DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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(Signature of candidate)

…… day of …….2005

ABSTRACT

The main aim of this thesis has been to study the way in which Fe(III) and Co(II) incorporation into Si-MCM-41 synthesis gels affects the properties of the unmodified material. Another aim was to investigate the influence of these hetero-atoms on the dispersion and particle size distribution as well as the catalytic activity of supported Au nanoparticles in the CO oxidation reaction.

Si-MCM-41 has been successfully synthesized in this work using mixtures containing CTAB as a structure-directing agent (SDA) and water-glass as a SiO_2 source. Replacement of water-glass with pre-calcined Si-MCM-41 for SiO_2 source in the secondary synthesis step has produced Si-MCM-41 with improved structural properties (XRD, HRTEM and Raman spectroscopy), including restructured and more crystalline pore walls (Raman spectroscopy).

The conventional shortcomings of Si-MCM-41 as a support for catalytically-active (transition) metal components such as low hydrothermal stability, low PZC, lack of cation exchange capacity and no reducibility have been partially addressed by modification with Fe(III) and Co(II). The premodification was achieved both during framework synthesis and after synthesis by the incipient wetness impregnation (IWI) method. As opposed to the one-pot synthesis of metal-containing derivatives, the IWI method gave materials with high metal loadings and maximal retention of the properties of pristine Si-MCM-41. On the other hand, metal incorporation during synthesis to a loading of ~8.8 wt% using aqueous solutions of metal precursors showed some collapse of the mesostructure. Consequently methods were sought to incorporate this amount of metal (and up to double, i.e., 16 wt%) with maximal retention of the MCM-41 characteristics. These methods included (i) using Si-MCM-41 as a SiO_2 source, (ii) dissolving the metal precursors in an acid solution before inclusion into the synthesis gel, and (iii) using freshly precipitated alkali slurries of the metal precursors. The first method produced a highly ordered 16wt% Fe-MCM-41 material with excellent reducibility (TPR showed three well-resolved peaks) and pore-wall structure (Raman spe-

ctroscopy). Like the aqueous route, the acid-mediated metal incorporation route did not produce ordered materials at metal contents of ~16 wt%. The base precipitate route produced highly ordered composite materials up to 16 wt% metal content, with characteristics similar to those of Si-MCM-41 (XRD, BET and HRTEM), although some metal phases were observed as a separate phase on the SiO_2 surface. Thus, metal-containing MCM-41 materials could be obtained with conservation of MCM-41 mesoporosity. Raman spectroscopic studies have shown that the effect of transition metal incorporation in MCM-41-type materials is to strengthen the pore walls (shift of Si-O-Si peaks to higher frequencies), while TPR studies revealed that the essentially neutral framework of Si-MCM-41 could be rendered reducible by transition metal incorporation.

Gold-containing mesoporous nanocomposites were prepared by both direct synthesis and post-synthetically. Catalysts prepared by direct hydrothermal synthesis were always accompanied by formation of large Au particles because of the need to calcine the materials at 500 ^{o}C in order to remove the occluded surfactant template. The presence of transition metal components in Me-MCM-41 (Me = Fe and Co) has been found to play a significant role in the particle size distribution and also the dispersion of Au nanoparticles when these materials were used as supports. In general, a base metal-containing support was found to produce smaller Au nanoparticles than the corresponding siliceous support. It has been proposed that the transition metal components serve as anchoring or nucleation sites for the Au nanoparticles, which are likely to sinter during calcination. The anchoring sites thus retard the surface mobility of Au at calcination temperatures above their $T_{Tammann}$.

The use of the Au/Me-MCM-41 materials as catalysts in the CO oxidation reaction has led to the following observations: (i) catalyst on metal-containing supports showed better activity than those on Si-MCM-41, probably due to the induced reducibility in metal-MCM-41, (ii) catalysts prepared by direct synthesis showed inferior activity owing to large Au particles, (iii) increasing Au content improves the catalytic performance, (iv) increasing the Fe content of the support

at constant Au improves the catalytic performance, and (v) changing the base metal component of the support from Fe to Co led to a significant improvement in catalytic activity. The similarity of the apparent activation energies (E_a) for the 5 wt% Au-containing 5 wt% Fe- and 5 wt% Co-MCM-41 suggested that the difference in catalytic activity is associated with the number of active sites possessed by each catalyst system. The observed order of catalytic activity of these 5 wt% Au-containing systems in terms of the support type is: Co-MCM-41 > Fe-MCM-41 > Si-MCM-41. This was further supported by the average Au particle size, which, in terms of the support, followed the order Co-MCM-41 < Fe-MCM-41 < Si-MCM-41. Thus, metal-support interactions between Au and MCM-41 have been enhanced by introducing Fe(III) and Co(II), which also induced framework charge, ion exchange capacity (IEC) and reducibility in the neutral siliceous support.

