ตัวเร่งปฏิกิริยาคอปเปอร์โครไมต์สำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิด

ของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์

นาย มงคลชนก ปราโมทย์ธนา

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

COPPER CHROMITE CATALYST FOR THE SELECTIVE HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL

Mr. Mongkolchanok Pramottana

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มงคลชนก ปราโมทย์ธนา: ตัวเร่งปฏิกิริยาคอปเปอร์โครไมต์สำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์(COPPER CHROMITE CATALYST FOR THE SELECTIVE HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL) อ. ที่ปรึกษา : ศ. ดร. ปิยะสาร ประเสริฐธรรม, 51 หน้า ISBN 974-03-0418-4.

งานวิจัยนี้เป็นการศึกษาปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์ ด้วยตัวเร่งปฏิกิริยาคอปเปอร์โครไมท์ซึ่งประกอบด้วยคอปเปอร์ออกไซด์และโครเมียมออกไซด์ร้อยละ 45 และ 46 โดยน้ำหนัก ตามลำดับ ทำการศึกษาปฏิกิริยาโดยใช้เครื่องปฏิกรณ์แบบกะชนิดหม้ออัดความดันที่มีใบกวน พบว่า ภาวะที่เหมาะสมในการทำปฏิกิริยาคือ อุณหภูมิ 125 องศาเซลเซียส ความดัน 120 ปอนด์ต่อตารางนิ้ว และปริมาณตัวเร่งปฏิกิริยา 1.05 กรัมต่อปริมาตรเฟอฟูรอล 15 ลูกบาศก์เซนติเมตร จากผลการทดลองพบว่า การรีดิวซ์ด้วยแก๊สไฮโดรเจนก่อนการทำปฏิกิริยาที่อุณหภูมิ 300 องศาเซลเซียสเป็นเวลา 4 ชั่วโมง จะทำให้เกิดการเปลี่ยนของเฟอฟูรอลสูงสุด เมื่อเพิ่มเวลาการรีดิวซ์จะเกิดการหลอมรวมตัวของโลหะทองแดงบนพื้นผิวตัวเร่งปฏิกิริยาทำให้เกิดการเปลี่ยนของเฟอฟูรอลลดลง ดังนั้นสามารถสรุปได้ว่าโลหะทองแดงบนพื้นผิวเป็นตำแหน่งที่ว่องไวสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์

ภาควิชา……วิศวกรรมเคมี…….. ลายมือชื่อนิสิต……

สาขาวิชา……วิศวกรรมเคมี…… ลายมือชื่ออาจารย์ที่ปรึกษา……

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MONGKOLCHANOK PRAMOTTHANA: COPPER CHROMITE CATALYST FOR THE SELECTIVE HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL, THESIS ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing., 51 pp. ISBN 974-03-0418-4.

In this research, the selective hydrogenation of furfural to furfuryl alcohol is investigated by using copper chromite catalyst containing copper oxide and chromium oxide 45 wt% and 46 wt%, respectively. The batch autoclave reactor with the propeller is used for this study. The appropriate operating conditions are found at the temperature of 125°C, the pressure of 120 psi, and the catalyst weight of 1.05 g per the furfural volume of 15 ml. From the experimental results, the maximum furfural conversion is observed after H_2 reduction at the temperature of 300°C for 4 h. Increasing reduction time causes the sintering of copper metal on the surface catalysts which decreases the furfural conversion. It can be concluded that the accessible copper metal is the active sites for the selective hydrogenation of furfural to furfuryl alcohol.

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จุฬาลงกรณ์มหาวิทยาลัย

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CHAPTER I
INTRODUCTION

In general, the catalyst is extensively used as an important component in chemical reaction processes. It does not only decrease significantly the processing time, but also selectively produces the desired product. For example, the palladium based catalyst is chosen to convert acetylene to only ethylene for the acetylene hydrogenation [Meksikorin (1995)] or copper chromite catalyst which is a catalyst used to covert C=O only to C-O-H for the hydrogenation of carbonyl compound [Liaw and Chen (2000)].

Copper chromite catalyst is an important catalyst that has been used for various industrial processes for decade years. The use of copper chromite catalyst for the selective hydrogenation concerns that selective product can be produced with its capability to selectively hydrogenate carbonyl bonds while leaving unsaturated C=C bonds virtually untouched. Various reactions are catalysed by copper chromite catalyst, e.g., selective hydrogenation of furfural to furfuryl alcohol [Soner and Dogu (1996)], partial reduction of conjugated dienes to monoenes [Capece and co-workers (1982)] and hydrogenation of crotonaldehyde to 1-butanol [Rao *et al.* (1997)].

The selective hydrogenation of furfural over copper chromite catalyst is a process typically used to produce furfuryl alcohol, which is an important reagent for many approaches, e.g., wetting agent, furan polymers, corrosion-resistant sealants and cements, solvent for dyes and resins, etc.[Irving and Lewis (1981)]. Furfural, C_4H_3OCHO, is a suitable compound to test the ability of a catalyst to selectively hydrogenate a carbonyl bond because of the presence of both C=O and unsaturated C=C bond in the structure. However, the chromium component in the copper chromite catalyst for the selective hydrogenation of furfural reaction has become a serious environmental problem. New restrictions prevent the used chromite catalysts from being deposited; they provide an incentive for developing a new replaceable copper catalyst, free of chromium or containing a lower content of chromium, powerful from a pretreatment.

Influencing parameters for pretreatment of copper chromite catalyst has been studied so far. Variety of pretreatment with hydrogen on copper chromite used for the reductive alkylation of aniline with acetone was studied and concluded that Cu^{1+} species were the active sites in this reaction [Pillai (1994)]. The maximum specific activity coincided with the large amount of Cu^{1+} which was reduced by hydrogen at 300°C for 4 h. On the other hand, Rao *et al.* investigated the effect of the reduction time on hydrogenation of crotonaldehyde to 1-butanol and proposed that the coexistence between Cu^{1+} and Cu^{0} species was required for this reaction due to a large amount of Cu^{0} produced after reduction.

It was additionally reported that the dissociative N_2O adsorption at 90°C has been used to measure the metallic Cu surface as shown in equation (1) [Dandekar and Vannice (1998)]:

$$N_2O(g) + 2Cu^0_s \rightarrow Cu_2O + N_2(g) \qquad (1)$$

Thus, an increase of Cu^{1+} surface, which was proposed to be active species for the selective hydrogenation of furfural to furfuryl alcohol, is presumably possible by pretreatment with N_2O. Hence, N_2O is used to study the active species for the selective hydrogenation of furfural to furfuryl alcohol.

1.1) Thesis objective

To study the active species on copper chromite catalysts for the selective hydrogenation of furfural to furfuryl alcohol by N_2O.

1.2) The scope of this study

1.2.1) Use commercial copper chromite catalyst in reaction

1.2.2) Use pressurisation and stirring batch reactor in study reaction

1.2.3) Study the effect of nitrous oxide after reduction with hydrogen on reaction

1.2.4) Use N_2O for measurement of accessible copper metal on surface

1.2.5) Study the catalytic performance after pretreatment with nitrous oxide in system:

Furfural	15 ml
Ethanol	500 ml
Total pressure (balance with hydrogen gas)	120 psi
Reaction temperature	125 $^{\circ}$C

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CHAPTER II
LITERATURE REVIEWS

It was generally recognized that copper-containging oxide catalyst was highly active for reactions of hydrogenation, for example, the hydrogenation of the carbonyl groups of organic compounds and of carbon monoxide to alcohols. Copper chromite, a type of copper-containing oxide catalysts, has been extensively used for many years in various industrial processes such as the hydrogenation of polyunsaturated compounds [Hubaut *et al.*, 1989], the hydrogenation of fatty acids [Narasimhan *et al.*, 1987], the hydrogenation of edible oils [Fang and co-workers, 1989], the hydrogenation of fatty esters [Miya *et al*., 1966], the hydrogenation of dienes [Bechara *et al*., 1985], the selective hydrogenation of furfural [Rao and co-workers, 1997], the hydrogenation of crotonaldehyde [Liaw and Chen, 2000], the reductive alkylation of aniline with acetone [Pillai, 1994], methanol synthesis [Herman and co-workers, 1979] and dehydration of alcohol [Thomas, 1970]. The utilization of this catalyst in hydrogenation reactions stemmed from its capability to selectively hydrogenate carbonyl bonds while leaving unsaturated C=C bonds virtually untouched. Liaw and Chen (2000) studied the hydrogenation of monofunctional compounds over copper chromite catalyst and found that the reactivities were in the following order: C=O (in aldehyde) > C=O (in ketone) >> C=C. The reactivity of C=C was largely enhanced by its delocalization with conjugated C=C or C=O group. In case of C=C with conjugated C=C, the most product was monoenes. In another case, C=C with conjugated C=O was hydrogenated on C=C and subsequently on C=O, therefore, the most product became saturated alcohol.

Successful use of copper chromite catalyst for the selective hydrogenation of furfural to furfuryl alcohol has been reported for over five decades. The influence of pretreatment on copper chromite with hydrogen was also studied. Pillai (1994) studied the pretreatment of copper chromite with hydrogen used for the reductive alkylation of aniline with acetone and concluded that the optimum temperature for pretreatment of copper chromite to gain maximum the activity and the amount of Cu^{1+}

was 300°C for 4 h. Rao *et al.* (1997) concluded that optimum temperature for pretreatment of copper chromite to gain maximum activity for crotonaldehyde hydrogenation was 300°C for 4 h. Yurieva (1999) studied the influence of hydrogen pretreatment on copper chromite used for the hydrogenation of acetone to isopropanol and concluded that the optimum temperature for the pretreatment of copper chromite to gain maximum activity was 300°C for 4 h. However, not many studies characterized these copper chromite systems, especially the state of the surface. Reaction mechanisms of the reaction and the activated hydrogen species as well as the role they play in the hydrogenation processes are not yet clearly understood. The state of copper chromite surface associating with activity in various hydrogenation reactions was proposed in many literatures. Most reactions over copper chromite catalyst were presumably active constituting Cu^{+1} state, e.g., reductive alkylation of aniline with acetone [Pillai (1994)], methanol synthesis [Herman and co-workers (1979), Monnier *et al.* (1985)], hydrogenation of dienes [Hubaut and co-workers (1986)], double-bond isomerization [Capece and Co-workers (1982)] and hydrogenation of dienes [Bechara *et al.* (1985)]. However, Cu^{0} was also proposed as active species on copper chromite surface for hydrogenation of conjugated dienes [Capece and Co-workers (1982)]. Many literatures proposed the state of Cu^{+1} on copper chromite to be necessary for hydrogenation reaction. However, the reduction of copper chromite by using hydrogen has limitation of Cu^{+1} content. Thus, it is interesting to study the effect of Cu^{+1} on the catalytic activity.

This research is aimed to study the active species of copper chromite catalyst for the selective hydrogenation of furfural to furfuryl alcohol via N_2O treatment.

CHAPTER III
THEORY

This chapter will explain about the theory concerning copper chromite catalyst. The furfural hydrogenation and thermodynamic data of such reaction are described in the next sections.

3.1 Nature of the interaction between hydrogen and copper chromite

It is found that nature of the interaction between hydrogen and copper chromite surface is affected by both the starting and final temperatures of the reduction of the copper chromite. Structure of copper chromite may change significantly upon reduction conditions. Delafossite structure containing Cu^{1+} was seen when copper chromite was kept in air atmosphere at 500°C, and then reduced at higher temperature [Moroz *et al.* (1987)]. Gradually heating from room temperature to above 450°C in flowing hydrogen caused the decomposition of the chromite to produce copper metal and chromia [Makarova *et al*. (1993), Rachkovskii and Boreskov (1970)]. Complex processes were observed if flowing hydrogen was passed through a bed of copper chromite in the temperature region 120-350°C [Makarova *et al.* (1993)]. No change in the phase composition of the sample was observed by XRD when the temperature was raised to 200°C. At 250°C, the copper ions were partially (50-60%) reduced to form Cu^{0} in the form of flat particles (see Figure 3.1(b)) on the surface of spinel crystals [Makarova *et al.* (1993)]. These Cu^{0} particles are well faceted particles, 50×100×100 Å in size, which are bonded epitaxially to the spinel surface. The compatibility between the reciprocal lattice (111) planes of the spinel and the (111) planes of copper can be seen from superposition of the reflections (220) of copper and the (440) reflections of chromite in the electron diffraction patterns. This state was destroyed at temperatures above 400°C: about 100% of the copper ions were reduced at 450°C, the particles of metallic copper becoming rounded and weakly bonded to the surface of chromium oxide (Figure 3.1(c)).

