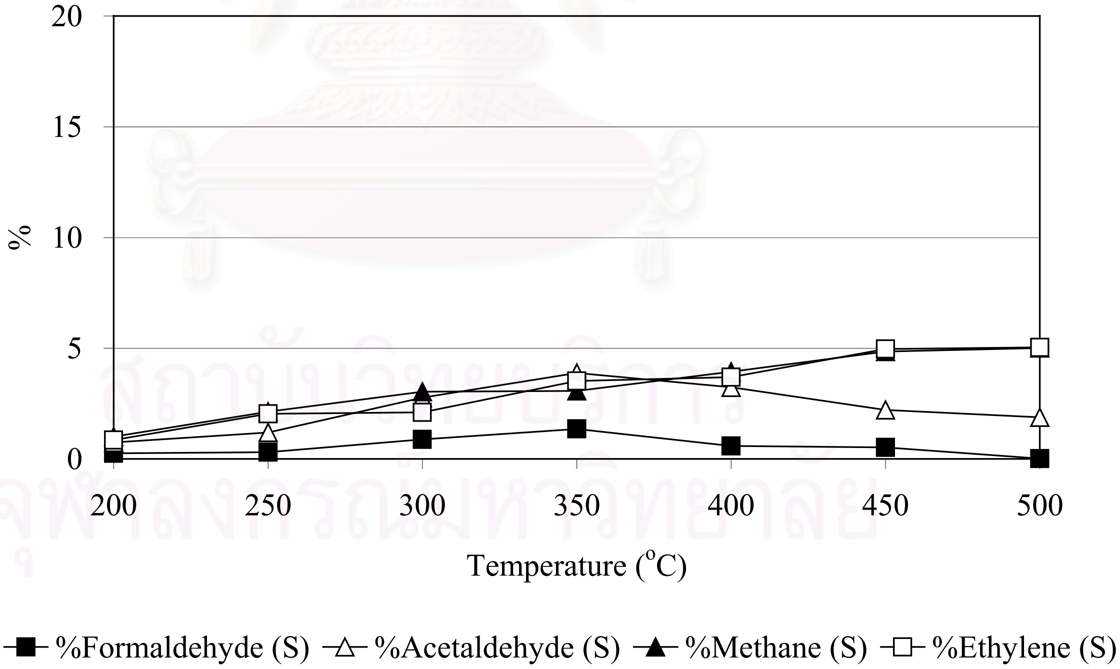

Figure 5.31b C1-C2 products of 8Cr10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

Figure 5.32 showed the summary of the effect of MgO loading for the Cr-oxide catalysts at the reaction temperature of 400°C.

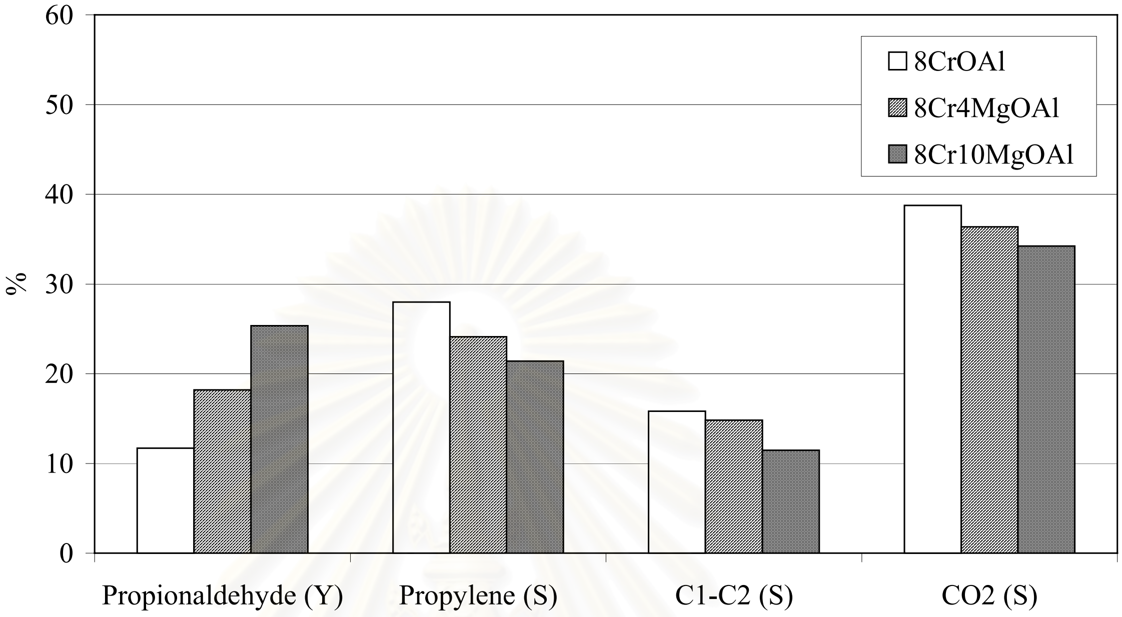

Figure 5.32 The catalytic properties of 1-propanol oxidation for Cr-oxide catalysts at 400°C

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5.3.3 Manganese oxide catalyst

a) 8Mn4MgOAl

The behavior of the 8Mn4MgOAl catalyst in 1-propanol oxidation is described in Figures 5.33a and 5.33b. Increasing the reaction temperature from 200°C to 350°C results in an increase in 1-propanol conversion from 18% to 88%. Further increasing the temperature, 96% conversion is obtained at the reaction temperature of 500°C.

In the beginning (reaction temperature range 200-350°C), the main reaction products are propionaldehyde and propylene, some formation of CO_2. At the reaction temperature higher than 350°C CO_2 is the main product. Some products of propionaldehyde and propylene are still detected. The selectivity of propionaldehyde substantially falls from 89% to 13% with increasing reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 36% at 300°C.

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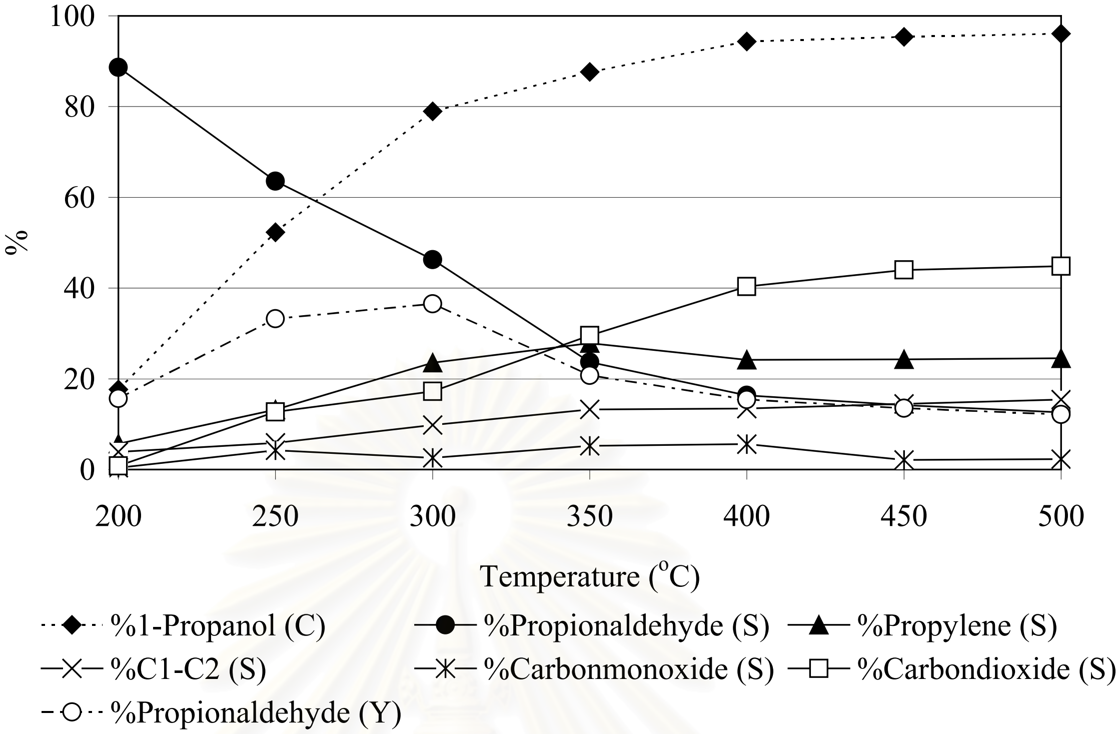

Figure 5.33a Catalytic property of 8Mn4MgOAl catalyst in the 1-propanol oxidation

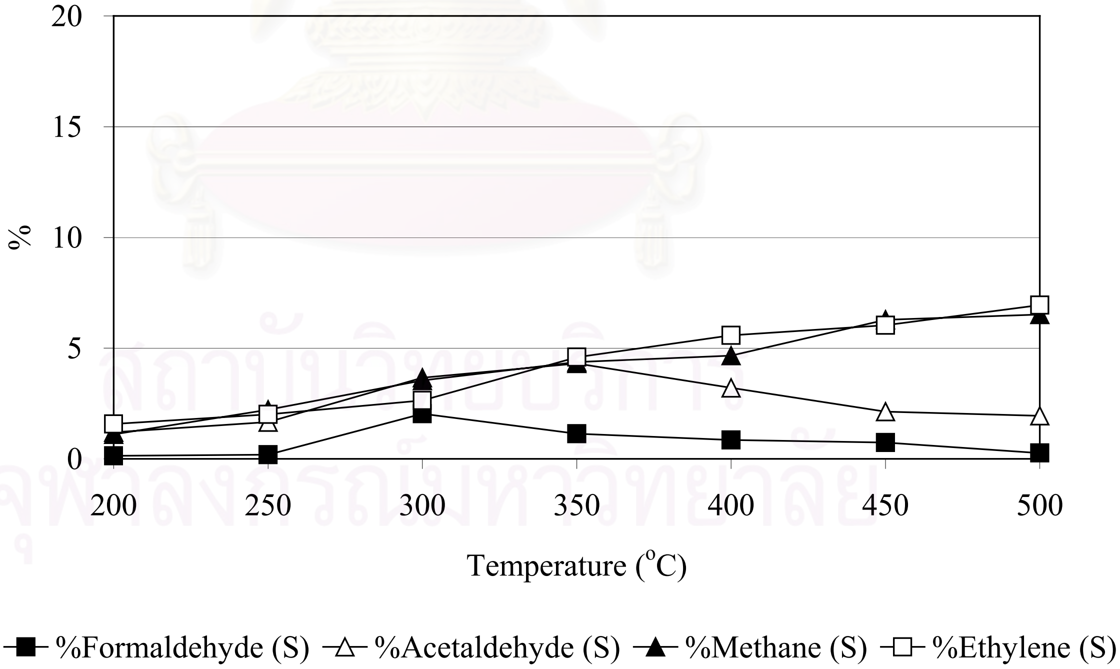

Figure 5.33b C1-C2 products of 8Mn4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Mn10MgOAl

The catalytic results, obtained in the oxidation of 1-propanol on 8Mn10MgOAl are illustrated in Figures 5.34a and 5.34b. The conversion of 1-propanol increases from 10% to 80% on the increase of reaction temperature from 200°C to 350°C and the slightly increases up to 92% at 500°C. At low 1-propanol conversions the main product is propionaldehyde, whose selectivity progressively decreases (89% to 18%). An increase in the formation of CO_2 (1% to 42%) is observed between 250°C and 500°C, together with formation of propylene, methane, ethylene and acetaldehyde and traces of formaldehyde. The maximum yield of propionaldehyde is ca. 35% at 300°C.

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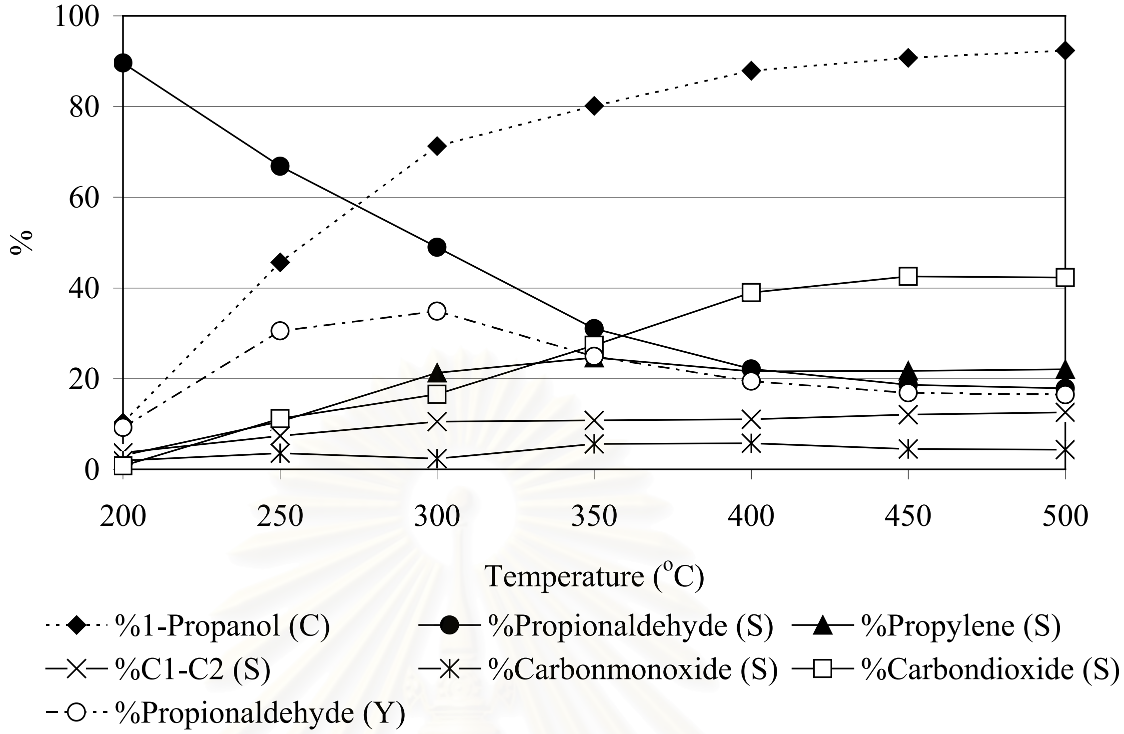

Figure 5.34a Catalytic property of 8Mn10MgOAl catalyst in the 1-propanol oxidation

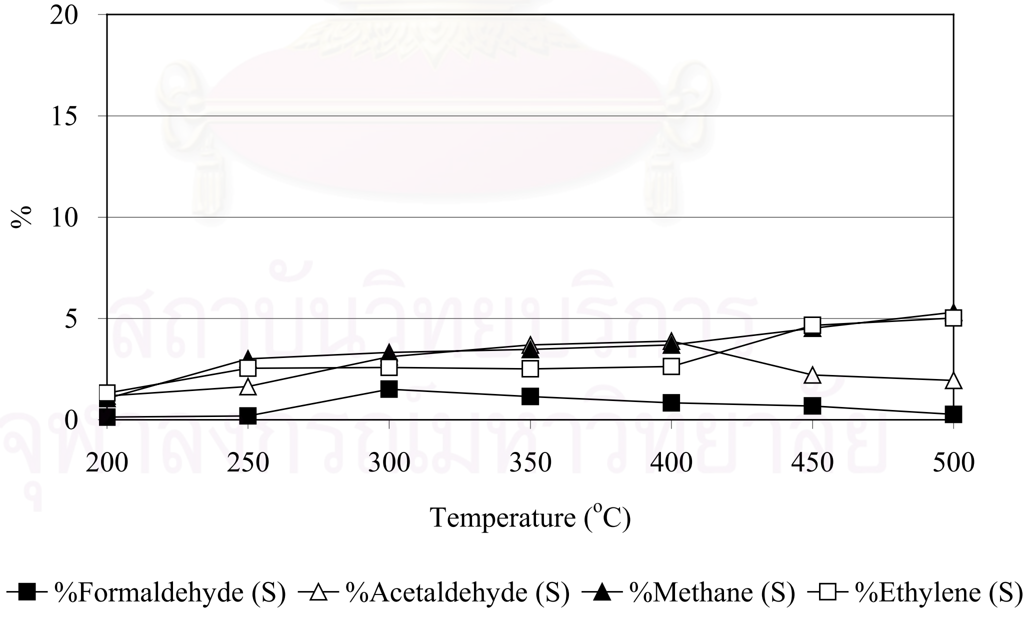

Figure 5.34b C1-C2 products of 8Mn10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

Figure 5.35 showed the summary of the effect of MgO loading for the Mn-oxide catalysts at the reaction temperature of 400°C.

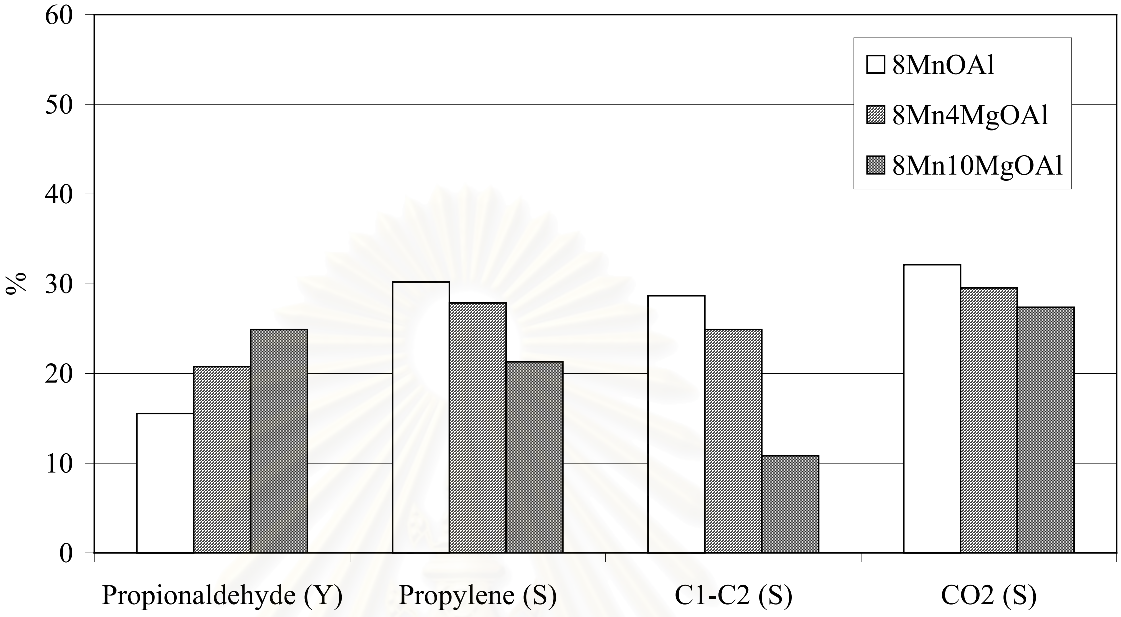

Figure 5.35 The catalytic properties of 1-propanol oxidation for Mn-oxide catalysts at 400°C

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5.3.4 Iron oxide catalyst

a) 8Fe4MgOAl

Figures 5.36a and 5.36b demonstrate the catalytic property of 8Fe4MgOAl in the 1-propanol oxidation. The conversion of 1-propanol increases from 10% to 83% on the increase of reaction temperature from 200°C to 400°C and gradually rises from 83% to 90% at 500°C. An increase of reaction temperature from 200°C to 500°C causes selectivity to propionaldehyde steadily falls from 92% to 42% while CO_2 and propylene selectivity rises from 1% to 16% and 1% to 16%, respectively. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO are detected. The maximum yield of propionaldehyde is ca. 45% at 400°C.

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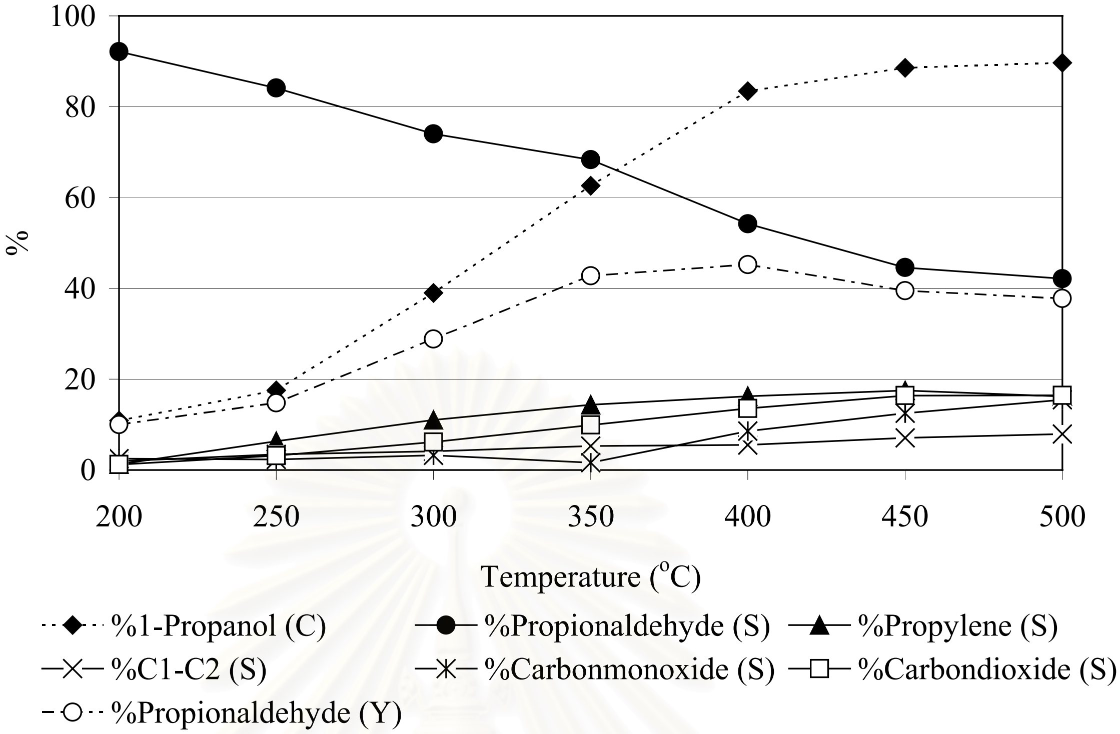

Figure 5.36a Catalytic property of 8Fe4MgOAl catalyst in the 1-propanol oxidation

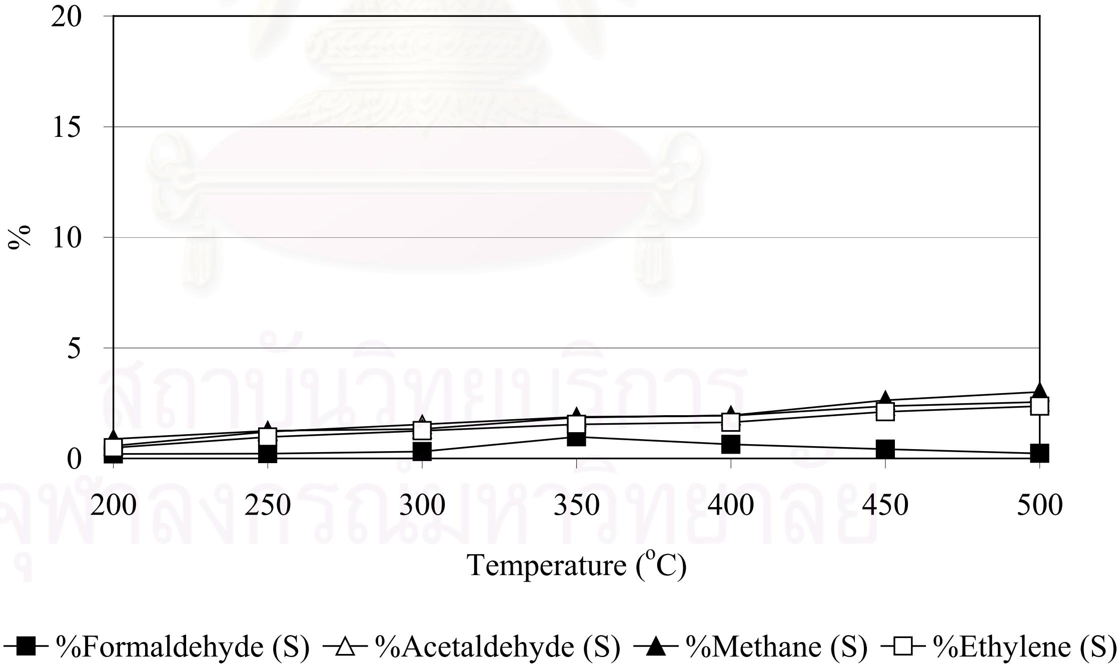

Figure 5.36b C1-C2 products of 8Fe4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Fe10MgOAl

The behavior of the 8Fe10MgOAl catalyst is described in Figures 5.37a and 5.37b. The conversion of 1-propanol steadily increases from 4% to 78% on the increase of reaction temperature from 200°C to 400°C. Further increasing temperature 84% conversion is obtained at reaction temperature 500°C. At low propanol conversions the main product is propionaldehyde, whose selectivity progressively decreases (94% to 46%), with some formation of CO_2 and propylene together with traces amounts of methane, ethylene, formaldehyde and acetaldehyde. The maximum yield of propionaldehyde is ca. 42% at 350°C.

