SURFACTANT-ASSISTED SYNTHESIS AND CHARACTERIZATION OF SILICA-DOPED ZIRCONIA AND ITS APPLICATION IN CHROMIUM REMOVAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

Masters of Science
in
Chemistry

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This is to certify that the dissertation entitled "**Surfactant-assisted synthesis and characterization of silica-doped zirconia & its application in chromium removal**" being submitted by Ashis Das to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa for the award of the degree of Master of Science is a research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University/Institute for the award of any Degree/Diploma.

N.I.T, Rourkela — Dr. Aparna Mondal
Date: — (Supervisor)

DECLARATION

I Mr. Ashis Das, NIT, Rourkela declare that all my research works are original & no part of this thesis has been submitted for any other degree or diploma. All the given information & works done are true to my sense & knowledge.

Ashis Das

Date:-

ACKNOWLEDGEMENT

I owe this unique opportunity to place on record my deep sense of gratitude & indebtedness to my superviser **Dr. Aparna Mondal**, Department of Chemistry, National Institute of technology,Rourkela for his scholastic guidance, prudent suggestions & persistent endeavor throughout the course of investigation.

I owe a deep sense of reverence to **Prof. B.G Mishra**, H.O.D,Dept. of chemistry,National Institute of technology, Rourkela for her suggestive guidance, immense poatronage, constructive criticism & enthusiastic encouragement.

My sincere gratitude is to **Dr. B.B. Nayak,** dept. of ceramic Engineering and **Miss Priyadarshini Nayak,** for their overall guidance, immense help, valuable suggestions, constructive criticism and painstaking efforts in doing the experimental work & preparing the thesis.

I express my profound gratitude to **Mr. Bappaditya Mondal**, **Miss.Abhipsa Mohapatra, Miss.Tapaswini padhee, Miss Subhraseema, Mr. Sandeep Mondal, Sitakanta, Harikrishna, Sushmita and Sushree Sabinaya** for their ceaseless encouragement, immense help, hearty encouragement during my project work.

Lastly I express my abysmal adoration & heartfelt devotion to **my beloved parents** for their countless blessings, unmatchable love, affection & incessant inspiration that has given me strength to fight all odds & shaped my life, career till today.

In the end I must record my special appreciation to **GOD** who has always been a source of my strength, inspiration & my achievements.

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ABSTRACT

Purpose of taking silica-doped zirconia system was aimed to obtain high surface area, temperature stability which possibly shows novel catalytic, adsorption behaviour as well. A novel synthesis of silica-doped zirconia nanoparticles with 5, 10, 15, and 20 mol% silica have been prepared by co-precipitation method. X-ray diffraction analysis indicates the transformation of monoclinic to tetragonal phase of zirconia in the presence of silica at higher temperature. Moreover from UV analysis it confirms the formation of t-phase. FT-IR analysis has been used to elucidate the presence of Si-O-Zr bond, Si-O-Si network in silica-doped zirconia nanopowder.

CHAPTER I

INTRODUCTION

1.1 General Introduction

The significance of using Zirconia (i.e Zirconium dioxide, ZrO_2) as template for synthesis of nanomaterial was due to its wide application in many technological fields, such as high performance ceramics, catalysts, high-temp fuel cells, oxygen sensor, damage resistant optical coatings and bioceramics such as orthopaedic and dental implants.[1] Recently considered attention has been focused on the utilization of powder, composite material with controlled purity and nanocrystalline structures showing distinct properties, such as increased strength, surface to volume ratio, hardness ratio because of the nature of atomic structure in the interfacial region and the small grain size which increases its strength & hardness. Coatings are applied for tailoring the surface and interfacial properties of particles. Moreover the purpose of taking silica-doped zirconia system was aimed to obtain high surface area, temperature stability which possibly shows novel catalytic, adsorption behaviour. There are large numbers of techniques available to synthesize different type of nanomaterials in the form of colloids, clusters, powder etc. such as physical method (Hydrothermal, microwave etc.), chemical method (Co-precipitation, sol-gel etc), hybrid technique (spray-pyrolysis, freeze-drying etc), Biological method (fungi, bacteria etc). The method of synthesis applied here was Wet chemical method due to its easy operation. Powders with a small particle size obtained by wet chemical processing often were heavily aggregated. Also, aggregation and agglomeration of the particles occurs when the precursor materials are calcined at temperatures above 600^0C.