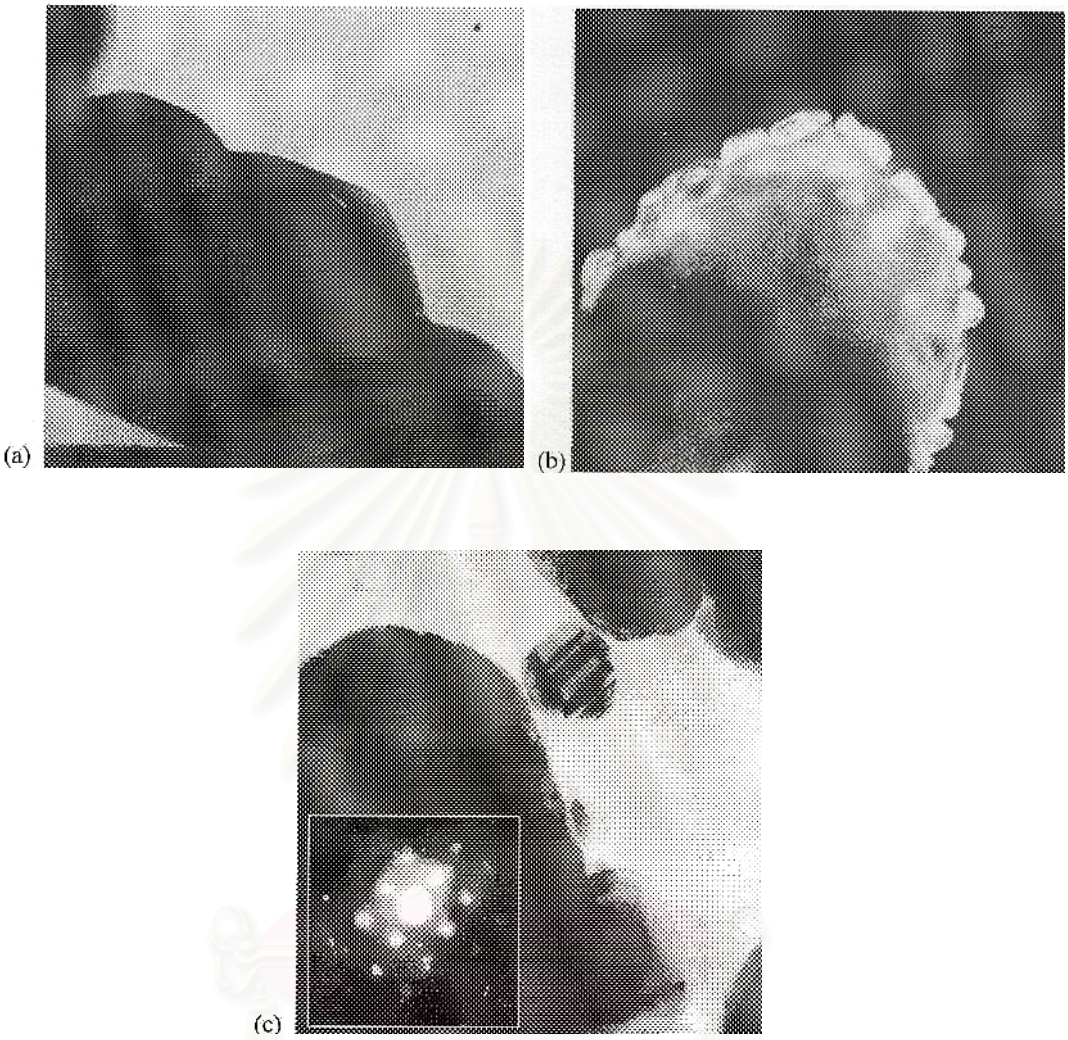


Figure 3.1 Electron microscopic images (x 400,000) of the samples; initial $CuCr_2O_4$ (a); reduced in H_2 at 320°C, the dark-field image of Cu^0 particles with identical orientation (b); and reduce in H_2 at 450°C (c).[Makarova *et al.* (1993)]

The spinel phase was stable in flowing hydrogen up to 400°C. However, the tetragonal distortion disappeared at temperature as low as 250°C (compared with 580° C in air) [Ustyantsev *et al.* (1973)] and the spinel acquired a cubic lattice with a lattice constant of a=8.342 Å characterized by a diffraction pattern (Figure 3.2(a), curve 2) in

which the line intensity distribution was noticeably different from that observed for the chromite before the treatment with H_2 (Figure 3.2(a), curve1). The difference increased as the temperature was increased to 320°C (Figure 3.2(a), curve 3). IR spectroscopic data (Figure 3.2(b)) showed that the absorption bands assigned to the vibration of the (CuO_4) groups of the spinel decreased in intensity following reduction at 250°C (Figure 3.2(b), curves 1, 2) and almost disappeared on reduction at 320°C (Figure 3.2(b), curve 3). However, it should be emphasized that the XRD data showed that no more than approximately half of the copper ions were released as metal particles under these conditions.

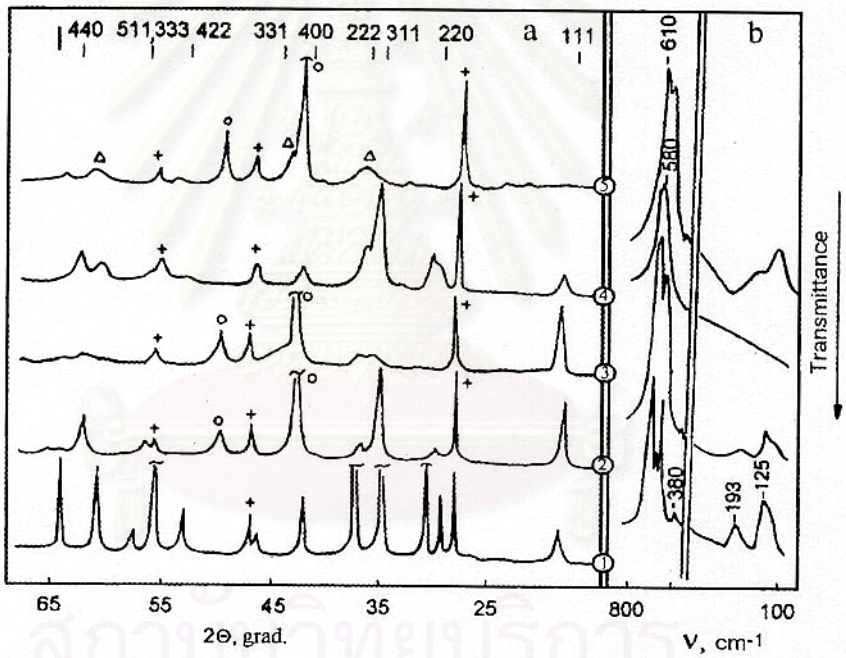


Figure 3.2 X-ray diffraction patterns (a) and IR spectra (b) of copper chromite; (1) initial sample; (2),(3),(5) reduced in H_2 at 250°,320° and 450°C,respectively; (4) sample 3 calcined in He at 320°C for 10h; (°), (+), (Δ) reflections from the Cu^0, silicon and NaCl-type structure, respectively. Positions of the reflections from a cubic type of $CuCr_2O_4$ spinel are marked on the top. [Ustyantsev *et al.* (1973)]

Kinetic studies of the interaction between hydrogen and the chromite at temperatures from 20-300°C [Khasin *et al.* (1994), Simentsova *et al*. (1996)] demonstrated a dependence of the interaction rate on the extent of reduction of the chromite. The rate of interaction of copper ions with the hydrogen in the surface layer increased as the reduction proceeded, reached a maximum, and then decreased. The maximum rate at 300°C was attained when the quantity of hydrogen consumed corresponded to the reduction of 0.3% of the copper ions of the chromite (ca. 60% of the surface copper ions). Only part of the hydrogen consumed formed water. The fraction of water-producing hydrogen also depended on the extent of reduction of the chromite; the greatest amount of water (40% with respect to the sorbed hydrogen at that moment) was formed at the earliest moment of exposure of the sample to hydrogen, when the extent of reduction of the chromite was low. As the chromite was reduced, the fraction of water-producing hydrogen decreased rapidly, being less that 4% at an overall hydrogen uptake corresponding to the reduction of 3-4% of the copper ions. The total hydrogen uptake corresponded to reduction of ca. 3% of the copper ions of the chromite after a 2 h run in the temperature range 250-320°C. There was slow hydrogen uptake at temperature 20-200°C and a much higher rate of uptake at the temperatures 250-300°C as shown in Fig.3.3 [Khasin *et al*. (1999)]. The nature of the desorbed hydrogen that did not produce water will be discussed below.

The composition of the reduced copper chromite underwent considerable transformations in an atmosphere of flowing helium at 320°C over a period of 10 h as shown by in situ XRD (Figure 3.2(b), curve 4). The X-ray diffraction patterns showed that the intensities of copper metal reflections decreased to very low values and that the intensity distribution of the spinel reflections changed towards those found for the freshly prepared oxidized spinel. The IR spectra showed absorption bands which can be assigned to vibration of the tetrahedral groups of (CuO_4) which approached the intensity found for the fresh spinel.

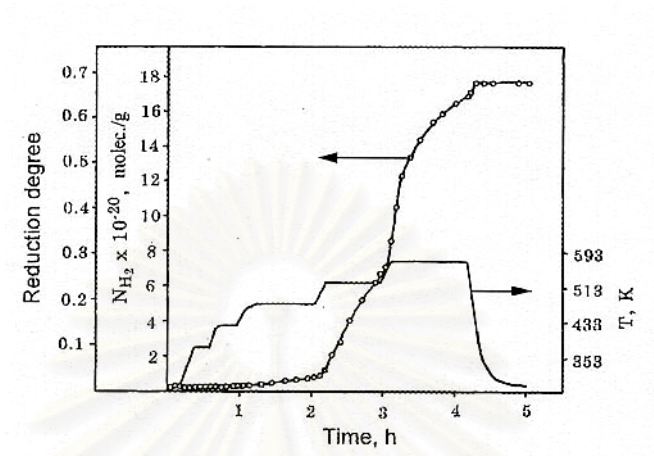


Figure 3.3 The dependence of the amount of reacted hydrogen, N_{H2}, and chromite reduction degree on time and temperature. P_{H2} = (3.9-8.1) x 10^4 Pa. [Khasin *et al*. (1999)]

Hence, they concluded that the initial oxidized state of the sample can be restored in flowing helium. Repeated reduction in flowing hydrogen resulted in full reproduction of the reduced state of the sample described above.

The presence of oxygen microimpurities in the He (below 0.05 vol%) provides an increase in the rate of hydrogen desorption and allows hydrogen to be removed completely and copper ions to move back to the spinel lattice. The electron transfer from copper to protons can be made much easier due to an intermediate interaction with the compound to be hydrogenated, for example by the reaction with oxygen:

$$2Cu^0 + O_2 + 4H^+ \leftrightarrow 2Cu^{2+} + 2H_2O$$

Removal of the hydrogen ions from the lattice and return of the copper ions to the spinel structure can be also achieved in flowing acetone, isopropyl alcohol being

formed. At the same time, the direct oxidation of the metallic copper oxide, but no return of copper ions to spinel occurred in flowing air [Makarova *et al*. (1993)].

$$2Cu^0 + O_2 \leftrightarrow 2CuO$$

If the sample oxidized in flowing air was reduced subsequently with hydrogen, copper metal was formed as round-shaped particles which were similar to the particles produced during the reductive destruction of the spinel at 450°C (Figure 3.1(c)). It should be noted that a comparatively high rate of reoxidation of the chromite observed during experiments in the in situ XRD studies of the phase transformations occurring [Makarova *et al*. (1993)] may have been as a result of leakage of traces of oxygen into the XRD in situ chamber.

The in situ XRD technique was used to study the composition of the sample as a function of the time of exposure to hydrogen at 320°C. The study showed that there was only a small increase in the amount of copper metal formed (from 40-50 to 50-60%) [Krieger *et al.* (1996)] over periods of time varying from 2 to 8 h, but that a considerable change in the spinel structure was observed. Therefore, in addition to the reduction of the surface to form water (which results in no structural change), two alternative processes take place in hydrogen. One of these is completed in the first 2-3 h and is apparently the exchange interaction between the hydrogen and the copper ions. Another is completed not earlier than 8 h from the initial exposure.

Neutron diffraction data obtained for this sample [Plyasova *et al*. (1996)] show that the composition of the chromite after the 2 h exposure to hydrogen can be presented as follows:

$$Cu_{0.53} \quad [Cu_{0.33}]^a[H^+_{0.30}]^e{}_4[Cu_{0.07}H_{0.38}]^c{}_2[Cr^{+3}]^d{}_2O_4 \qquad (1)$$

Where a, c, d, e are the crystallographic positions of the ions in the spinel structure.

Hydrogen atoms are located simultaneously at two types of positions: (I) at 32e positions, in tetrahedral whose centers (8a positions) have been occupied by copper ions before the reduction; (ii) at 16c positions, at the centers of empty octahedrons of the spinel.

The neutron diffraction data obtained were analyzed to determine the interatomic distances. For the hydrogen located at the tetrahedral, one distance for the H-O was equal to 0.96 Å and three distances were equal to 2.33 Å while, for 16c positions, all the six H-O distances were 2.12 Å. Hence, the proton formed as a result of the exchange interaction with the copper ion in the tetrahedron reacts with one of the oxygen ions of the tetrahedron to form a covalent O-H bond resembling one of the O-H bond of a water molecule. Further studies are needed to establish the state of the hydrogen housed in the octahedral.

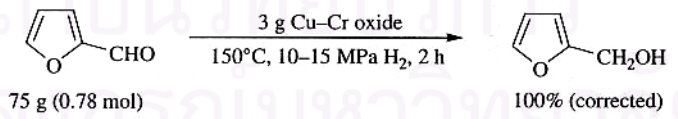
Thus, the interaction of copper chromite with hydrogen over the temperature range from 20°C to 320°C can be presented as follows. A portion of the surface oxygen ions starts to react with hydrogen at low temperature to yield water. As a result, reduced copper species (Cu^{1+} or Cu^{0}) are formed at the chromite surface. Copper species cause a homolytic rupture of the bond in a hydrogen molecule and the hydrogen atoms formed are dissolved in the spinel. Two processes occur at high temperatures, one being the exchange interaction of a copper ion with two hydrogen atoms from neighboring octahedral; producing copper atoms which are released as epitaxially bonded flat particles on the spinel surface, and two protons bonded covalently with oxygen atoms at the tetrahedral vertices. The nature of the other, slower process is less well understood. They can only suppose that the copper ions are transferred from tetrahedral to octahedral coordination, e.g. due to an exchange interaction of the ion with a hydrogen atom from the neighboring octahedron; as a result, a Cu^{1+} ion as well as a proton bonded covalently to the oxygen at a tetrahedral vertex are formed. The reverse reaction is observed in an inert atmosphere for the processes involving the exchange interaction between protons and copper atoms; the chromite is restored to its initial state. The rate of hydrogen desorption decreases as

the concentration of dissolved hydrogen decreases but the rate may be increased by allowing it to promote a hydrogenation reaction, for example by feeding acetone or a small amount of oxygen. At the same time, the direct oxidation of copper to copper oxides, which does not imply the removal of the hydrogen solute and returning copper ions back to the spinel, proceeds both in air and in an oxygen medium.

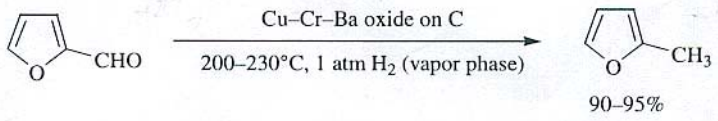
3.2 Hydrogenation of furfural [Nishimura (2001)]

Hydrogenation of furfural and related compounds has been the subject of a large number of investigations, since furfural may be prepared industrially by the action of water or dilute acid on pentosan-containing materials such as corncobs, wood, the hulls of oats, rice, and peanuts, and is the most important starting compound for various furans and their derivatives.

Furfural, although it is an aldehyde of aromatic character, such as benzaldehyde, can be converted to furfuryl alcohol in virtually quantitative yield over copper-chromium oxide as catalyst at high pressures and at temperature lower than 175^0C, at which point the catalyst has little or no effect on the furan ring (eqn. 2). This transformation may also be performed in the presence of other catalysts, although in most cases the hydrogenation tends to proceed over the stage of furfuryl alcohol.



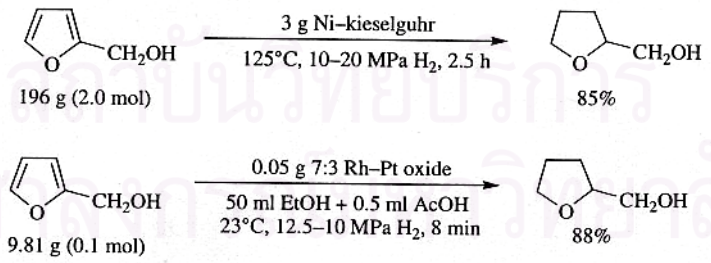
(2)



(3)

Conversion of furfural to 2-methylfuran was achieved in 90-95% yields by vapor-phase hydrogenation over copper-chromium-barium oxide dispersed on activated charcoal at 1 atm H_2 and 200-230^oC (eqn. 3).

Furfural was converted to tetrahydrofurfyl alcohol in 96-98% yields by hydrogenation over copper-chromium oxide at 150-160^oC and 10-20 Mpa H_2, followed by hydrogenation with added Raney Ni at 100-115^oC. The hydrogenation was performed in one step in 70-80% yields with use of either Raney Ni or a mixture of copper-chromium oxide and Raney Ni at 170-180^oC and 6.9-10.3 Mpa H_2. Tetra-hydrofurfuryl alcohol was also obtained in 73% yield in hydrogenation over a ruthenium catalyst in ethanol in the presence of magnesium oxide at 110^oC and 15 MPa H_2, although a better yield (89%) was reported in the hydrogenation over ruthenium dioxide at 100^oC and 10 MPa H_2. Tetrahydrofurfuryl alcohol is usually obtained in higher yields by hydrogenation of furfuryl alcohol than of furfuryl. The hydrogenation of furfuryl alcohol over Ni-kieselguhr at 125^oC and 10-20 MPa H_2 gave tetrahydrofurfuryl alcohol in 85% yield (eqn. 4). Tetrahydrofurfuryl alcohol was also obtained in an 88% yield in hydrogenation over an Adams-type rhodium-platinum oxide in ethanol with addition of a small amount of acetic acid at 23^oC and 12.5-10 MPa H_2 (eqn. 5).



(4)

(5)

3.3 Thermodynamic calculation [Yaws (1999)]

The thermodynamic data can provide important information needed, i.e., the heat of reaction (ΔH_r^o) and the Gibbs free energy of equilibrium constant (K_p) from ΔG_r^o. With the equilibrium constant known, the equilibrium product yield for a given set of reactions can be estimated.

Based on works reported in the literatures, reaction scheme of the selective hydrogenation of furfural to furfuryl alcohol can be viewed as follows:

$$C_4H_3O\text{-}CHO + H_2 \longrightarrow C_4H_3O\text{-}CH_2OH \qquad (6)$$

Knowing the ΔG_r^o values for all the potential surface reactions that may occur during the hydrogenation of furfural over a temperature range of 25–1500°C allows us to determine the feasibility of a given reaction and to predict the expected equilibrium distribution of reactants and products. The thermodynamic feasibility of a reaction is defined by the criteria illustrated in Table 3.1. The ΔG_r^o and ΔH_r^o values for reaction (eqn.6) are plotted versus temperature and the results are illustrated in Figures 3.4 and 3.5. The hydrogenation reaction, equation (6), is significantly exothermic.

The ΔG_r^o values for the reactions (6) are presented in Figure 3.5. All of the reactions are thermodynamically spontaneous between 25 and 900°C, which suggests the feasibility of good product yields. Consequently, the temperatures that favor good equilibrium yields for the furfural hydrogenation.

The log K_{eq} values for these reactions were plotted versus temperature and the results are presented in Figure 3.6.

Table 3.1: The criteria for thermodynamic feasibility [Neramittagapong (2000)]

ΔG_r^o (kcal.mol^{-1})	Feasibility
1. Very negative; < 10	Very high equilibrium conversion possible
2. Moderately negative; 0 to –10	Fairly high equilibrium conversion possible
3. Moderately positive; 0 to 10	Low equilibrium conversion depending upon process conditions
4. Very positive; > 10	Very low equilibrium conversion, generally not significant reactions

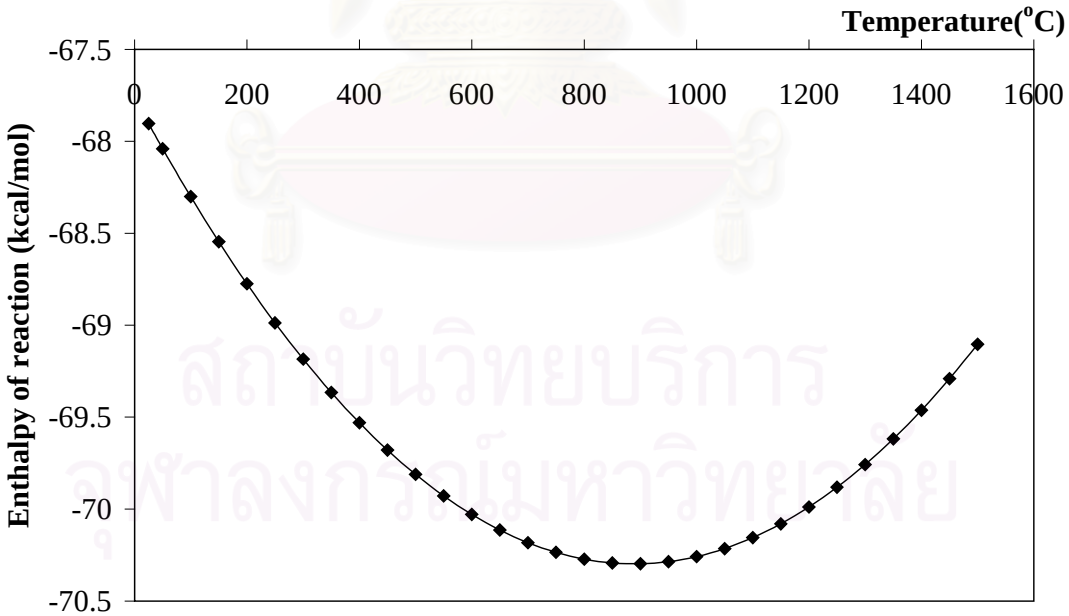


Figure 3.4 Enthalpy of reaction versus temperature for the selective hydrogenation of furfural to furfuryl alcohol. [Yaws (1999)]

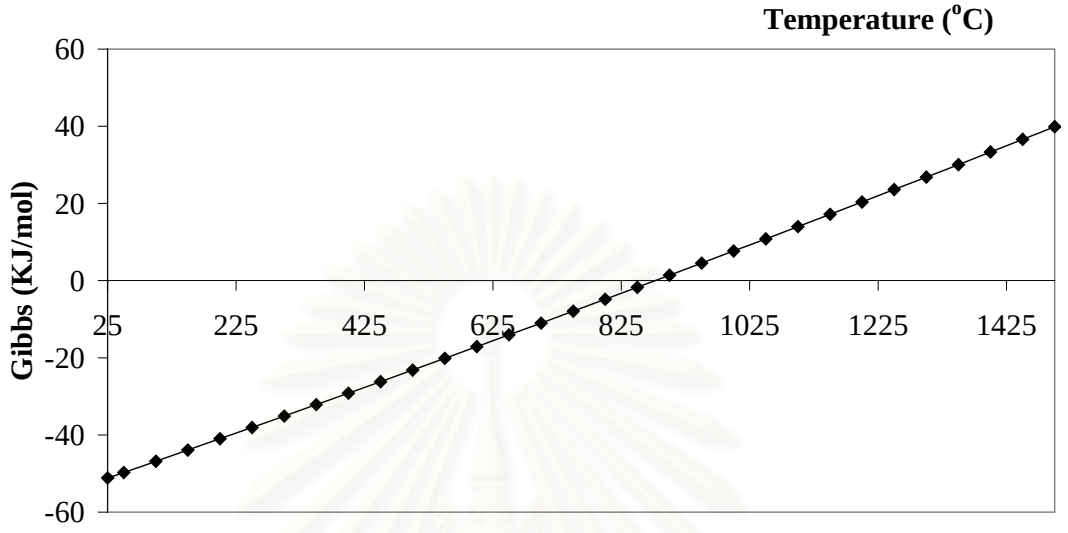


Figure3.5 Gibbs free energy of reaction versus temperature for the selective hydrogenation of furfural to furfuryl alcohol. [Yaws (1999)]

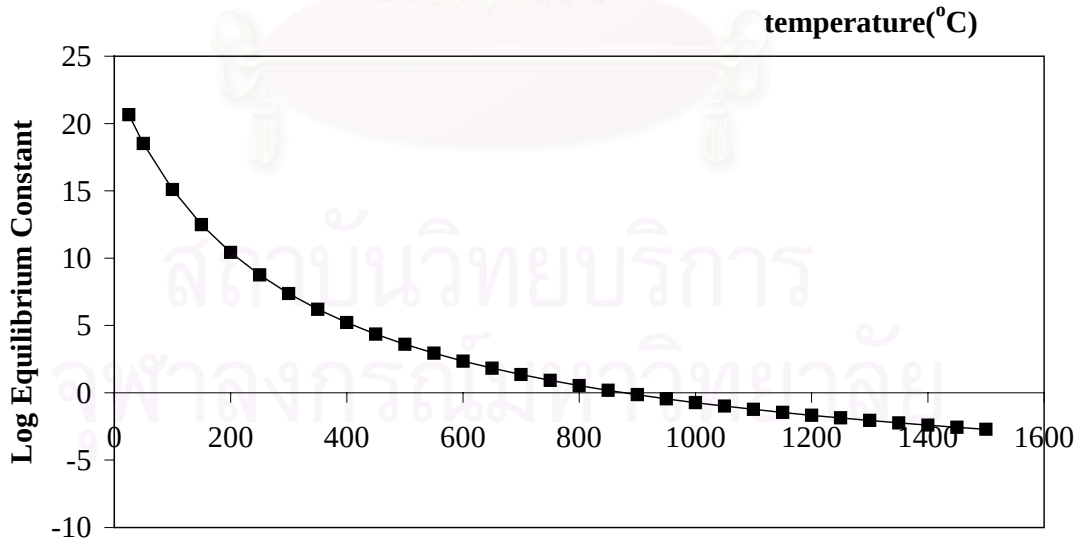


Figure 3.6 Log of the equilibrium constants for the selective hydrogenation. [Yaws (1999)]

CHAPTER IV
EXPERIMENTAL

The experiments in this chapter are divided into two major parts including the catalytic reaction and catalyst characterization, respectively. The first part is catalytic reaction which is presented in section 4.1. The catalyst characterizations, i.e., XRD, BET, TGA, XRF and nitrous adsorption, are illustrated in the second part (section 4.2).

4.1) The catalytic reaction

4.1.1 Chemicals and reagents

The reactions are prepared with the following reagents:

1) High purity grade Hydrogen (99.99 vol.%), supplied by Thai Industrial Gases Limited.
2) High purity grade Nitrogen of (99.99 vol.%) supplied by Thai Industrial Gases Limited.
3) Furfural ($C_5H_4O_2$) available from Merck, >98 vol.%
4) Absolute Ethyl alcohol (C_2H_6O) available from Carlo Erba, 99.8 vol.%
5) Copper chromite (Cu-1135 P) available from Engelhard Corporation

4.1.2 Instruments and Apparatus

The schematic diagram of the reaction apparatus for the selective hydrogenation of furfural is shown in Figure 4.1.

1) Autoclave reactor: the autoclave is made of stainless steel with a volume of 2000 ml and 10 cm inside diameter. It consists of four valves, which are used to feed or vent the reactant and a stirring core. This autoclave can be operated at moderate temperature (0-300°C) and pressure (0-300 psi) as shown in Figures 4.2a and 4.2b.

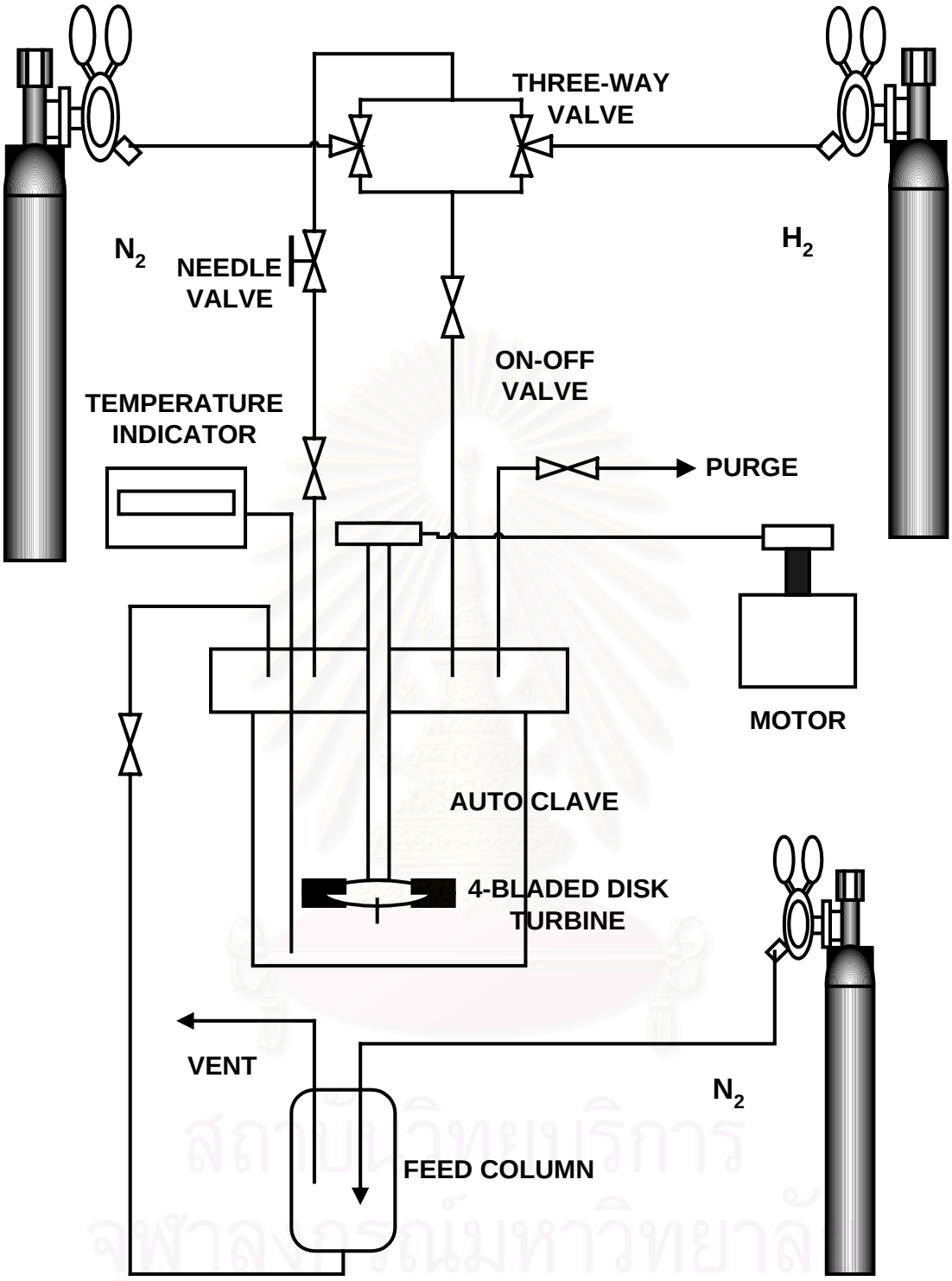


Figure 4.1 Flow diagram of the liquid hydrogenation system.

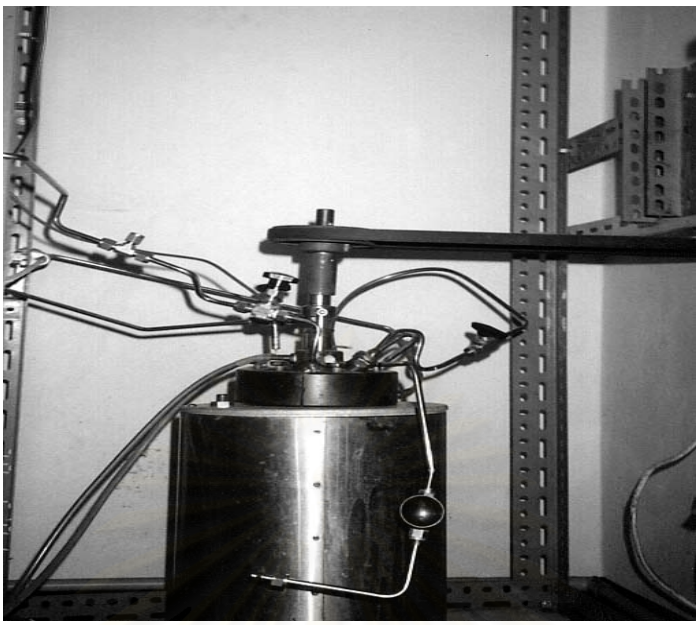


Figure 4.2 a Autoclave and Propeller

Figure 4.2 b Autoclave and Propeller

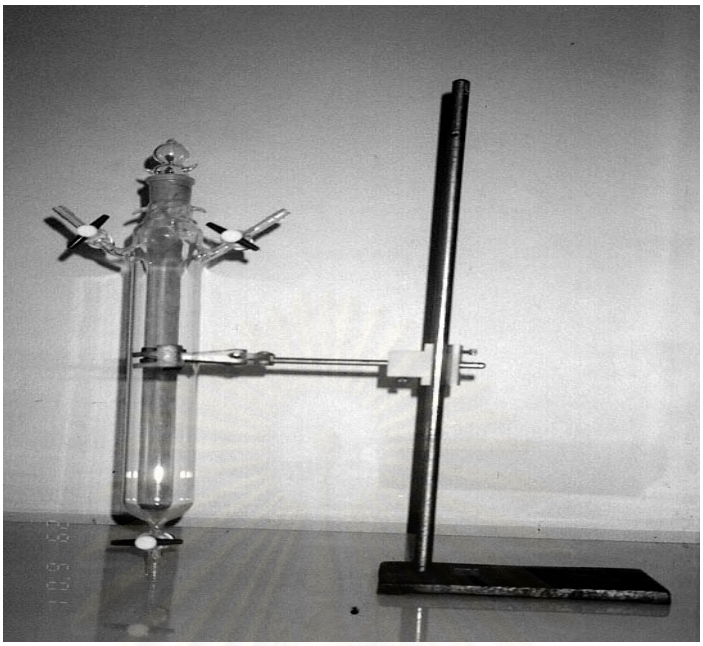


Figure 4.3 Feed column

2) Automatic temperature controller: The automatic temperature controller consists of a magnetic switch connected to a variable voltage transfer and a RKC temperature controller, which is connected to a 1 mm diameter thermocouple for temperature measurement of the system. A dial setting establishes a set point at any temperature within the range 0 to 400°C

3) Electrical furnace (Heater): This supplies the required temperature to the autoclave for reaction. The autoclave can be operated from room temperature up to 300°C at voltage of 150 volts.

4) Gas controlling system: Nitrogen cylinder is equipped with a pressure regulator (0-2000 psi). Hydrogen gas is allowed to flow into the autoclave by using a pressure regulator (0-350 psi). A needle valve is used to release gas from the autoclave. A ball valve is used to supply and adjust the gas for the autoclave.