DEDICATION

This thesis is dedicated to the memory of my brother

Malesela Simon Mokhonoana

1970-2003

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry
BET	Brunnauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BMS	Bimodal silica
CIT-5	California Institute of Technology number 5
CO	Carbon monoxide
CMC	Critical micelle concentration
CMK	Carbon Mesostructures at KAIST
CP	Coprecipitation
COHb	Carboxyhemoglobin
CTAB	Cetyltrimethylammonium bromide
CTMAOH	Cetyltrimethylammonium hydroxide
CVD	Chemical vapour deposition
DAM-1	Dallas Amorphous Material # 1
DP	Deposition-precipitation
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
DRS UV-Vis	Diffuse Reflectance Spectroscopy (UV-Vis)
DTA	Differential Thermal Analysis
EDS	Energy-dispersive X-ray spectrometry
EDTA	Ethylenediamine tetraacetate
EDX	Energy-dispersive X-ray Analysis
EHC	Electrically heated catalyst
en	Ethylenediamine

EPA	Environmental Protection Agency
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance
EXAFS	Extended X-ray Absorption Fine Structure
FMMS	Functionalized Monolayers on Mesoporous Supports
FMS-16	Folded Sheet Mesoporous material, 16 designates a 16 C surfactant template
(FT)IR	Fourier Transform Infrared
FTS	Fischer-Tropsch Synthesis
g	Lande factor or gyromagnetic ratio
HCs	Hydrocarbons
HDP	Homogeneous deposition-precipitation
HDS	Hydrodesulphurization
HMS	Hexagonal mesoporous silica
(HR)TEM	High resolution transmission electron microscopy
(HR)SEM	High Resolution Scanning Electron Microscopy
ICP	Inductively-coupled plasma
IEC	Ion exchange capacity
IEP	Isoelectric point
IUPAC	International Union of Pure and Applied Chemistry
IWI	Incipient wetness impregnation
KAIST	Korea Advanced Institute of Science and Technology
LAT	Ligand-assisted templating
LCT	Liquid-crystal templating
MCM	Mobil's Composition of Matter

MFI	Mobil Five
MSU-G, -X	Michigan state university-G or X
MTS	Micelle-templated silica
NOx	Nitrogen oxides
NMR	Nuclear Magnetic Resonance
O_2Hb	Oxyhemoglobin
OMS	Ordered Mesoporous Silica
ORMOSILs	Organically-Modified Silicas
PE	Polyethylene
PP	Polypropylene
PGMs	Platinum Group Metals
PHCs	Porous Clay Heterostructures
PILCs	Pillared Clays
PNNL	Pacific Northwest National Laboratory
PSD	Particle size distribution
PVD	Physical Vapour Deposition
PZC	Point of Zero Charge
RS	Raman spectroscopy
SAMMS	Self-Assembled Monolayers on Mesoporous Supports
SBA	Santa Barbara
SCTA	Sample Controlled Thermal Analysis
SDA	Structure-directing agent
SFE	Supercritical Fluid Extraction
SIB	Ship-in-a-bottle

SMSIs	Strong metal-support interactions
SV	Space velocity
T_{50}	Light-off temperature
TBHP	Tertiarybutylhydroperoxide
TCD	Thermal conductivity detector
TEA	Triethanolamine
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
TIE	Template ion-exchange
TMCS	Trimethyl chlorosilane
TMMPS	Tris(methoxy)mercaptopropylsilane
TMOS	Tetramethyl orthosilicate
TMS-1	Transition-metal mesoporous molecular sieves
TOS	Time on stream
TPGS	α-Tocopheryl polyethylyne glycol 1000 succinate
TPR	Temperature-Programmed Reduction
TUD-1	Technical University of Delft # 1
TWC	Three-way catalyst
USY	Ultrastable Y zeolite
UTD	University of Texas at Dallas
UV-Vis	Ultraviolet and Visible spectrophotometry
VAM	Vinyl acetate monomer
VPI-5	Virginia Polytechnic Institute # 5
XANES	X-ray Absorption Near-Edge Spectroscopy