CHAPTER II

LITERATURE REVIEW

2.1. Literature review

Preparation of silica-coated ZrO_2 nanoparticles by microwave irradiation confirms the formation of thin and uniform silica layer on zirconia nanoparticle.[1]

Synthesis of zirconia and silica-doped zirconia nanopowder with 5, 10, 15 and 20 mol% silica by oxalate processing confirms the formation of t-ZrO_2 to m-ZrO_2 at higher temperatute in the presence of silica.[2]

Stabilization of ZrO_2 in ZrO_2-SiO_2 binary oxide confirms the transformation of tetragonal to monoclinic zirconia with increase in silica content.[3]

The effect of small addition of silica on the microstructural, and mechanical properties of 3 mol% yttria-stabilized zirconia ceramics has been discussed[4].

Synthesis of mesoporous sulfated silica-zirconia materials with various Si/Zr molar ratios (2.0-5.0) by using tri-block copolymer as template and has studied its acidic catalytic study.[5]

The sol-gel preparation method used to obtain zirconia/silica mixed oxides to modify the textural and catalytic properties of the mixed oxides[6].

The effects of key process parameters on the properties of the mesoporous silica-zirconia materials were investigated, including the choice of Zr (IV) source (zirconium oxychloride or nitrate), the ZrO2 content and the synthesis pressure (i.e. ambient pressure or hydrothermal conditions).[7]

Study of possible cluster models of the intergranular interfaces phase for SiO_2/ZrO_2 binary oxides optimized by the density-functional theory (DFT/B3LYP) [8].

2.2 Objective of present work

- To synthesize high surface area, thermally stabilized zirconia–silica mixed oxide by co-precipitation method.
- Role of silica on crystal structure of zirconia.
- Effect of calcination temperature on phase transformation of zirconia.

CHAPTER III

EXPERIMENTAL TECHNIQUE AND MEASUREMENTS

3.1. Procedure

The starting reagents were zirconium oxychloride $ZrOCl_2.8H_2O$, Tetraethoxy silane (TEOS), $Si(OC_2H_5)_4$, Dodecylamine(DDA), and Isopropanol. Precise amount of the zirconium oxychloride and TEOS were weighed and dissolved separately in distilled water, isopropanol respectively. After obtaining homogeneous solution, the reagents were mixed using magnetic stirring. Then the surfactant DDA was added to the above solution slowly dropwise. After stirring 1h the pH of the solution mixture was adjusted by adding sodium hydroxide, NaOH. Then the precipitate was washed with distilled water, followed by ethanol. Finally it was dried with acetone and kept in an oven at 70^0C temperature for 24h, then powdered and calcined at 400^0C for 2h in furnace. All the composition of 5 mol%, 10 mol% and 20 mol% silica doped ZrO_2 nanoparticle were synthesized by this method.

3.2. Characterization and Measurements

Formation of SiO_2 coated ZrO_2 nanomaterial was characterised by XRD, UV, FT-IR spectroscopy. The surface morphology was examined by Scanning electron microscopy (SEM) method.

3.2.1. X-Ray Diffraction

X-ray diffraction was used to perform phase analysis. The sample for this measurement was prepared by using a glass slide with a groove as the sample holder. The powder was placed in the groove and was compressed with the help of another glass slide. The excess powder was removed. The sample with the flat surface at the slide was used to measure its characteristic X-ray diffraction pattern by using PHILIPS XPERT PRO X-ray diffractometer with following set up.

Target CuKα of wavelength λ = 0.1540 nm,

Range of diffraction angle 2θ (20° - 80°)

Scanning speed 0.04°/ s.

For a crystalline solid, the structure may be specific in terms of crystal unit cell and translations symmetry, the lattice leading to sharp Bragg peaks, which are characteristic of the diffraction pattern of the crystalline solids. The structure of the amorphous solid, on the other hand, is characterized by a lack of symmetry, periodicity and long-range order, resulting in a diffraction pattern. By using the XRD plot and Bragg's law the peaks were identified and subsequently phases were identified. Average crystallite size in the sample has been calculated from widths $\Delta 2\theta_{1/2}$ in characteristic diffraction peaks with the Debye – Schemer's formula, $D = 0.89\lambda / [(\Delta 2\theta_{1/2}) \cos\theta_B]$, where $2\theta_B$ is the peak position in diffractogram.

3.2.2. FT-IR Spectroscopy

The IR spectrum was measured in the 400 to 4000 cm^{-1} region for sample dispersed in KBr pellets (in 1:4 ratios) with Perkin-Elmer spectrophotometer. The reported values of frequencies are accurate to ± 2 cm^{-1} in the case of the sharp bands and ± 5 cm^{-1} or even larger in the case of the broad bands

3.2.3 SEM

SEM measurements were carried out to investigate the detailed morphology, surface roughness and structure of the powders. The sample was prepared for SEM analysis by taking a pinch of sample with ethanol, then sonicating it 5 to 10 min, followed by taking it in a glass piece, dried in an oven at 70^0C for few min.

3.2.4 UV Spectroscopy

The UV-Vis spectra of powder samples were obtained on a Schimadzu UV-2450 ultraviolet-visible spectrophotometer, and $BaSO_4$, used as internal standard. UV-Vis spectroscopy has been used to study the phase transformation as well as to determine the incorporation of silica into zirconia lattice.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. XRD Analysis

The XRD patterns of surfactant (DDA) assisted ZrO_2-SiO_2 precursor calcined at 400^0C for 2 h are shown in figure 2 in below. It shows the X-ray diffractogram of pure ZrO_2, along with 5 mol%, 10 mol% and 20 mol%. Silica-doped ZrO_2. Analysis of X-ray diffractogram provides phase analysis as well as an analysis of average crystallite size. From Figure 1, it has been confirmed that pure ZrO_2 and 5 mol% silica-doped ZrO_2 show only tetragonal polymorph at 400^0C. But 10 mol%, 20 mol% doped sample in 400^0C calcined temperature reflect still in amorphous phase.

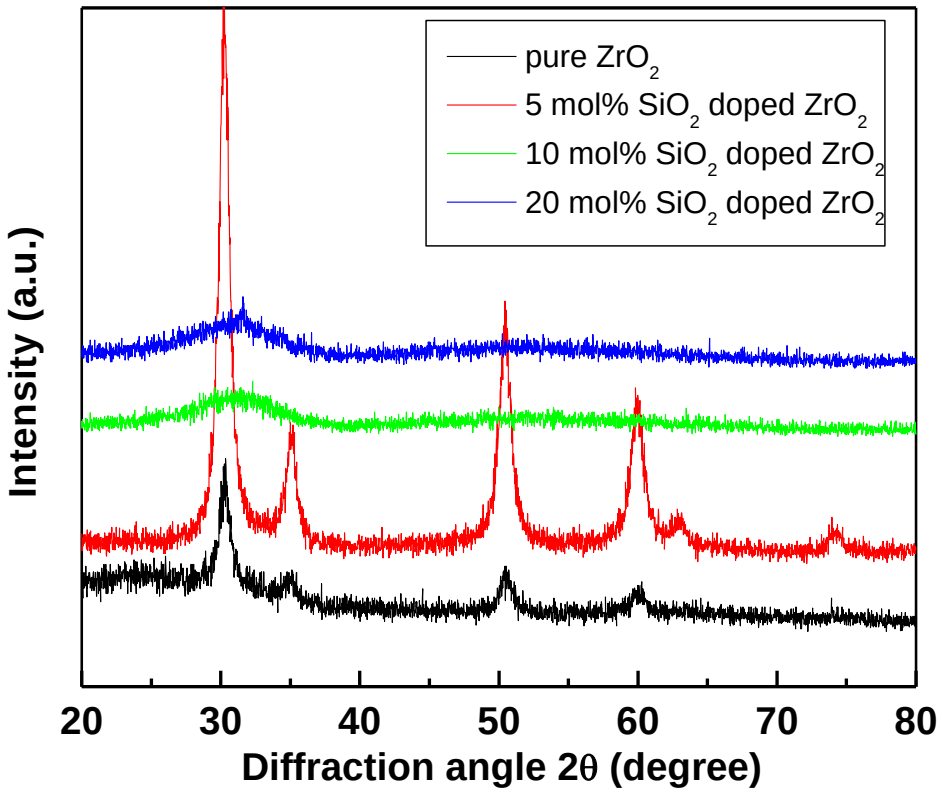


Fig.1. XRD patterns of pure ZrO_2 along with 5 mol%, 10 mol%, and 20 mol% silica doped at 400^0C calcined temperature.

Moreover at higher calcined temperature of 600^0C all the compositions attain tetragonal polymorph. The calculated‘d’ value for major peaks matched with the ‘d’ values given in JCPDS card no. 80-0784 confirms the formation of tetragonal polymorph. Moreover the crystallinity size decreases with increase in silica doping.

4.2. FT-IR Spectroscopy

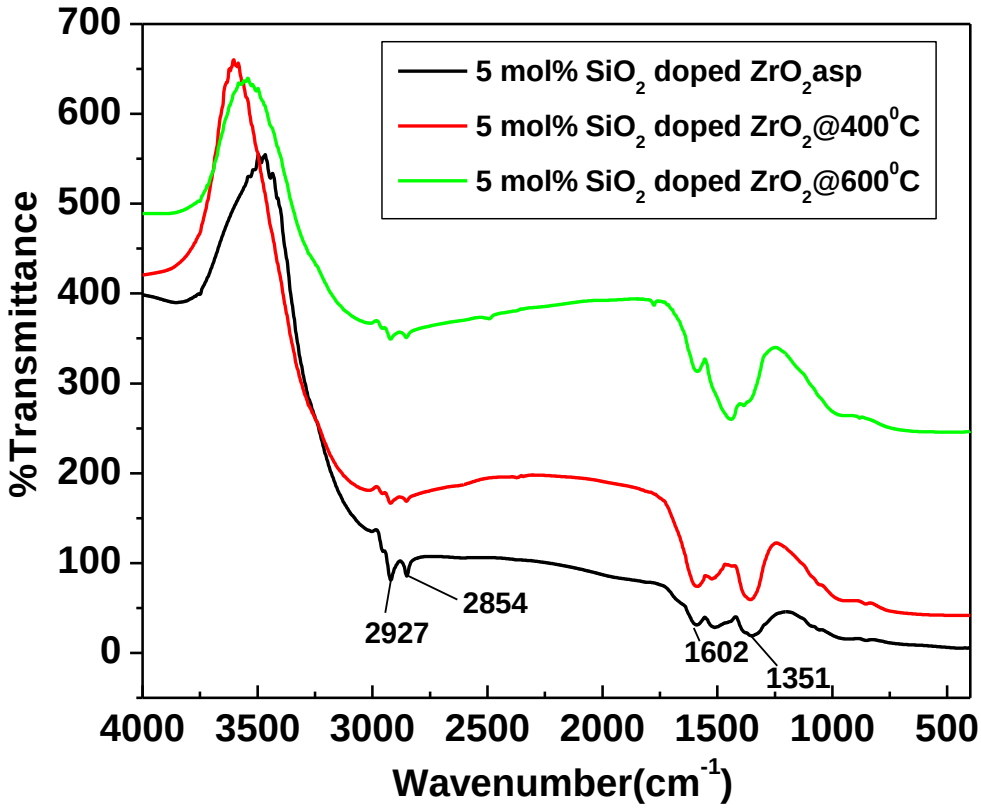


Fig.2. IR spectrum of 5 mol% silica-doped ZrO_2 of pure sample along with 400^0C, 600^0C calcined temperature.

