ตัวเร่งปฏิกิริยาของโคปเปอร์โครไมต์สำหรับปฏิกิริยาไฮโดรเจนชั่วคราวแบบเลือกเกิด
ของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์

นาย มงคลชนก ปราโมทย์ธนา

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

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Chemical Engineering

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งานวิจัยนี้เป็นการศึกษาปฏิกิริยาไฮโดรเจนแบบเลือกเกิดของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์ด้วยตัวเร่งปฏิกิริยาคอปเปอร์โครไมต์ซึ่งประกอบด้วยคอปเปอร์ออกไซด์และโครเมียมออกไซด์อย่าง 45 และ 46 โดยน้ำหนัก ตามลำดับ ทำการศึกษาปฏิกิริยาโดยใช้เครื่องปฏิกรณ์แบบชนิดหนึ่งความดันที่มีใบกวน พบว่า ภาวะที่เหมาะสมในการทำปฏิกิริยาคือ อุณหภูมิ 125 องศาเซลเซียส ความดัน 120 ปอนด์ต่อตารางนิ้ว และปริมาณตัวเร่งปฏิกิริยา 1.05 กรัมต่อปริมาตรเฟอฟูรอล 15 ลูกบาศก์เซนติเมตร จากผลการทดลองพบว่า การรีดิวซ์ด้วยแก๊สไฮโดรเจนก่อนการทำปฏิกิริยาที่อุณหภูมิ 300 องศาเซลเซียสเป็นเวลา 4 ชั่วโมง จะทำให้เกิดการเปลี่ยนของเฟอฟูรอลสูงสุด เมื่อเพิ่มเวลาการรีดิวซ์จะเกิดการละลายของตัวของโลหะทองแดงบนตัวเร่งปฏิกิริยาทำให้เกิดการเปลี่ยนของเฟอฟูรอลลง ดังนั้นสามารถสรุปได้ว่าโลหะทองแดงบนตัวเร่งปฏิกิริยาเป็นตัวแปรที่สำคัญต่อการทดลองแบบเลือกเกิดของเฟอฟูรอลเป็นเฟอฟูริลแอลกอฮอล์
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 H₂ 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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VITA

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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, C₄H₅OCHO, 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$_2$O adsorption at 90°C has been used to measure the metallic Cu surface as shown in equation (1) [Dandekar and Vannice (1998)]:

$$\text{N}_2\text{O}(g) + 2\text{Cu}^{0} \rightarrow \text{Cu}_2\text{O} + \text{N}_2(g)$$  \hspace{1cm} (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$_2$O. Hence, N$_2$O 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 N₂O.

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 N₂O 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 °C
CHAPTER II
LITERATURE REVIEWS

It was generally recognized that copper-containing 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=O, 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 [Cappece 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 [Capcece 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$_2$O 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)).
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 \(a=8.342 \text{ Å}\) 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 H₂ (Figure 3.2(a), curve 1). 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 (CuO₄) 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 H₂ at 250°, 320° and 450°C, respectively; (4) sample 3 calcined in He at 320°C for 10h; (○), (+), (Δ) reflections from the Cu⁰, silicon and NaCl-type structure, respectively. Positions of the reflections from a cubic type of CuCr₂O₄ 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 (CuO₄) which approached the intensity found for the fresh spinel.
Figure 3.3  The dependence of the amount of reacted hydrogen, \( N_{\text{H}_2} \), and chromite reduction degree on time and temperature. \( P_{\text{H}_2} = (3.9-8.1) \times 10^4 \text{ Pa.} \) [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:

\[
2\text{Cu}^0 + \text{O}_2 + 4\text{H}^+ \leftrightarrow 2\text{Cu}^{2+} + 2\text{H}_2\text{O}
\]

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)].

\[ 2\text{Cu}^0 + \text{O}_2 \leftrightarrow 2\text{CuO} \]

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:

\[
\text{Cu}_{0.53} [\text{Cu}_{0.33}]^a [\text{H}^+_{0.30}]^e [\text{Cu}_{0.07} \text{H}_{0.38}]^c [\text{Cr}^{3+}]^d_2 \text{O}_4
\]

(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°C, 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.

\[
\text{Furfural} + 3 \text{Cu-Cr oxide} \xrightarrow{150^\circ \text{C}, 10-15 \text{ MPa H}_2 \text{, 2h}} \text{Furfuryl alcohol} 
\]
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 H₂ and 200-230°C (eqn. 3).

