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

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Thesis submitted in fulfillment of requirements
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DEDICATION

I dedicate this dissertation to my family and many friends. My deep feeling of gratitude is to my loving parents, Haji Husin and Hajah Zainab, whose words of encouragement always motivate me to work harder. *Al-fatihah* to my late wife, Rozieyati, without whose caring supports it would not have been possible for me to complete this work during her life. To my loving children, Fathin, Hakim, Arief, and Hafiz thank you for your patience and understanding.

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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, FTIR, 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, FTIR, 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. Dengan kehadiran CH_4, Cu/SBA-15 disediakan dengan menggunakan kaedah pengubahsuaian pH telah menunjukkan aktiviti pemangkinan yang lebih tinggi. Penguraian lebih daripada 80% penukaran dicapai pada 500 °C bagi tindak balas penurunan N_2O dengan CH_4.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES