# STUDY ON COPPER INCORPORATED MESOPOROUS SILICA SBA-15 FOR $N_2O$ CATALYTIC DECOMPOSITION

MOHD HAIZAL MOHD HUSIN

Thesis submitted in fulfillment of requirements
for the award of degree of
Doctor of Philosophy

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

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## TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

## LIST OF ABBREVIATIONS

| | |
|---|---|
| $N_2O$ | nitrous oxide |
| Cu | copper |
| Si | silica |
| SBA-15 | Santa Barbara acids - 15 |
| HCl | hydrochloric acid |
| TEOS | tetraethyl orthosilicate |
| HMTA | hexamethylenetetramine |
| $CH_4$ | methane |
| XRD | X-ray diffraction |
| TEM | Transmission Electron Microscopy |
| SEM | Scanning Electron Microscopy |
| FT-IR | Fourier transform infrared spectroscopy |
| TGA | Thermogravimetric analysis |
| AAS | Atomic absorption spectroscopy |
| TPR | Temperature programmed reduction |
| EDX | Energy-dispersive X-ray |
| XPS | X-ray photoelectron spectroscopy |
| W/F | Weight of catalysts / gas flowrate (g s/mL) |
| PP bottle | polypropylene bottle |

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## ABSTRACT

Nitrous oxide ($N_2O$) is an environmental pollutant because it is a relatively strong greenhouse effect gas and contributes towards the destruction of ozone in the stratosphere. Direct decomposition of $N_2O$ by catalysts represents one of the potential solutions to minimize $N_2O$ emissions. This research focuses on Cu incorporation into SBA-15 mesoporous silica by pH modification method using hexamethylenetetramine (HMTA) as an internal pH-modifier and its potential use as a catalyst for $N_2O$ decomposition. The effect of acidity on SBA-15 preparation through different initial HCl concentration and the addition of HMTA as pH modifier were investigated. The SBA-15 formed well-ordered hexagonal mesoporous structure at high acidity (2.0 M) and poor ordered hexagonal pore structure at low acidity condition (0.005 M). It was found that under moderate acidic condition (0.1 M HCl) with addition of HMTA (HMTA:Si molar ratio 1:10), well-ordered hexagonal mesoporous SBA-15 could be produced. Meanwhile, copper was chosen for further studies on metal incorporation of SBA-15 (M/SBA-15) because Cu-containing SBA-15 has the highest catalytic activity for $N_2O$ decomposition compared to that of other first row transition metals impregnated on SBA-15. Copper incorporated mesoporous silica (Cu-SBA-15) has been successfully prepared by direct synthesis under medium acidic condition with addition of HMTA as a pH modifier. The Cu/SBA-15 produced were characterised using XRD, $N_2$ adsorption-desorption, TEM, SEM, FT-IR, UV-vis, XPS and TPR. The results indicate that Cu was mainly incorporated into the framework of SBA-15. The unit-cell, surface area, pore volume and wall thickness increased after the incorporation of the copper ions in SBA-15. HMTA plays a very important role to increase internal pH in order to introduce copper into the framework of SBA-15 silica. Cu loading on Cu/SBA-15 determined using AAS is almost the same to the initial Cu amount, when the pH value is above isoelectronic of silica (pH=2) due to addition of HMTA. Higher amount of HMTA, however, lead to the destruction of SBA-15 structure. Compared with Cu/SBA-15 impregnation method, Cu/SBA-15 prepared through pH modification method shows much higher activity for $N_2O$ catalytic decomposition due to 80% $N_2O$ conversion at 550 °C and reached 100% at 600 °C. The activation energy for the reaction catalysed by Cu/SBA-15 prepared through pH modification method is 91.9 – 121.6 kJ/mol. This is much lower compared to that catalysed by Cu/SBA-15 prepared though impregnation, that is in the range between 148.5 – 173.9 kJ/mol. Cu/SBA-15 incorporated sample also has higher activity due catalytic activity started at 300 °C and reaches more 80% conversion at 500 °C for catalytic reduction of $N_2O$ by $CH_4$.

