

PHYSICO-CHEMICAL CHARACTERISTICS OF MIXED
METAL OXIDES USED IN NUCLEAR TECHNOLOGY

A THESIS

Submitted to
Chemistry Department, Faculty of Science,
Ain Shams University

BY
TAREK KHALIL KHALIL KHALIL
B.Sc.

5-6.72
T.K

In Partial Fulfilment of
The Requirements for
The Degree of Master of Science
(Chemistry)



1988

27283



PHYSICO-CHEMICAL CHARACTERISTICS OF MIXED
METAL OXIDES USED IN NUCLEAR TECHNOLOGY

The Advisors:

Approved

1. Prof. Dr. Mohamed Abdel-Khalik Mohamed,
2. Prof. Dr. Hisham Fouad Aly, and
3. Prof. Dr. Farid Hosny Abou El-Nour.

Mohamed Abdel-Khalik Mohamed
Hisham Fouad Aly
Farid Hosny Abou El-Nour

Head of Chemistry Department

Nabila Massak

Prof. Dr. Nabila Massak *Genady*



Y

NOTE

Besides the work carried out in this thesis, the candidate has attended graduate courses for one year , covering the following topics :

1. Nuclear chemistry and its applications.
2. Solvent extraction and chromatography.
3. Spectroscopic applications of group theory.
4. Advanced polarography and corrosion.
5. Analytical chemistry (advanced instrumental analysis).
6. Computer science .
7. Inorganic reaction mechanisms.
8. Organometallic compounds.

He has successfully passed a written examination in these courses.

Prof. Dr. N. M. Guindy

Head of Chemistry Department,

Σ

TO
MY MOTHER, FATHER,
SISTER AND FIANCÉE.

ACKNOWLEDGEMENT

The author would like to express his sincere gratitude and appreciation to Prof. Dr. Mohamed Abdel-Khalik Mohamed, Professor of Physical Chemistry, Faculty of Science, Ain Shams University, for his supervision, continuous help and fruitful discussions throughout the course of this work.

Thanks are also due to Prof. Dr. Hisham Fouad M. Aly, Prof. of Nuclear Chemistry and Head of Hot Lab. Center, Atomic Energy Authority, not only for his supervision but also for his continuous encouragement and fruitful discussions during the progress of this study.

The author is grateful for Prof. Dr. Farid Hosny Abou El-Nour, Prof. of Physical Chemistry, Nuclear Chemistry Department, Nuclear Research Center, Atomic Energy Authority, not only for suggesting and supervising this work, but also for the significant encouragement and constructive criticism of the manuscript.

Thanks are also due to Associate Prof. Dr. Ahmed Sayed Abdel-Halim, Metallurgy Department, Nuclear Research Center, A.E.A., for his co-supervision during this study.

Thanks are also to Dr. Nabil Arafat Belacy, lecturer of Physical Chemistry, Nuclear Chemistry Department, N.R.C., A.E.A., for continuous help and helpful guiding throughout the scope of the work.

7

I would also like to thank Eng. Yousry Kamal Afifi,
Assistant lecturer, Metallurgy Department, N.R.C., A.E.A.,
for his help.

The auther is specially grateful to the members of the
Nuclear Chemistry Department, Hot Lab. Center and Metallur-
gy Department, A.E.A. for their valuable assistance and co-
operation.

CONTENTS

	Page
Aim of the Work	i

CHAPTER I

DEVELOPMENT OF NICKEL PROMOTED WITH METAL OXIDES
AS A CATALYST FOR THE ISOTOPIIC EXCHANGE OF
DEUTERIUM BETWEEN HYDROGEN AND WATER VAPOUR.