Figure 2 compares IR spectra of as prepared 5 mol% silica-doped ZrO_2 along with its calcined sample at 400^0C and 600^0C with surfactant. The broad band corresponding to –OH stretching recorded in the 3000 to 3700 cm^{-1} range. Two peaks at 2927 cm^{-1} and 2854 cm^{-1} show C-H stretching band of hydrocarbon chain of DDA. The peak at 1602 cm^{-1} corresponds

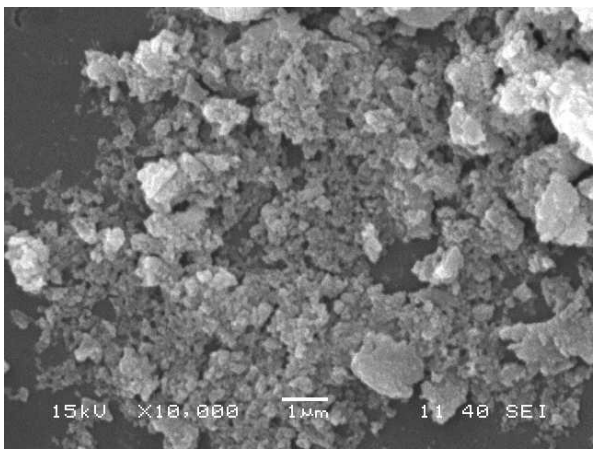
to N-H bending of amine group present in DDA. The band at 1351 cm^{-1} assign to the deformation vibration of Zr-OH. The weak peak at 966 cm^{-1} is due to stretching vibration of Zr-O-Si bond. Similar IR spectra of 10 mol%, 20 mol% doped silica were obtained The absorption band due to stretching vibration of different functional groups, bonds are tabled below.

IR Absorption range/peak(cm^{-1})	**Assignment**
3200-3700	OH stretching
2927,2854	C-H stretching of hydrocarbon chain of DDA
1602	N-H deformation of amine group of DDA
1351	Zr-OH deformation
966	Zr-O-Si stretching

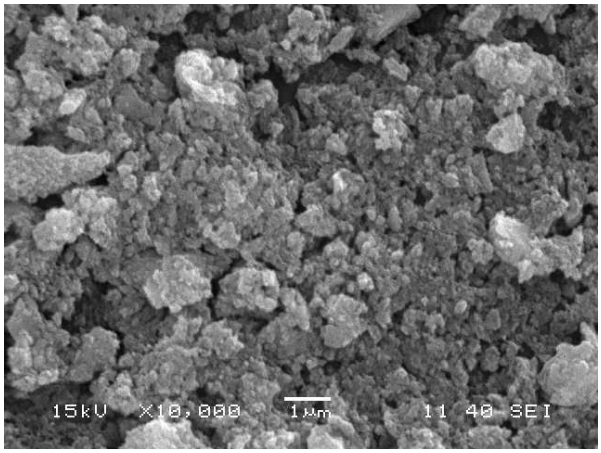
Therefore, it confirms the formation of heterogeneous Si-O-Zr bond at the interface of SiO_2-ZrO_2 mixed oxide along with Si-O-Si network over zirconia nanoparticles. It also reflects removal of peak corresponds to N-H stretching, C-H Stretching of organic residue of surfactant DDA at higher calcined temperature.