5) Gas chromatograph: A gas chromatograph (Shimadzu GC-9A) equipped with a flame ionization detector (FID) was used to analyze liquid feed and product. The operating conditions for GC and detector are shown in Table 4.1.

Table 4.1 Operating conditions for the gas chromatograph

Gas Chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	15% Carbowax 20M/Chromosorb WAW-DMSC (80/100)
Carrier gas	N_2
Flow rate of carrier gas	30 ml/min
Column temperature - Initial - Final	 120^oC 140^oC
Detector temperature	200^oC
Injector temperature	250^oC
Analyzed gas	furfural, furfuryl alcohol, furan, 2-methylfuran, 1-pentanol, 2-pentene-1-ol, ethyl alcohol

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4.1.3 Hydrogenation procedure

The hydrogenation procedures are described in the details below that compose of 2 steps of reaction.

1. Reduction step

0.85 - 1.25 gram of catalyst was placed in the autoclave located in the electrical furnace. The autoclave was purged with nitrogen to remove remaining air.

Sequentially, hydrogen was switched at a volumetric flow rate of 100 ml/min. Next, the temperature was heated from room temperature to the appropriate value (300°C) with the heating rate of 3°C min^{-1}. This temperature was held for 3-10 h. After that the autoclave was cooled by hydrogen.

2. Reactant preparation and hydrogenation step

500 ml of ethyl alcohol and 15 ml of furfural were mixed in a beaker, and then set in the 600 ml feed column (Figure 4.3). The mixture was then flushed with nitrogen. Afterwards, hydrogen was purged to remove a remained nitrogen and heated to reaction temperature (100-140°C) at a heating rate of 3°C min^{-1}. The stirring was carried out with a stirring core until the reaction temperature was constant. The autoclave was finally pressurized to 80-200 psi with hydrogen. After 3 h the heating and stirring were stopped. The autoclave was cooled down to room temperature, before the slow releasing of pressure.

The feed and product were collected with the liquid syringe and injected to the gas chromatograph for analysis.

The results of hydrogenation reaction were calculated in the terms of:

$$\% \text{ A converted} = \frac{\text{mole of A reacted}}{\text{mole of A in feed}} \times 100\%$$

$$\% \text{ selectivity to B} = \frac{\text{mole of A converted to B}}{\text{mole of A reacted}} \times 100\%$$

where A and B are reactant and desired product, respectively.

4.1.4 Nitrous oxide pretreatment

From the hydrogenation procedure, the nitrous oxide pretreatment was proceeded after the reduction step. Nitrogen is used to remove the remained hydrogen. The reactor was heated from room temperature to 90°C under the nitrogen flow of 100 ml/min and

held for 20 minutes . Nitrous oxide was released into the autoclave and then pressed to 14.7 psi for 2 minutes and subsequently removed. Afterward the autoclave was cooled by nitrogen. Finally the hydrogen was used to remove nitrogen at room temperature.

4.2) Characterization of the catalyst samples

4.2.1 X-Ray Diffraction (XRD)

XRD Patterns of the catalyst samples were determined by using Ni-filtered Cu Kα radiation in the 2θ range of 10° to 80° (SIEMENS XRD D5000, Petrochemical Engineering Research Laboratory, Chulalongkorn University).

4.2.2 Specific Surface Area Measurement

The BET surface area was determined by nitrogen adsorption in an automatic apparatus ASAP-2000 constructed by Micromeritics. The data obtained were recorded by microcomputer. This unit is located at Analysis Center of Department of Chemical Engineering, Chulalongkorn University. The operating conditions are listed as follows:

Table 4.2 Operating conditions for BET surface area measurement

Sample weight:	0.3 g
Degas temperature:	150^oC
Vacuum pressure:	<10 μHg
Pressure table :	5 points

4.2.3 Thermogravimetric Analysis

The amount of copper in each state (Cu^{1+}, Cu^{0}) was determined by thermogravimetric analysis (TGA) in a Shimadzu TA-50 thermal analyzer (Petrochemical Engineering Research Laboratory, Chulalongkorn University). The operating conditions are listed as follows:

Example: Reduction of copper chromite with H_2 at 300°C for 10 h

Sample weight: 11 - 15 mg

Step	Rate (^{o}C/min)	Final Temperature (^{o}C)	Time (min)
1	1	40	40
2	2	300	150
3	-2 (Cool)	100	60
4	2	300	240
5	0.5	305	360

Note: step 1-3: nitrogen flow,
step 4-6: hydrogen flow .
(+): heating , (-): cooling

4.2.4 X-Ray Fluorescence Spectroscopy

The component of catalyst samples was determined by using Wavelength Dispersive X-Ray Fluorescence Spectrometer (Philips Model PW 2400). This unit is located at the Scientific and Technology Research Equipment Center, Chulalongkorn University (STREC).

4.2.5 Copper metal sites measurement by N_2O adsorption method

The number of metal active sites were measured by N_2O adsorption technique on the assumption that only one N_2O molecule adsorbed and reacted with two copper metal sites, as the equation 4.1. Quantity of catalyst used is 0.01 g. Helium 99.99% was used as a carrier gas. Nitrous oxide was used as an adsorbent and a standard gas. The reaction temperature was 90°C. The flow diagram of the N_2O adsorption apparatus was shown in Figure 4.4. The amount of adsorbed N_2O was measured by the thermal conductivity detector.

$$2Cu^{0} + N_2O \longrightarrow N_2 + Cu\text{-}O\text{-}Cu \qquad (4.1)$$

Table 4.3 Operating condition of gas chromatograph for copper metal sites measurement

Gas chromatography	GC GOW-MAC Series 750
Detector	TCD
Packed column	PORAPAK - QS
Helium flow rate	30 ml/min
Column temperature	80°C
Detector / injector temperature	80°C
Detector current	80 mA

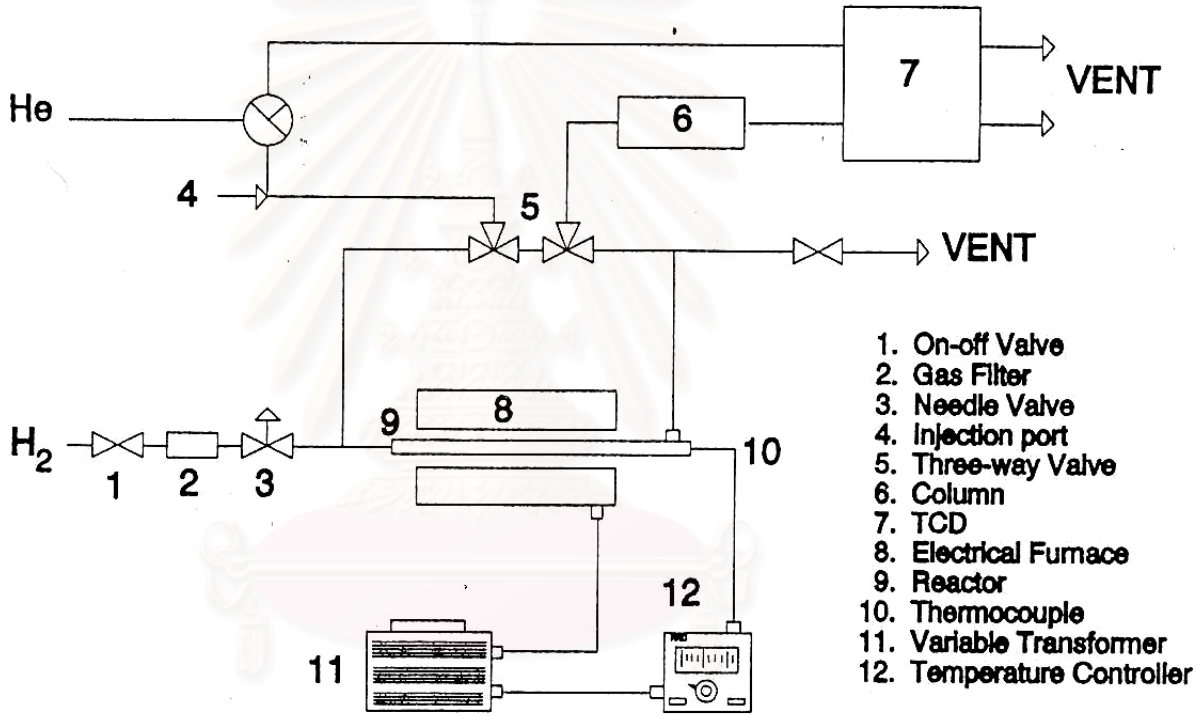

Figure 4.4 Flow Diagram of the nitrous oxide reaction for measurement of copper metal sites

CHAPTER V
RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two major parts including the catalyst characterization and the catalytic reaction test.

5.1 Catalyst characterization

5.1.1 Determination of composition content and BET surface area

The metal oxide composition and BET surface area of a commercial catalyst are summarized in Table 5.1.

Table 5.1 The composition and the BET surface area of a commercial catalyst.

Catalyst	copper chromite
Copper oxide content (% by wt)	45
Chromium oxide content (% by wt)	46
BET surface area (m^2/g)	38
Single point surface area (m^2/g)	36

5.1.2 X-Ray Diffraction (XRD)

The XRD patterns are shown in Figure 5.1. It is observed that the XRD pattern of a fresh copper chromite catalyst is in general agreement with the literatures [Stroupe (1949), Pillai (1994), and Rao *et al.* (1997)]. The dominant peak at 2θ value of 35.4° corresponded to the feature of cupric chromite ($CuCr_2O_4$). The XRD pattern of a reduced copper chromite catalyst shows two well-defined peaks

appeared at 43.0° and 51.0° and a weak broaden peak at 36.5°, assigned to the characteristic of metallic copper and cuprous chromite ($CuCrO_2$), respectively [Pillai (1994), and Rao *et al.* (1997)]. For a reduced catalyst pretreated by nitrous oxide, its XRD profile is similar to that of a reduced catalyst. However, it can be seen that the intensities of the two peaks at 43° and 51.0° are obviously decreased, whereas the intensity of a peak at 36.5° is slightly increased. It is suggested that the dissociative adsorption of nitrous oxide should occur on metallic copper surface [Dandekar *et al.* (1999)].

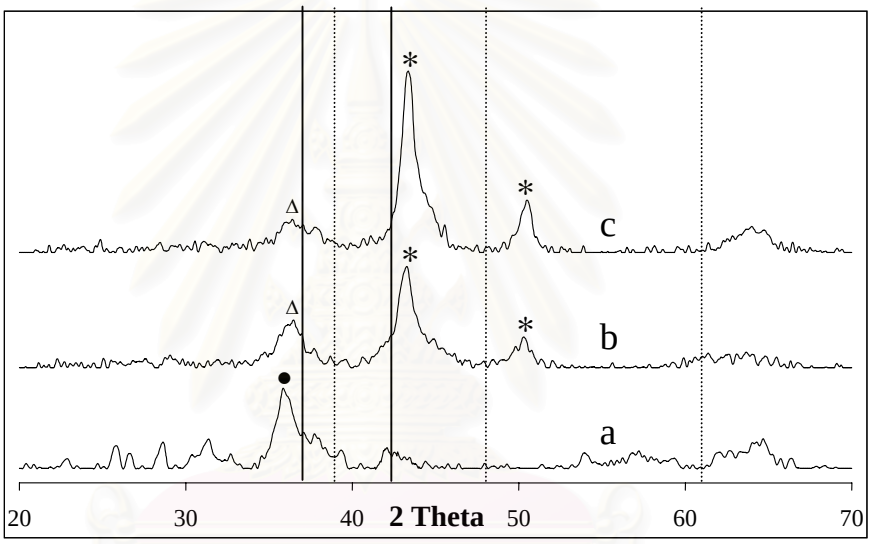

Figure 5.1 XRD patterns for copper chromite catalysts:(a) a fresh catalyst; (b) after reduction at 300°C for 4 h and subsequently N_2O pretreatment at 90°C; (c) after reduction at 300°C for 4 h. The following phases are denoted: Cu^0 (∗). $CuCrO_2$ (●). $CuCr_2O_4$ (Δ). XRD patterns of cuprous oxide (—). XRD patterns of cupric oxide (·····). [Stroupe (1949), Pillai (1994), and Rao *et al.* (1997)]