I.1.	Hydrogen/Deuterium Isotopic Exchange Reaction	1
I.2.	Promoted Nickel Catalysts	4
I.2.1.	Ni/Al ₂ O ₃ system	6
I.2.2.	Ni/Cr ₂ O ₃ system	6
I.2.3.	Miscellaneous nickel/metal oxide catalysts	7
I.2.4.	Ni/Cr ₂ O ₃ /Al ₂ O ₃ catalysts	9
I.2.5.	Ni/Cr ₂ O ₃ /MgO catalysts	9
I.2.6.	Ni/Cr ₂ O ₃ /ZrO ₂ catalysts	11
I.3.	Different Methods for Preparation of Nickel Catalysts Promoted with Metal Oxides	15
I.3.1.	Impregnation technique	15
I.3.2.	Co-precipitation technique	16
I.4.	Crystallite Lattice Parameters and Structure of Metal Oxide Promoters	18

^

Page

CHAPTER II

PREPARATION OF URANIUM DIOXIDE MICROSPHERES BY GELATION TECHNIQUES

II.	Sol-Gel and Gelation Processes	22
II.1.	Sol-Gel Processes	22
II.1.1.	Water extraction gelation	22
II.1.2.	External chemical gelation	26
II.1.3.	Internal chemical gelation	27
II.2.	Chemical Gelation Processes	28
II.2.1.	External gelation processes	29
II.2.2.	Internal gelation processes	31
II.2.2.1.	Hydrolysis process	31
II.3.	Thermal Treatment of Uranium Oxides ...	37
II.3.1.	Phase transfer of uranium oxides	37
II.3.2.	Reduction and sintering of uranium oxides	41

CHAPTER III

SURFACE CHARACTERISTICS OF METALS AND METAL OXIDES

III.1.	Surface Feature of Solids	48
III.2.	Adsorption of Gases on Solid Surface ..	49

	Page
III.3.	The BET-Equation 51
III.4.	Classification of Pore Sizes 56
III.5.	Analysis of Isotherms (t-plots) 59
III.6.	Porosity and Catalytic Activity 62

CHAPTER IV

EXPERIMENTAL AND RESULTS

PART 1

Preparation and Characterization of Nickel
Promoted with Chromia/Thoria as a Catalyst
for the H/D Isotopic Exchange Reaction
between Hydrogen and Water Vapour.

IV.1.1.	Preparation of Ni/Cr ₂ O ₃ /ThO ₂ catalysts. 64
IV.1.2.	H/D isotopic exchange over Ni/Cr ₂ O ₃ /ThO ₂ catalysts 65
IV.1.2.1.	Isotopic exchange apparatus 65
IV.1.2.2.	Catalytic activity measurements for H/D exchange 68
IV.1.3.	Surface area measurements 71
IV.1.3.1.	BET-apparatus 71
IV.1.3.2.	Measuring technique 73
IV.1.3.3.	Adsorption-desorption isotherms 74
IV.1.3.4.	Calculation of specific surface area ... 83

	Page
IV.1.3.5. Detection of micro- and meso pores (V_{1-t} plots)	84
IV.1.4. Hydrogen chemisorption measurements ..	94
IV.1.4.1. Surface area of supported nickel	94
IV.1.4.2. Degree of dispersion and average particle size	95
IV.1.5. Measurements of liquid phase catalytic activity	97
IV.1.6. Thermodynamics and rate equation	100
IV.1.7. Catalyst investigations	114
IV.1.7.1. X-Ray examination	114
IV.1.7.2. Thermal analysis	114

PART 2

Preparation and Characterization of Uranium Trioxide and Uranium Dioxide Microspheres by the Developed Internal Gelation Method (Hydrolysis Process).