Furfural was converted to tetrahydrofurfuryl alcohol in 96-98% yields by hydrogenation over copper-chromium oxide at 150-160°C and 10-20 Mpa H₂, followed by hydrogenation with added Raney Ni at 100-115°C. 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°C and 6.9-10.3 Mpa H₂. Tetrahydrofurfuryl alcohol was also obtained in 73% yield in hydrogenation over a ruthenium catalyst in ethanol in the presence of magnesium oxide at 110°C and 15 MPa H₂, although a better yield (89%) was reported in the hydrogenation over ruthenium dioxide at 100°C and 10 MPa H₂. 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°C and 10-20 MPa H₂ 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°C and 12.5-10 MPa H₂ (eqn. 5).
3.3 Thermodynamic calculation [Yaws (1999)]

The thermodynamic data can provide important information needed, i.e., the heat of reaction ($\Delta H_r^o$) and the Gibbs free energy of equilibrium constant ($K_p$) from $\Delta G_r^o$. 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:

$$C_4H_3O-CHO + H_2 \rightarrow C_4H_3O-CH_2OH \quad (6)$$

Knowing the $\Delta G_r^o$ 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 $\Delta G_r^o$ and $\Delta H_r^o$ 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 $\Delta G_r^o$ 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)]

<table>
<thead>
<tr>
<th>$\Delta G^o_r$ (kcal.mol$^{-1}$)</th>
<th>Feasibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Very negative; &lt; 10</td>
<td>Very high equilibrium conversion possible</td>
</tr>
<tr>
<td>2. Moderately negative; 0 to –10</td>
<td>Fairly high equilibrium conversion possible</td>
</tr>
<tr>
<td>3. Moderately positive; 0 to 10</td>
<td>Low equilibrium conversion depending upon process conditions</td>
</tr>
<tr>
<td>4. Very positive; &gt; 10</td>
<td>Very low equilibrium conversion, generally not significant reactions</td>
</tr>
</tbody>
</table>

Figure 3.4 Enthalpy of reaction versus temperature for the selective hydrogenation of furfural to furfuryl alcohol. [Yaws (1999)]
Figure 3.5  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 (C₅H₄O₂) available from Merck, >98 vol.%
4) Absolute Ethyl alcohol (C₂H₆O) 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
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

<table>
<thead>
<tr>
<th>Gas Chromatograph</th>
<th>SHIMADZU GC9A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>FID</td>
</tr>
<tr>
<td>Packed column</td>
<td>15% Carbowax</td>
</tr>
<tr>
<td></td>
<td>20M/Chromosorb WAW-DMSC (80/100)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>N₂</td>
</tr>
<tr>
<td>Flow rate of carrier gas</td>
<td>30 ml/min</td>
</tr>
<tr>
<td>Column temperature</td>
<td></td>
</tr>
<tr>
<td>- Initial</td>
<td>120°C</td>
</tr>
<tr>
<td>- Final</td>
<td>140°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Analyzed gas</td>
<td>furfural, furfuryl alcohol, furan, 2-methylfuran, 1-pentanol, 2-pentene-1-ol, ethyl alcohol</td>
</tr>
</tbody>
</table>

**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>
<thead>
<tr>
<th>Table 4.2 Operating conditions for BET surface area measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample weight:</td>
</tr>
<tr>
<td>Degas temperature:</td>
</tr>
<tr>
<td>Vacuum pressure:</td>
</tr>
<tr>
<td>Pressure table:</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Step</th>
<th>Rate (°C/min)</th>
<th>Final Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>-2 (Cool)</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>300</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>305</td>
<td>360</td>
</tr>
</tbody>
</table>

