STRUCTURE-ACTIVITY CORRELATIONS OF Cu/ZnO CATALYSTS DERIVED FROM DIFFERENT PRECURSORS AS A FUNCTION OF AGING

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By

ERNEE NORYANA BINTI MUHAMAD

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für meine Familie..

"…… a happy ending story"

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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February 2006

Chairman : Associate Professor Dr. Irmawati Ramli, PhD

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Structural modifications of Cu/ZnO catalysts for methanol steam reforming (MSR) have been investigated as a function of precipitate aging in the catalyst preparation process. Freshly precipitated Cu,Zn-hydroxycarbonate precursor (HC) and Cu,Zn-hydroxynitrate precursor (HN) were aged in their mother liquor for 120 min followed by washing, drying, calcination and reduction. The characteristics of the precursors before and after aging were determined by means of TG/MS, XRD, and SEM. Generally, more pronounced aging effect was observed for HC precursor (reference catalyst) while no significant effect of aging was observed for HN precursor.

In order to determine the microstructural changes as a function of aging, the bulk structure of the Cu/ZnO catalysts was investigated by in-situ XRD, XAS, ^{63}Cu NMR and HRTEM. The observed increase in the activity of the catalysts prepared by HC aging coincides with a decrease in copper crystallite size (i.e. an increase in Cu surface area) and an increase in the microstrain in the copper clusters presumably because of the improved interface between Cu and ZnO in comparison to the HN

prepared catalysts. Aging of the HN precursors results in large, separated and less strained Cu and ZnO particle with an inferior catalytic activity compared to aging of the HC precursors.

An increase in catalytic activity of HN and HC was observed significantly after temporary addition of oxygen was done to the feed mixture. The higher catalytic activity does not correlate with an increase in copper surface area, microstrain or oxygen in copper cluster (Cu-EXAFS), but due to slight changes of the catalyst in the medium range order of Cu and ZnO in XAS analysis. Furthermore, the HRTEM and ^{63}Cu NMR investigations revealed that the copper particles get more sintered resulting in less interfacial contact of Cu to ZnO as was observed after the O_2 pulse. Based on these comparative investigations, a structural model of the active catalyst as a function of aging was proposed for the HN preparative route.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PERKAITAN ANTARA STRUKTUR-AKTIVITI MANGKIN Cu/ZnO YANG DIHASILKAN DARIPADA PREKURSOR YANG BERBEZA SEBAGAI FUNGSI PENUAAN

Oleh

ERNEE NORYANA BINTI MUHAMAD

Febuari 2006

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Kajian ke atas modifikasi struktur mangkin Cu/ZnO bagi proses pembentukan semula stim metanol (MSR) telah dilakukan sebagai fungsi masa penuaan. Mendakan prekursor Cu,Zn-hidroksikarbonat (HC) dan Cu,Zn-hidroksinitrat (HN) telah dimatangkan di dalam cecair bahan tindakbalas selama 120 minit dan diikuti dengan proses pembasuhan, pengeringan, pengkalsinan dan penurunan. Teknik TG/MS, XRD dan SEM telah digunakan untuk mencirikan prekursor-prekursor sebelum dan selepas masa penuaan tersebut. Secara keseluruhannya, kesan penuaan yang ketara telah diperhatikan ke atas prekursor HC (mangkin rujukan) manakala tiada perubahan yang sangat ketara dapat diperhatikan dari prekursor HN.

Bagi menentukan kesan modifikasi mikrostruktur sebagai fungsi masa penuaan, struktur pukal mangkin Cu/ZnO telah dikaji secara in-situ XRD, in-situ XAS, ^{63}Cu NMR dan HRTEM. Hasil daripada kajian menunjukkan peningkatan di dalam aktiviti mangkin yang dihasilkan dari prekursor HC adalah sejajar dengan faktor penurunan saiz kristal kuprum (iaitu peningkatan luas permukaan kuprum) dan peningkatan daya

mikro regangan di dalam kekisi kuprum yang disebabkan oleh peningkatan antara muka Cu dan ZnO. Manakala penuaan prekursor HN menghasilkan prekursor yang bersaiz besar, terpisah dan kurang daya regangan antara partikel Cu dan ZnO. Ini menyebabkan kadar aktiviti yang lebih rendah bagi mangkin Cu/ZnO yang dihasilkan melalui proses penuaan prekursor HN berbanding HC.