Figures 5.2 and 5.3 illustrate the XRD patterns of cuprous oxide (Cu_2O) and cupric oxide (CuO), respectively. Comparing with the XRD curve of the reduced catalyst through the N_2O pretreatment, it is found that the absence of a separate phase for cuprous oxide is determined by the absence of reflections at 42.3° and 61.4° and no cupric oxide is demonstrated, seeing from the absence of reflections

at 48.8°. Hence, the copper component in copper chromite catalyst after the N_2O pretreatment should be not cuprous oxide but it is distinctly in form cuprous chromite. From XRD data, it can be propose the mechanism for the reduction and the oxidation of copper chromite as follows.

$$CuCr_2O_4 \xrightarrow{\text{Reduction}} CuCrO_2 \rightleftarrows Cu^0$$

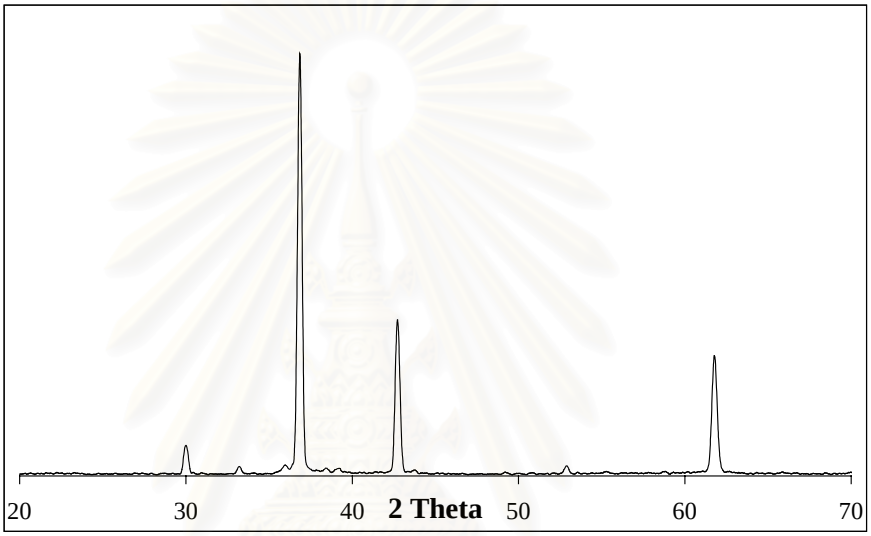

Figure 5.2 XRD patterns of cuprous oxide.

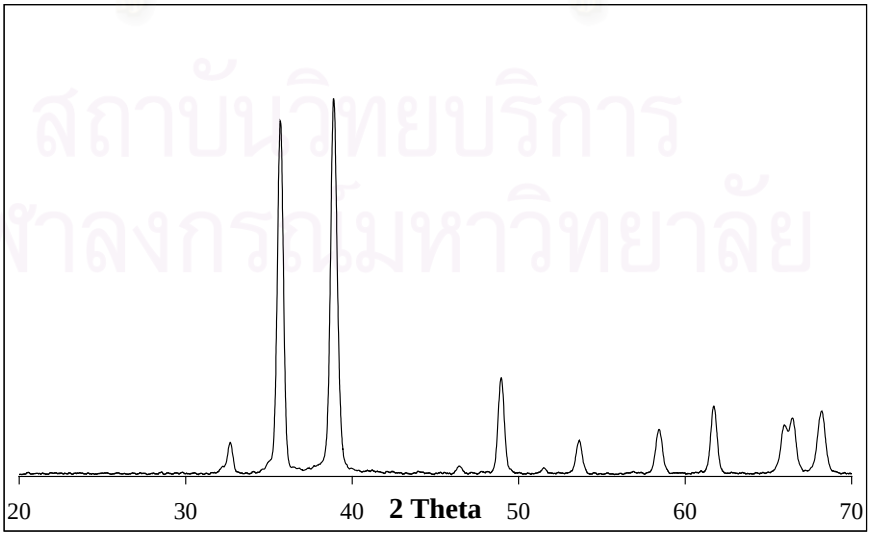

Figure 5.3 XRD patterns of cupric oxide.

5.1.3 Thermogravimetric analysis (TGA)

The loss of catalyst species, as in heating program, can be determined in term of the weight loss by using the thermogravimetric analysis. Each thermogram consists of three curves, i.e., temperature curve, weight curve, and differentiate weight (dtg) curve. In this work, it can be implied that the weight loss of catalyst during the heating under the hydrogen flow represents to the disappearance of oxygen content due to the reduction process as proposed in the below equation:

$$\text{Cupric chromite} \rightarrow \text{Cuprous chromite} \leftrightarrow \text{Metallic copper} \qquad (1)$$

Figure 5.4 shows TGA curves of a fresh copper chromite catalyst. It is found that the weight loss during the reduction step begins at 130°C and decreases dramatically in the temperature interval between 130 and 300°C. However, the catalyst weight is almost constant after the reduction temperature is held at 300°C. Hence, the reduction process as shown in equation (1) should be severely carried out during the increasing reduction temperature step. The TGA curves of cuprous oxide and cupric oxide are also observed as shown in Figures 5.5 and 5.6, respectively. The reduction temperature peaks of cuprous oxide and cupric oxide appeared at 200°C and 250°C, respectively. It can be concluded that cupric oxide is more stable than cuprous oxide.