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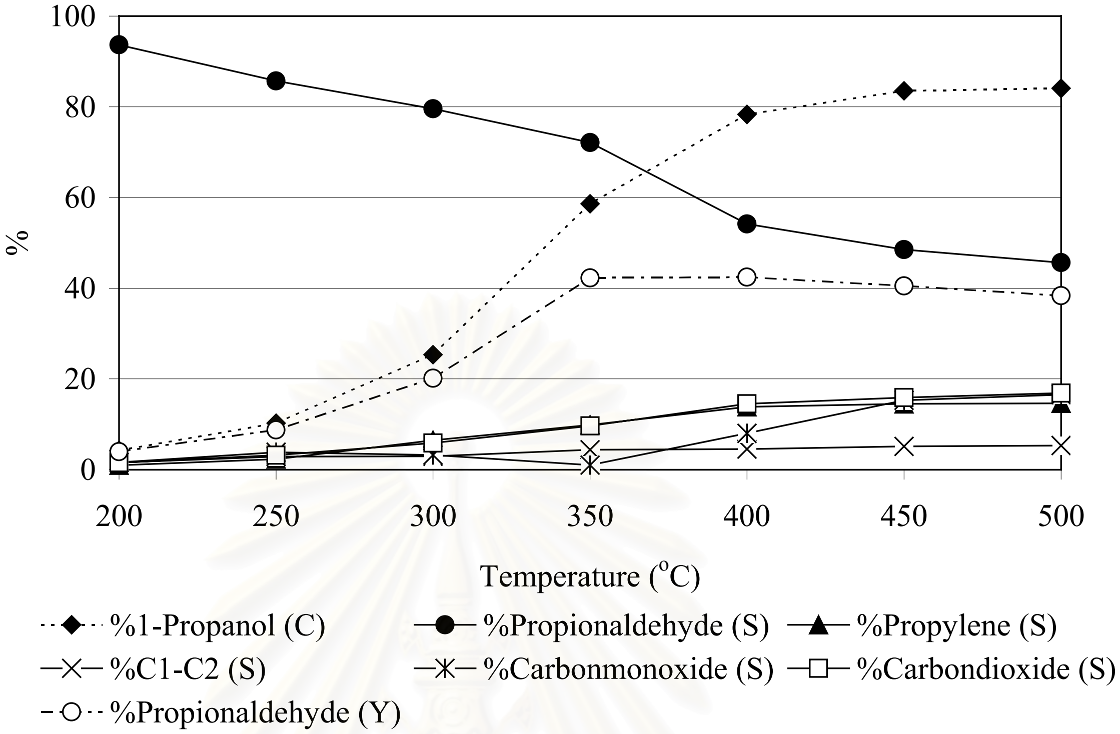

Figure 5.37a Catalytic property of 8Fe10MgOAl catalyst in the 1-propanol oxidation

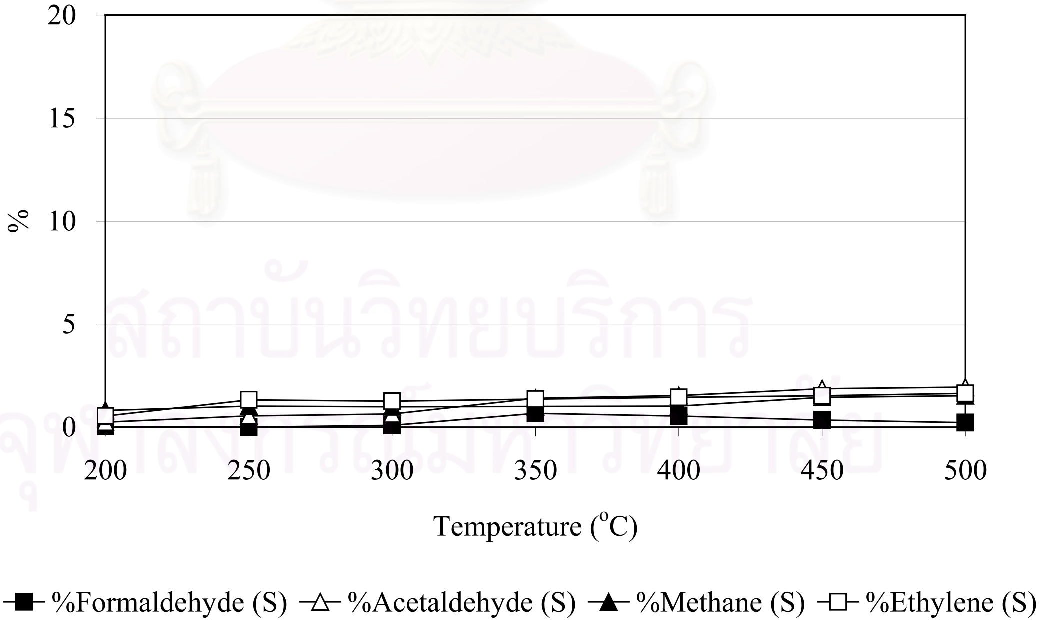

Figure 5.37b C1-C2 products of 8Fe10MgOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

Figure 5.38 showed the summary of the effect of MgO loading for the Fe-oxide catalysts at the reaction temperature of 400^{o}C.

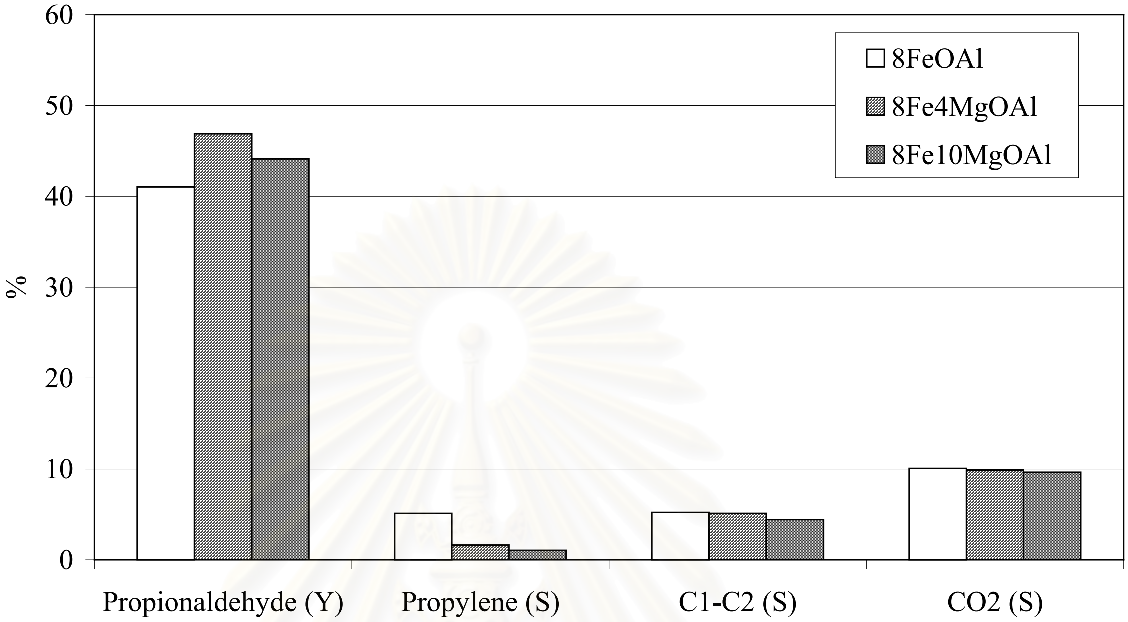

Figure 5.38 The catalytic properties of 1-propanol oxidation for Fe-oxide catalysts at 400^{o}C

5.3.5 Cobalt oxide catalyst

a) 8Co4MgOAl

Figures 5.39a and 5.39b demonstrate the catalytic property of 8Co4MgOAl in the 1-propanol oxidation. At reaction temperature range 200-400^{o}C the conversion of 1-propanol increases from 6% to 85% and gradually increases to 93% at 500^{o}C.

At low 1-propanol conversion the main oxidation product is propionaldehyde with small amount of propylene and CO_2. At high 1-propanol conversion (above 300^{o}C) propionaldehyde selectivity rapidly decreases while CO_2 and propylene selectivities quickly increase. The maximum selectivities to CO_2 and propylene are about 21% and 25% at 500^{o}C, respectively. The maximum yield of propionaldehyde is ca. 51% at 400^{o}C.

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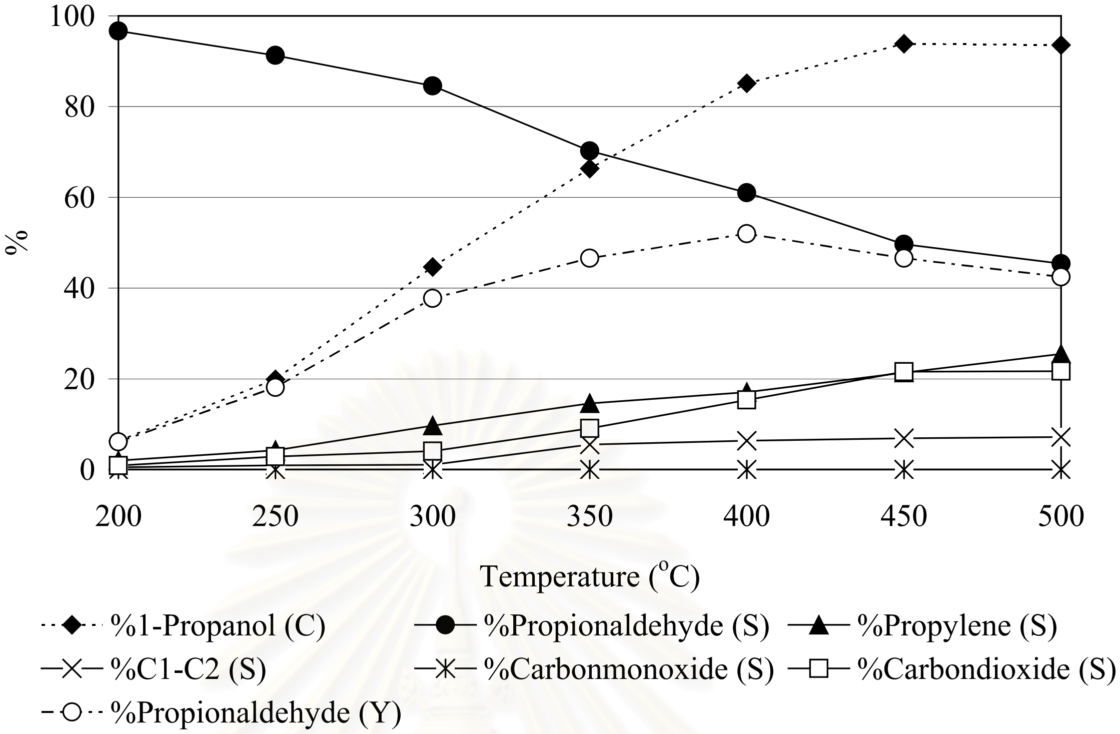

Figure 5.39a Catalytic property of 8Co4MgOAl catalyst in the 1-propanol oxidation

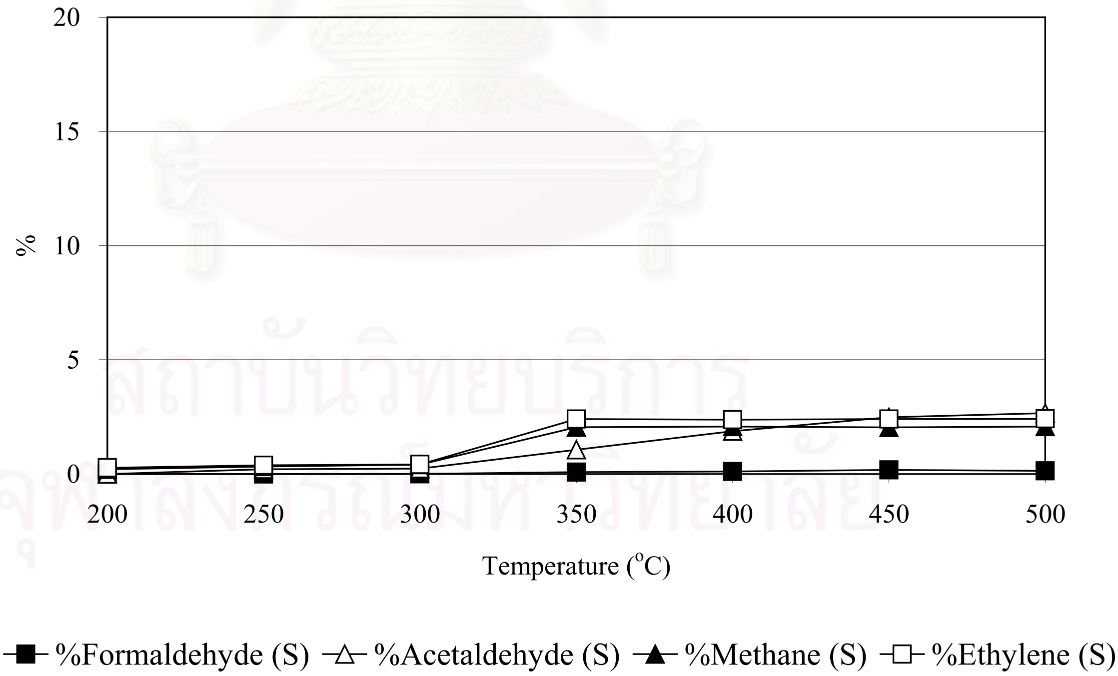

Figure 5.39b C1-C2 products of 8Co4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Co10MgOAl

The results of catalytic test on 8Co10MgOAl catalyst are shown in Figures 5.40a and 5.40b. The conversion of propionaldehyde increases from 6% to 83% on the increase of reaction temperature from 200°C to 400°C and the slightly increases up to 92% at 500°C. An increase of reaction temperature from 200°C to 500°C causes selectivity to propionaldehyde steadily falls from 96% to 51% while CO_2 and propylene selectivity rises from 1% to 19% and 1% to 16%, respectively. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO_2 are detected. The maximum yield of propionaldehyde is ca. 50% at 400°C.

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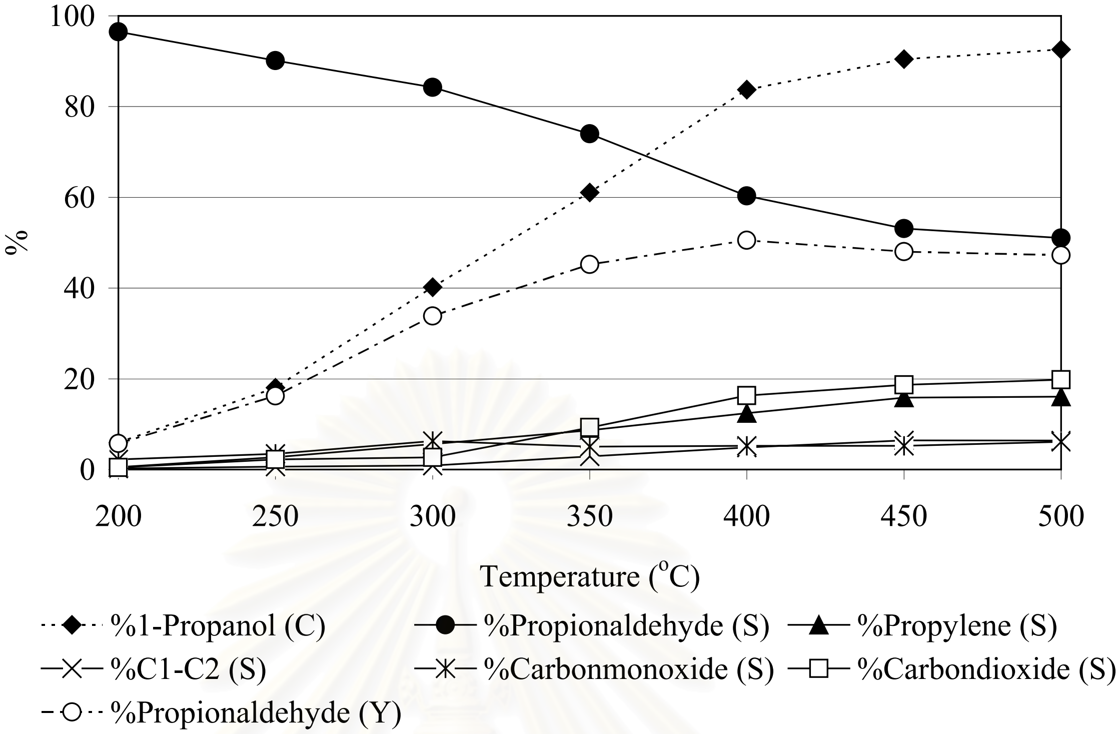

Figure 5.40a Catalytic property of 8Co10MgOAl catalyst in the 1-propanol oxidation

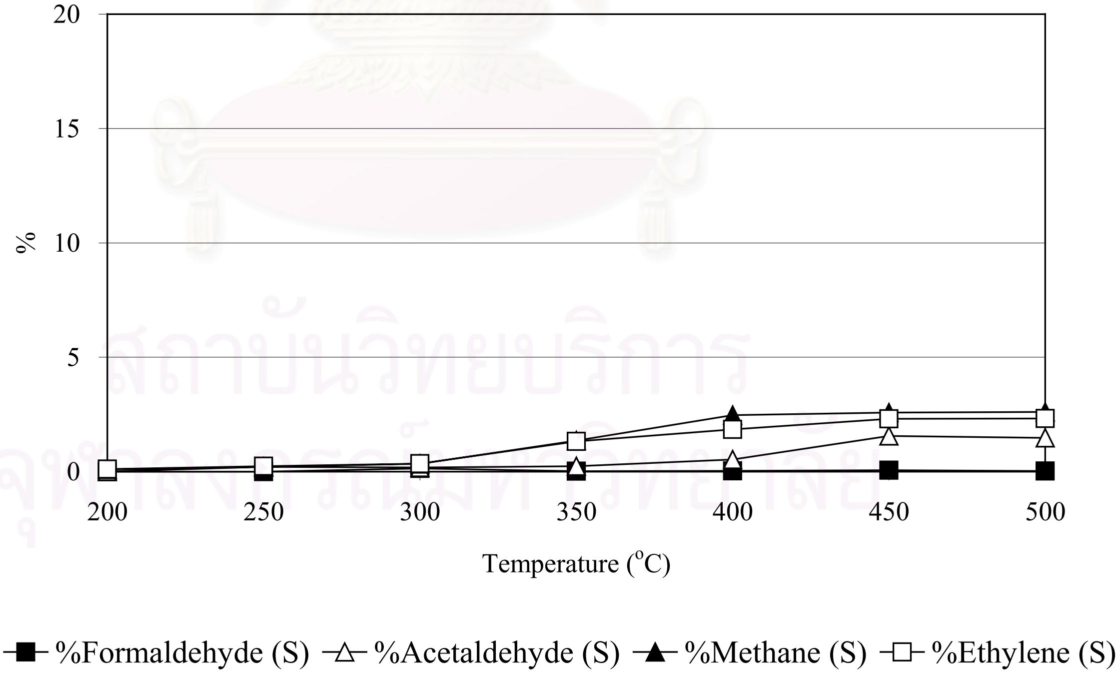

Figure 5.40b C1-C2 products of 8Co10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

Figure 5.41 showed the summary of the effect of MgO loading for the Co-oxide catalysts at the reaction temperature of 400°C.

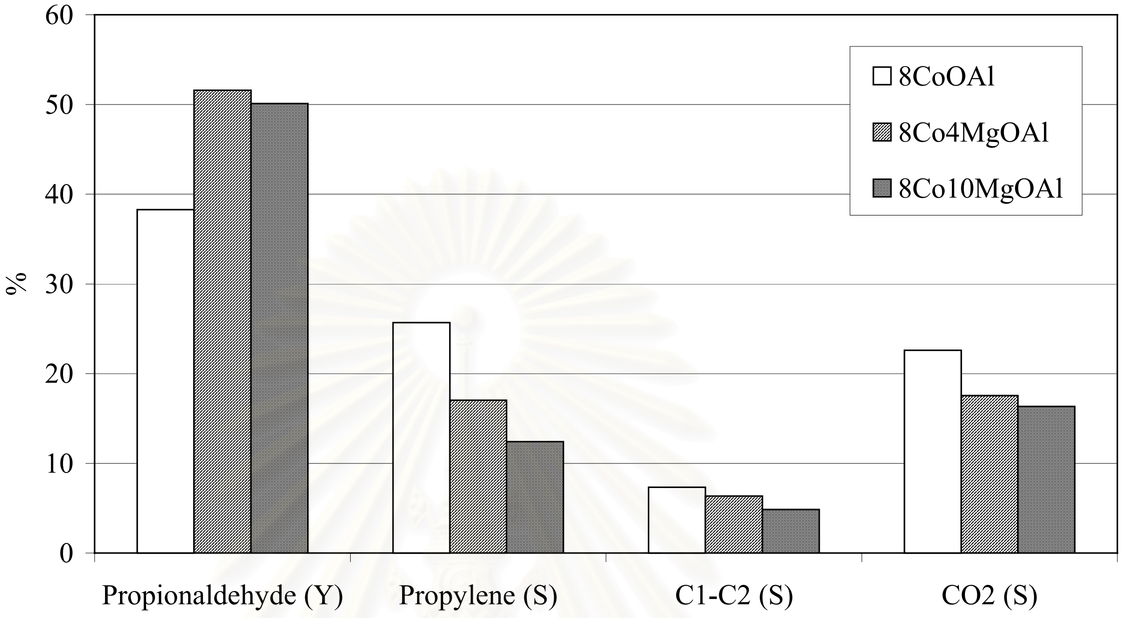

Figure 5.41 The catalytic properties of 1-propanol oxidation for Co-oxide catalysts at 400°C

5.3.6 Nickel oxide catalyst

a) 8Ni4MgOAl

Figures 5.42a and 5.42b demonstrate the catalytic property of 8Ni4MgOAl in the 1-propanol oxidation. At reaction temperature range 200-400^{o}C the conversion of 1-propanol increases from 4% to 88% and gradually increase to 92% at 500^{o}C.

At low 1-propanol conversion the main oxidation product is propionaldehyde with small amount of propylene and CO_2. At high 1-propanol conversion (above 300^{o}C) propionaldehyde selectivity rapidly decreases while CO_2 and propylene selectivities quickly increase. The maximum selectivities to CO_2 and propylene are about 40% and 21% at 500^{o}C, respectively. The maximum yield of propionaldehyde is ca. 31% at 350^{o}C.

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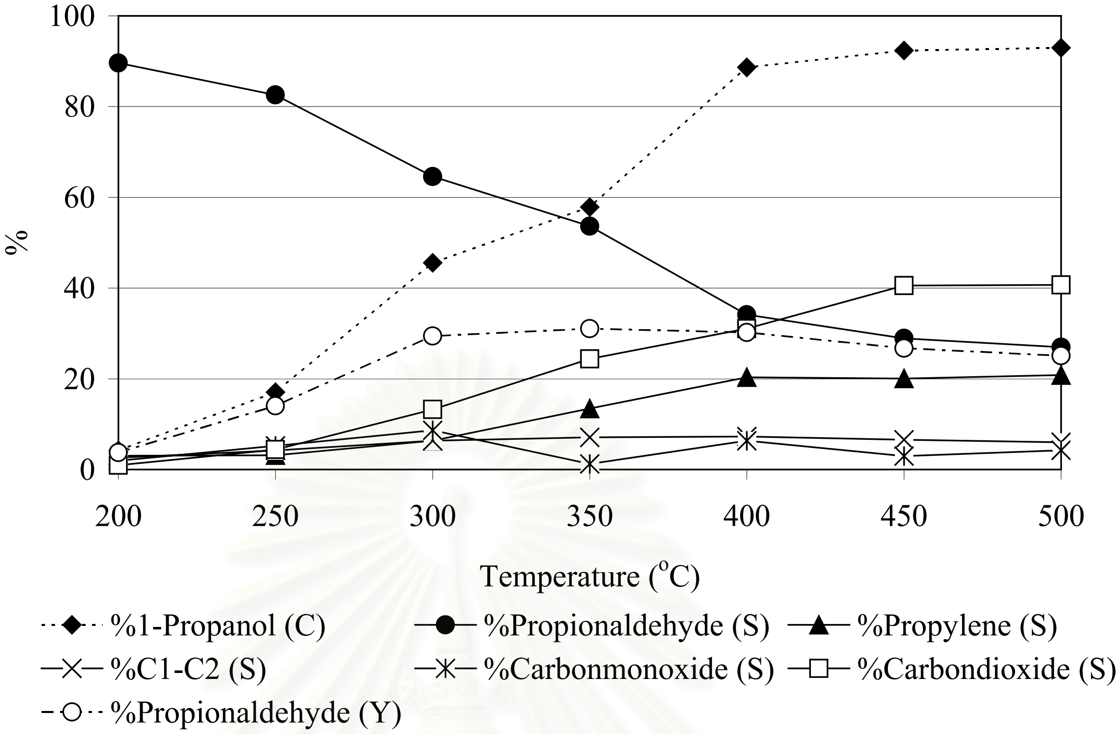

Figure 5.42a Catalytic property of 8Ni4MgOAl catalyst in the 1-propanol oxidation

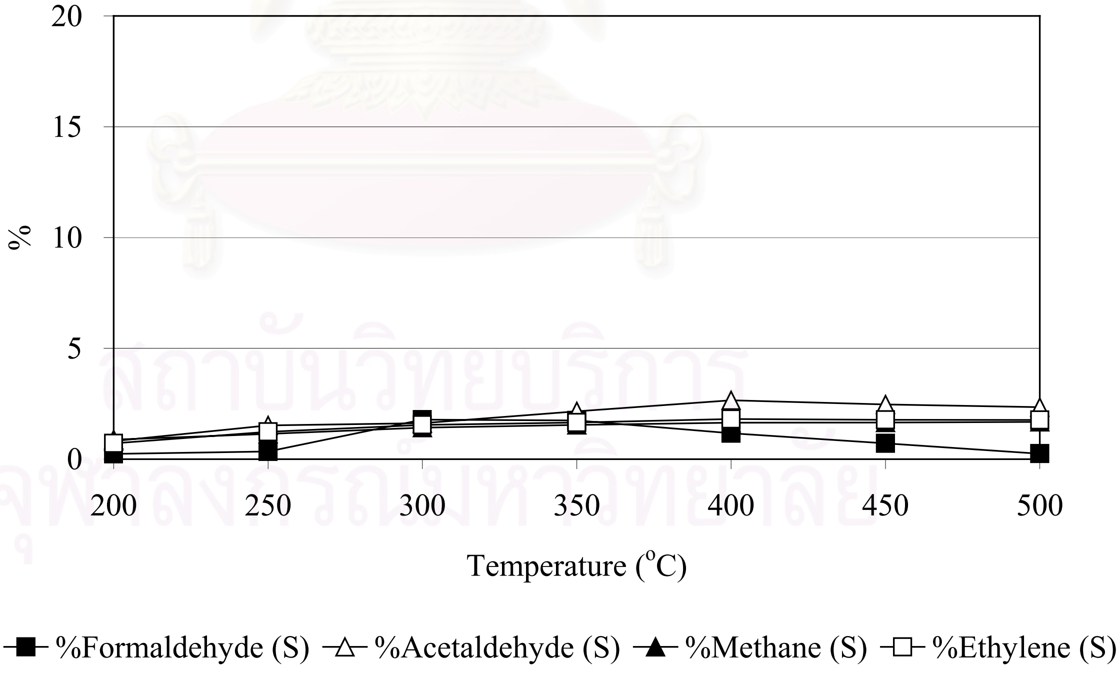

Figure 5.42b C1-C2 products of 8Ni4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Ni10MgOAl

The behavior of the 8Ni10MgOAl catalyst in 1-propanol oxidation is described in Figures 5.43a and 5.43b. Increasing the reaction temperature from 200°C to 400°C results in the increase in 1-propanol conversion from 3% to 85%. Further increasing temperature 89% conversion is obtained at reaction temperature 500°C.