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$_2$O adsorption method

The number of metal active sites were measured by N$_2$O adsorption technique on the assumption that only one N$_2$O 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$_2$O adsorption apparatus was shown in Figure 4.4. The amount of adsorbed N$_2$O was measured by the thermal conductivity detector.

$$2Cu^0 + N_2O \rightarrow N_2 + Cu-O-Cu \quad (4.1)$$

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

<table>
<thead>
<tr>
<th>Gas chromatography</th>
<th>GC GOW-MAC Series 750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>TCD</td>
</tr>
<tr>
<td>Packed column</td>
<td>PORAPAK - QS</td>
</tr>
<tr>
<td>Helium flow rate</td>
<td>30 ml/min</td>
</tr>
<tr>
<td>Column temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Detector / injector temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Detector current</td>
<td>80 mA</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>copper chromite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper oxide content (% by wt)</td>
<td>45</td>
</tr>
<tr>
<td>Chromium oxide content (% by wt)</td>
<td>46</td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>38</td>
</tr>
<tr>
<td>Single point surface area (m²/g)</td>
<td>36</td>
</tr>
</tbody>
</table>

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 (CuCr₂O₄). 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 (\(\text{CuCrO}_2\)), 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 \(\text{N}_2\text{O}\) pretreatment at 90°C; (c) after reduction at 300°C for 4 h. The following phases are denoted: \(\text{Cu}_0\) (*), \(\text{CuCrO}_2\) (●), \(\text{CuCr}_2\text{O}_4\) (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 (\(\text{Cu}_2\text{O}\)) and cupric oxide (\(\text{CuO}\)), respectively. Comparing with the XRD curve of the reduced catalyst through the \(\text{N}_2\text{O}\) 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 N₂O 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.

\[
\begin{align*}
\text{Reduction} & \\
\text{CuCr}_2\text{O}_4 & \rightarrow \text{CuCrO}_2 & \text{Cu}^0
\end{align*}
\]

**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:

\[
\text{Cupric chromite} \rightarrow \text{Cuprous chromite} \leftrightarrow \text{Metallic copper} \quad (1)
\]

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$_{\text{XRF}}^0$), 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$_{\text{measure}}^0$) 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$_{\text{XRF}}^0$ and Cu$_{\text{measure}}^0$ 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).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu$_{\text{measure}}^0$ (% by wt)</th>
<th>Cu$_{\text{XRF}}^0$ (% by wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper chromite</td>
<td>25.66</td>
<td>36.34</td>
</tr>
<tr>
<td>Cupric oxide (CuO)</td>
<td>80.38</td>
<td>79.87</td>
</tr>
<tr>
<td>Cuprous oxide (Cu$_2$O)</td>
<td>88.96</td>
<td>88.81</td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th>Reduction time (h)</th>
<th>Cu\textsubscript{measure} (mg)</th>
<th>Cu\textsubscript{XRF} (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>25.66</td>
<td>36.34</td>
</tr>
<tr>
<td>5</td>
<td>26.38</td>
<td>36.34</td>
</tr>
<tr>
<td>10</td>
<td>28.05</td>
<td>36.34</td>
</tr>
<tr>
<td>20</td>
<td>28.77</td>
<td>36.34</td>
</tr>
</tbody>
</table>
5.1.4 Copper metal sites measurement by N$_2$O 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](image_url)

**Figure 5.9** Effect of reaction pressure on the selective hydrogenation of furfural at $T = 125$ °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 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.