4.3. SEM

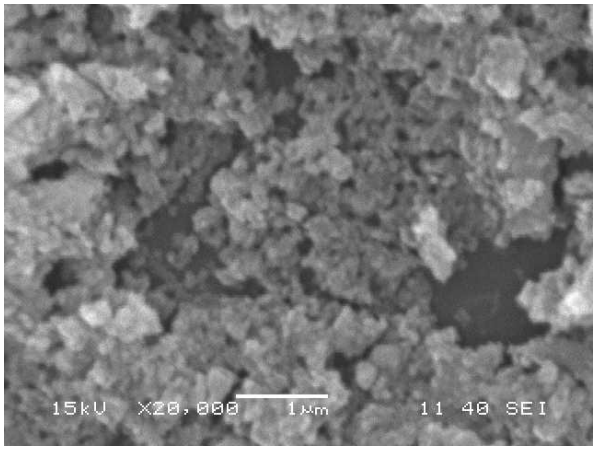
Figure 3 shows the morphology of silica-doped ZrO_2 of different composition. Particles are in agglomerated in nature with size of around 2 μm as observed from the SEM micrographs.



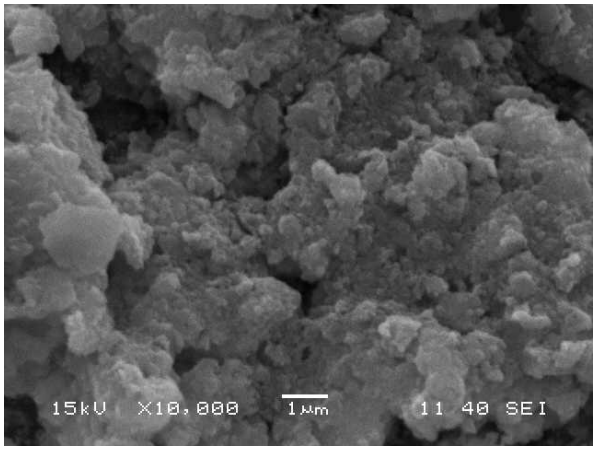
(a)



(b)



(c)



(d)

Fig.3. SEM micrograph of as prepared sample of (a) pure, (b) 5 mol%, (c) 10 mol%, (d) 20 mol% silica-doped ZrO_2.

4.4. UV Spectroscopy

Figure 4 shows the UV spectra of surfactant assisted 5 mol% Silica-doped ZrO_2 nanoparticle at different calcined temperature.