In the beginning (reaction temperature 200-350°C), the main reaction product is propionaldehyde with some formation of CO_2 and propylene. At the reaction temperature higher than 400°C CO_2 is the main product. Some products of propionaldehyde and propylene are also detected. The selectivity of propionaldehyde substantially falls from 90% to 38% with increasing the reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 29% at 300°C.

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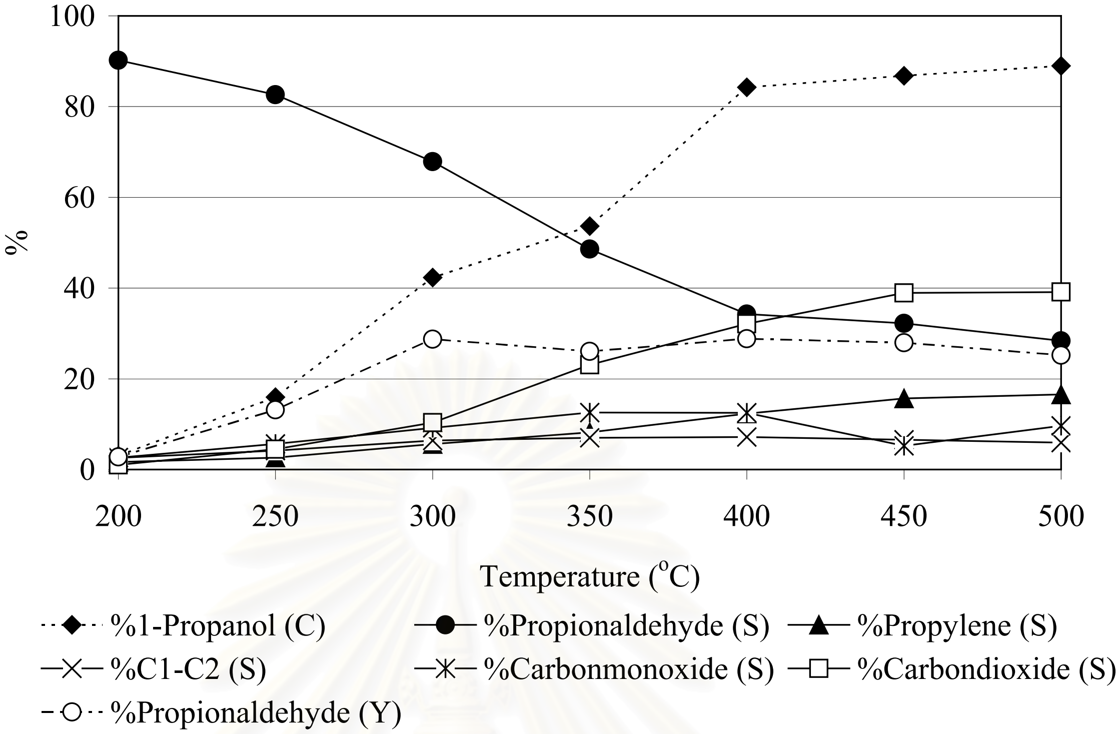

Figure 5.43a Catalytic property of 8Ni10MgOAl catalyst in the 1-propanol oxidation

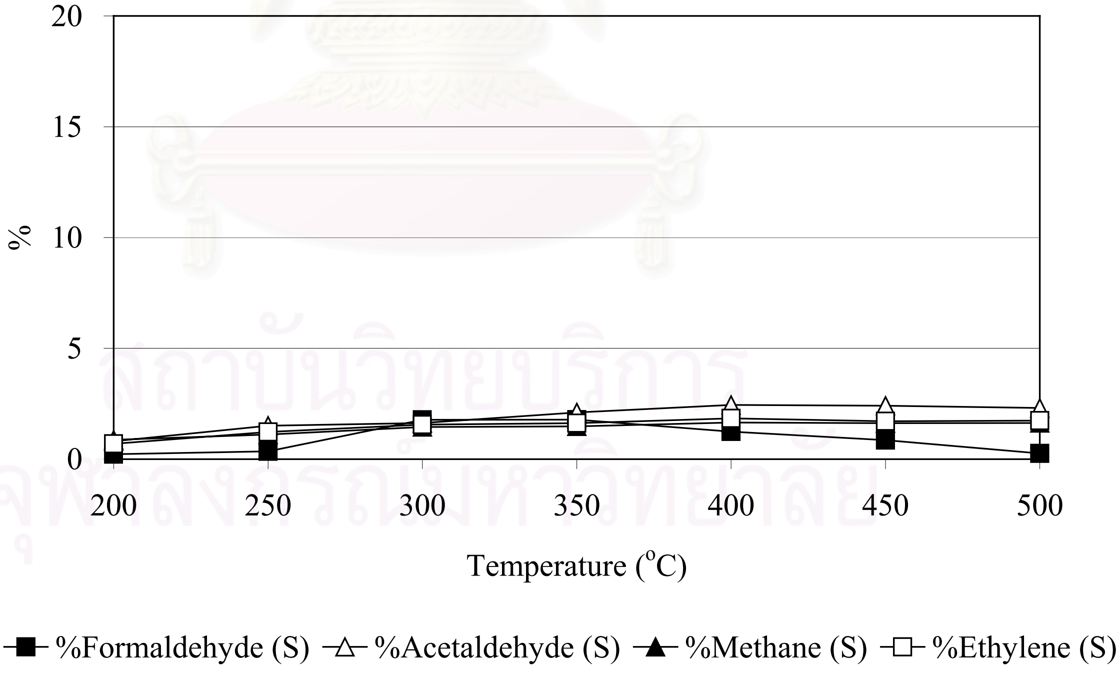

Figure 5.43b C1-C2 products of 8Ni10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

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Figure 5.43 showed the summary of the effect of MgO loading for the Ni-oxide catalysts at the reaction temperature of 400°C.

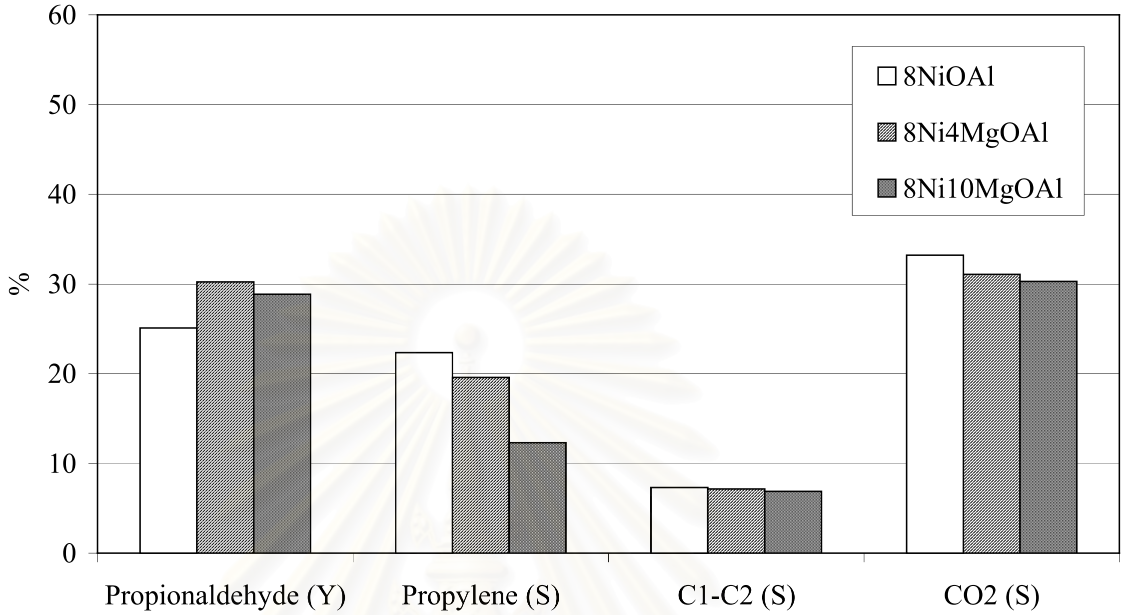

Figure 5.43 The catalytic properties of 1-propanol oxidation for Ni-oxide catalysts at 400°C

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5.3.7 Copper oxide catalyst

a) 8Cu4MgOAl

The catalytic results, obtained in the oxidation of 1-propanol on 8Cu4MgOAl are illustrated in Figures 5.44a and 5.44b. The conversion of 1-propanol increases from 12% to 86% on the increase of reaction temperature from 200^{o}C to 350^{o}C and the slightly increases up to 95% at 500^{o}C. At low 1-propanol conversions the main product is propionaldehyde, whose selectivity progressively decreases (89% to 28%). An increase in the formation of CO_2 (1% to 43%) is observed between 250^{o}C and 500^{o}C, together with small amounts of propylene, methane, ethylene and acetaldehyde and traces of formaldehyde. The maximum yield of propionaldehyde is ca. 39% at 300^{o}C.

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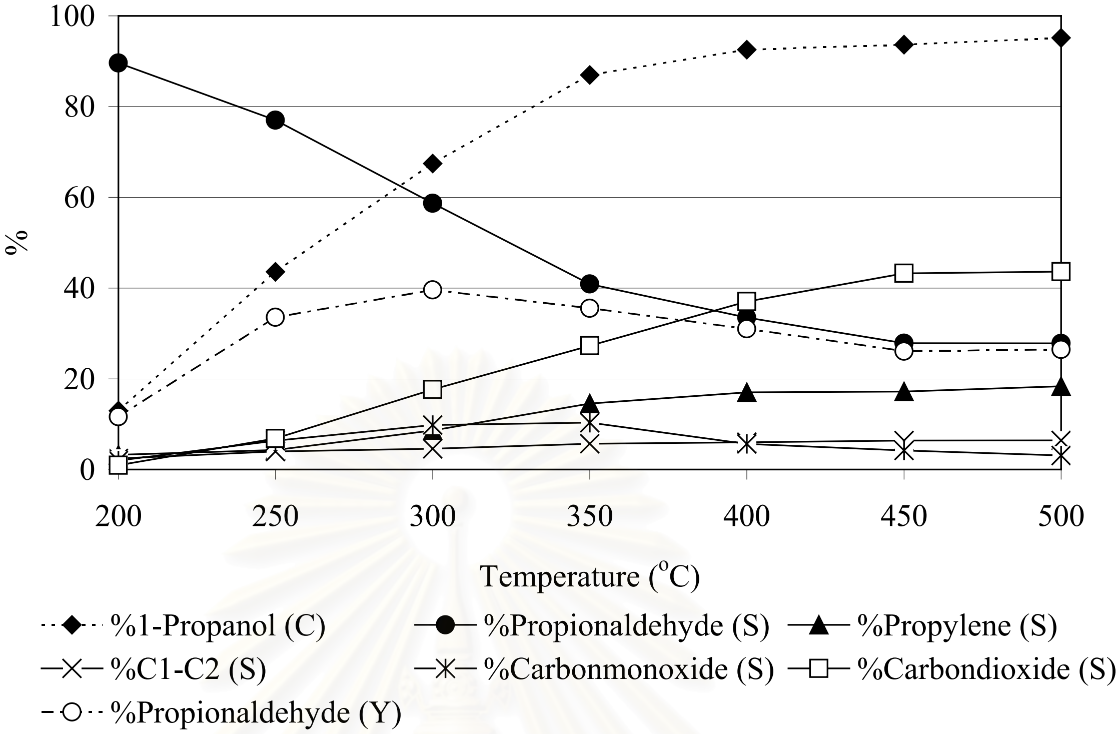

Figure 5.44a Catalytic property of 8Cu4MgOAl catalyst in the 1-propanol oxidation

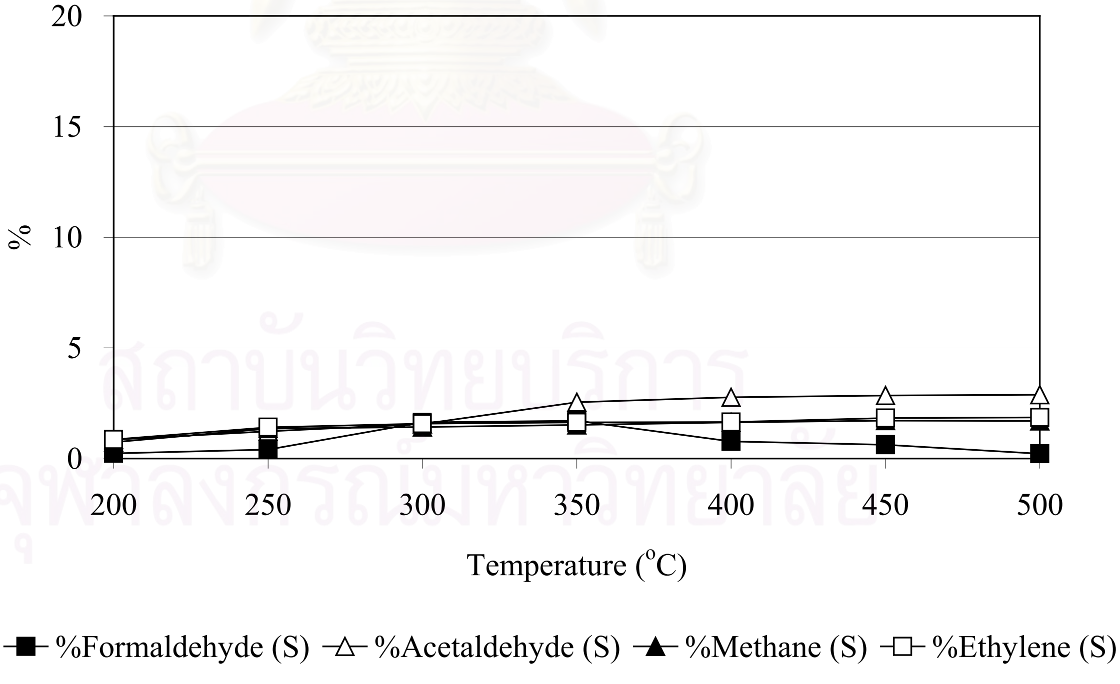

Figure 5.44b C1-C2 products of 8Cu4MgOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

b) 8Cu10MgOAl

The behavior of the 8Cu10MgOAl catalyst in 1-propanol oxidation is described in Figures 5.45a and 5.45b. Increasing the reaction temperature from 200°C to 400°C results in the increase in 1-propanol conversion from 10% to 88%. Further increasing temperature 92% conversion is obtained at reaction temperature 500°C. In the beginning (reaction temperature 200-350°C), the main reaction products are propionaldehyde and CO_2, some formation of propylene. At the reaction temperature higher than 400°C CO_2 is the main product. Some products of propionaldehyde and propylene are detected. The selectivity of propionaldehyde substantially falls from 91% to 32% with increasing reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 38% at 300°C.

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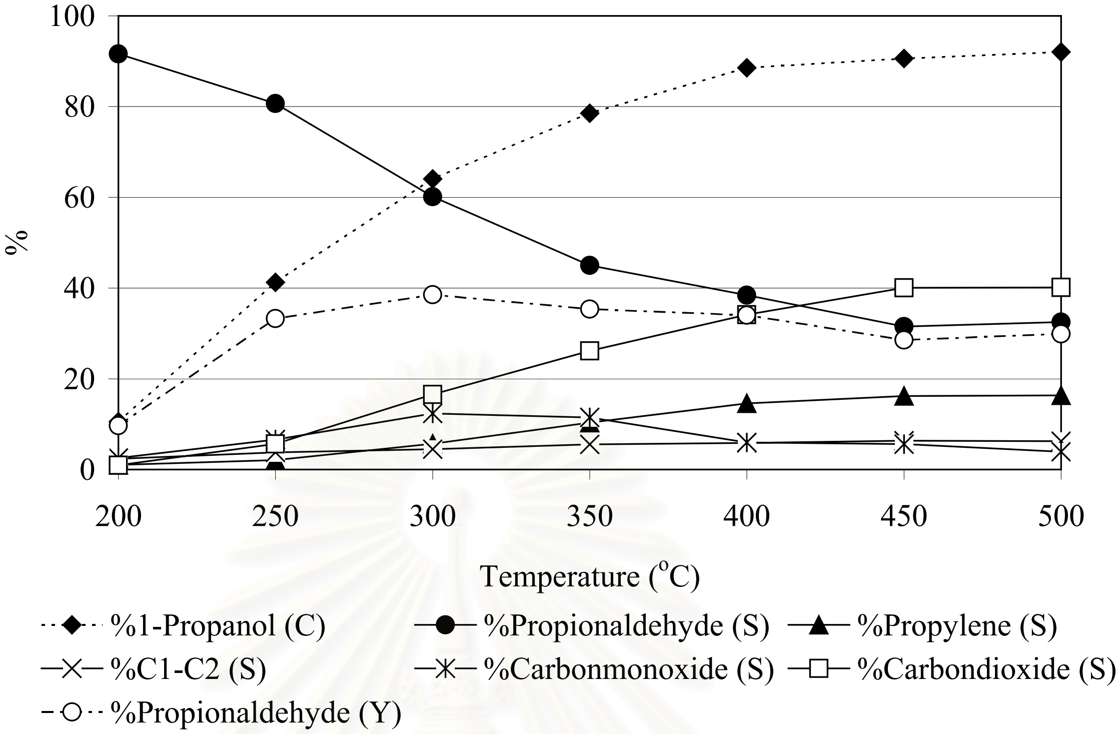

Figure 5.45a Catalytic property of 8Cu10MgOAl catalyst in the 1-propanol oxidation

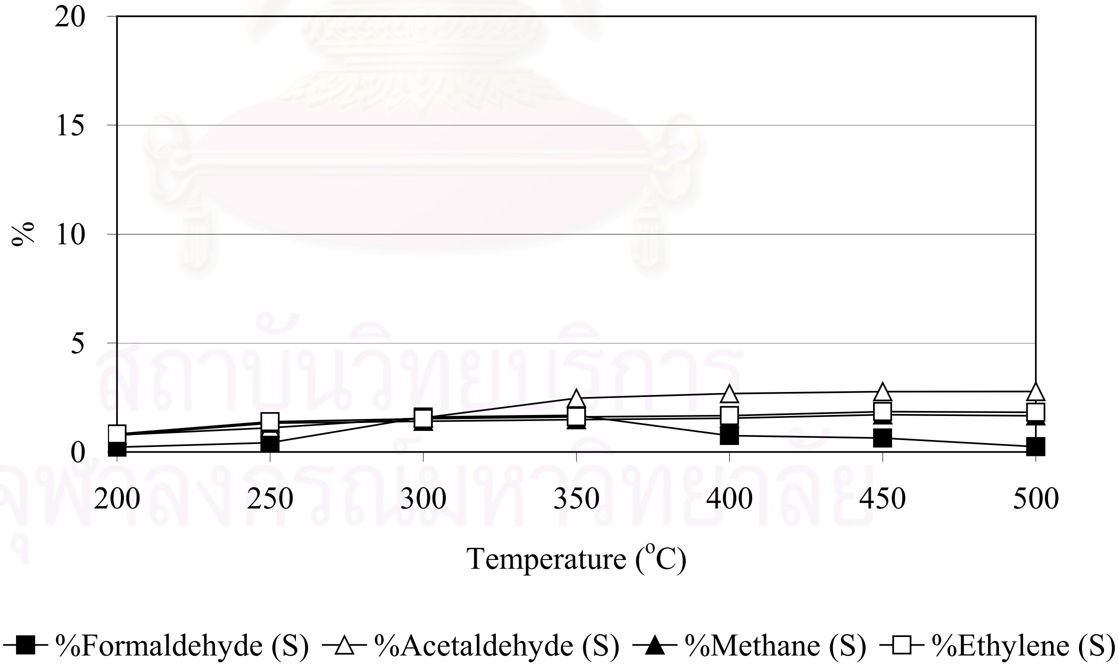

Figure 5.45b C1-C2 products of 8Cu10MgOAl catalyst in the 1-propanol oxidation
(C-Conversion, S-Selectivity, Y-Yield)

Figure 5.46 showed the summary of the effect of MgO loading for the Cu-oxide catalysts at the reaction temperature of 400°C.

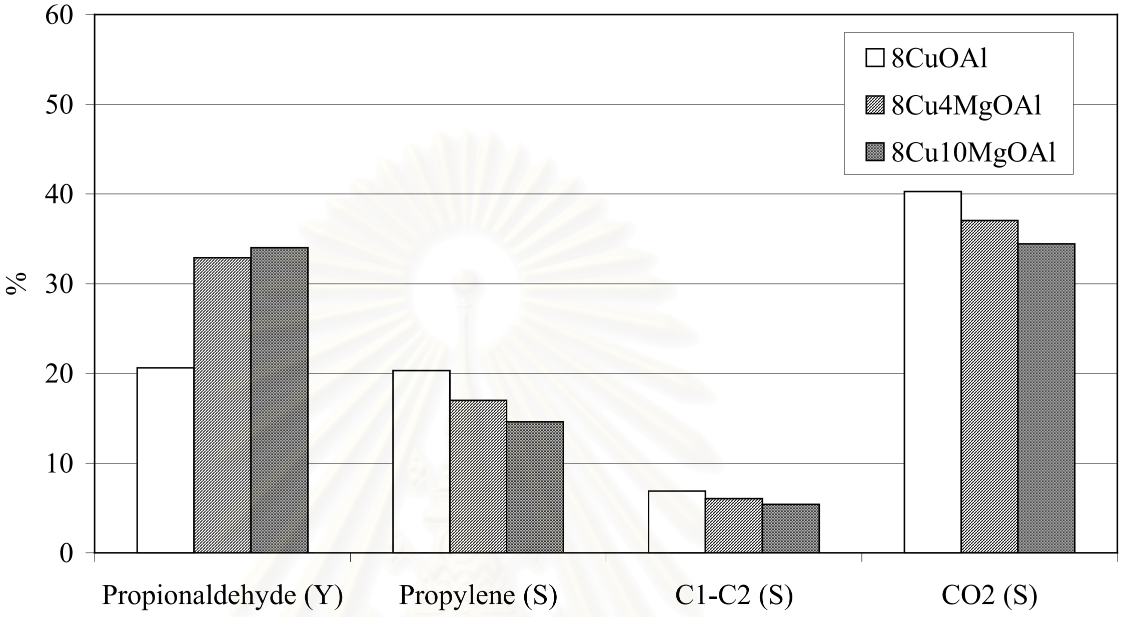

Figure 5.46 The catalytic properties of 1-propanol oxidation for Cu-oxide catalysts at 400°C

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5.3.8 Zinc oxide catalyst

a) 8Zn4MgOAl

The behavior of the 8Zn4MgOAl catalyst is described in Figures 5.47a and 5.47b. The conversion of 1-propanol gradually increases from 3% to 14% on the increase of reaction temperature from 200°C to 250°C and rapidly increases up to 90% at 450°C. Further increasing temperature 93% conversion is obtained at reaction temperature 500°C.

In the beginning (reaction temperature range 200-300°C), the main reaction products are propionaldehyde with some formation of propylene and CO_2. At the reaction temperature higher than 350°C propionaldehyde, propylene and CO_2 are the main products. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO_2 are also detected. The selectivity of propionaldehyde substantially falls from 91% to 42% with increasing reaction temperature from 200-500°C. The maximum yield of propionaldehyde is ca. 46% at 400°C.