## ABSTRAK

Nitrus oksida ($N_2O$) adalah bahan pencemar alam sekitar kerana ia merupakan gas kesan rumah hijau yang agak kuat dan boleh menyebabkan kemusnahan ozon dalam stratosfera. Penguraian langsung $N_2O$ menggunakan kaedah pemangkin merupakan salah satu penyelesaian yang berpotensi meminimumkan pelepasan $N_2O$. Kajian ini menumpu kepada penyediaan mangkin Cu yang digabungkan dengan SBA-15 silika berliang meso melalui sintesis langsung secara pengubahsuaian pH dengan menggunakan heksametiltetramin (HMTA) sebagai pengubah pH dalaman dan potensi penggunaan bahan ini sebagai mangkin bagi tindak balas penguraian $N_2O$. Kajian kesan keasidan dalam penyediaan SBA-15 berdasarkan perbezaan kepekatan awalan larutan HCl dan penambahan HMTA sebagai pH diubahsuai telah dilakukan. Bahan SBA-15 yang terhasil menunjukkan struktur heksagon berliang meso yang teratur pada keasidan yang tinggi (2.0 M HCl) manakala struktur liang heksagon yang tidak teratur terbentuk pada keadaan keasidan yang rendah (0.005 M HCl). Hasil kajian menunjukkan keadaan berasid sederhana (0.1 M HCl) dengan penambahan HMTA (HMTA: Si nisbah molar 1:10) mampu menghasilkan struktur heksagon berliang meso yang teratur. Sementara itu, kuprum telah dipilih untuk kajian lanjutan terhadap logam digabungkan dengan SBA-15 (M/SBA-15). Ini kerana sampel SBA-15 yang mengandungi Cu (Cu-SBA-15) menunjukkan aktiviti paling aktif dalam tindak balas penguraian $N_2O$ berbanding sampel yang mengandungi logam peralihan baris pertama yang lain yang telah disediakan melalui kaedah pengisitepuan. Kuprum yang bergabung dengan silika berliang meso (Cu/SBA-15) telah dihasilkan menggunakan keadaan berasid sederhana berserta dengan penambahan HMTA sebagai agen pengubah pH. Sampel Cu/SBA-15 yang terhasil dicirikan menggunakan XRD, $N_2$ penjerapan-penyahjerapan, TEM, SEM, FT-IR, UV-vis, XPS dan TPR. Dapatan analisa menunjukkan bahawa atom Cu telah bergabung ke dalam kerangka silika SBA-15. Unit-sel, luas permukaan, isi padu liang dan ketebalan dinding meningkat selepas penggabungan ion kuprum dalam SBA-15. HMTA memainkan peranan yang amat penting untuk meningkatkan pH dalaman larutan supaya dapat memasukkan kuprum ke dalam rangka silika SBA-15. Muatan Cu yang diukur menggunakan AAS menunjukkan kuantiti Cu yang hampir sama dengan kuantiti awal, apabila nilai pH melebihi titik isoelektronik silika (pH = 2) melalui penambahan HMTA. Namun begitu penambahan berlebihan HMTA membawa kepada kemusnahan struktur SBA-15. Dalam perbandingan, dengan sampel Cu-SBA-15 yang disediakan melalui kaedah pengisitepuan, sampel Cu/SBA-15 yang disediakan melalui pengubahan pH adalah lebih aktif bagi aktiviti penguraian bermangkin $N_2O$ berdasarkan 80% penukaran $N_2O$ pada suhu 550 °C dan mencapai 100% pada suhu 600 °C. Tenaga pengaktifan bagi tindak balas yang dimangkinkan Cu/SBA-15 kaedah penggabungan adalah 91.9 - 121.6 kJ/mol iaitu lebih rendah berbanding dengan nilai bagi Cu/SBA-15 kaedah pengisitepuan iaitu di antara 148.5 - 173.9 kJ/mol. Cu/SBA-15 disediakan dengan menggunakan kaedah pengubahsuaian pH juga telah menunjukkan aktiviti pemangkinan yang lebih tinggi berdasarkan aktiviti pemangkinan yang bermula pada suhu 300 °C dan mencapai lebih daripada 80% penukaran pada suhu 500 °C bagi tindak balas penurunan $N_2O$ dengan kehadiran $CH_4$.

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