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 °C and Reduction Time = 4 h
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$^0_{\text{actual}}$) 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 N₂O 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 N₂O 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, $T = 125^\circ$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.

\[
\text{Reduction} \quad \text{CuCr}_2\text{O}_4 \rightarrow \text{CuCrO}_2 \rightarrow \text{Cu}^0
\]

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 \(\text{CuCrO}_2\) instead of \(\text{Cu}_2\text{O}\) during the \(\text{N}_2\text{O}\) pretreatment on copper chromite catalyst should be further studied in more detail.
REFERENCES

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

\[
F = \frac{(A/W)_{\text{COMPONENT}}}{(A/W)_{\text{STANDARD}}} \tag{A-1}
\]

Given ethanol is standard component (F=1)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Weight (W) (gram)</th>
<th>Area (A)</th>
<th>Correction Factor (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>0.0153</td>
<td>104962</td>
<td>1.05</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>1.1210</td>
<td>7323062</td>
<td>1.00</td>
</tr>
<tr>
<td>Furfuryl Alcohol</td>
<td>0.0533</td>
<td>425786</td>
<td>1.22</td>
</tr>
</tbody>
</table>
APPENDIX B

CALCULATION OF NUMBER OF MOLE

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

\[
\text{Number of mole} = \frac{\text{Area} \times (MW \times F)}{\sum \text{Area} \times (MW \times F)} \times \text{Total mole}
\]

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

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Area</th>
<th>MW</th>
<th>Correction Factor (F)</th>
<th>Number of mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>346540</td>
<td>96.09</td>
<td>1.05</td>
<td>0.23</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>7266886</td>
<td>46.09</td>
<td>1.00</td>
<td>10.77</td>
</tr>
<tr>
<td>Furfuryl Alcohol</td>
<td>0</td>
<td>98.01</td>
<td>1.22</td>
<td>0</td>
</tr>
</tbody>
</table>
APPENDIX C

Calculation of copper from TG data

Calculation of the \( \text{Cu}^{1+} \), the \( \text{Cu}^0 \) 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 \( \text{Cu}^{2+} \rightarrow \text{Cu}^0 \)

- 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 = (12.37 x 36.34) / 100 mg.

\[
\text{Cu}^0_{\text{XRF}} = \frac{12.37 \times 36.34}{100} \text{mg} \quad (1)
\]

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

\[
(12.37 - 11.46) = 0.91 \text{ mg of oxygen} = 0.057 \text{ mmol of oxygen}
\]

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

\[
= 0.057 \text{ mmol of copper metal} = 3.62 \text{ mg of copper metal} \quad (2)
\]

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

\[
\text{Cuprous chromite content} = \frac{4.50 - 3.62}{\text{mg}} = 0.88 \text{ mg} \quad (3)
\]
APPENDIX D
Calculation of copper metal active site on catalyst

The weight of catalyst used = \( w \) g.
Area of N\(_2\)O peak after adsorption = \( A \) unit.
Average area of 50 \( \mu \)l. standard N\(_2\)O peak = \( B \) unit.
Amounts of N\(_2\)O adsorbed on catalyst = \( \sum (B - A) \) unit.
Volume of N\(_2\)O adsorbed on catalyst = \( \frac{\sum (B - A)}{B} \times 50 \) \( \mu \)l.
Volume of gas 1 mole at 30 \( ^\circ \)C = 24.86\( \times \)10\(^6\) \( \mu \)l.
Mole of N\(_2\)O adsorbed on catalyst (mole) = \( \left[ \frac{\sum (B - A)}{B} \times \left( \frac{50}{24.86 \times 10^6} \right) \right] \)

1 mole is 6.02\( \times \)10\(^{23}\) molecule
Then, Molecule of N\(_2\)O adsorbed on catalyst
\( = 2.01 \times 10^{-6} \times \left[ \frac{\sum (B - A)}{B} \right] \times 6.02 \times 10^{23} \) molecules

1 molecule of N\(_2\)O reacts with 2 molecules of copper metal as the equation

\[ 2\text{Cu}^0 + \text{N}_2\text{O} \rightarrow \text{N}_2 + (\text{Cu}-0-\text{Cu}) \]

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