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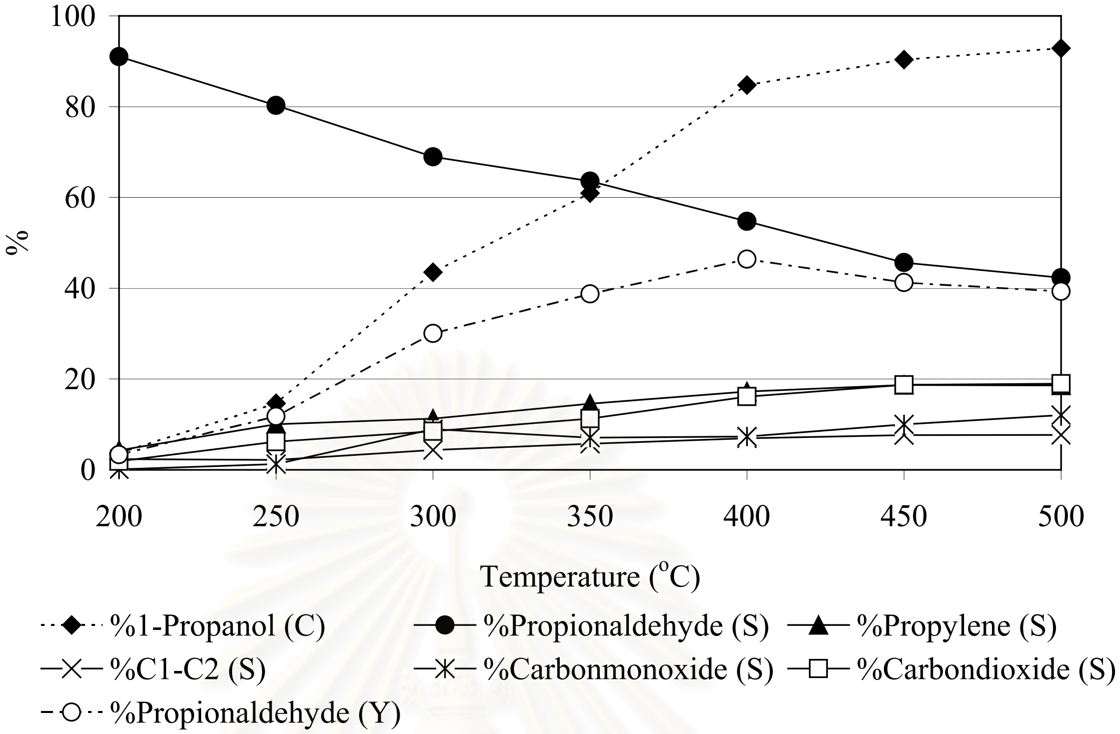

Figure 5.47a Catalytic property of 8Zn4MgOAl catalyst in the 1-propanol oxidation

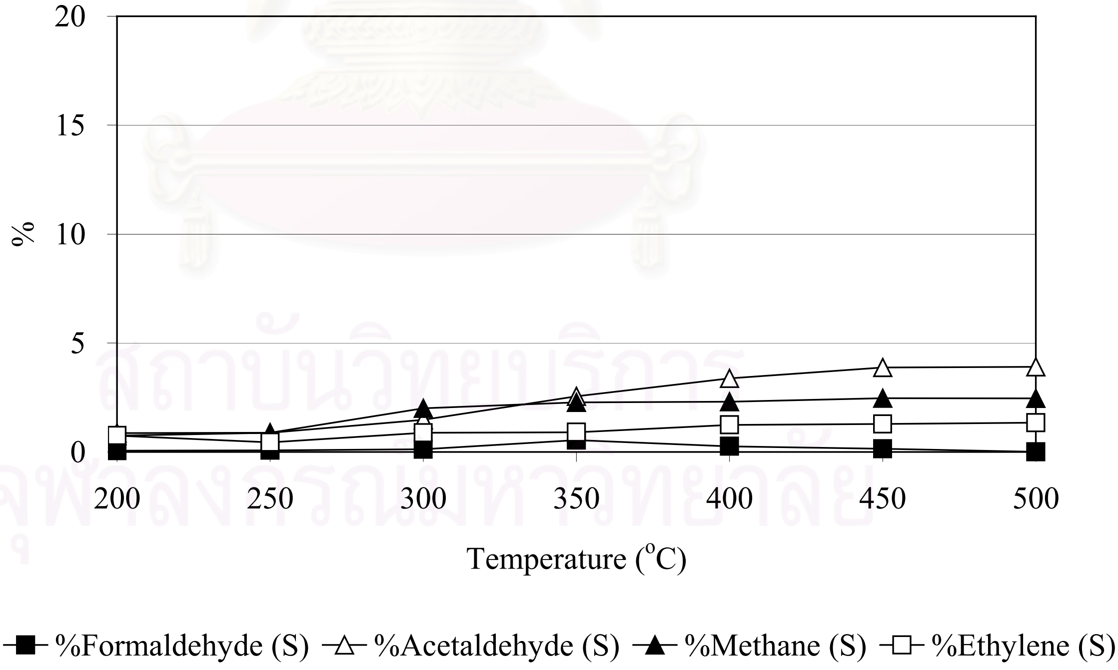

Figure 5.47b C1-C2 products of 8Zn4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Zn10MgOAl

Figures 5.48a and 5.48b demonstrate the catalytic property of 8Zn10MgOAl in the 1-propanol oxidation. The conversion of propionaldehyde increases from 2% to 81% on the increase of reaction temperature from 200°C to 400°C and gradually rises from 81% to 87% at 500°C. An increase of reaction temperature from 200°C to 500°C causes the selectivity to propionaldehyde steadily falls from 94% to 46% while CO_2 and propylene selectivity rises from 1% to 22% and 1% to 20%, respectively. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO are also detected. The maximum yield of propionaldehyde is ca. 44% at 400°C.

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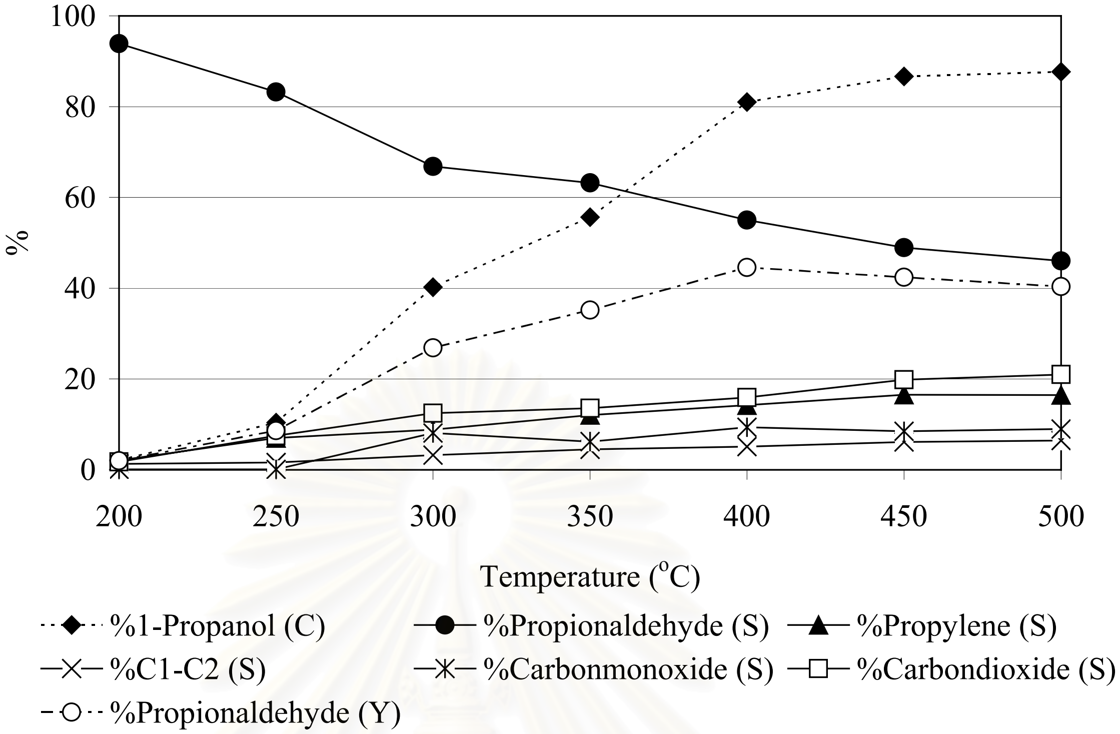

Figure 5.48a Catalytic property of 8Zn10MgOAl catalyst in the 1-propanol oxidation

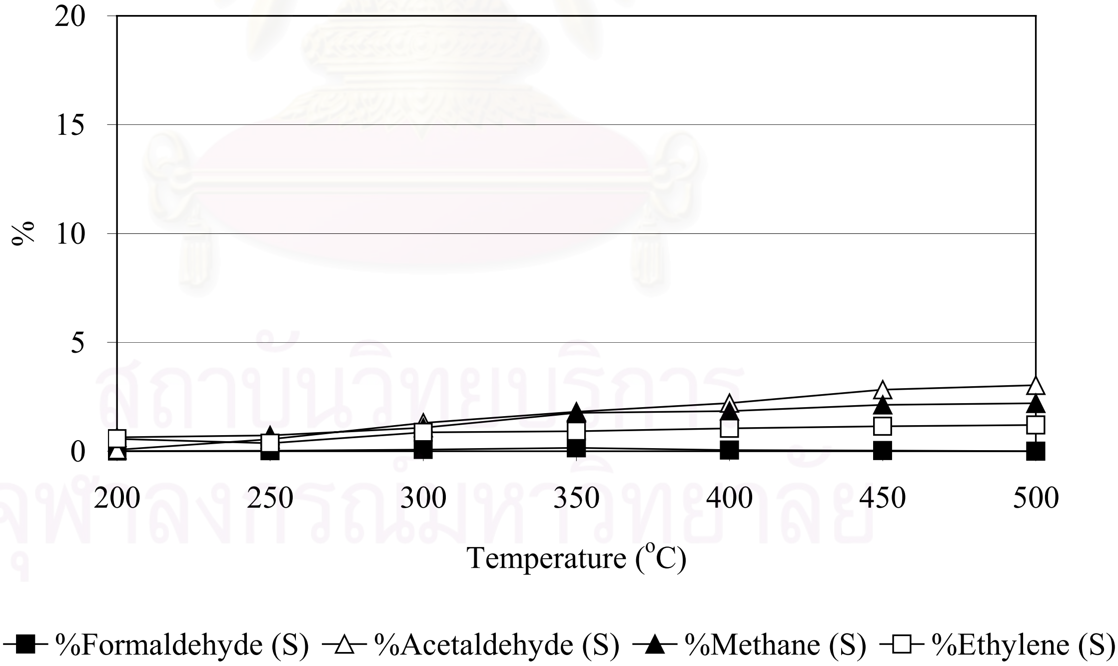

Figure 5.48b C1-C2 products of 8Zn10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

Figure 5.49 showed the summary of the effect of MgO loading for the Zn-oxide catalysts at the reaction temperature of 400°C.

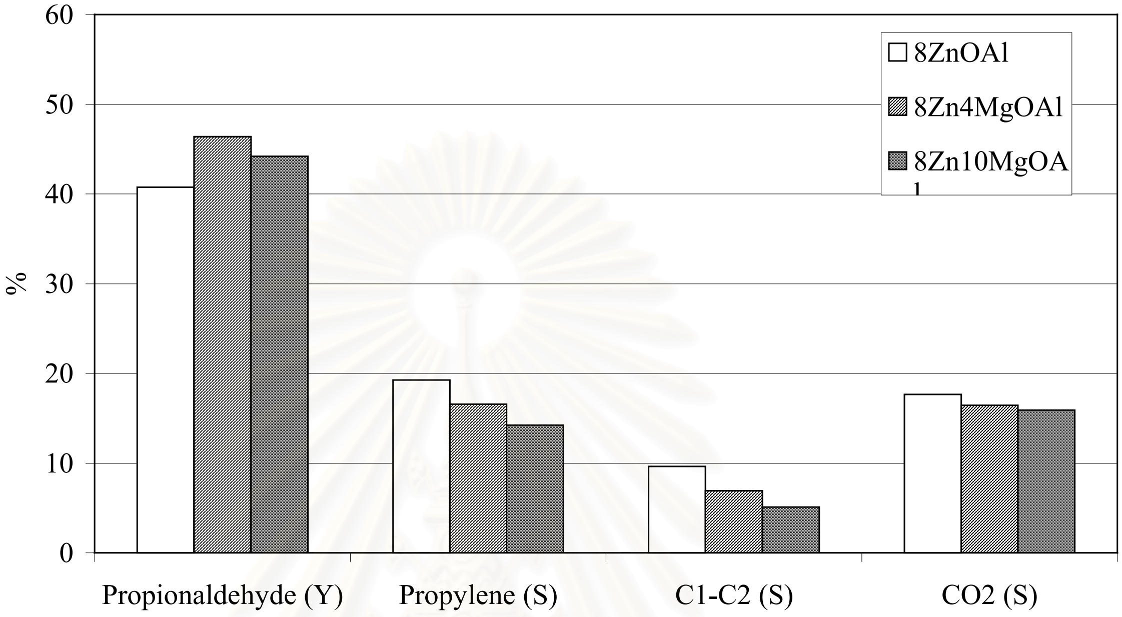

Figure 5.49 The catalytic properties of 1-propanol oxidation for Zn-oxide catalysts at 400°C

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5.3.9 Molybdenum oxide catalyst

a) 8Mo4MgOAl

The catalyst property of 8Mo4MgOAl catalyst on 1-propanol oxidation is illustrated in Figures 5.50a and 5.50b. The 1-propanol conversion increased from 1% to 88% at the temperature range of 200–400°C and steadily increased until the temperature reach 500°C, which the conversion was about 93%.

At low 1-propanol conversion (200-300°C) the major reaction products are propionaldehyde and propylene. Also, there are some formations of CO_2 with traces of formaldehyde, acetaldehyde, methane, ethylene, and CO. While at high 1-propanol conversion (300-500°C) the main products are propionaldehyde, propylene and CO_2 and some formation of formaldehyde, acetaldehyde, methane and ethylene. Consequently, the selectivity of propionaldehyde moderately falls from 90% to 28% and the selectivities of CO_2 slightly rise from 0% to 16% with increasing reaction temperature from 200-500°C. However the propylene selectivity rises form 3% to 21% in the temperature range 200-500°C. The maximum yield of propionaldehyde is ca. 29% at 450°C.

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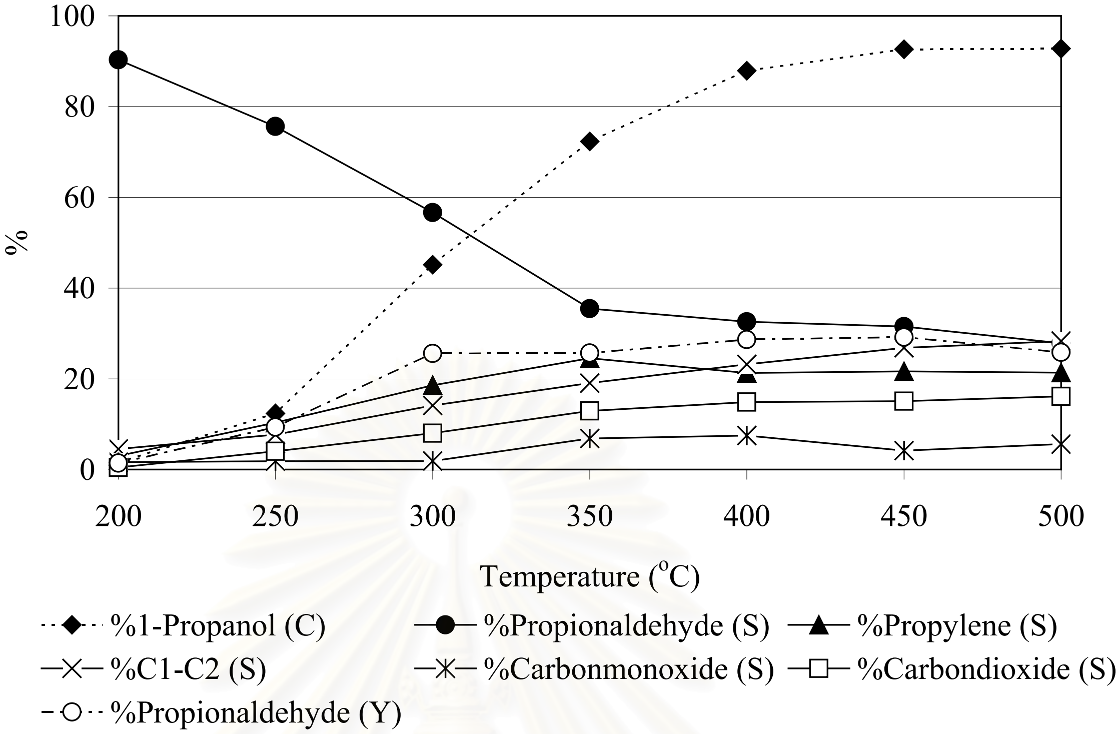

Figure 5.50a Catalytic property of 8Mo4MgOAl catalyst in the 1-propanol oxidation

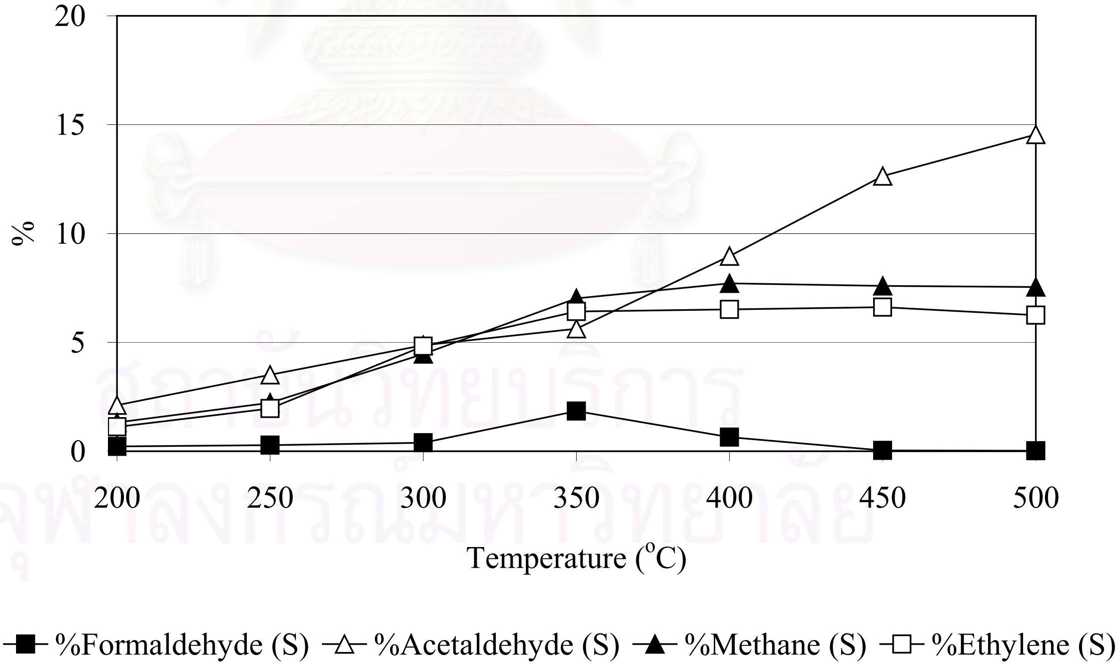

Figure 5.50b C1-C2 products of 8Mo4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8Mo10MgOAl

The catalytic results, obtained in the oxidation of 1-propanol on 8Mo10MgOAl are illustrated in Figures 5.51a and 5.51b. The conversion of 1-propanol increases from 1% to 78% on the increase of reaction temperature from 200°C to 400°C and the slightly increases up to 90% at 500°C. At low propanol conversions the main product is propionaldehyde, whose selectivity progressively decreases (90% to 28%). An increase in the formation of CO_2, propylene and acetaldehyde is observed at 250°C, together with small amounts of methane and ethylene and traces of formaldehyde. The maximum yield of propionaldehyde is ca. 28% at 450°C.

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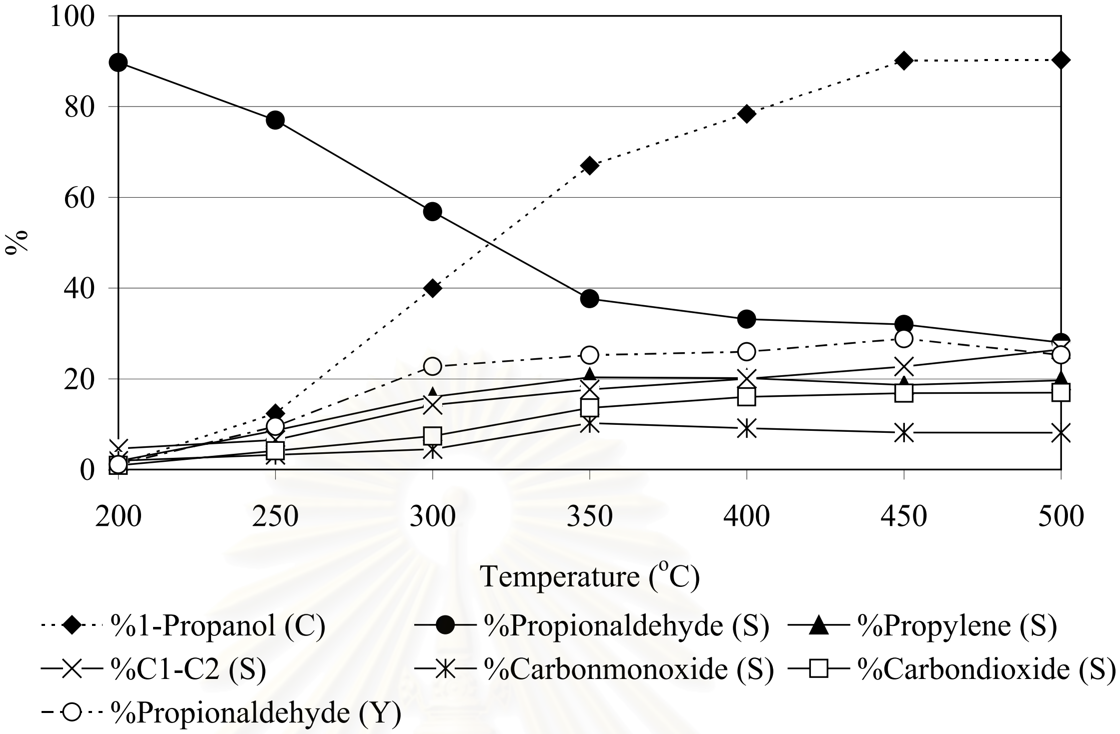

Figure 5.51a Catalytic property of 8Mo10MgOAl catalyst in the 1-propanol oxidation

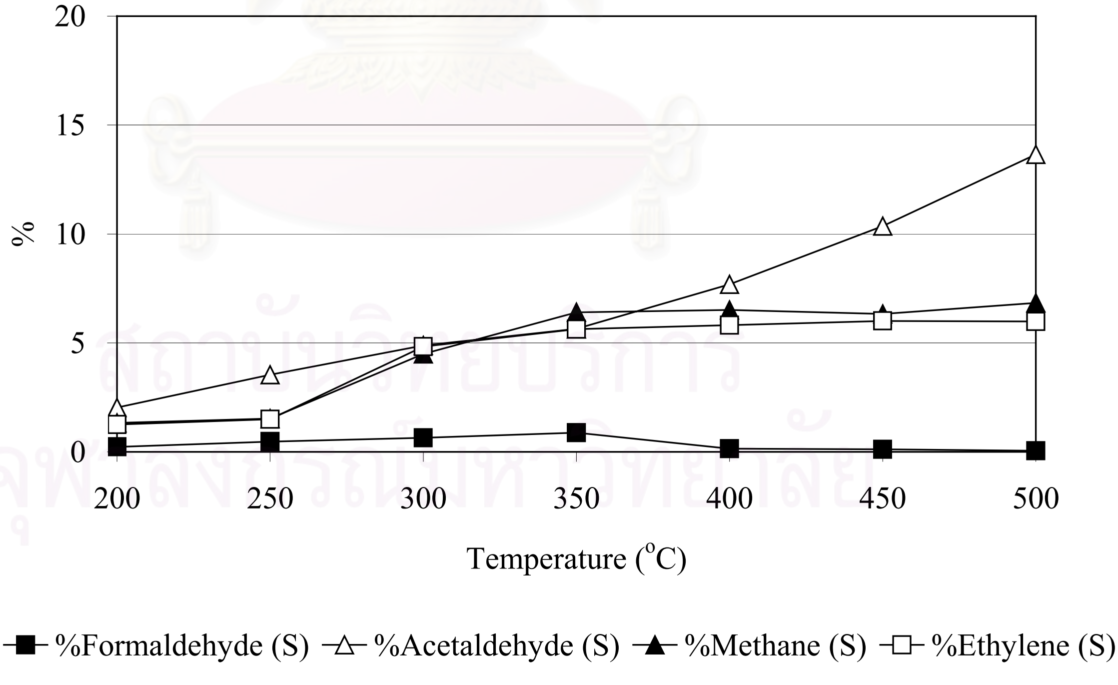

Figure 5.51b C1-C2 products of 8Mo10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

Figure 5.52 showed the summary of the effect of MgO loading for the Mo-oxide catalysts at the reaction temperature of 400°C.

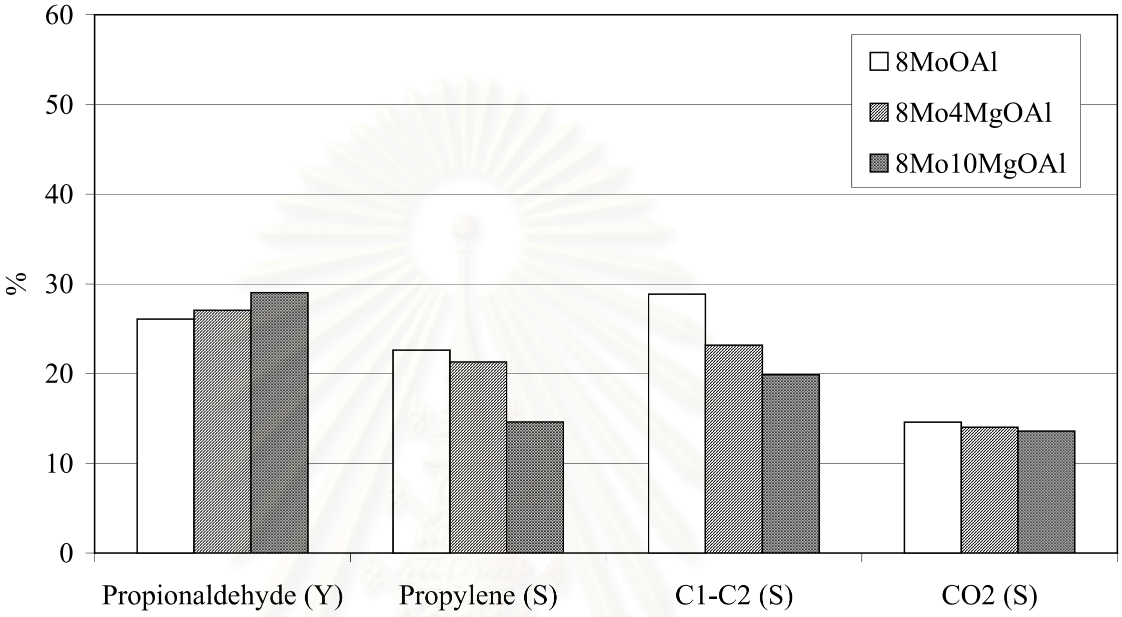

Figure 5.52 The catalytic properties of 1-propanol oxidation for Mo-oxide catalysts at 400°C

5.3.10 Tungsten oxide catalyst

a) 8W4MgOAl

The catalytic results, obtained in the oxidation of 1-propanol on 8W4MgOAl are illustrated in Figures 5.53a and 5.53b. The conversion of 1-propanol increases from 7% to 85% on the increase of reaction temperature from 200°C to 400°C and the slightly increases up to 92% at 500°C. At low propanol conversions the main products are propionaldehyde, whose selectivity progressively decreases (80% to 26%) and propylene, whose selectivity progressively increases (4% to 27%). An increase in the formation of CO_2 and acetaldehyde is observed at 250°C, together with small amounts of methane and ethylene and traces of formaldehyde. The maximum yield of propionaldehyde is ca. 27% at 400°C.