Peningkatan yang ketara dalam aktiviti mangkin Cu/ZnO bagi HC dan HN dapat diperhatikan selepas penambahan sementara oksigen ke dalam bahan suapan. Peningkatan aktiviti yang tinggi ini didapati tidak berkaitan dengan peningkatan luas permukaan kuprum, daya mikro regangan atau oksigen yang terdapat di dalam susunan gabungan atom – atom kuprum (Cu-EXAFS), tetapi adalah disebabkan oleh sedikit perubahan yang berlaku di antara jarak pertengahan Cu dan ZnO seperti yang diperhatikan di dalam analysis XAS. Tambahan pula, kajian HRTEM dan ^{63}Cu NMR menunjukan partikel kuprum menjadi semakin besar yang menyebabkan kurang interaksi antara muka Cu dan ZnO selepas penambahan sementara oksigen. Oleh itu, berdasarkan kajian ini, satu model struktur bahan mangkin aktif yang dihasilkan dari proses penuaan HN telah dicadangkan.

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I certify an Examination Committee met on 10th February 2006 to conduct the final examination of Ernee Noryana Binti Muhamad on her Master of Science thesis entitled "Structure-Activity Correlations of Cu/ZnO Catalysts Derived from Different Precursors As A Function of Aging" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

_____

ERNEE NORYANA BINTI MUHAMAD

Date : 20th March 2006

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LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetric
DWF	Debye-Waller factor
EDX	Energy Dispersive X-ray
EXAFS	Extended X-ray Absorption Fine Structure
FWHM	Full width at half maximum
HC	Hydroxycarbonate
HN	Hydroxynitrate
HRTEM	High Resolution Transmission Electron Microscopy
ICDD-PDS	International Centre for Diffraction Data – Powder Diffraction Standard
ICSD	Inorganic Crystal Structure Database
IUPAC	International Union of Pure and Applied Chemistry
MS	Mass Spectrometer
MSR	Methanol Steam Reforming
NMR	Nuclear Magnetic Resonance
RDF	Radial Distribution Function
RFC	Reactive Frontal Chromatography
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TG	Thermogravimetric
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1

INTRODUCTION

In general, this chapter represents some background of the well known Cu-based catalysts especially Cu/ZnO which is related to this study. Towards the end of this chapter, the application of the catalysts in hydrogen production particularly in Methanol Steam Reforming (MSR) reaction is described.

1.1 Cu/ZnO Catalyst

Copper catalysts are widely used for a variety of selective hydrogenation and dehydrogenation processes and it has been known at least since the 1920's. For instance, Cu/ZnO catalyst formulation is well known for low-pressure methanol synthesis [1,2] and low-temperature water-gas shift reaction (WGS) [3]. Recently a lot of studies discussed its application for the production of hydrogen from methanol by steam reforming and/or partial oxidation reaction especially for fuel cell application [4,5]. Cu/ZnO catalysts also have been used in hydrogenation of carbon monoxide [6-8], carbon dioxide [9], unsaturated hydrocarbons and certain reactions of amines [10].

The performance of these catalysts is sensitive to the preparation methods, the choice of oxide phase used in them and the presence of small amounts of dopants such as alkali and alkaline earth compounds as well as of Group VIII metal. Most of the published studies reported the use of simple copper/zinc binary system as the

precursors of these catalysts rather than three or four components in one system. The implication of more components in one system makes the system much more complicated to understand and because of that, most of the extensive publications on these catalysts have concentrated on the simple copper/zinc oxide binary system. The incorporation of zinc oxide into the copper catalyst is of primary importance in making and maintaining a good dispersion of copper metal crystallites and also prevents the copper particles from sintering [1]. Moreover, the high activity of this particular system is believed to result from a strong interaction of the two phases (Cu/ZnO) leading to a specific quality of the active copper material which is a subject under discussion. In fact, this is widely documented in several reviews [10-13] which brought into evidences that controversial issues are yet lively.

However, there are some controversies respective to the roles of Cu and ZnO that make this system interesting for investigations (i.e. the effects of structural and chemical promotion). Although the process (e.g. methanol synthesis) involving copper-based catalysts are well established industrially, debates still exist as to:

i. the influence of the preparation method
ii. the role of the reduced copper species on the surface of catalysts
iii. the identification of the active sites
iv. role of ZnO and Al_2O_3 in the catalytic process (as Al_2O_3 is normally added to Cu/ZnO catalyst for industry)

Cu-Zn-Al oxide catalysts have attracted great interest in the last decade after the the first paper was published by Klier [2]. Klier suggested that Cu is incorporated in the

ZnO phase on interstitial and substitutional sites, assuming three possible valence states Cu^0, Cu^+ and Cu^{2+}. Klier's proposals were made within the framework of bulk defect equilibria based on scanning transmission electron microscopy (STM), X-ray data and optical spectra [10]. He found that the defect structure and therefore the bulk of the catalyst determine the catalytic activity.