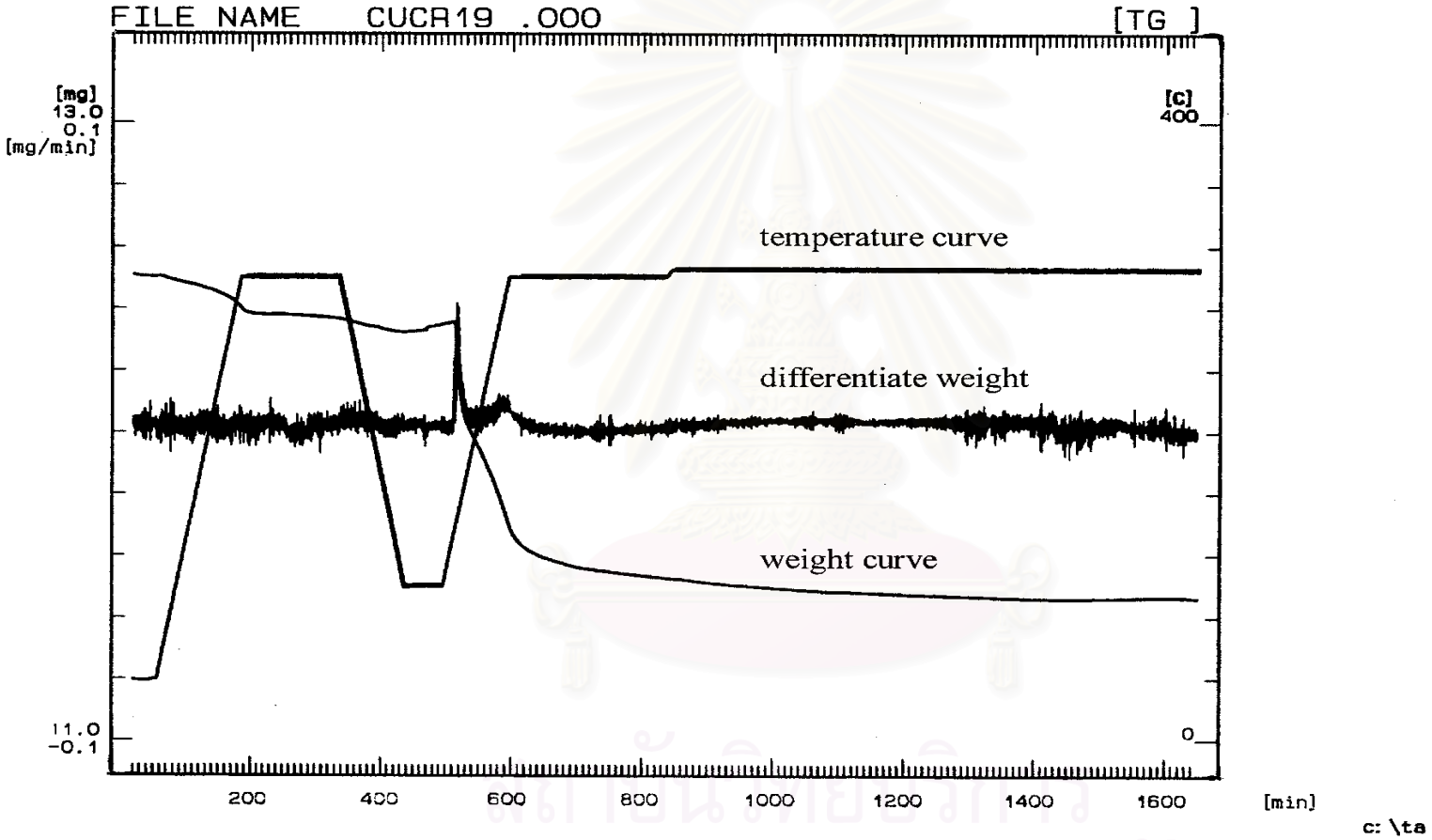

Figure 5.4 TGA thermogram of fresh copper chromite

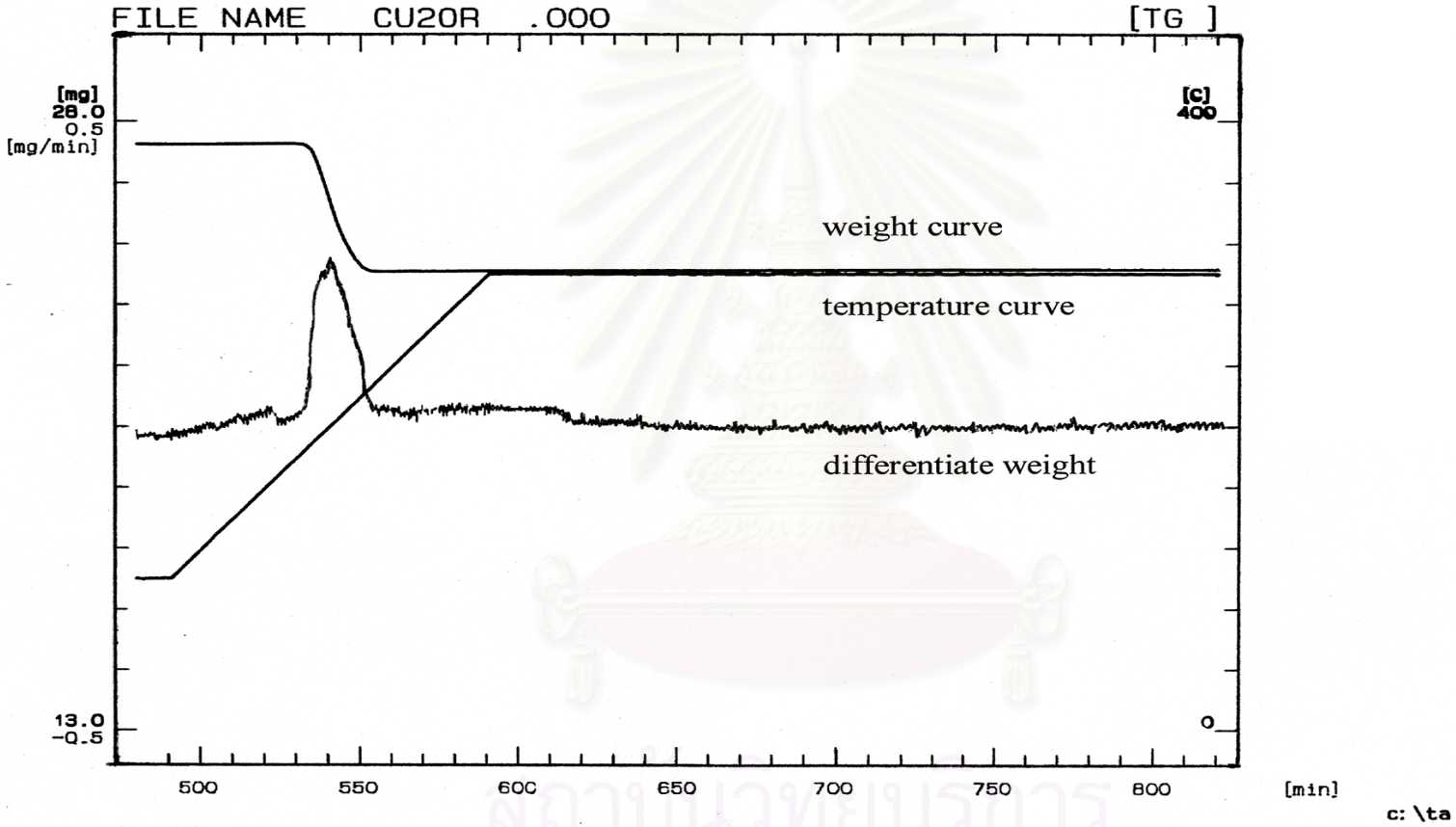

Figure 5.5 TGA thermogram of cuprous oxide

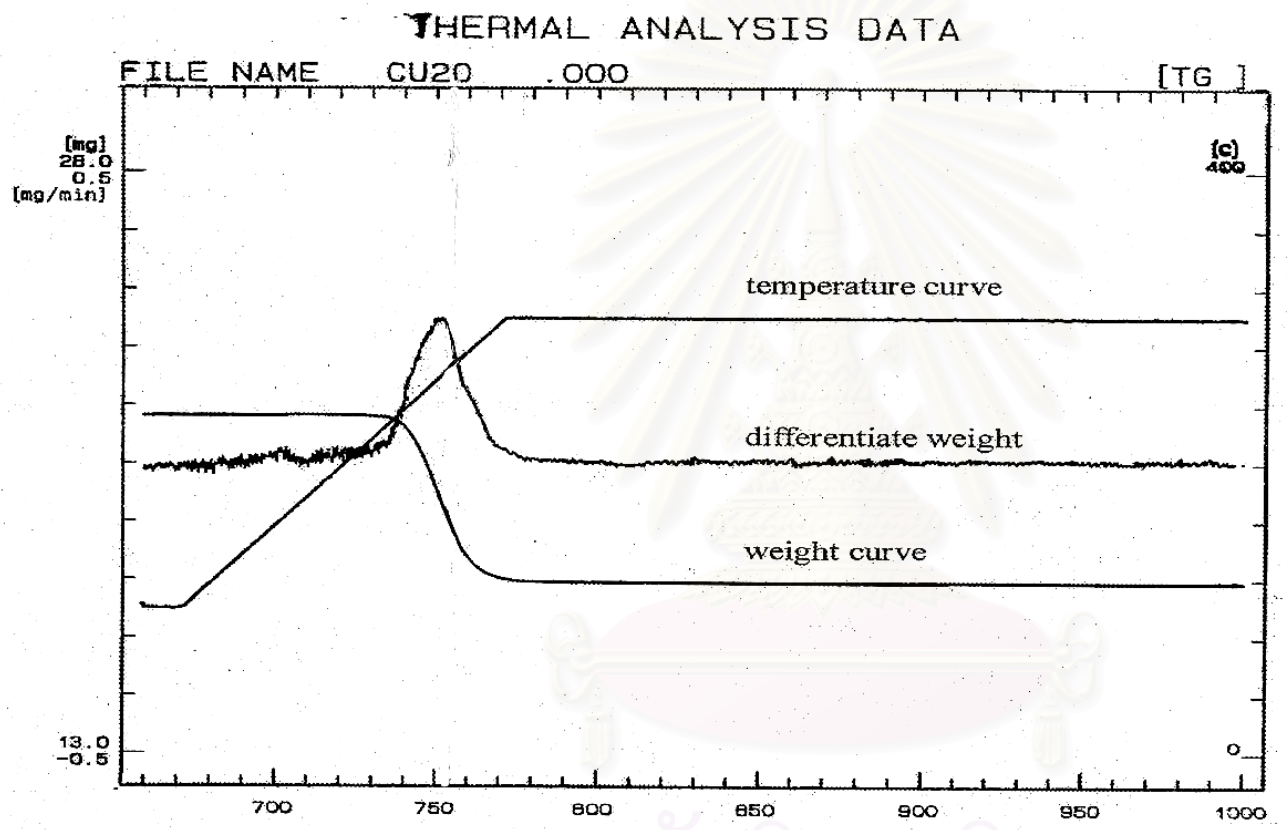

Figure 5.6 TGA thermogram of cupric oxide

The maximum metallic copper content (Cu^0_{XRF}), which exists possibly on copper chromite catalyst, can be calculated from the assumption that the copper oxide content obtained by X-Ray Fluorescence Spectroscopy (XRF) in Table 5.1 is completely converted to metallic copper. This content is compared with the actual metallic copper content ($Cu^0_{measure}$) which is calculated in form of bulk copper metal obtained from the TGA curves as illustrated in Table 5.2. The detail for calculation both Cu^0_{XRF} and $Cu^0_{measure}$ values was shown in Appendix C. From Table 5.2, it was found that all of copper in cupric oxide and cuprous oxide can be reduced to metallic copper while some of copper in copper chromite can be reduced to copper metal.

Table 5.2 The maximum and actual copper contents in copper chromite, cupric oxide and cuprous oxide (The actual copper contents are obtained from TGA curves after reduction at 300°C for 4 h).

Catalysts	$Cu^0_{measure}$ (% by wt)	Cu^0_{XRF} (% by wt)
Copper chromite	25.66	36.34
Cupric oxide (CuO)	80.38	79.87
Cuprous oxide (Cu_2O)	88.96	88.81

In addition, increasing the reduction time at 300°C, the amounts of metallic copper in copper chromite are shown in Table 5.3. It is obvious that the actual metallic copper content from experimental is less than the maximum metallic copper content. Hence, the copper in copper chromite catalyst cannot be completely reduced to metallic copper though increasing the reduction time up to 20 h.

Table 5.3 The maximum and actual copper contents in copper chromite (The actual copper contents are obtained from TGA curves after reduction at 300°C with various reduction time).

Reduction time (h)	$Cu^0_{measure}$ (mg)	Cu^0_{XRF} (mg)
4	25.66	36.34
5	26.38	36.34
10	28.05	36.34
20	28.77	36.34

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5.1.4 Copper metal sites measurement by N_2O adsorption method

The relationship between copper metal active sites and furfural conversion is shown in Figure 5.8. Basically, the reduction by hydrogen could make copper molecule in copper chromite become copper metal. However, this accessible copper metal depends on the reduction time. It is observed that the amounts of accessible copper metal at reduction time of 4 h is more than those of 10 h because the long reduction time results in sintering of copper metal on the surface catalyst which decreased furfural conversion.

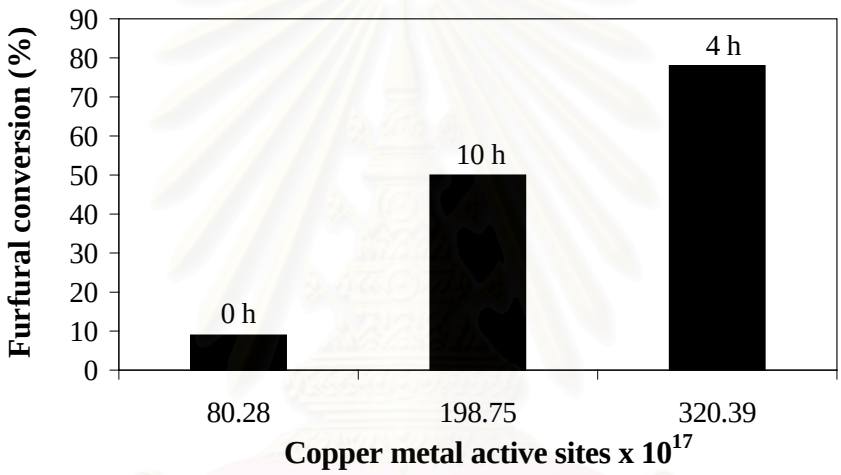

Figure 5.7 Correlation between copper metal active sites and furfural conversion.

5.2 Catalytic reaction test

5.2.1 Effect of the reaction temperature

The temperature dependence on the catalytic activity and selectivity of copper chromite catalyst on the selective hydrogenation of furfural is shown in Figure 5.8. Increase in the reaction temperature from 100°C to 125°C results in the increase in furfural conversion from 33% to 78% with a relatively constant of furfuryl alcohol selectivity at 92%. The furfural conversion at the temperature up above 125°C is slightly increased while the selectivity towards furfuryl alcohol is slightly decreased. Another product is 2-methylfuran. The possible explanation for this observation is that the reaction rate is usually increased with increasing reaction temperature with unnoticeable effect on the selectivity. The negligible effect of increasing temperature on the selectivity could possibly be attributed to the fact that the C=C bonds in furfural ring are conjugated and they are therefore stabilized. The reaction temperature at 125°C is then chosen to further study.

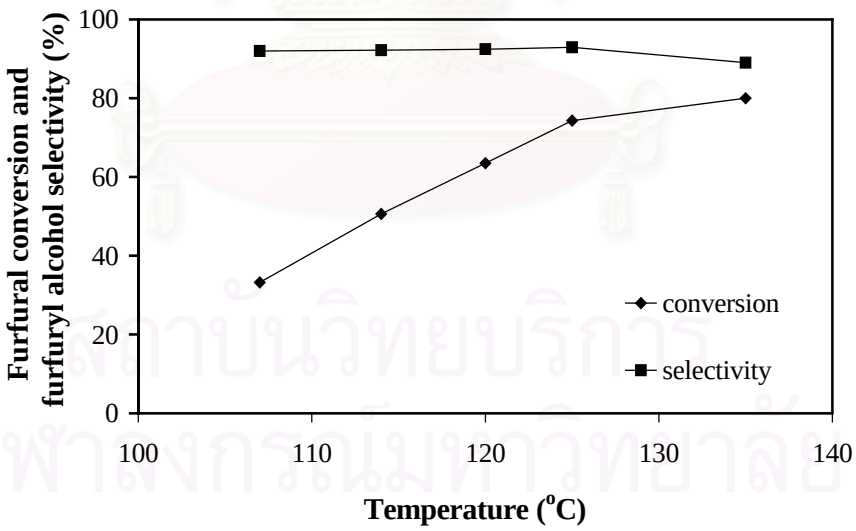

Figure 5.8 Effect of reaction temperature on the selective hydrogenation of furfural at P=120 psi, Catalyst Weight =1.05 g and Reduction Time = 4 h.

5.2.2 Effect of the reaction pressure

Effect of the reaction pressure is depicted in Figure 5.9. Variation of the reaction pressure in the range 80 psi to 200 psi results in the increase in furfural conversion from 48% to 90% with a constant value of the furfuryl alcohol selectivity at 92%. This is in a good agreement with that reported in the literature [Rao *et al.* (1999)] that the rate of reaction depends on partial pressure of hydrogen. Thus the reaction pressure is kept constant at 120 psi for further study.

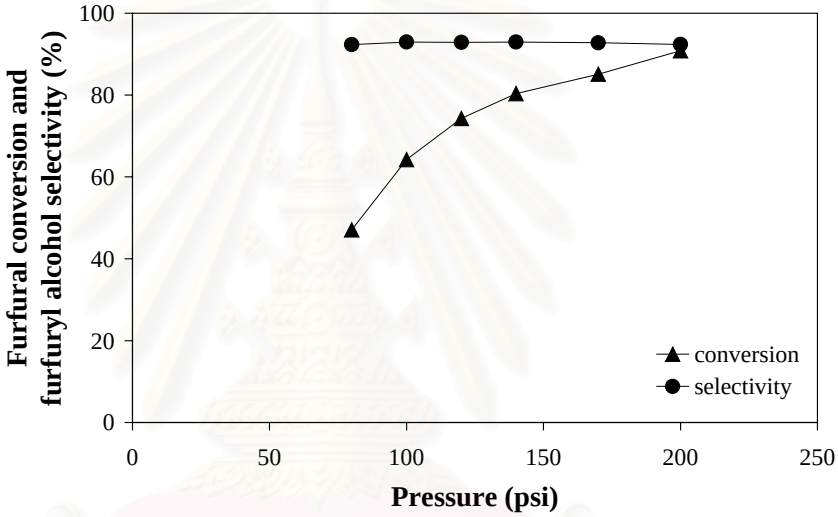

Figure 5.9 Effect of reaction pressure on the selective hydrogenation of furfural at T = 125 ^{o}C, Catalyst Weight = 1.05 g and Reduction Time = 4 h.