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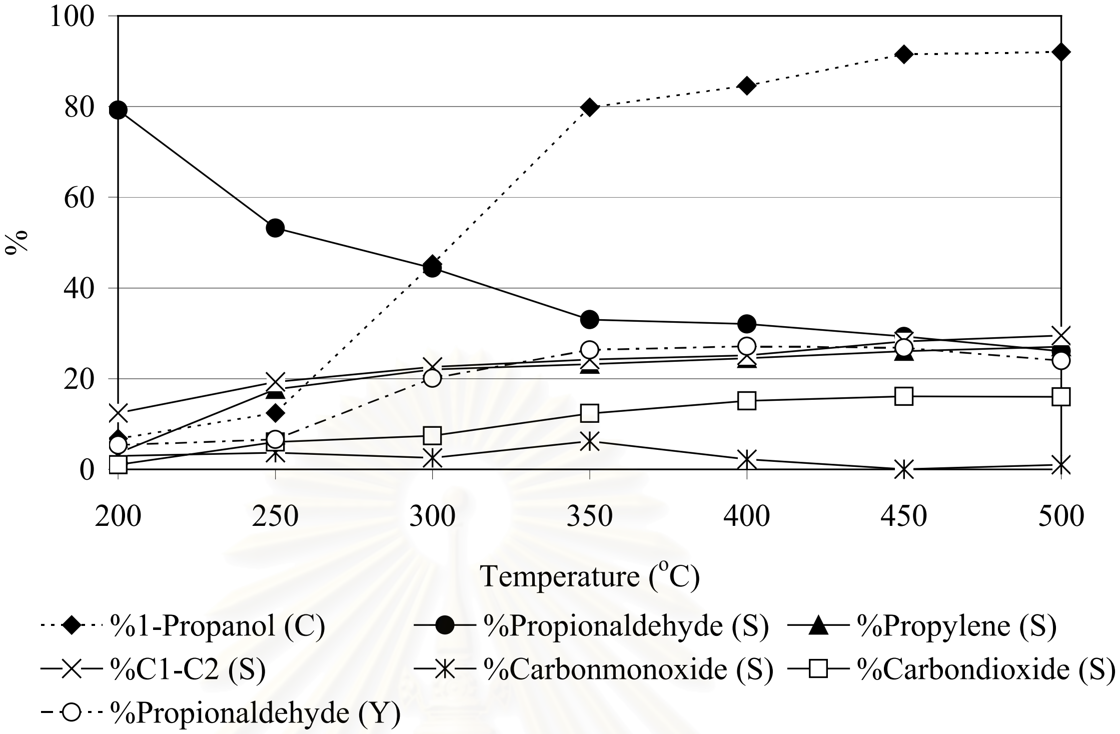

Figure 5.53a Catalytic property of 8W4MgOAl catalyst in the 1-propanol oxidation

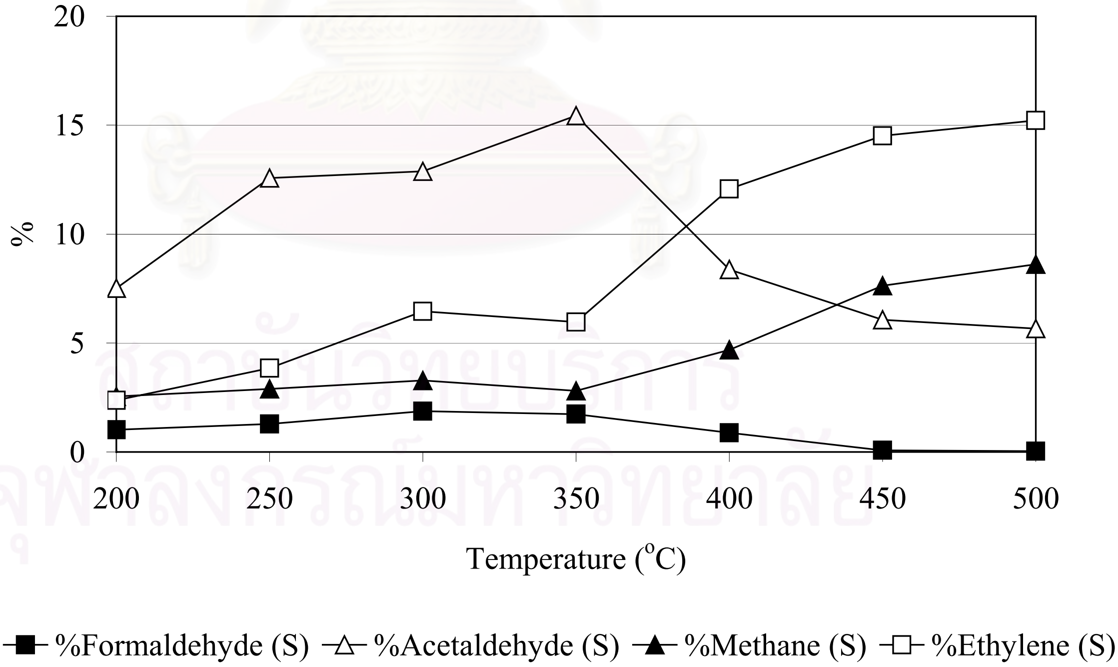

Figure 5.53b C1-C2 products of 8W4MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

b) 8W10MgOAl

The result of catalytic test on 8W10MgOAl catalyst is shown in Figures 5.54a and 5.54b. The conversion of 1-propanol increases from 4% to 83% on the increase of reaction temperature from 200°C to 400°C and the slightly increases up to 90% at 500°C. An increase of reaction temperature from 200°C to 500°C causes the selectivity to propionaldehyde steadily falls from 85% to 30% while CO_2 rises from 1% to 16%. The propylene selectivity rises from 3% to 25% on the increase of reaction temperature from 200°C to 500°C. Traces of formaldehyde, acetaldehyde, methane, ethylene and CO are also detected. The maximum yield of propionaldehyde is ca. 28% at 400°C.

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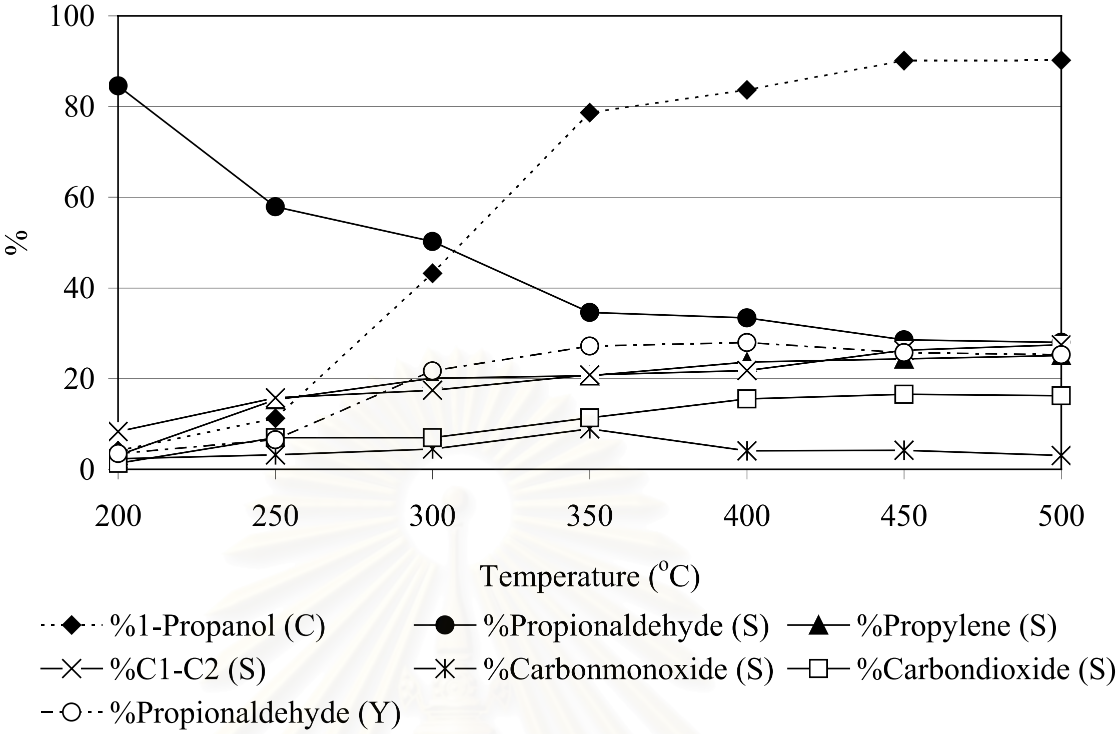

Figure 5.54a Catalytic property of 8W10MgOAl catalyst in the 1-propanol oxidation

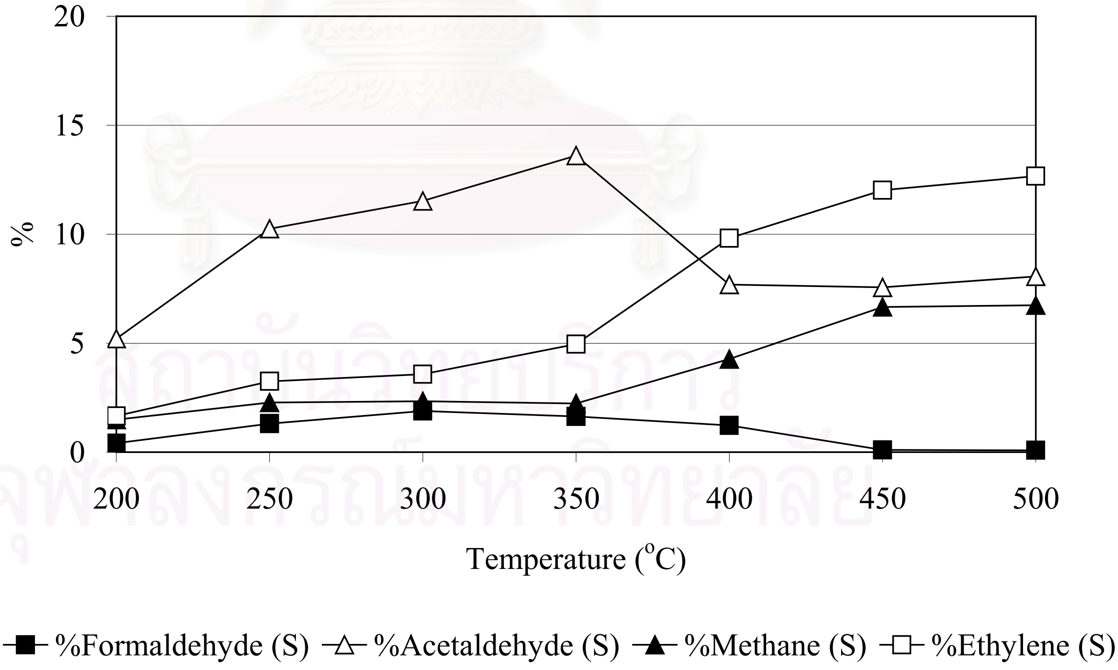

Figure 5.54b C1-C2 products of 8W10MgOAl catalyst in the 1-propanol oxidation (C-Conversion, S-Selectivity, Y-Yield)

Figure 5.55 showed the summary of the effect of MgO loading for the W-oxide catalysts at the reaction temperature of 400^{o}C.

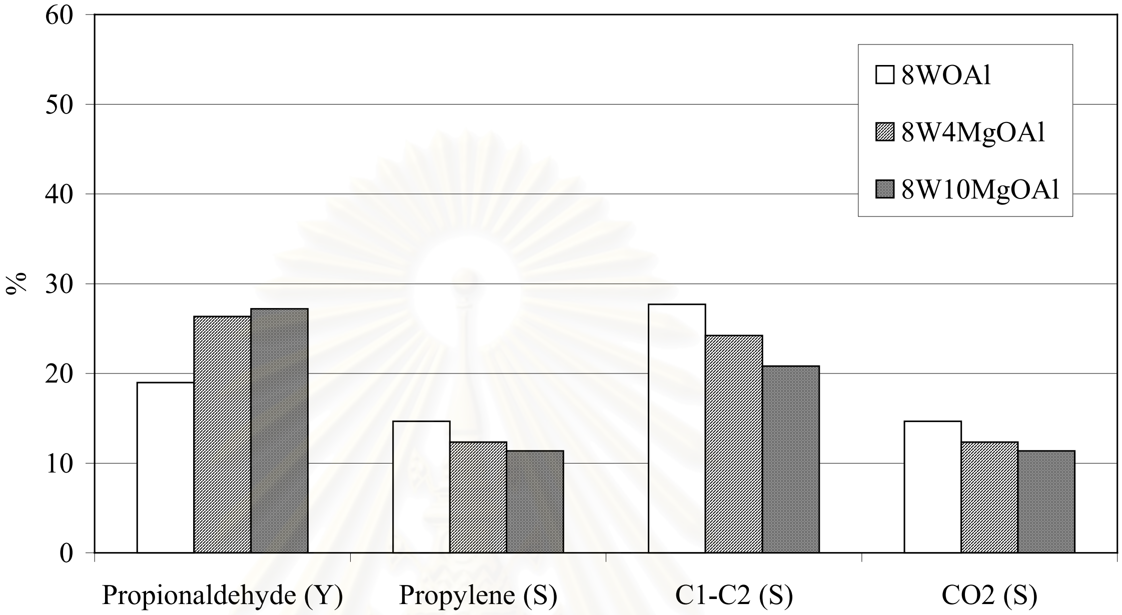

Figure 5.55 The catalytic properties of 1-propanol oxidation for W-oxide catalysts at 400^{o}C

The relevant behavior observed over all catalysts after promoting with MgO is the slightly decreased of 1-propanol conversion. Additionally, selectivity to other undesired products except propionaldehyde decreases considerably. It is believed that the number of acidic sites which promote dehydration of 1-propanol to propylene and C1-C2 products decrease with MgO addition. Additionally, MgO may inhibit the pathway for the conversion of propionaldehyde to CO_2. Nevertheless, there is no direct proportion between the content of MgO addition and propionaldehyde yield. Therefore, an appropriate combination between acidic and basic sites should exist to improve the catalyst activity by adding alkaline metal and types of transition metal addition.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The conclusions of the present research are the following:

1. Higher redox sites, 8CrOAl, 8MnOAl, and 8CuOAl will cause higher CO_2 formation. Instead, lower redox sites 8MoOAl and 8WOAl can not perform a good selective oxidation reaction of 1-propanol to form propionaldehyde product as well.

2. 8VOAl, 8CoOAl, 8FeOAl and 8ZnOAl show good catalytic activity for selective oxidation of 1-propanol to propionaldehyde

3. Not only acid-base properties but also redox properties affected the catalytic activities and selectivity for the selective oxidation of 1-propanol

4. The catalytic behavior was essentially independent on MgO. But the presence of magnesium oxide on the transition metal oxide/alumina catalyst decreased the acidity of the catalyst leading to the reduction of dehydration and cracking reaction.

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6.2 Recommendations for future studies

From the previous conclusions, the following recommendations for future studies are proposed.

1. Due to the other factors such as: strength and type of oxygen on the catalyst surface, additional more surface characterizations should be carried out.

2. Because the acid property influences the catalytic property, therefore the role of Bronsted/Lewis acid sites (during the oxidation process) should be further studied.

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APPENDICES

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APPENDIX A

CALCULATION OF CATALYST PREPARATION

Preparation of 8CoOAl, 8Co4MgOAl and 8Co10MgOAl catalysts by the Wet Impregnation Method is shown as follow:

Reagent: - Cobalt acetate tetrahydrate [$Co(CH_3COO)_2 \cdot 4H_2O$]
Molecular weight = 249 g
- Magnesium nitrate [$Mg(NO_3)_2$]
Molecular weight = 256.41 g
Support - Alumina [Al_2O_3]

Calculation for the preparation of the 8CoOAl catalyst.

The 8CoOAl aqueous solution used in catalyst preparation consists of Co 8wt% and Al_2O_3 92wt%. The amount of cobalt in 8CoOAl catalyst is calculated as follows:

Basis: Al_2O_3 1 g
If the weight of catalyst was 100 gram, 8CoOAl would compose of cobalt 8 g. and Al_2O_3 92 g. Therefore, in this system,

the amount of Co $= 8/92 \times 1$
$= 0.0869$ g

Cobalt (Co) 0.0869 g. was prepared from $Co(CH_3COO)_2 \cdot 4H_2O$ 99% and molecular weight of Co = 59, then

the $Co(CH_3COO)_2 \cdot 4H_2O$ content $= (249 \times 0.0869 \times 100)/(59 \times 99)$
$= 0.3705$ g

Calculation for the preparation of the 8Co4MgOAl catalyst.

The 8Co4MgOAl aqueous solution used in catalyst preparation consists of Co 8wt% and Al_2O_3 92wt%. The amount of cobalt in 8Co4MgOAl catalyst is calculated as follows:

Basis: Al_2O_3 1 g
If the weight of catalyst was 100 gram, 8Co4MgOAl would compose of cobalt 8 g. and Al_2O_3 92 g Therefore, in this system,
the amount of Co = 8/92 × 1
= 0.0869 g

Cobalt (Co) 0.0869 g was prepared from $Co(CH_3COO)_2{\cdot}4H_2O$ 99% and molecular weight of Co = 59, then
the $Co(CH_3COO)_2{\cdot}4H_2O$ content = (249×0.0869×100)/(59×99)
= 0.3705 g

Then, the Mg : (Support+Co) weight ratio = 4:100
The amount of Mg = 4×(0.0869+1)/100
= 0.04348 g.

Magnesium (Mg) 0.04348 g was impregnated from $Mg(NO_3)_2$ solution 99% and molecular weight of Mg = 24.305 g
Thus, the amount of $Mg(NO_3)_2$ used = (256.41/24.305)×0.04348×(100/99)
= 0.4633 g

Calculation for the preparation of the 8Co10MgOAl catalyst.

The 8Co10MgOAl aqueous solution used in catalyst preparation consists of Co 8wt% and Al_2O_3 92wt%. The amount of cobalt in 8Co10MgOAl catalyst is calculated as follows:

Basis: Al_2O_3 1 g
If the weight of catalyst was 100 gram, 8Co10MgOAl would compose of cobalt 8 g and Al_2O_3 92 g Therefore, in this system,
the amount of Co = $8/92 \times 1$
= 0.0869 g

Cobalt (Co) 0.0869 g was prepared from $Co(CH_3COO)_2{\cdot}4H_2O$ 99% and molecular weight of Co = 59, then
the $Co(CH_3COO)_2{\cdot}4H_2O$ content = $(249\times0.0869\times100)/(59\times99)$
= 0.3705 g

Then, the Mg : (Support+Co) weight ratio = 10:100
The amount of Mg = $10\times(0.0869+1)/100$
= 0.10869 g

Magnesium (Mg) 0.10869 g was impregnated from $Mg(NO_3)_2$ solution 99% and molecular weight of Mg = 24.305 g
Thus, the amount of $Mg(NO_3)_2$ used = $(256.41/24.305)\times0.10869\times(100/99)$
= 1.1582 g

The calculation for the preparation of other catalysts, 8VOAl, 8V4MgOAl, 8V10MgOAl, 8CrOAl, 8Cr4MgOAl, 8Cr10MgOAl, 8MnOAl, 8Mn4MgOAl, 8Mn10MgOAl, 8FeOAl, 8Fe4MgOAl, 8Fe10MgOAl, 8NiOAl, 8Ni4MgOAl, 8Ni10MgOAl, 8CuOAl, 8Cu4MgOAl, 8Cu10MgOAl, 8ZnOAl, 8Zn4MgOAl, 8Zn10MgOAl, 8MoOAl, 8Mo4MgOAl, 8Mo10MgOAl, 8WOAl, 8W4MgOAl, 8W10MgOAl, is the same as the preparation of 8CoOAl, 8Co4MgOAl, 8Co10MgOAl catalysts.

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APPENDIX B

CALCULATION OF DIFFUSIONAL LIMITATION EFFECT

In the present work there are doubts whether the external and internal diffusion limitations interfere with the propane reaction. Hence, the kinetic parameters were calculated based on the experimental data so as to prove the controlled system. The calculation is divided into two parts; one of which is the external diffusion limitation, and the other is the internal diffusion limitation.

1. External diffusion limitation

The 1-propanal oxidation reaction is considered to be an irreversible first order reaction occurred on the interior pore surface of catalyst particles in a fixed bed reactor. Assume isothermal operation for the reaction.

In the experiment, 8% 1-propanol, 5% O_2 balance with nitrogen was used as the unique reactant in the system. Molecular weight of 1-propanol and air (O_2 5%) are 60 and 28.2, respectively. Thus, the average molecular weight of the gas mixture was calculated as follows:

$$
\begin{aligned}
M_{AB} &= 0.08 \times 60 + 0.92 \times 28.2 \\
&= 30.744 \text{ g/mol}
\end{aligned}
$$

<u>Calculation of reactant gas density</u>

Consider the 1-propanol oxidation is operated at low pressure and high temperature. We assume that the gases are respect to ideal gas law. The density of such gas mixture reactant at various temperatures is calculated in the following.

$$\rho = \frac{PM}{RT} = \frac{1.0 \times 10^5 \times 30.744 \times 10^{-3}}{8.314T}$$

We obtained : $\rho = 0.782$ kg/m^3 at T = 200^{o}C

$\rho = 0.706$ kg/m^3 at T = 250^{o}C

$\rho = 0.645$ kg/m^3 at T = 300^{o}C

$\rho = 0.594$ kg/m^3 at T = 350^{o}C

Calculation of the gas mixture viscosity

The simplified methods for determining the viscosity of low pressure binary are described anywhere (Reid, 1988). The method of Wilke is chosen to estimate the gas mixture viscosity.

For a binary system of 1 and 2,

$$\mu_m = \frac{y_1\mu_1}{y_1 + y_2\Phi_{12}} + \frac{y_2\mu_2}{y_2 + y_1\Phi_{21}}$$

where μ_m = viscosity of the mixture

μ_1, μ_2 = pure component viscosity

y_1 , y_2 = mole fractions

$$\phi_{12} = \frac{\left[1+\left(\frac{\mu_1}{\mu_2}\right)^{1/2}\left(\frac{\mathrm{M}_1}{\mathrm{M}_2}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{\mathrm{M}_1}{\mathrm{M}_2}\right)\right]^{1/2}}$$

$$\phi_{21} = \phi_{12}\left(\frac{\mu_2}{\mu_1}\right)\left(\frac{\mathrm{M}_1}{\mathrm{M}_2}\right)$$

M_1, M_2 = molecular weight

Let 1 refer to 1-propanol and 2 to air (O_2 5%)

M_1 = 60 and M_2 = 28.2

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From Perry the viscosity of pure 1-propanol at 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 500°C are 0.0124, 0.0135, 0.015 and 0.0162 cP, respectively. The viscosity of pure air at 200^{o}C, 250^{o}C, 300^{o}C and 350^{o}C are 0.0248, 0.0265, 0.0285 and 0.030 cP, respectively.

At 200^{o}C :

$$\phi_{12} = \frac{\left[1+\left(\frac{0.0124}{0.0248}\right)^{1/2}\left(\frac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60}{28.2}\right)\right]^{1/2}} = 0.502$$

$$\phi_{21} = 0.502\left(\frac{0.0248}{0.0124}\right)\left(\frac{60}{28.2}\right) = 2.14$$

$$\mu_m = \frac{0.08\times 0.0124}{0.08+0.92\times 0.502} + \frac{0.92\times 0.0248}{0.92+0.08\times 2.14} = 0.0227cP = 2.27\times 10^{-5}\,kg/m-\sec$$

At 250^{0}C :

$$\phi_{12} = \frac{\left[1+\left(\frac{0.0135}{0.0265}\right)^{1/2}\left(\frac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60}{28.2}\right)\right]^{1/2}} = 0.506$$

$$\phi_{21} = 0.506\left(\frac{0.0265}{0.0135}\right)\left(\frac{60}{28.2}\right) = 2.113$$

$$\mu_m = \frac{0.08\times 0.0135}{0.08+0.92\times 0.506} + \frac{0.92\times 0.0265}{0.92+0.08\times 2.113} = 0.0244cP = 2.44\times 10^{-5}\,kg/m-\sec$$

At 300^{o}C :

$$\phi_{12} = \frac{\left[1+\left(\frac{0.015}{0.0285}\right)^{1/2}\left(\frac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60}{28.2}\right)\right]^{1/2}} = 0.512$$

$$\phi_{21} = 0.512\left(\frac{0.0285}{0.015}\right)\left(\frac{60}{28.2}\right) = 2.07$$

$$\mu_m = \frac{0.08\times 0.015}{0.08+0.92\times 0.512} + \frac{0.92\times 0.0285}{0.92+0.08\times 2.07} = 0.0263cP = 2.63\times 10^{-5}\,kg/m-\sec$$

At 350°C :
$$\phi_{12} = \frac{\left[1+\left(\frac{0.0162}{0.030}\right)^{1/2}\left(\frac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60}{28.2}\right)\right]^{1/2}} = 0.517$$

$$\phi_{21} = 0.517\left(\frac{0.030}{0.0162}\right)\left(\frac{60}{28.2}\right) = 2.037$$

$$\mu_m = \frac{0.08\times 0.0162}{0.08+0.92\times 0.517} + \frac{0.92\times 0.030}{0.92+0.08\times 2.037} = 0.0278cP = 2.78\times 10^{-5} kg/m-\sec$$

Calculation of diffusion coefficients

Diffusion coefficients for binary gas system at low pressure calculated by empirical correlation are proposed by Reid (1988). Wilke and Lee method is chosen to estimate the value of D_{AB} due to the general and reliable method. The empirical correlation is

$$D_{AB} = \frac{\left(3.03-\frac{0.98}{\mathrm{M}_{AB}^{1/2}}\right)\left(10^{-3}\right)T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^{2}\Omega_D}$$

where D_{AB} = binary diffusion coefficient,cm^2/s

T = temperature,K

M_A ,M_B = molecular weights of A and B ,g/mol

$$\mathrm{M}_{AB} = 2\left[\left(\frac{1}{\mathrm{M}_A}\right)+\left(\frac{1}{\mathrm{M}_B}\right)\right]^{-1}$$

P = pressure,bar

σ = characteristic length,^{0}A

Ω_D = diffusion collision integral, dimensionless

The characteristic Lennard-Jones energy and Length, ε and σ , of air and propanol are as follows: (Reid,1988)

For C_3H_7OH : σ (C_3H_7OH) = 4.549 ^{0}A, ε/k = 576.7
For air : σ (air) = 3.711 ^{0}A , ε/k = 78.6

The sample rules are usually employed.