The formation of Cu^+ has also been reported by several authors [13,14]. In particular, Fujitani *et al*. [14] in their study on the interaction between support and metal catalyst suggested that the active component was not only Cu^+ but also Cu^0. Thus the support may play the role to control the Cu^+/Cu^0 ratio on which the catalytic activity depends. Other pronounces support effect was found by Bartley and Burch [15] when different copper catalysts are tested for the methanol synthesis from both CO/H_2 and CO_2/H_2 mixtures. In particular, Burch *et al*. [15,16] and Spencer [17] have proposed that the role of ZnO is to act as a reservoir for hydrogen and to promote the hydrogen spill-over.

In other point of view, the morphology effect, proposed by Yoshihara and Campbell [18], Ovesen *et al*. [19], Hadden *et al*. [20], and Topsøe and Topsøe [21], in which the morphology of copper particles on a ZnO support is responsible for the effect of ZnO upon the methanol synthesis, is also a controversial issue. The view, so far described, is further complicated by the fact that, depending on the experimental condition and on the catalyst preparation history, the formation of a Cu-Zn alloy may also occur [22,23]. As a result, this makes the system more complicated to understand, and hence point a great interest for further investigation.

Recent works carried out by Kniep *et al*. [24,25] and Günter *et al*. [26,27] show that the methanol synthesis and methanol steam reforming activity for binary Cu/ZnO catalysts can be related to the microstrain in copper particles. Extensive in-situ XRD analysis, for determining the microstructural strain in both Cu and ZnO, clearly indicates that the specific Cu surface area of Cu/ZnO samples alone cannot unequivocally account for the observed methanol production rates of the systems. Structural defects of Cu resulting from presence of ZnO in Cu metal, incomplete reduction or epitaxial orientation to ZnO are believed to cause strain which modifies the Cu surface area and, thus, influence the catalytic activity.

In contrast from the idea that ZnO also plays an important role in the catalytic activity of Cu/ZnO catalysts (i.e. methanol synthesis), a contradiction appeared when, Chinchen *et al*. [1,12] reported that the methanol synthesis reactions occur exclusively on the surface of metallic copper and ZnO acts as carrier to prevent sintering of the copper particles. Therefore, ZnO has no special role towards copper in the synthesis of methanol.

In summary, the complexity in understanding the synergetic effect between copper and zinc oxide, the active states of copper and the effects of ZnO are still subjected to some debates, hence a great interest in research area. The origin for all of these issues are the knowledge-based of the relationships between catalytic activity, surface structure and bulk structure in order to come to a rational catalyst design. Therefore, a better understanding of the precursor phases is needed since precursor structure plays a unique role in determining the interdispersion and the activity of the final catalysts.

Different types of mechanism and conditions have been used in the preparation of catalyst precursor resulting in the formation of various types of crystalline phases.

1.2 The Hydrogen Production From Methanol

Hydrogen (H_2) is used in vast quantities in the chemical industry for production of various bulk, fine and special chemicals, in food processing, for fuel production in refineries, in the steel industry and also directly as a fuel. The largest portion of hydrogen in the world is manufactured at ammonia production units and consumed on site in the process. Other large consumers are the processes for methanol and hydrogen peroxide production.

Hydrogen can be produced from both fossil and renewable sources. The largest quantities are manufactured from natural gas. However, in the future it can be produced by electrolysis of water using solar energy. In this case it can clearly be viewed as a sustainable source of energy. Hydrogen is the cleanest fuel available and ideally produces only water during combustion, which makes it an interesting alternative to decrease the anthropogenic emission of carbon dioxide (CO_2). The most important driving force for using hydrogen in automotive applications is the potential of obtaining low emissions of hazardous compounds. Hydrogen can be used in internal combustion engines or in fuel cell engines.

However, storing hydrogen on board a vehicle poses many concerns regarding safety and handling and can affect customer acceptance in a negative way. Hydrogen can be stored as a compressed gas at high pressures, as liquid at cryogenic temperature, in