IV.2.1. Experimental set-up and equipment for UO_3 production	115
IV.2.2. Preparation of UO_3 - and UO_2 microspheres	120
IV.2.3. Characterization of uranium oxide microspheres	128
IV.2.3.1. Density and porosity	128

	Page
IV.2.3.2. Surface area, total pore volume and pore radius measurements	139
IV.2.3.3. TGA and DTA measurements	195
IV.2.3.2.1 Determination of O/U-ratio	195
IV.2.3.3.2 DTA and TG behaviour of uranium oxide microspheres	199
IV.2.3.4. X-Ray diffraction measurements	203

CHAPTER V

DISCUSSION OF THE RESULTS

V.1. Ni/Cr ₂ O ₃ /ThO ₂ Catalysts for H/D Isoto- pic Exchange Reaction	204
V.1.1. Vapour phase activity	205
V.1.2. Liquid phase activity	207
V.1.3. Kinetic and thermodynamic behaviour ..	208
V.2. Uranium Oxide Microspheres	210
V.2.1. Effect of preparation conditions on density and porosity of UC ₃ microsphe- res	210
V.2.2. Effect of preparation conditions on surface area, total pore volume and pore radius of UC ₃ microspheres	212
V.2.3. Effect of reduction temperature and time on the density of UC ₂ microspheres.	213

	Page
V.2.4. Effect of preparation conditions on density and porosity of UO ₂ microspheres	215
V.2.5. Effect of preparation conditions on surface area, total pore volume and pore radius of UO ₂ microspheres	216
V.2.6. Effect of sintering temperature on the density of UO ₂ -samples	219
V.2.7. DTA and TG analysis	221
V.2.7.1. Effect of washing conditions	222
V.2.7.2. Effect of feed solution aging	222
V.2.7.3. Effect of soaking conditions	223
V.2.8. X-Ray diffraction analysis	223
SUMMARY	227
REFERENCES	231
APPENDIX TABLES	242
Arabic Summary .	

AIM OF THE WORK

Metal oxides have a wide application in many fields. One of these is their use in nuclear technology. As fuel, uranium dioxide, UO_2 , has particular interest in nuclear technology. It is the nuclear fuel now most widely used in energy producing reactors, such as light water reactors (LWR), fast breeder reactors (FBR) and high temperature gas cooled reactors (HTGR).

Uranium dioxide used as nuclear fuel must fulfil certain specifications⁽¹⁾. Different techniques may be followed to produce UO_2 nuclear fuel to fulfil the required specifications. From the advantages of UO_2 fuel are its high melting point of $2828 \pm 20^\circ C$, its corrosion resistance to radiation damage, and its irradiation stability. The physico-chemical characteristics of UO_2 such as density, surface area, pore structure, grain size, crystallite size, sphericity, oxygen to uranium ratio ... etc. depend mainly on the method of its preparation⁽²⁾.

UO_2 -fuel must be shaped into different forms such as rods, tubes, pellets or spheres. Spherical fuel can be produced by either dry (e.g. powder agglomeration and pellet crushing) or wet methods⁽³⁾. The second methods are preferred and yield more valuable fuel than the first ones^(4,5). In addition, the wet chemical methods became an almost universal for producing spherical nuclear fuel. The spherical form of the fuel produced by the wet

chemical processes has several advantages over the conventional methods⁽⁶⁾. Therefore, sol-gel processes appear to be particularly promising methods for the production of nuclear fuel microspheres⁽⁷⁾. The sol-gel processes were developed and applied at the Oak Ridge National Laboratory, ORNL, USA⁽⁸⁾, AERE, United Kingdom⁽⁹⁾, KEMA, Netherlands⁽¹⁰⁾, CNEN, Italy⁽¹¹⁾, KFA Jülich, FRG⁽¹²⁾, and Tokai, Japan⁽¹³⁾ for preparation of high density thorium and/or uranium microspheres. In these processes three major operations take place:

- i- Preparation of an aqueous sol,
- ii- Removing of water producing UO_3 gel particles, and
- iii- Thermal treatment of the UO_3 -gel particles to produce a dense UO_2 -microspheres.

In Chapter II of the present study the different gelation methods were described, while in the second experimental part of Chapter IV a developed gelation process, internal gelation hydrolysis process, was applied to produce a dense UO_2 -microspheres suitable as nuclear fuel. The physico-chemical characteristics of UO_3 - and UO_2 -microspheres produced at different experimental conditions were studied and optimized to obtain UO_2 -microspheres of maximum % theoretical density suitable as nuclear fuel.