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{4.549 + 3.711}{2} = 4.13$$

$$\varepsilon_{AB}/k = \left(\frac{\varepsilon_A \varepsilon_B}{k^2}\right)^{1/2} = (576.7 \times 78.6)^{1/2} = 212.9$$

Ω_D is tabulated as a function of kT/ε for the Lennard-Jones potential. The accurate relation is

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

where $T^* = \frac{kT}{\varepsilon_{AB}}$, A = 1.06036 , B = 0.15610 , C = 0.19300 , D = 0.47635 , E = 1.03587 , F = 1.52996 , G = 1.76474 , H = 3.89411

Then $T^* = \frac{473}{212.9} = 2.222$ at 200°C

$T^* = \frac{523}{212.9} = 2.456$ at 250°C

$T^* = \frac{573}{212.9} = 2.691$ at 300°C

$T^* = \frac{623}{212.9} = 2.926$ at 350°C

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$

Ω_D = 1.038 ; 200°C

Ω_D = 1.006 ; 250°C

Ω_D = 0.979 ; 300°C

Ω_D = 0.956 ; 350°C

With Equation of D_{AB},

At 200°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})473^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 1.038}$

$= 3.01\times10^{-5}$ m^2/s

At 250°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})523^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 1.006}$

$= 3.62\times10^{-5}$ m^2/s

At 300°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})573^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 0.979}$

$= 4.26\times10^{-5}$ m^2/s

At 350°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})623^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 0.956}$

$= 5.04\times10^{-5}$ m^2/s

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Reactant gas mixture was supplied at 100 ml/min. in tubular microreactor used in the 1-propanol oxidation system at 30^{o}C

1-propanol flow rate through reactor = 100 ml/min. at 30^{o}C

The density of 1-propanol , $\rho = \frac{1.0\times10^{5}\times30.744\times10^{-3}}{8.314(273+30)} = 1.236$ kg/s

Mass flow rate = $1.236\left(\frac{100\times10^{-6}}{60}\right) = 2.06\times10^{-6}$ kg/s

Diameter of quartz tube reactor = 8 mm

Cross-sectional area of tube reactor = $\frac{\pi(8\times10^{-3})^{2}}{4} = 5.03\times10^{-5}$ m^2

Mass Velocity , G = $\frac{2.06\times10^{-6}}{5.03\times10^{-5}} = 0.04$ kg/m^2-s

Catalyst size = 40-60 mesh = 0.178-0.126 mm

Average catalyst size = (0.126+0.178)/2 = 0.152 mm

Find Reynolds number, Re$_p$, which is well known as follows:

$$\mathrm{Re}_p = \frac{d_p G}{\mu}$$

We obtained

<u>At 200^{o}C</u> : $\mathrm{Re}_p = \frac{(0.152\times10^{-3}\times0.04)}{2.27\times10^{-5}} = 0.268$

<u>At 250^{o}C</u> : $\mathrm{Re}_p = \frac{(0.152\times10^{-3}\times0.04)}{2.44\times10^{-5}} = 0.249$

<u>At 300^{o}C</u> : $\mathrm{Re}_p = \frac{(0.152\times10^{-3}\times0.04)}{2.63\times10^{-5}} = 0.231$

<u>At 350^{o}C</u> : $\mathrm{Re}_p = \frac{(0.152\times10^{-3}\times0.04)}{2.78\times10^{-5}} = 0.219$

Average transport coefficient between the bulk stream and particles surface could be correlated in terms of dimensionless groups, which characterize the flow conditions. For mass transfer the Sherwood number, kmρ/G, is an empirical function of the Reynolds number, d_pG/μ, and the Schmit number, $\mu/\rho D$. The j-factors are defined as the following functions of the Schmidt number and Sherwood numbers:

$$j_D = \frac{k_m \rho}{G}\left(\frac{a_m}{a_t}\right)(\mu / \rho D)^{2/3}$$

The ratio (a_m/a_t) allows for the possibility that the effective mass-transfer area a_m, may be less than the total external area, a_t, of the particles. For Reynolds number greater than 10, the following relationship between j_D and the Reynolds number well represents available data.

$$j_D = \frac{0.458}{\varepsilon_B}\left(\frac{d_p G}{\mu}\right)^{-0.407}$$

where G = mass velocity(superficial) based upon cross-sectional area of empty reactor
(G = uρ)
d_p = diameter of catalyst particle for spheres
μ = viscosity of fluid
ρ = density of fluid
ε_B = void fraction of the interparticle space (void fraction of the bed)
D = molecular diffusivity of component being transferred

Assume $\varepsilon_B = 0.5$

At 200°C ; $j_D = \frac{0.458}{0.5}(0.268)^{-0.407} = 1.565$

At 250°C ; $j_D = \frac{0.458}{0.5}(0.249)^{-0.407} = 1.613$

<u>At 300°C</u> ; $j_D = \dfrac{0.458}{0.5}(0.231)^{-0.407} = 1.663$

<u>At 350°C</u> ; $j_D = \dfrac{0.458}{0.5}(0.219)^{-0.407} = 1.699$

A variation of the fixed bed reactor is an assembly of screens or gauze of catalytic solid over which the reacting fluid flows. Data on mass transfer from single screens has been reported by Gay and Maughan. Their correlation is of the form

$$j_D = \frac{\varepsilon k_m \rho}{G}(\mu / \rho D)^{2/3}$$

Where ε is the porosity of the single screen.

Hence, $k_m = \left(\dfrac{j_D G}{\mu}\right)(\mu / \rho D)^{2/3}$

$$k_m = \left(\frac{0.458G}{\varepsilon_B \rho}\right)\mathrm{Re}^{-0.407}\ Sc^{-2/3}$$

Find Schmidt number, Sc : $Sc = \dfrac{\mu}{\rho D}$

<u>At 200°C</u> : $Sc = \dfrac{2.27*10^{-5}}{0.782*3.01*10^{-5}} = 0.964$

<u>At 250°C</u> : $Sc = \dfrac{2.44*10^{-5}}{0.706*3.62*10^{-5}} = 0.955$

<u>At 300°C</u> : $Sc = \dfrac{2.63*10^{-5}}{0.645*4.26*10^{-5}} = 0.957$

<u>At 350°C</u> : $Sc = \dfrac{2.78*10^{-5}}{0.594*5.04*10^{-5}} = 0.928$

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Find k_m : At 200°C, $k_m = \left(\dfrac{1.565\times 0.04}{0.782}\right)(0.964)^{-2/3} = 0.082\,\text{m/s}$

At 250°C, $k_m = \left(\dfrac{1.613\times 0.04}{0.706}\right)(0.955)^{-2/3} = 0.094\,\text{m/s}$

At 300°C, $k_m = \left(\dfrac{1.663\times 0.04}{0.645}\right)(0.957)^{-2/3} = 0.106\,\text{m/s}$

At 350°C, $k_m = \left(\dfrac{1.699\times 0.04}{0.594}\right)(0.928)^{-2/3} = 0.12\,\text{m/s}$

Properties of catalyst

Density = 0.375 g/ml catalyst

Diameter of 40-60 mesh catalyst particle = 0.152 mm

Weight per catalyst particle $= \dfrac{\pi(0.152\times 0^{-1})^3\times 0.375}{6} = 6.895*10^{-7}$ g/particle

External surface area per particle $= \pi(0.152\times 10^{-3})^2 = 7.26\times 10^{-7}$ m^2/particle

$a_m = \dfrac{7.26\times 10^{-7}}{6.895\times 10^{-7}} = 1.052\times 10^{-2}$ m^2/gram catalyst

Volumetric flow rate of gaseous feed stream = 100 ml/min

Molar flow rate of gaseous feed stream $= \dfrac{(1\times 10^5)\left(\dfrac{100\times 10^{-6}}{60}\right)}{8.314(273+30)} = 6.62\times 10^{-5}$ mol/s

1-propanol molar feed rate = $0.08\times 6.62\times 10^{-5} = 5.29\times 10^{-6}$ mol/s

1-propanol conversion (experimental data): 1.78 % at 200°C
5.73 % at 250°C
28.07 % at 300°C
59.93 % at 350°C

The estimated rate of 1-propanol oxidation reaction is based on the ideal plug flow reactor which there is no mixing in the direction of flow and complete mixing perpendicular to the direction of flow (i.e., in the radial direction). The rate of reaction will vary with reaction length. Plug flow reactors are normally operated at steady state so that properties at any position are constant with respect to time. The mass balance around plug flow reactor becomes

$$\{\text{rate of i into volume element}\} - \{\text{rate of i out of volume element}\}$$
$$+ \{\text{rate of production of i within the volume element}\}$$
$$= \{\text{rate of accumulation of i within the volume elecment}\}$$

$$F_{Ao} = F_{Ao}(1\text{-}x) + (r_W W)$$
$$(r_W W) = F_{Ao} - F_{Ao}(1\text{-}x) = F_{Ao} = F_{Ao}x$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.0178}{0.1} = 4.717 \times 10^{-7} \text{ mol/s-gram catalyst at } 200^{o}\text{C}$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.0573}{0.1} = 1.518 \times 10^{-6} \text{ mol/s-gram catalyst at } 250^{o}\text{C}$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.28}{0.1} = 7.42 \times 10^{-6} \text{ mol/s-gram catalyst at } 300^{o}\text{C}$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.599}{0.1} = 1.587 \times 10^{-5} \text{ mol/s-gram catalyst at } 350^{o}\text{C}$$

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At steady state the external transport rate may be written in terms of the diffusion rate from the bulk gas to the surface. The expression is:

$$R_{obs} = k_m a_m (C_b\text{-}C_s)$$
$$= \frac{\text{1 - propanol converted (mole)}}{\text{(time)(gram of catalyst)}}$$

where C_b and C_s are the concentrations in the bulk gas and at the surface, respectively.

<u>At 200°C</u>, $(C_b\text{-}C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{4.717\times10^{-7}}{0.082\times1.052\times10^{-1}} = 5.47\times10^{-4}\ \text{mol/m}^3$

<u>At 250°C</u>, $(C_b\text{-}C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{1.518\times10^{-6}}{0.094\times1.052\times10^{-1}} = 1.53\times10^{-4}\ \text{mol/m}^3$

<u>At 300°C</u>, $(C_b\text{-}C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{7.42\times10^{-6}}{0.106\times1.052\times10^{-1}} = 6.65\times10^{-3}\ \text{mol/m}^3$

<u>At 350°C</u>, $(C_b\text{-}C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{1.587\times10^{-5}}{0.12\times1.052\times10^{-1}} = 1.26\times10^{-3}\ \text{mol/m}^3$

From C_b (1-propanol) = 1.59 mol/m^3

Consider the difference of the bulk and surface concentration is small. It means that the external mass transport has no effect on the 1-propanol oxidation reaction rate.

2. Internal diffusion limitation

Next, consider the internal diffusion limitation of the 1-propanol reaction. An effectiveness factor, η, was defined in order to express the rate of reaction for the whole catalyst pellet, r_p, in terms of the temperature and concentrations existing at the outer surface as follows:

$$\eta = \frac{\text{actual rate of whole pellet}}{\text{rate evaluated at outer surface conditions}} = \frac{r_p}{r_s}$$

The equation for the local rate (per unit mass of catalyst) may be expected functionally as r = f(C,T).

Where C represents, symbolically, the concentrations of all the involved components

Then, $r_p = \eta r_s = \eta f(C_s,T_s)$

Suppose that the 1-propanol oxidation is an irreversible reaction A→B and first order reaction, so that for isothermal conditions $r = f(C_A) = k_1C_A$. Then $r_p = \eta k_1 (C_A)_s$.

For a spherical pellet, a mass balance over the spherical-shell volume of thickness Δr. At steady state the rate of diffusion into the element less the rate of diffusion out will equal the rate of disappearance of reactant with in the element. This rate will be $\rho_p k_1 C_A$ per unit volume, where ρ_p is the density of the pellet. Hence, the balance may be written, omitting subscript A on C,

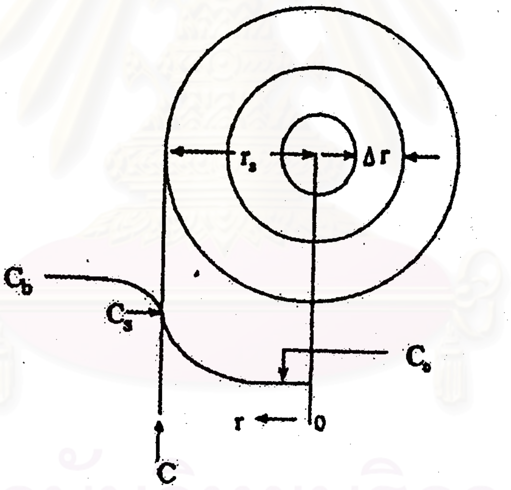

Figure B1. Reactant (A) concentration vs. position for first-order reaction on a spherical catalyst pellet.

$$\left(-4\pi r^2 D_e \frac{dC}{dr}\right)_r - \left(-4\pi r^2 D_e \frac{dC}{dr}\right)_{r+\Delta r} = -4\pi r^2\, \Delta r_p k_1 C$$

Take the limit as $\Delta r \to 0$ and assume that the effective diffusivity is independent of the concentration of reactant, this difference equation becomes

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$$\frac{d^2C}{dr^2} + 2\frac{dC}{dr} - \frac{k_1\rho_p C}{D_e} = 0$$

At the center of the pellet symmetry requires

$$\frac{dC}{dr} = 0 \text{ at } r = 0$$

and at outer surface

$C = C_s$ at $r = r_s$

Solve linear differential equation by conventional methods to yield

$$\frac{C}{C_s} = \frac{r_s \sinh\left(3\phi_s \frac{r}{r_s}\right)}{r \sinh 3\phi_s}$$

where ϕ_s is Thiele modulus for a spherical pellet defined by $\phi_s = \frac{r_s}{3}\sqrt{\frac{k_1\rho_p}{D_e}}$

Both D_e and k_1 are necessary to use $r_p = \eta k_1 (C_A)_s$. D_e could be obtained from the reduced pore volume equation in case of no tortuosity factor.

$$D_e = (\varepsilon_s^2 D_{AB})$$

<u>At 200°C</u>, $D_e = (0.5)^2\ (3.01\times10^{-5}) = 7.53\times10^{-6}$

<u>At 250°C</u>, $D_e = (0.5)^2\ (3.62\times10^{-5}) = 9.04\times10^{-6}$

<u>At 300°C</u>, $D_e = (0.5)^2\ (4.26\times10^{-5}) = 1.06\times10^{-5}$

Substitute radius of catalyst pellet, $r_s = 0.107\times10^{-3}$ m with ϕ_s equation

$$\phi_s = \frac{0.076\times10^{-3}\ \text{m}}{3}\sqrt{\frac{k(\text{m}^3/\text{s - kg cat.})\times1000(\text{kg/m}^3)}{7.53\times10^{-6}(\text{m}^2/\text{s})}}\text{, at 200°C}$$

$\phi_s = 0.292\sqrt{k}$ (dimensionless) at 200°C

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$\phi_s = 0.266\sqrt{k}$ (dimensionless) at 250°C

$\phi_s = 0.246\sqrt{k}$ (dimensionless) at 300°C

Find k (at 200°C) from the mass balance equation around plug-flow reactor.

$$r_w = \frac{F_{Ao}\,dx}{dW}$$

where $r_w = kC_A$

Thus,

$$kC_A = \frac{F_{Ao}\,dx}{dW}$$

$$kC_{Ao}(1\text{-}x) = \frac{F_{Ao}\,dx}{dW}$$

$$W = \frac{F_{Ao}}{kC_{Ao}}\int_0^{0.1}\frac{1}{1-x}\,dx$$

$$W = \frac{F_{Ao}}{kC_{Ao}}\left[-\ln(1-x)\right]_0^{0.1} = \frac{F_{Ao}}{kC_{Ao}}(-\ln(0.9))$$

$$k = \frac{F_{Ao}}{WC_{Ao}}(-\ln(0.9822))$$

$$k = \frac{5.29\times10^{-6}\ (\text{mol/s})}{0.1\times10^{-3}\ (\text{kg})\times1.03(\text{mol/m}^3)}(-\ln(0.9822)$$

$$= 0.92\times10^{-4}\ \text{m}^3/\text{s-kg catalyst}$$

Calculate $\phi_s : \phi_s = 0.292\sqrt{0.92\times10^{-4}} = 0.0028$ at 200°C

$\phi_s = 0.266\sqrt{3.03\times10^{-3}} = 0.015$ at 250°C

$\phi_s = 0.246\sqrt{1.68\times10^{-2}} = 0.032$ at 300°C

For such small values of ϕ_s it was concluded that the internal mass transport has no effect on the rate of 1-propanol oxidation reaction.

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APPENDIX C

CALCULATION OF SPECIFIC SURFACE AREA

From Brunauer-Emmett-Teller (BET) equation

$$\frac{p}{n(1-p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C} \qquad (C1)$$

Where, p = Relative partial pressure of adsorbed gas, P/P_0

P_0 = Saturated vapor pressure of adsorbed gas in the condensed state at the experimental temperature, atm

P = Equilibrium vapor pressure of adsorbed gas, atm

n = Quantity of gas adsorbed at pressure P, ml. at the NTP/g of sample

n_m = Quantity of gas adsorbed at monolayer, ml. at the NTP/g of sample

C = Exp $[(H_C - H_l)/RT]$

H_C = Heat of condensation of adsorbed gas on all other layers

H_l = Heat of adsorption into the first layer

Assume $C \rightarrow \infty$, then

$$\frac{p}{n(1-p)} = \frac{p}{n_m}$$

$$n_m = n(1-p) \qquad (C2)$$

The surface area, S, of the catalyst is given by

$$S = S_b \times n_m \qquad (C3)$$

From the gas law

$$\frac{P_b V}{T_b} = \frac{P_t V}{T_t} \qquad (C4)$$

Where, P_b = Pressure at 0ºC

P_t = Pressure at tºC

T_b = Temperature at 0ºC = 273.15 K

T_t = Temperature at tºC = 273.15 + t K

V = Constant volume

Then, $P_b = (273.15/T_t) \times P_t = 1$ atm

Partial pressure

$$P = \frac{[\text{Flow of }(\text{He}+\text{N}_2) - \text{Flow of He}]}{\text{Flow of }(\text{He}+\text{N}_2)} \tag{C5}$$

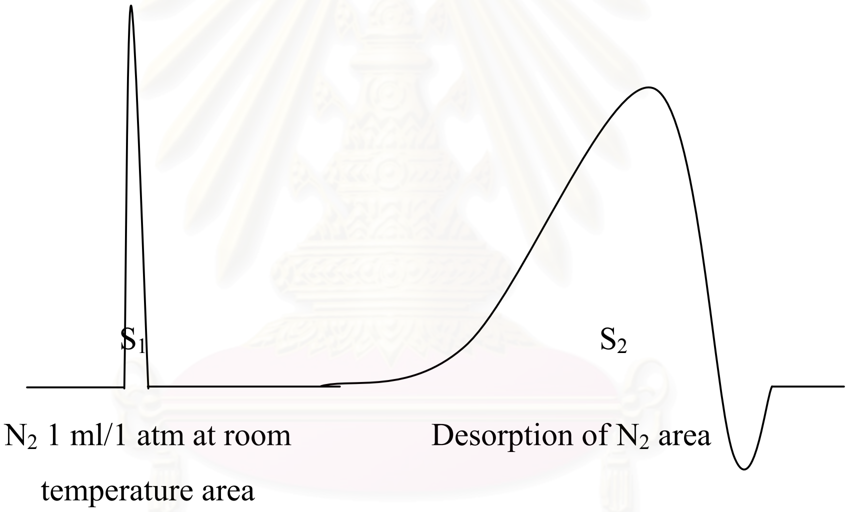
$$= 0.3 \text{ atm}$$

For nitrogen gas, the saturated vapor pressure equals to

$P_0 = 1.1$ atm

then, $p = P/P_0 = 0.3/1.1 = 0.2727$

To measure the volume of nitrogen adsorbed, n



$$n = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \text{ ml. /g of catalyst} \tag{C6}$$

Where, S_1 = N_2 1 ml/1 atm at room temperature area

S_2 = Desorption of N_2 area

W = Sample weight, g

T = Room temperature, K

Therefore,

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times (1-p)$$

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$$n_m = \frac{S_2}{S_1}\times\frac{1}{W}\times\frac{273.15}{T}\times 0.7272 \qquad \text{(C2.1)}$$

Whereas, the surface area of nitrogen gas from literature equal to

S_b = 4.373 m^2/ml of nitrogen gas

Then,

$$S = \frac{S_2}{S_1}\times\frac{1}{W}\times\frac{273.15}{T}\times 0.7272\times 4.343$$

$$S = \frac{S_2}{S_1}\times\frac{1}{W}\times\frac{273.15}{T}\times 3.1582\ \text{m}^2/\text{g} \qquad \text{(C7)}$$

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APPENDIX D

CALIBRATION CURVE

Flame ionization detector gas chromatographs, model 14A and 14B, were used to analyze the concentrations of oxygenated compounds and light hydrocarbons, respectively. 1-propanol, formaldehyde, acetaldehyde, and propionaldehyde were analyzed by GC model 14A while methane, ethylene, propane, and propylene were analyzed by GC model 14B.

Gas chromatograph with the thermal conductivity detector, model 8A, was used to analyze the concentration of CO_2 by using Porapak-Q column.

The calibration curves of methane, ethylene, propane, propylene, 1-propanol, 2-propanol, CO_2, formaldehyde, acetaldehyde, and propionaldehyde are illustrated in the following figures.