XPS	X-ray Photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
WGC	World Gold Council
WGS	Water-gas shift
ZSM-5	Zeolite Saucony Mobil # 5

SCOPE AND CONTENT OF THE THESIS

Pure silica has a neutral framework in which the Si^{4+} is tetrahedrally bonded to four bridging O atoms, and consequently cannot show cation exchange properties. Metal components can be introduced into the silica to induce cation exchange capacity, redox properties and nucleation sites for the growth or development of metal nanoparticles. This thesis examines Si-MCM-41 and metal-containing variants, i.e., Fe- and Co-MCM-41 as supports for Au catalysts. Au catalysts have recently gained popularity because of their ability to catalyze a wide range of reactions at low temperature.

Chapter 1 covers the literature on inorganic porous materials, with particular reference to addressing the issue of shape selectivity in microporous materials and improving the surface area of the resulting materials. The survey includes a discussion of the first templated synthesis of a mesoporous family of zeolitic materials, designated M41S, to which belong a range of interesting materials such as MCM-41, MCM-48 and MCM-50. The survey includes the synthesis, characterization, catalytic and technical applications of the Si-MCM-41 materials.

Chapter 2 presents the results of the work carried out on pure silica MCM-41 materials that were prepared in this thesis. Covered in this study are the role of various synthetic variables (i.e. optimization of the synthesis conditions) that lead to a highly ordered Si-MCM-41 with improved structural integrity, as well as enhanced thermal and hydrothermal stability. These variables include the crystallization time and reaction temperature, the synthesis gel composition (SiO_2/CTAB molar ratio and the water content), inclusion of additives as co-templates in the synthesis gel, the pH of the synthesis gel, and the nature of the silica source. These materials were characterized using X-ray diffraction (XRD) to assess structural integrity, High Resolution Transmission Electron Microscopy (HRTEM) to evaluate the microstructure of the pores, and Brunauer-Emmett-Teller (BET) surface area analysis. Conclusions at the end of the chapter are based on the findings of these characterization techniques. The optimized Si-MCM-41

materials so obtained were used as benchmarks in the synthesis of base metal-containing mesoporous MCM-41 materials described in **chapter 3**.

Chapter 3 focuses on Fe- and Co-MCM-41 materials, with particular emphasis on their synthesis and characterization. The metal precursors were introduced at various stages of the synthesis, and in various forms (i.e., as solutions or as freshly-prepared gelatinous precipitates). The synthesis was carried out under both ambient and hydrothermal temperature conditions, and the amount of the heterometal that was incorporated into the mesostructure with structural retention has been optimized. Incipient wetness impregnation was also used for the synthesis of Fe- and Co-MCM-41 derivatives. Physicochemical characterization of the resulting materials included XRD, HRTEM, BET, temperature programmed reduction (TPR), ESR spectroscopy and Raman spectroscopy. Conclusions are also included at the end of this chapter, based on the observations from these characterization techniques. These heteroatom-containing mesoporous materials, with their associated redox and cation exchange properties, were used as supports in the preparation of supported Au catalysts discussed in **chapter 4**.

Chapter 4 focuses on an investigation of different methods used to prepare supported gold nanoparticles. These methods range from deposition-precipitation, co-deposition-precipitation (both Fe(III) or Co(II) and Au(III) deposited simultaneously on Si-MCM-41), co-precipitation of Au(III) with either Fe(III) or Co(II) in the presence of a preformed Si-MCM-41, or direct one-pot hydrothermal synthesis where the metal components form part of the initial synthesis gel. Characterization of the final materials involved XRD, HRTEM, BET and EDS techniques. These materials and other related materials were evaluated for catalytic activity as described in **chapter 5**.

Chapter 5 describes the catalytic properties of the Au/Me-MCM-41 materials, with Me = Si, Fe and Co, in the reaction:

$$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g), \qquad \Delta G_{298\ K} = -257.1\ kJ/mol$$

The results are interpreted in terms of the light-off temperature, i.e., the temperature at which the catalyst starts converting carbon monoxide into carbon dioxide. Conclusions based on the observed catalytic behaviour are found at the end of the chapter.

Chapter 6 presents the summary of the work done, and the main conclusions of the study entailed in this thesis.