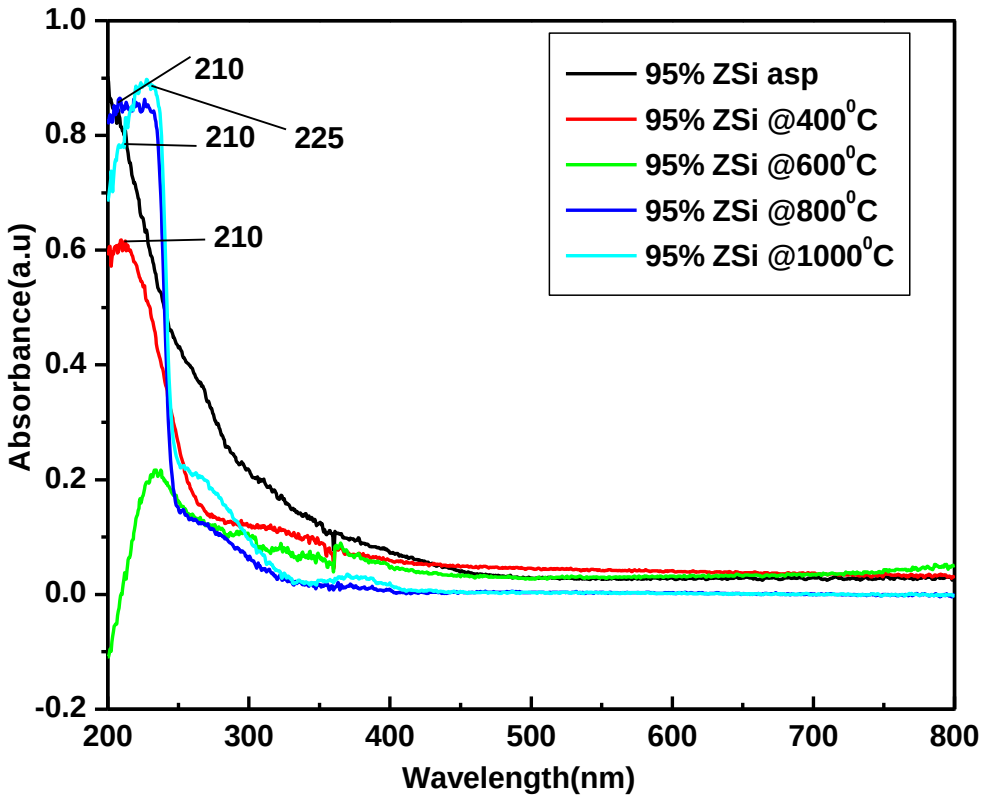


Fig.4. UV spectra of 5 mol% SiO_2-doped ZrO_2 of pure, along with 400^{0}C, 600^{0}C, 800^{0}C, 1000^{0}C calcined temperature.

The absorption peak at 210 nm shows due to t-phase of ZrO_2. The band at 225nm corresponds to m-phase. The above bands correspond to ligand to metal charge transfer band (LMCT) from O^{2-} to an isolated Zr^{4+} ion in tetrahedral configuration[5]. From the above result discussion it confirms the stabilization of t-phase at higher temperature of SiO_2-doped ZrO_2.

CHAPTER V

APPLICATION IN CHROMIUM REMOVAL

The chromium adsorption study of silica-doped ZrO_2 samples is shown in figure 5 below.

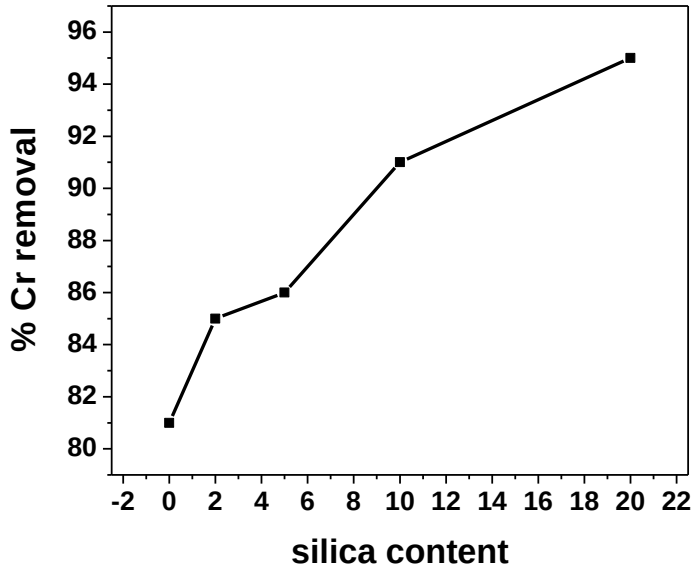


Fig.5. % of Cr removal with different composition of silica doping.

The experiment was carried out to study the adsorption property of silica-doped ZrO_2 as prepared sample of different composition with different pH of chromium solution. It was found that at pH 1, the 20 mol% silica-doped ZrO_2 show maximum Cr (VI) adsorption. Further experiments need to be carried out for better adsorption results.

CHAPTER VI

CONCLUSIONS & FUTURE WORK

- Synthesized nanomaterial shows stabilization up to 600°C calcined temperature.
- Characterization by XRD followed by UV spectroscopy confirms the stabilization of metastable t-phase polymorph of silica-doped ZrO_2 nanomaterial.
- From FTIR, it infers the formation of heterogeneous Si-O-Zr bond at the interface of SiO_2-ZrO_2 prepared sample.
- Decomposition of organic residues at higher calcined temperature.
- From above study it is concluded that the silica-doped ZrO_2 nanomaterial can be used as to study the adsorption or catalytic application.
- Further analysis of the sample for TG-DSC, TEM, BET.

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