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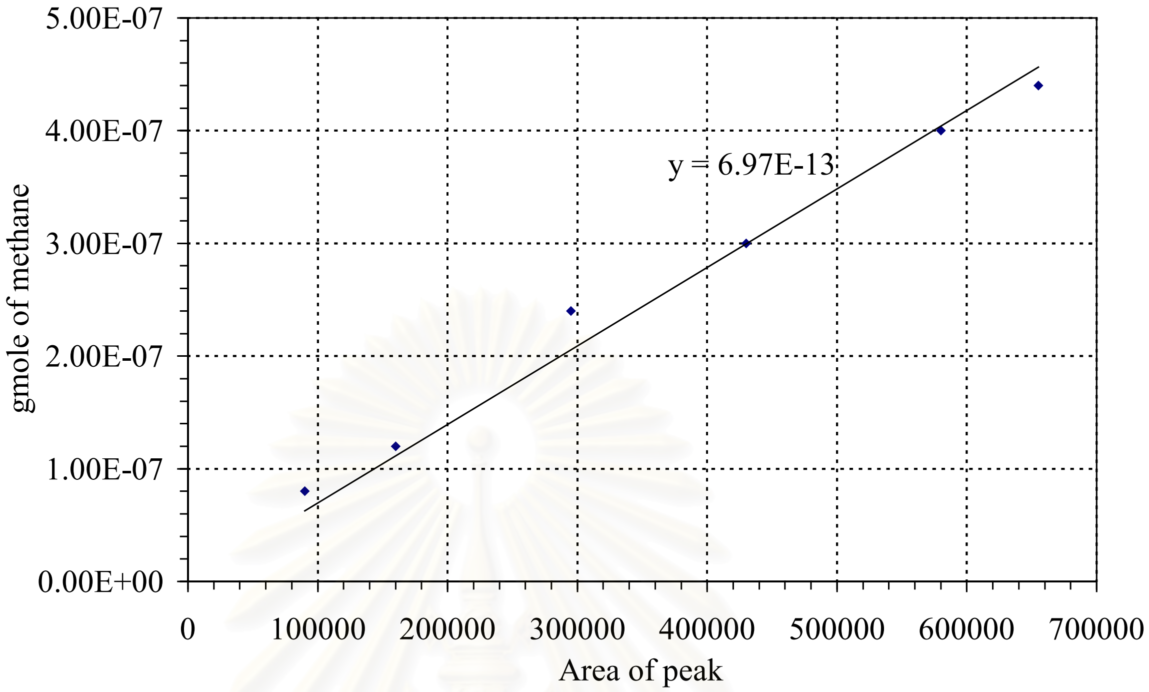

Figure D1 The calibration curve of methane

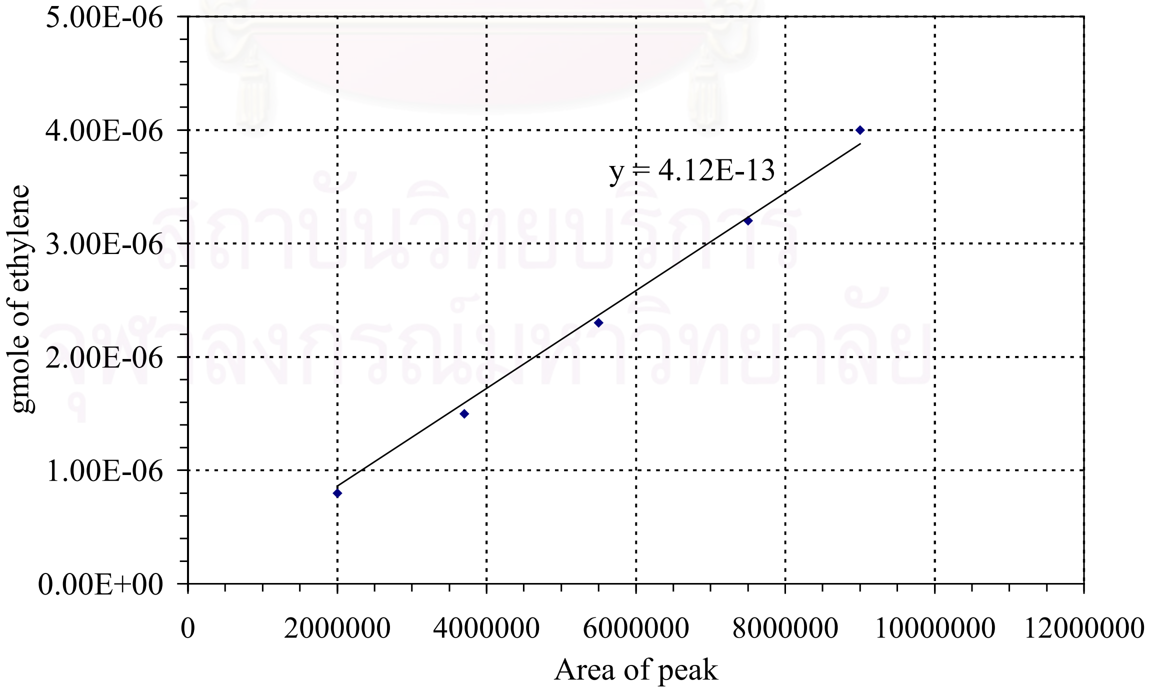

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Figure D2 The calibration curve of ethylene

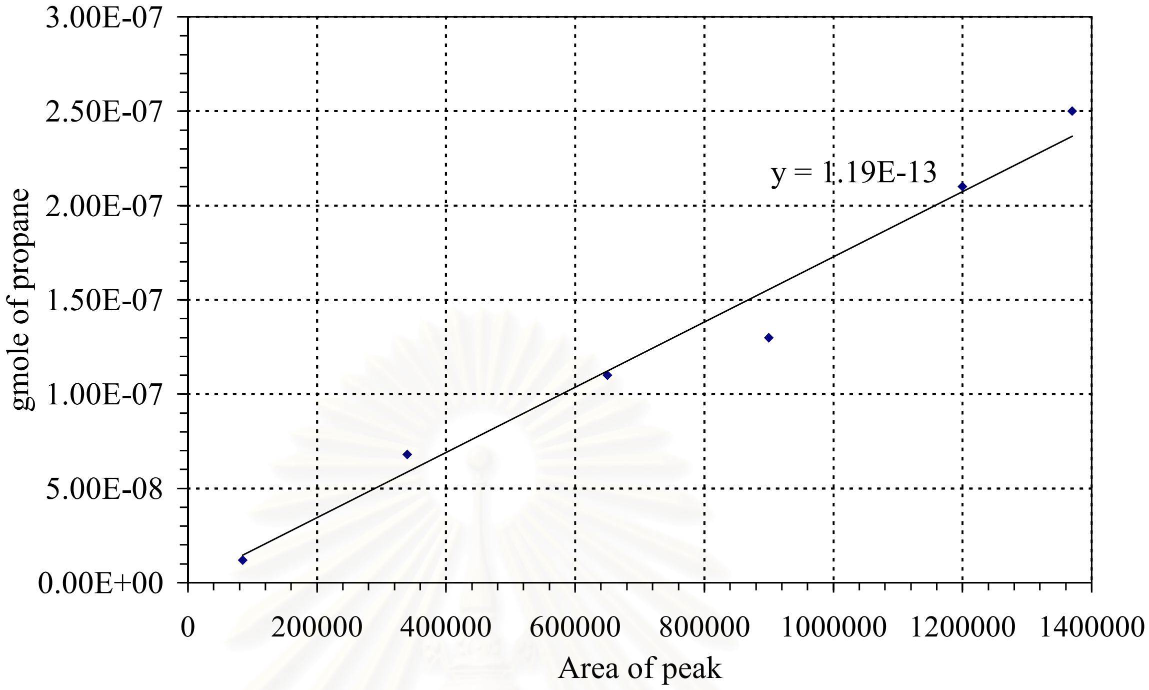

Figure D3 The calibration curve of propane

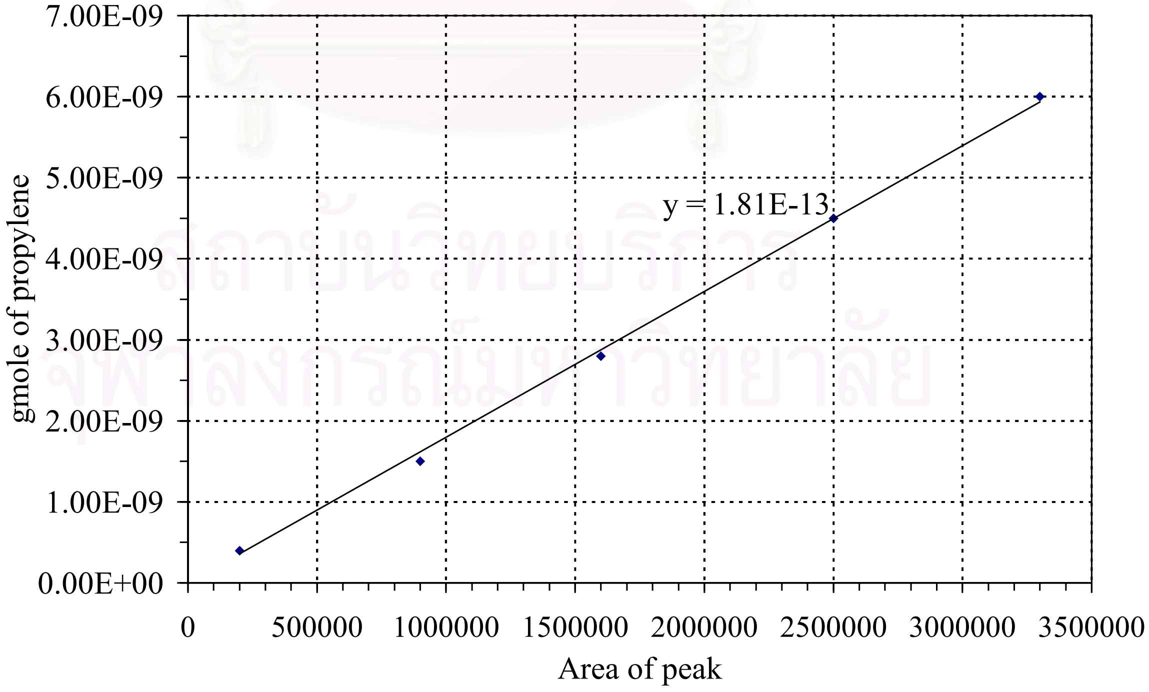

Figure D4 The calibration curve of propylene

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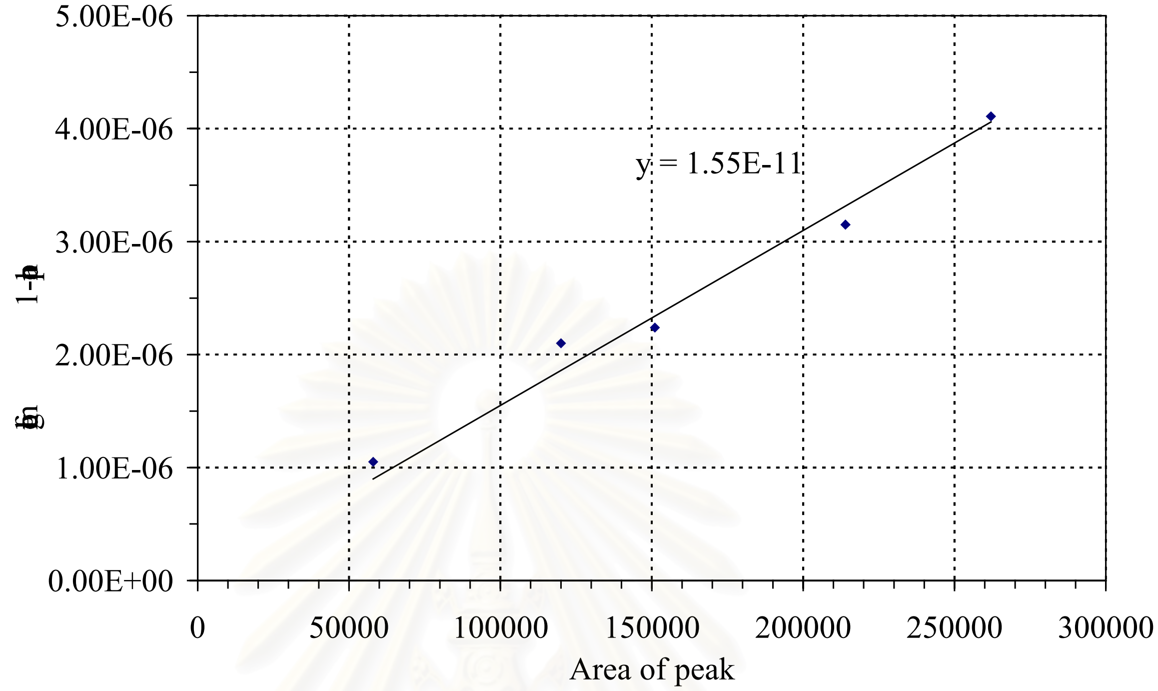

Figure D5 The calibration curve of 1-propanol

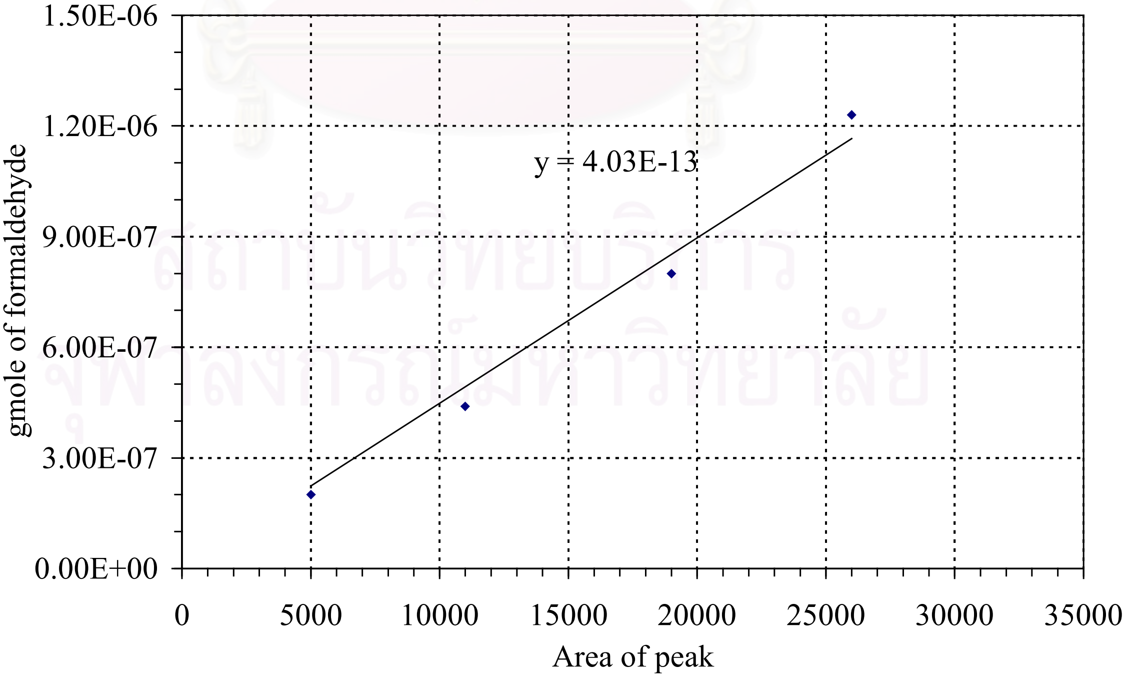

Figure D6 The calibration curve of formaldehyde

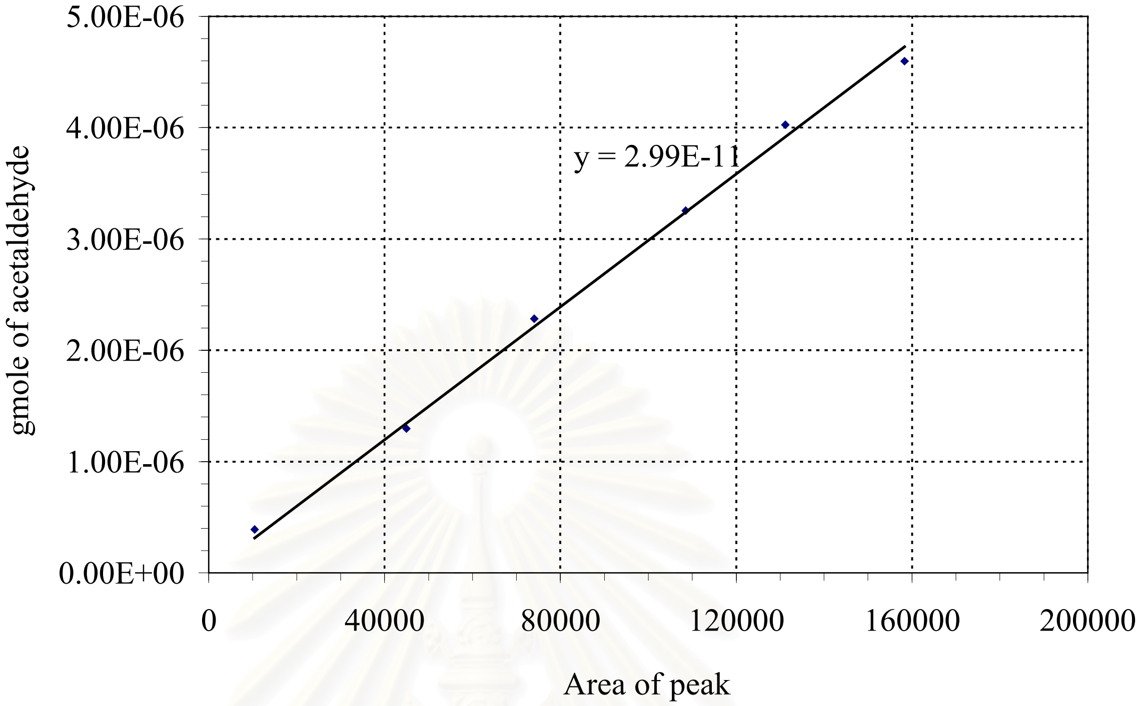

Figure D7 The calibration curve of acetaldehyde

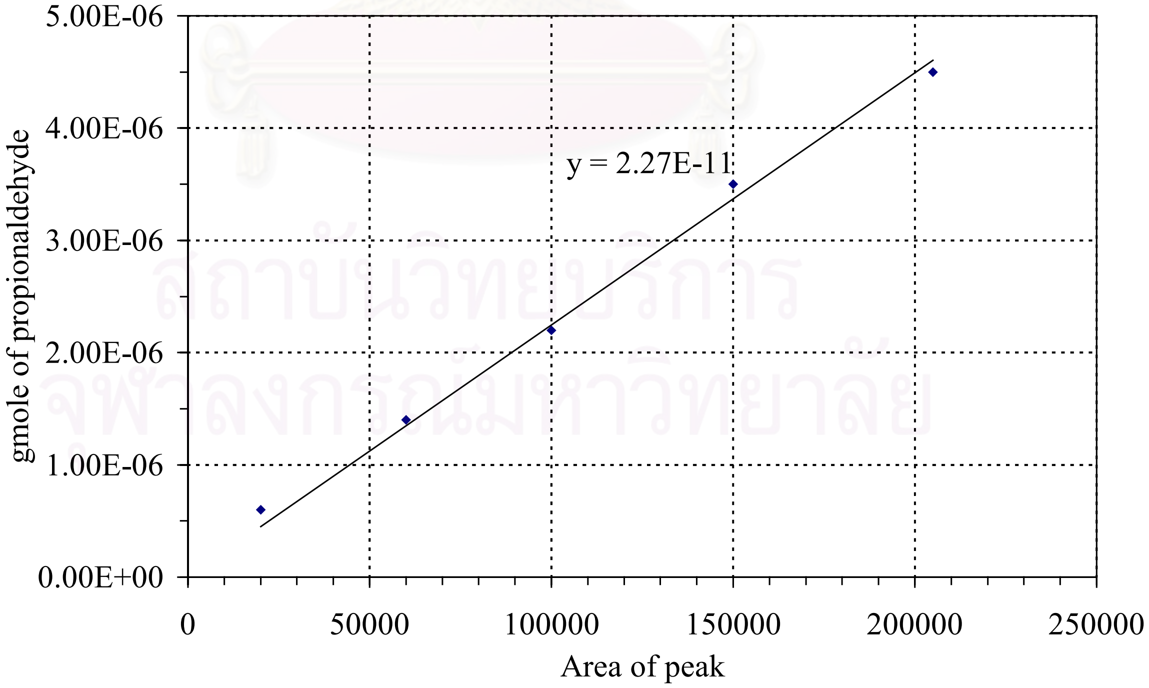

Figure D8 The calibration curve of propionaldehyde

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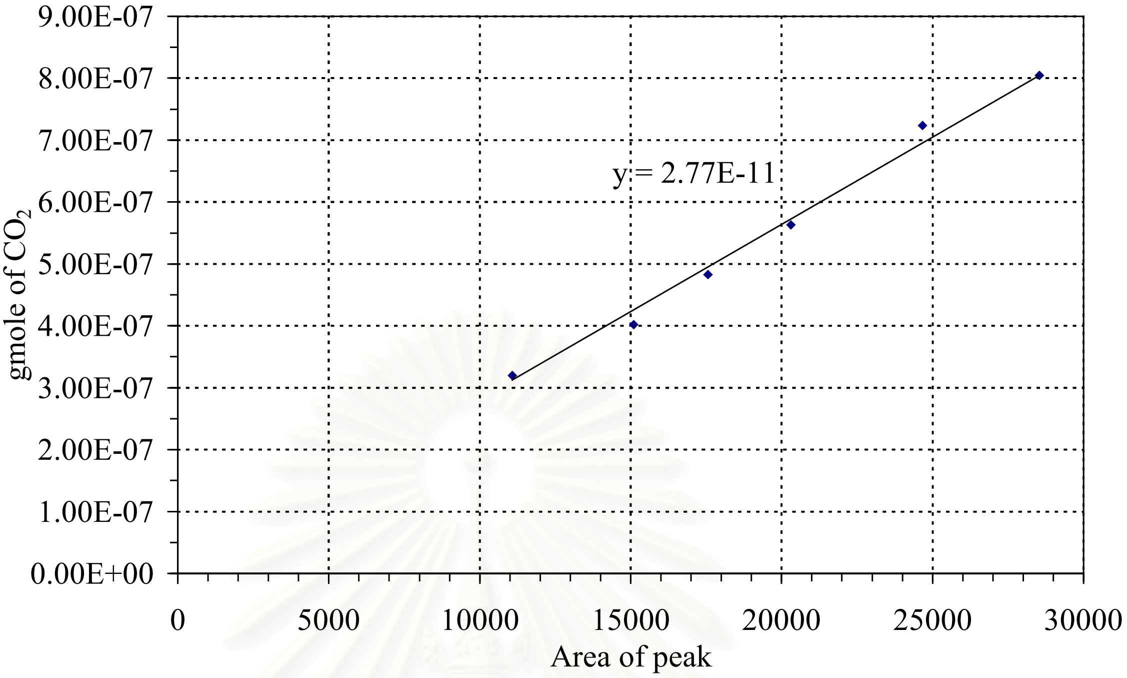

Figure D9 The calibration curve of carbondioxide

APPENDIX E

DATA OF EXPERIMENTS

Table E1a data of Figure 5.11a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	8.79	25.66	58.74	72.44	88.94	95.14	95.64
%Propionaldehyde (S)	92.14	78.02	66.08	59.88	47.55	40.98	35.66
%Propylene (S)	3.11	12.33	14.96	18.62	20.17	22.85	23.68
%C1-C2 (S)	2.68	4.58	7.62	9.82	12.75	14.22	14.63
%Carbonmonoxide (S)	0.22	0.88	3.56	2.03	2.51	1.20	2.14
%Carbondioxide (S)	0.72	3.84	6.74	8.65	16.34	19.88	22.31
%Propionaldehyde (Y)	8.10	20.02	38.82	43.38	42.29	38.99	34.11

Table E1b data of Figure 5.11b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.14	0.37	2.66	2.89	3.01	1.02	0.33
%Acetaldehyde (S)	0.89	1.58	2.31	3.67	4.22	5.14	5.21
%Methane (S)	0.92	1.63	2.96	3.01	3.98	4.06	4.32
%Ethylene (S)	0.87	1.37	2.35	3.14	4.55	5.02	5.10

Table E2a data of Figure 5.12a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	27.88	57.31	84.97	92.66	94.61	96.88	96.91
%Propionaldehyde (S)	85.34	57.19	33.96	25.63	12.37	9.21	6.65
%Propylene (S)	8.85	17.56	25.68	26.88	27.98	28.66	31.44
%C1-C2 (S)	2.50	7.03	11.00	14.29	15.83	15.91	15.59
%Carbonmonoxide (S)	1.96	5.66	8.41	5.44	4.58	1.06	1.08
%Carbondioxide (S)	0.87	10.62	18.33	27.55	38.77	45.01	44.69
%Propionaldehyde (Y)	23.79	32.78	28.86	23.75	11.70	8.92	6.44

Table E2b data of Figure 5.12b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.21	0.23	0.87	1.69	0.68	0.59	0.47
%Acetaldehyde (S)	0.64	1.31	1.45	3.64	3.88	2.67	1.89
%Methane (S)	0.88	3.08	4.66	4.85	5.39	6.69	7.15
%Ethylene (S)	0.77	2.41	4.02	4.11	5.88	5.96	6.08

Table E3a data of Figure 5.13a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	34.60	64.97	90.62	97.69	97.33	97.18	99.01
%Propionaldehyde (S)	83.52	55.22	32.52	15.89	12.69	9.89	5.84
%Propylene (S)	9.96	16.96	26.54	30.21	27.58	27.05	28.25
%C1-C2 (S)	4.67	8.70	16.02	17.05	16.21	15.13	16.31
%Carbonmonoxide (S)	0.38	3.58	3.63	3.25	0.18	0.19	1.01
%Carbondioxide (S)	1.03	15.48	21.07	32.11	43.31	47.58	48.56
%Propionaldehyde (Y)	28.90	35.88	29.47	15.52	12.35	9.61	5.78

Table E3b data of Figure 5.13b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.22	0.26	1.66	1.26	1.32	1.66	0.98
%Acetaldehyde (S)	1.85	2.25	4.01	4.28	3.81	3.01	2.07
%Methane (S)	1.25	3.65	5.33	5.85	5.45	5.14	6.85
%Ethylene (S)	1.35	2.54	5.02	5.66	5.63	5.32	6.41

Table E4a data of Figure 5.14a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	12.02	18.54	38.95	67.85	84.59	91.56	92.88
%Propionaldehyde (S)	89.63	79.61	70.36	62.54	49.68	43.25	41.26
%Propylene (S)	2.99	8.62	13.58	16.02	18.88	19.33	18.02
%C1-C2 (S)	2.09	3.27	3.50	5.21	5.76	6.98	8.46
%Carbonmonoxide (S)	3.05	2.96	4.25	5.11	9.02	12.36	13.55
%Carbondioxide (S)	1.25	4.77	7.01	10.05	14.52	16.55	16.63
%Propionaldehyde (Y)	10.77	14.76	27.41	42.43	42.02	39.60	38.32

Table E4b data of Figure 5.14b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.14	0.61	0.78	0.88	1.2	0.74	0.52
%Acetaldehyde (S)	0.28	1.34	1.33	2.31	2.40	3.14	3.25
%Methane (S)	0.85	0.95	1.05	1.65	1.74	1.99	2.69
%Ethylene (S)	0.96	0.98	1.12	1.25	1.62	1.85	2.52

Table E5a data of Figure 5.15a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	7.12	20.33	46.81	65.27	87.62	94.56	95.83
%Propionaldehyde (S)	92.11	85.97	77.84	64.11	43.69	38.07	30.01
%Propylene (S)	3.57	6.82	12.34	18.75	25.69	27.85	35.17
%C1-C2 (S)	2.14	3.02	3.70	6.18	7.32	7.99	9.19
%Carbonmonoxide (S)	0.00	0.02	0.03	0.02	0.10	0.00	0.00
%Carbondioxide (S)	1.24	3.28	5.66	10.58	22.59	25.01	25.14
%Propionaldehyde (Y)	6.56	17.48	36.44	41.84	38.28	36.00	28.76

Table E5b data of Figure 5.15b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0	0.01	0.02	0.24	0.34	0.45	0.43
%Acetaldehyde (S)	0.74	0.88	0.94	2.31	3.14	3.28	3.31
%Methane (S)	0.95	1.12	1.52	1.86	1.95	2.54	2.67
%Ethylene (S)	0.45	1.02	1.24	2.01	2.23	2.17	3.21

Table E6a data of Figure 5.16a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	5.14	20.34	50.28	62.81	90.58	93.85	94.56
%Propionaldehyde (S)	86.96	78.55	56.33	41.22	27.69	24.51	22.14
%Propylene (S)	5.51	6.86	12.44	17.41	22.34	21.61	23.17
%C1-C2 (S)	2.88	4.71	6.47	7.19	7.31	6.73	6.40
%Carbonmonoxide (S)	2.01	3.96	8.63	8.55	9.02	2.85	3.01
%Carbondioxide (S)	1.01	5.55	14.66	25.07	33.21	44.22	45.08
%Propionaldehyde (Y)	4.47	15.98	28.32	25.89	25.08	23.00	20.94

Table E6b data of Figure 5.16b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.25	0.39	1.85	1.74	1.21	0.61	0.36
%Acetaldehyde (S)	0.88	1.51	1.63	2.22	2.75	2.63	2.41
%Methane (S)	0.91	1.25	1.47	1.57	1.63	1.68	1.75
%Ethylene (S)	0.84	1.56	1.52	1.66	1.72	1.81	1.88