5.2.3 Effect of ratio between catalyst weight and furfural volume

Figure 5.10 demonstrates the influence of the ratio between the catalyst weight and the furfural volume used on the catalytic activity for the selective hydrogenation of furfural. Increasing the ratio of the catalyst weight and the furfural volume from 0.85 g/15 ml to 1.05 g/15 ml results in the increase in furfural conversion from 60% to 78% while the furfuryl alcohol selectivity remains constant at 92%. Increase of the ratio between the catalyst weight and the furfural volume does

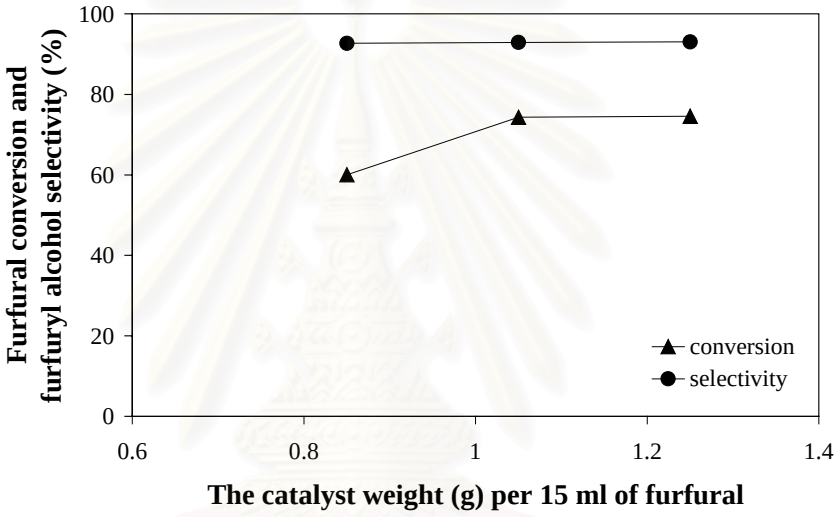

Figure 5.10 Effect of the ratio between the catalyst weight and the furfural volume on the selective hydrogenation of furfural at P = 120 psi, T = 125 ^{o}C and Reduction Time = 4 h

not longer influence either the furfural conversion or the selectivity to furfuryl alcohol when the ratio is above 1.05 g/15 ml. It is concluded from the experimental results that 1.05 g of catalyst are enough to convert 15 ml of furfuryl and thus this ratio was used for further study.

5.2.4 Effect of reduction time

Figure 5.11 shows the correlation between the reduction time and the catalytic performance in terms of furfuryl conversion and selectivity to furfuryl alcohol. It is seen thus conversion increases from 65% to 78% with increasing the reduction time whereas the selectivity remains constant at 92%. The decrease in furfural conversion is observed with longer reduction time, i.e., from 62% at 5 h to 50% at 10 h, while the selectivity is still not influenced. The copper chromite catalyst reduced at 300°C for 4 h give the highest rate and specific activity which is in agreement with the literatures [Rao *et al.* (1997), and Pillai (1994)]. From Table 5.3, the consideration of the actual metallic copper content (Cu^0_{actual}) observed after the reduction at 5 and 10 h shows the relatively similar values. This should be a possible reason of the above results observed at 5th and 10th h of the reduction. The slightly different conversions seen after the different reduction time (4, 5 and 10 h) suggest that the reduction for 4 h should be used.

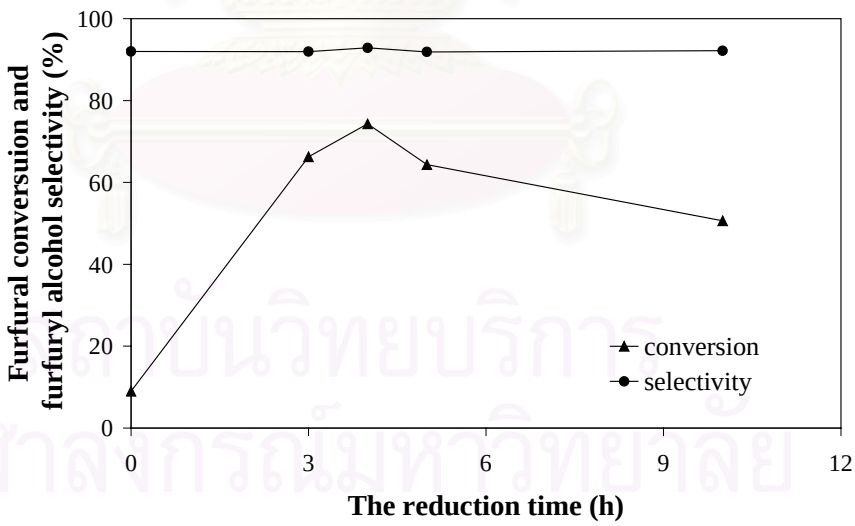

Figure 5.11 Effect of reduction time for the selective hydrogenation of furfural at P = 120 psi, T = 125°C and Catalyst Weight = 1.05 g.

5.2.5 Effect of nitrous oxide

The influence of pretreatment with nitrous oxide on the catalytic activity and selectivity for the selective hydrogenation of furfural is studied and the results are shown in Figure 5.12. After N_2O pretreatment, copper chromite catalyst shows less activity, i.e., it leads to the decrease in furfural conversion from 78% to 48% with a constant selectivity at 92%. It is elucidated that cuprous chromite in copper chromite catalyst was increased after N_2O pretreatment.

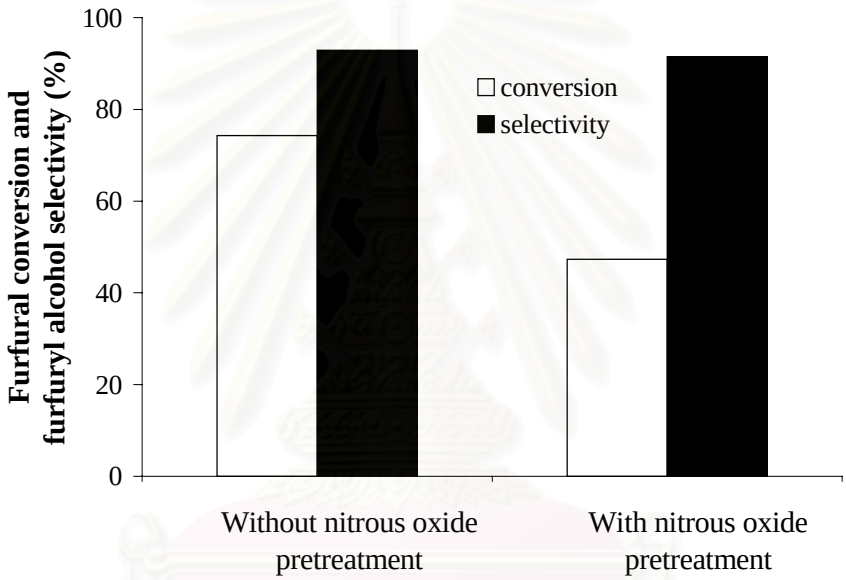

Figure 5.12 Effect of the pretreatment with nitrous oxide on the catalytic activity and selectivity of copper chromite catalyst for the selective hydrogenation of furfural at P = 120 psi, T = 125°C and Catalyst Weight = 1.05 g.

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

This chapter will be focused on the conclusions of the research experimental data. The recommendations for future works will be also emerged.

6.1) Conclusions

The conclusions of the present research are the following:

1. Accessible copper metal is active species for selective hydrogenation of furfural to furfuryl alcohol.

2. Long reduction time causes the loss of accessible copper sites and results in sintering.

3. The mechanism for the reduction and the oxidation of copper chromite can be proposed as follows.

$$\xrightarrow{\text{Reduction}}$$

$$CuCr_2O_4 \longrightarrow CuCrO_2 \rightleftharpoons Cu^0$$

6.2 Recommendations

From the previous conclusions, recommendations for future studies are as follows:

1. Study of the effect of chromite on copper distribution should be done.
2. The mechanism for the state transformation of copper metal to $CuCrO_2$ instead of Cu_2O during the N_2O pretreatment on copper chromite catalyst should be further studied in more detail.

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APPENDICES

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APPENDIX A

CORRECTION FACTOR

Correction factor for GC with column 15%Carbowax 20M/Chromosorb

Correction factor, $F = \frac{(A/W)_{COMPONENT}}{(A/W)_{STANDARD}}$ (A-1)

Given ethanol is standard component (F=1)

Reactants	Weight (W) (gram)	Area (A)	Correction Factor (F)
Furfural	0.0153	104962	1.05
Ethanol (EtOH)	1.1210	7323062	1.00
Furfuryl Alcohol	0.0533	425786	1.22

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APPENDIX B

CALCULATION OF NUMBER OF MOLE

Number of mole of each component can be calculated by using correction factors from Appendix A.

$$\text{Number of mole} = \frac{Area/(MWxF)_{component}}{\Sigma(Area)/(MWxF)_{component}} \times \text{Total mole}$$

For example; Batch reactor

Reaction conditions;

temperature = 125°C, speed level = 700 rpm, catalyst weight = 1.05 g,

time = 0 min, EtOH = 500 ml , Furfural = 15 ml, Furfuryl Alcohol = 0 ml

Reactants	Area	MW	Correction Factor (F)	Number of mole
Furfural	346540	96.09	1.05	0.23
Ethanol (EtOH)	7266886	46.09	1.00	10.77
Furfuryl Alcohol	0	98.01	1.22	0

APPENDIX C

Calculation of copper from TG data

Calculation of the Cu^{1+}, the Cu^{0} of copper chromite catalyst from TG data (Figure 5.4)
Assumption: Catalyst weight loss from TG data is assumed to be the change in oxidation state of copper from $Cu^{2+} \rightarrow Cu^{0}$

- The copper contents of copper chromite from XRF data are equal to 36.34 %wt.
- The initial weight of copper chromite is equal to 12.37 mg.
- The final weight of copper chromite is equal to 11.46 mg.

Maximum copper contents in initial weight of copper chromite = (12.37x36.34)/100 mg.

Cu^{0}_{XRF} = 4.50 mg (1)

(Initial weight - Final weight) of copper chromite = Disappearance of oxygen in copper chromite

(12.37-11.46) = 0.91 mg of oxygen

= 0.057 mmol of oxygen

Moles of oxygen disappearance = Moles of copper metal ($Cu^{0}_{measure}$) appearance

= 0.057 mmol of copper metal

= 3.62 mg of copper metal (2)

Therefore, Equations (1)-(2) is the cuprous chromite (Cu^{1+}) in reduced copper chromite.

Cuprous chromite content = 4.50 - 3.62 mg

= 0.88 mg (3)

APPENDIX D

Calculation of copper metal active site on catalyst

The weight of catalyst used	=	w	g.
Area of N_2O peak after adsorption	=	A	unit.
Average area of 50 μl. standard N_2O peak	=	B	unit.
Amounts of N_2O adsorbed on catalyst	=	$\sum$(B-A)	unit.
Volume of N_2O adsorbed on catalyst	=	$[\sum(B-A)/B]\times 50$	μl.
Volume of gas 1 mole at 30 ^oC	=	24.86×10^6	μl.

Mole of N_2O adsorbed on catalyst (mole) $= [[\sum(B-A)/B]\times(50/24.86\times 10^6)]$

1 mole is 6.02×10^{23} molecule

Then, Molecule of N_2O adsorbed on catalyst

$= 2.01\times 10^{-6}\times[\sum(B-A)/B]\times 6.02\times 10^{23}$ molecules

1 molecule of N_2O reacts with 2 molecules of copper metal as the equation

$$2Cu^0 + N_2O \longrightarrow N_2 + (Cu\text{-}0\text{-}Cu)$$

Metal active site $= 1.21\times 10^{18}\times[\sum(B-A)/B] / w$ molecules of Cu^0/g. cat.

VITA

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