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Table E7a data of Figure 5.17a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	15.44	45.66	69.87	88.97	92.36	95.67	95.78
%Propionaldehyde (S)	87.02	76.31	53.22	36.47	22.33	19.63	15.41
%Propylene (S)	6.07	7.11	12.34	16.98	20.33	20.85	22.34
%C1-C2 (S)	3.18	4.93	6.21	7.81	6.98	7.10	6.84
%Carbonmonoxide (S)	2.01	3.66	6.38	8.52	8.14	3.31	6.48
%Carbondioxide (S)	1.02	6.37	20.31	28.57	40.27	47.69	48.57
%Propionaldehyde (Y)	13.44	34.84	37.18	32.45	20.62	18.78	14.76

Table E7b data of Figure 5.17b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.36	0.45	1.52	1.74	0.84	0.61	0.23
%Acetaldehyde (S)	1.01	1.55	1.62	2.85	2.81	2.92	3.02
%Methane (S)	0.85	1.42	1.44	1.55	1.62	1.75	1.74
%Ethylene (S)	0.96	1.51	1.63	1.67	1.71	1.82	1.85

Table E8a data of Figure 5.18a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	4.84	16.85	45.22	62.07	85.16	92.54	93.14
%Propionaldehyde (S)	87.84	72.31	56.32	52.47	47.85	42.31	40.36
%Propylene (S)	6.89	12.63	13.85	16.39	19.25	20.04	20.55
%C1-C2 (S)	2.62	4.03	8.55	10.72	9.61	11.63	10.17
%Carbonmonoxide (S)	0.11	1.22	8.04	6.22	5.23	6.01	8.22
%Carbondioxide (S)	1.67	8.9	12.66	13.96	17.65	19.63	20.36
%Propionaldehyde (Y)	4.25	12.18	25.47	32.57	40.75	39.15	37.59

Table E8b data of Figure 5.18b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.11	0.14	0.47	0.99	0.48	0.23	0.1
%Acetaldehyde (S)	0.94	1.23	4.56	6.37	4.29	5.77	4.41
%Methane (S)	0.89	2.25	3.12	3	2.99	3.14	2.87
%Ethylene (S)	0.79	0.55	0.87	1.21	2.33	2.72	2.89

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Table E9a data of Figure 5.19a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	3.41	14.28	48.82	75.24	90.33	94.61	94.71
%Propionaldehyde (S)	87.41	71.22	52.14	32.45	30.21	29.14	26.98
%Propylene (S)	5.62	15.62	20.47	28.69	22.61	23.51	23.44
%C1-C2 (S)	4.64	8.48	16.19	22.89	28.86	29.17	31.51
%Carbonmonoxide (S)	0.58	1.05	2.14	2.06	2.33	2.88	2.36
%Carbondioxide (S)	0.67	3.45	8.44	13.66	14.58	14.69	15.47
%Propionaldehyde (Y)	2.98	10.17	25.45	24.42	27.29	27.57	25.55

Table E9b data of Figure 5.19b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.28	0.31	1.54	2.47	0.34	0.08	0.07
%Acetaldehyde (S)	2.34	5.47	6.98	9.64	12.33	15.51	16.22
%Methane (S)	1.22	1.49	4.59	6.33	7.61	6.25	6.84
%Ethylene (S)	1.08	1.52	4.62	6.92	8.92	7.41	8.45

Table E10a data of Figure 5.20a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	8.07	13.88	47.25	80.61	88.66	92.64	93.44
%Propionaldehyde (S)	76.14	45.85	32.51	23.55	23.89	14.25	8.04
%Propylene (S)	5.47	23.35	27.45	28.85	30.11	32.11	32.51
%C1-C2 (S)	14.17	24.29	28.85	27.68	29.90	37.18	41.93
%Carbonmonoxide (S)	2.52	0.85	3.14	4.52	1.05	0.06	1.02
%Carbondioxide (S)	1.22	5.49	7.74	14.66	14.85	16.02	16.16
%Propionaldehyde (Y)	6.14	6.36	15.36	18.98	21.18	13.20	7.51

Table E10b data of Figure 5.20b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.78	1.87	2.84	1.68	1.22	0.41	0.13
%Acetaldehyde (S)	8.47	16.37	18.74	16.01	12.31	12.68	13.66
%Methane (S)	2.99	2.25	3.12	3.25	5.01	9.81	11.52
%Ethylene (S)	2.71	5.67	6.99	8.42	12.58	14.69	16.75

Table E11a data of Figure 5.27a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	7.55	26.33	56.36	72.55	88.25	94.58	94.02
%Propionaldehyde (S)	93.41	84.52	72.63	67.41	53.66	45.61	40.21
%Propylene (S)	2.03	7.88	9.67	12.82	15.41	18.66	19.62
%C1-C2 (S)	2.51	4.62	7.52	9.23	14.15	15.30	15.77
%Carbonmonoxide (S)	1.32	0.85	3.25	2.85	3.41	1.85	3.67
%Carbondioxide (S)	0.64	2.04	6.04	7.21	13.25	18.52	19.62
%Propionaldehyde (Y)	7.05	22.25	40.93	48.91	47.35	43.14	37.81

Table E11b data of Figure 5.27b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.15	0.32	2.57	2.81	2.98	1.01	0.42
%Acetaldehyde (S)	0.84	1.62	2.21	3.08	5.62	5.31	5.01
%Methane (S)	0.88	1.63	2.96	3.01	3.98	4.66	4.88
%Ethylene (S)	0.79	1.37	2.35	3.14	4.55	5.33	5.88

Table E12a data of Figure 5.28a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	3.25	13.69	48.75	64.55	89.63	90.88	91.58
%Propionaldehyde (S)	94.58	87.55	74.69	70.44	50.14	45.66	42.11
%Propylene (S)	1.75	4.32	6.88	8.96	12.39	16.89	17.22
%C1-C2 (S)	1.69	4.44	7.41	8.27	12.75	15.66	15.90
%Carbonmonoxide (S)	0.17	0.51	4.87	5.28	11.22	2.05	4.01
%Carbondioxide (S)	0.81	2.66	6.04	6.08	12.41	19.05	20.18
%Propionaldehyde (Y)	3.07	11.99	36.41	45.47	44.94	41.50	38.56

Table E12b data of Figure 5.28b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0	0.08	1.88	2.69	2.04	1.06	0.41
%Acetaldehyde (S)	0.25	1.44	2.21	2.61	5.41	5.54	4.85
%Methane (S)	0.59	1.45	2.96	2.85	3.11	4.71	5.18
%Ethylene (S)	0.85	1.55	2.24	2.81	4.23	5.41	5.87

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Table E13a data of Figure 5.30a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	23.44	53.88	81.33	90.58	92.66	95.44	95.85
%Propionaldehyde (S)	88.52	66.31	43.05	31.25	19.63	15.01	14.45
%Propylene (S)	5.22	14.09	24.55	24.67	23.61	23.41	23.35
%C1-C2 (S)	2.66	6.26	9.96	13.12	14.83	14.15	14.56
%Carbonmonoxide (S)	1.85	3.85	5.52	4.86	5.69	3.58	2.38
%Carbondioxide (S)	0.95	9.01	16.38	25.69	35.47	43.25	44.32
%Propionaldehyde (Y)	20.75	35.73	35.01	28.31	18.19	14.33	13.85

Table E13b data of Figure 5.30b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.25	0.29	0.87	1.22	0.66	0.61	0.31
%Acetaldehyde (S)	0.74	1.22	2.69	3.44	3.75	2.85	1.74
%Methane (S)	0.98	2.42	3.01	3.69	5.14	5.58	6.31
%Ethylene (S)	0.69	2.33	3.39	4.77	5.28	5.11	6.20

Table E14a data of Figure 5.31a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	21.69	48.52	76.85	84.66	92.35	93.45	94.52
%Propionaldehyde (S)	90.23	69.31	49.02	38.52	27.44	19.63	19.25
%Propylene (S)	3.05	12.34	23.11	21.36	23.01	23.41	22.11
%C1-C2 (S)	2.87	5.68	8.80	11.84	11.46	12.54	11.95
%Carbonmonoxide (S)	2.08	3.95	4.39	5.09	5.04	3.11	4.66
%Carbondioxide (S)	0.88	8.65	14.63	22.36	32.56	40.96	41.22
%Propionaldehyde (Y)	19.57	33.63	37.67	32.61	25.34	18.34	18.20

Table E14b data of Figure 5.31b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.26	0.3	0.88	1.36	0.59	0.52	0.02
%Acetaldehyde (S)	0.75	1.2	2.77	3.88	3.24	2.21	1.88
%Methane (S)	1.01	2.14	3.04	3.08	3.94	4.85	5.01
%Ethylene (S)	0.85	2.04	2.11	3.52	3.69	4.96	5.04

Table E15a data Figure 5.33a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	17.66	52.31	78.94	87.64	94.33	95.38	96.07
%Propionaldehyde (S)	88.63	63.54	46.25	23.69	16.35	14.20	12.63
%Propylene (S)	5.69	13.20	23.54	27.85	24.21	24.31	24.51
%C1-C2 (S)	3.90	5.89	9.84	13.28	13.45	14.46	15.42
%Carbonmonoxide (S)	0.44	4.25	2.58	5.22	5.63	2.14	2.33
%Carbondioxide (S)	0.85	12.69	17.23	29.55	40.32	44.01	44.85
%Propionaldehyde (Y)	15.65	33.24	36.51	20.76	15.42	13.54	12.13

Table E15b data of Figure 5.33b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.14	0.19	2.04	1.14	0.85	0.74	0.27
%Acetaldehyde (S)	1.21	1.66	3.66	4.31	3.21	2.14	1.95
%Methane (S)	1.11	2.22	3.54	4.38	4.66	6.28	6.52
%Ethylene (S)	1.58	2.01	2.64	4.59	5.58	6.04	6.95

Table E16a data of Figure 5.34a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	10.28	45.66	71.27	80.17	87.88	90.71	92.33
%Propionaldehyde (S)	89.63	66.85	48.96	31.05	22.14	18.63	17.85
%Propylene (S)	3.08	10.58	21.30	24.62	21.63	21.69	22.07
%C1-C2 (S)	3.68	7.38	10.52	10.83	11.04	12.07	12.55
%Carbonmonoxide (S)	1.96	3.59	2.36	5.62	5.74	4.52	4.36
%Carbondioxide (S)	0.78	11.20	16.58	27.36	38.96	42.55	42.31
%Propionaldehyde (Y)	9.21	30.52	34.89	24.89	19.46	16.90	16.48

Table E16b data of Figure 5.34b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.13	0.19	1.51	1.15	0.84	0.68	0.27
%Acetaldehyde (S)	1.18	1.64	3.11	3.69	3.88	2.21	1.95
%Methane (S)	1.05	3.01	3.32	3.47	3.69	4.52	5.31
%Ethylene (S)	1.32	2.54	2.58	2.52	2.63	4.66	5.02

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Table E17a data of Figure 5.36a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	10.87	17.55	38.96	62.58	83.44	88.58	89.69
%Propionaldehyde (S)	92.11	84.11	74.01	68.35	54.22	44.58	42.11
%Propylene (S)	1.25	6.34	11.04	14.33	16.24	17.52	16.21
%C1-C2 (S)	1.93	3.43	4.12	5.27	5.51	7.10	7.92
%Carbonmonoxide (S)	2.52	2.32	3.22	1.62	8.55	12.52	15.44
%Carbondioxide (S)	1.22	3.14	6.14	9.89	13.58	16.41	16.44
%Propionaldehyde (Y)	10.01	14.76	28.83	42.77	45.24	39.49	37.77

Table E17b data of Figure 5.36b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.2	0.22	0.31	0.98	0.64	0.42	0.23
%Acetaldehyde (S)	0.57	1.21	1.54	1.88	1.93	2.36	2.55
%Methane (S)	0.88	1.25	1.33	1.85	1.95	2.63	3.01
%Ethylene (S)	0.48	0.97	1.25	1.54	1.63	2.11	2.36

Table E18a data of Figure 5.37a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	4.27	10.22	25.36	58.63	78.32	83.51	84.05
%Propionaldehyde (S)	93.65	85.66	79.55	72.11	54.17	48.52	45.63
%Propylene (S)	0.95	2.33	6.48	9.86	13.85	14.52	14.66
%C1-C2 (S)	1.58	2.88	2.97	4.42	4.52	5.16	5.31
%Carbonmonoxide (S)	1.63	3.85	3.25	1.02	8.01	15.30	16.55
%Carbondioxide (S)	1.52	3.20	5.89	9.63	14.52	15.88	16.89
%Propionaldehyde (Y)	4.00	8.75	20.17	42.28	42.43	40.52	38.35

Table E18b data of Figure 5.37b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0	0	0.09	0.66	0.53	0.34	0.22
%Acetaldehyde (S)	0.24	0.54	0.64	1.40	1.53	1.86	1.94
%Methane (S)	0.81	1.02	0.99	1.00	1.02	1.44	1.52
%Ethylene (S)	0.53	1.32	1.25	1.36	1.44	1.52	1.63

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Table E19a data of Figure 5.39a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	6.32	19.88	44.65	66.33	85.14	93.85	93.55
%Propionaldehyde (S)	96.64	91.29	84.55	70.25	61.02	49.66	45.38
%Propylene (S)	1.98	4.28	9.69	14.62	17.05	21.36	25.49
%C1-C2 (S)	0.49	0.93	1.07	5.53	6.34	6.93	7.17
%Carbonmonoxide (S)	0.00	0.00	0.01	0.02	0.00	0.00	0.00
%Carbondioxide (S)	0.87	2.88	4.08	9.07	15.33	21.56	21.68
%Propionaldehyde (Y)	6.11	18.15	37.75	46.60	51.95	46.61	42.45

Table E19b data of Figure 5.39b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0	0	0.01	0.08	0.11	0.18	0.14
%Acetaldehyde (S)	0	0.21	0.24	1.07	1.88	2.48	2.67
%Methane (S)	0.21	0.33	0.41	2.05	2.08	2.04	2.08
%Ethylene (S)	0.28	0.39	0.42	2.41	2.38	2.41	2.42

Table E20a data of Figure 5.40a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	5.95	18.02	40.18	61.08	83.74	90.47	92.58
%Propionaldehyde (S)	96.47	90.14	84.22	74.01	60.32	53.11	51.04
%Propylene (S)	0.57	2.74	5.62	8.69	12.41	15.86	16.08
%C1-C2 (S)	0.22	0.66	0.87	2.92	4.85	6.45	6.42
%Carbonmonoxide (S)	2.21	3.47	6.31	5.07	5.22	5.22	6.11
%Carbondioxide (S)	0.45	2.21	2.69	9.25	16.33	18.69	19.78
%Propionaldehyde (Y)	5.74	16.24	33.84	45.21	50.51	48.05	47.25

Table E20b data of Figure 5.40b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0	0	0.14	0.02	0.04	0.06	0.03
%Acetaldehyde (S)	0.01	0.21	0.18	0.24	0.53	1.56	1.48
%Methane (S)	0.1	0.21	0.34	1.36	2.47	2.58	2.61
%Ethylene (S)	0.11	0.24	0.35	1.32	1.85	2.31	2.33

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Table E21a data of Figure 5.42a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	4.21	17.04	45.58	57.85	88.63	92.36	92.96
%Propionaldehyde (S)	89.63	82.55	64.58	53.66	34.11	28.94	26.98
%Propylene (S)	3.08	3.15	6.37	13.44	20.33	20.07	20.83
%C1-C2 (S)	2.65	4.23	6.37	7.10	7.28	6.60	6.03
%Carbonmonoxide (S)	1.96	5.23	8.66	1.25	6.33	2.96	4.25
%Carbondioxide (S)	0.98	4.39	13.28	24.38	31.08	40.55	40.69
%Propionaldehyde (Y)	3.77	14.07	29.44	31.04	30.23	26.73	25.08

Table E21b data of Figure 5.42b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.24	0.34	1.78	1.75	1.17	0.71	0.25
%Acetaldehyde (S)	0.82	1.52	1.62	2.15	2.66	2.47	2.34
%Methane (S)	0.88	1.14	1.42	1.55	1.64	1.65	1.68
%Ethylene (S)	0.71	1.23	1.55	1.65	1.81	1.77	1.76

Table E22a data of Figure 5.43a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	3.07	15.96	42.33	53.63	84.25	86.78	88.96
%Propionaldehyde (S)	90.22	82.63	67.85	48.58	34.25	32.21	28.36
%Propylene (S)	1.68	2.64	5.61	8.22	12.31	15.66	16.57
%C1-C2 (S)	2.59	4.19	6.41	6.99	7.18	6.59	5.94
%Carbonmonoxide (S)	2.63	5.66	9.17	12.55	12.52	5.22	9.63
%Carbondioxide (S)	1.02	4.52	10.33	23.11	32.11	38.96	39.14
%Propionaldehyde (Y)	2.77	13.19	28.72	26.05	28.86	27.95	25.23

Table E22b data of Figure 5.43b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.22	0.35	1.77	1.78	1.24	0.85	0.26
%Acetaldehyde (S)	0.81	1.51	1.63	2.11	2.45	2.41	2.31
%Methane (S)	0.87	1.11	1.45	1.48	1.65	1.62	1.63
%Ethylene (S)	0.69	1.22	1.56	1.62	1.84	1.71	1.74

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Table E23a data of Figure 5.45a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	12.96	43.58	67.44	86.96	92.52	93.66	95.14
%Propionaldehyde (S)	89.62	77.02	58.69	40.88	33.52	27.86	27.81
%Propylene (S)	3.24	4.31	8.61	14.55	17.01	17.21	18.37
%C1-C2 (S)	2.45	4.00	4.57	5.69	6.05	6.40	6.45
%Carbonmonoxide (S)	1.99	6.33	9.85	10.36	5.66	4.20	3.11
%Carbondioxide (S)	0.96	6.85	17.66	27.31	37.05	43.25	43.61
%Propionaldehyde (Y)	11.61	33.57	39.58	35.55	31.01	26.09	26.46

Table E23b data of Figure 5.45b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.24	0.41	1.63	1.71	0.78	0.63	0.22
%Acetaldehyde (S)	0.85	1.23	1.57	2.54	2.77	2.85	2.89
%Methane (S)	0.74	1.36	1.42	1.52	1.63	1.72	1.70
%Ethylene (S)	0.86	1.41	1.58	1.63	1.65	1.83	1.86

Table E24a data of Figure 5.46a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	10.55	41.25	64.08	78.55	88.55	90.58	92.04
%Propionaldehyde (S)	91.63	80.69	60.14	45.01	38.41	31.52	32.51
%Propylene (S)	1.02	2.07	5.69	10.33	14.61	16.22	16.38
%C1-C2 (S)	2.36	3.82	4.49	5.57	5.90	6.33	6.26
%Carbonmonoxide (S)	2.55	6.63	12.36	11.52	5.96	5.63	3.96
%Carbondioxide (S)	0.98	5.66	16.54	26.14	34.11	40.05	40.14
%Propionaldehyde (Y)	9.67	33.28	38.54	35.36	34.01	28.55	29.92

Table E24b data of Figure 5.46b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.22	0.42	1.60	1.68	0.75	0.64	0.24
%Acetaldehyde (S)	0.78	1.11	1.56	2.47	2.68	2.77	2.78
%Methane (S)	0.76	1.32	1.41	1.49	1.55	1.71	1.66
%Ethylene (S)	0.82	1.39	1.52	1.61	1.67	1.85	1.82

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Table E25a data of Figure 5.48a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	3.69	14.66	43.52	60.95	84.77	90.35	92.86
%Propionaldehyde (S)	91.02	80.25	68.96	63.58	54.74	45.65	42.33
%Propylene (S)	4.32	10.05	11.28	14.55	17.25	18.69	18.58
%C1-C2 (S)	2.37	2.20	4.37	5.75	6.93	7.63	7.71
%Carbonmonoxide (S)	0.07	1.25	8.96	7.11	7.32	10.02	12.05
%Carbondioxide (S)	1.88	6.23	8.47	11.28	16.11	18.74	18.95
%Propionaldehyde (Y)	3.36	11.76	30.01	38.75	46.40	41.24	39.31

Table E25b data of Figure 5.48b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.06	0.08	0.13	0.54	0.26	0.14	0.01
%Acetaldehyde (S)	0.75	0.88	1.48	2.56	3.38	3.88	3.91
%Methane (S)	0.87	0.88	2.01	2.28	2.31	2.47	2.46
%Ethylene (S)	0.75	0.44	0.88	0.91	1.24	1.28	1.34

Table E26a data of Figure 5.49a

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%1-Propanol (C)	2.11	10.36	40.21	55.66	81.01	86.64	87.66
%Propionaldehyde (S)	93.87	83.22	66.81	63.21	55.01	48.95	46.02
%Propylene (S)	2.10	7.02	8.85	12.05	14.22	16.52	16.47
%C1-C2 (S)	1.28	1.64	3.25	4.50	5.10	6.11	6.44
%Carbonmonoxide (S)	0.08	0.09	8.11	6.22	9.36	8.47	8.99
%Carbondioxide (S)	1.74	7.49	12.47	13.58	15.92	19.83	21.01
%Propionaldehyde (Y)	1.98	8.62	26.86	35.18	44.56	42.41	40.34

Table E26b data of Figure 5.49b

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.01	0.02	0.08	0.15	0.05	0.03	0
%Acetaldehyde (S)	0.07	0.55	1.3	1.81	2.21	2.83	3.03
%Methane (S)	0.64	0.72	1.08	1.77	1.84	2.13	2.2
%Ethylene (S)	0.57	0.37	0.87	0.92	1.05	1.15	1.21

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Table E27a data of Figure 5.51a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	1.58	12.36	45.17	72.34	87.89	92.64	92.77
%Propionaldehyde (S)	90.32	75.62	56.63	35.48	32.58	31.52	27.85
%Propylene (S)	3.01	10.33	18.59	24.52	21.30	21.63	21.36
%C1-C2 (S)	4.55	7.70	14.16	19.06	23.18	26.85	28.34
%Carbonmonoxide (S)	1.63	1.85	1.89	6.85	7.52	4.15	5.62
%Carbondioxide (S)	0.45	4.02	8.01	12.95	14.88	15.06	16.14
%Propionaldehyde (Y)	1.43	9.35	25.58	25.67	28.63	29.20	25.84

Table E27b data of Figure 5.51b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.22	0.28	0.39	1.84	0.65	0.04	0.02
%Acetaldehyde (S)	2.11	3.51	4.87	5.62	8.96	12.64	14.55
%Methane (S)	1.32	2.23	4.47	7.02	7.71	7.59	7.54
%Ethylene (S)	1.12	1.96	4.82	6.42	6.51	6.62	6.25

Table E28a data of Figure 5.52a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	1.22	12.36	39.95	66.99	78.39	90.11	90.28
%Propionaldehyde (S)	89.69	77.02	56.85	37.63	33.14	32.01	28.01
%Propylene (S)	1.89	8.62	16.05	20.36	20.18	18.63	19.68
%C1-C2 (S)	4.62	6.56	14.21	17.68	20.02	22.70	26.47
%Carbonmonoxide (S)	1.95	3.25	4.52	10.25	9.14	8.14	8.11
%Carbondioxide (S)	0.95	4.14	7.36	13.58	16.02	16.85	16.95
%Propionaldehyde (Y)	1.09	9.52	22.71	25.21	25.98	28.84	25.29

Table E28b data of Figure 5.52b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.23	0.47	0.65	0.88	0.14	0.12	0.05
%Acetaldehyde (S)	2.04	3.54	4.88	5.64	7.69	10.36	13.65
%Methane (S)	1.33	1.52	4.5	6.41	6.51	6.33	6.84
%Ethylene (S)	1.25	1.5	4.83	5.63	5.82	6.01	5.98

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Table E29a data of Figure 5.54a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	6.77	12.41	45.28	79.81	84.61	91.52	92.01
%Propionaldehyde (S)	79.22	53.21	44.39	33.02	32.05	29.31	26.07
%Propylene (S)	3.62	17.69	22.04	23.17	24.51	26.08	27.06
%C1-C2 (S)	12.44	19.31	22.61	24.21	25.13	28.21	29.49
%Carbonmonoxide (S)	2.96	3.65	2.55	6.21	2.21	0.05	1.02
%Carbondioxide (S)	1.01	6.01	7.41	12.33	15.14	16.11	16.01
%Propionaldehyde (Y)	5.36	6.60	20.10	26.35	27.12	26.82	23.99

Table E29b data of Figure 5.54b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	1.02	1.28	1.87	1.74	0.88	0.08	0.04
%Acetaldehyde (S)	7.52	12.57	12.88	15.44	8.37	6.07	5.66
%Methane (S)	2.55	2.89	3.28	2.81	4.69	7.63	8.62
%Ethylene (S)	2.37	3.85	6.45	5.96	12.07	14.51	15.21

Table E30a data of Figure 5.55a

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%1-Propanol (C)	4.11	11.28	43.25	78.66	83.66	90.12	90.21
%Propionaldehyde (S)	84.56	57.88	50.22	34.58	33.41	28.55	28.01
%Propylene (S)	3.11	15.36	20.08	20.63	23.65	24.33	25.07
%C1-C2 (S)	8.36	15.78	17.43	20.81	21.78	26.24	27.46
%Carbonmonoxide (S)	2.33	3.21	4.52	8.96	4.07	4.22	3.04
%Carbondioxide (S)	1.36	7.01	6.99	11.36	15.52	16.54	16.25
%Propionaldehyde (Y)	3.48	6.53	21.72	27.20	27.95	25.73	25.27

Table E30b data of Figure 5.55b

Component	Temperature (^oC)						
	200	250	300	350	400	450	500
%Formaldehyde (S)	0.41	1.31	1.89	1.64	1.22	0.11	0.09
%Acetaldehyde (S)	5.21	10.25	11.52	13.61	7.69	7.56	8.06
%Methane (S)	1.49	2.28	2.33	2.24	4.27	6.66	6.74
%Ethylene (S)	1.66	3.25	3.58	4.96	9.82	12.02	12.66

VITA

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