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Comparative Study for the Synthesis of Ru-Nio Transition Bimetallic Catalyst Using Sonochemical Method & Characterization of the Effective Catalyst with the Cost Analysis

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Abstract: ***Sonochemical Method has been used in all the comparative experiments for the synthesis of Metal oxide nanoparticles. Five Catalysts were prepared in different proportions and the efficiency of each catalyst was calculated using the results obtained after hydrogen peroxide estimation result as well as the Congo Red Dye Degradation result. The final catalyst with high efficiency along with minimum cost was selected for further characterization including XRD and SEM.***

Keywords: Sonochemical method, XRD, SEM, H2O2 Estimation, Congo Red Dye, Optimization, Acoustic, Cavitation.

1. Introduction

The Chemical reaction forms the basis of any chemical transformation occurring in nature. The parameters that affect the chemical reactions are pressure and temperature which was applied using ultrasound energy. The Utilization of high intensity ultrasound offers a facile, versatile synthetic tool for nanostructured materials that are often unavailable by conventional methods. The primary physical phenomena associated with ultrasound that are relevant to materials synthesis are Cavitation [1]. Acoustic Cavitation creates extreme conditions inside the collapsing bubble and serves as the origin of most Sonochemical phenomena in liquids or liquid-solid slurries. The process utilizing the application of ultrasound to bring a chemical change is known as Sonication [2]. Here an attempt has been made to prepare oxides of transition metals by the process of sonication of the solutions of Metal salts in the presence of Ruthenium. The applications of these Metal oxides are in the field of catalysis, pollution abatement for heavy metal and colour removal.

2. Experimental Section

Preparation of six Bimetallic Catalysts in different ratios along with varying stabilizing agent

2.1 Sonication Parameter

1. Pulse : 05 ON / 02 OFF
2. Amp : 30%
3. Time : 1 hour
4. Set Point Temperature : 70 degree

Hydrogen peroxide estimation was obtained by titrating a fixed amount of sample against potassium permanganate solution [3] during the analysis of all six catalysts.

2.2 Catalyst 1

Ruthenium Chloride (0.5 gm) was dissolved in 20 ml of ethanol and 0.5 gm of Nickel Oxide dissolved in 80 ml of water. Combined both the solutions and kept on sonication for 1 hour [4]. Now add 1 gram of PVP which acts as a stabilizing agent, after the sonication is over, put the beaker in hot air oven at 110 degree Celsius till we achieve the powdered form catalyst. No calcination was done with this sample. The ratio of the catalyst is 1:1

Catalyst 2

Ruthenium chloride 0.2 gm was dissolved in 20 ml of ethanol and 0.5 gm of Nickel Chloride was mixed with 80 ml of water and then both solutions were combined with the addition of 1 gram of PVP and then kept for Sonication for 1 hour. Now after the sonication, the solution was subjected to Calcination at 450 degree Celsius in the muffle furnace. The ratio of the catalyst is 1:25

Catalyst 3

Ruthenium on Carbon (10%) (*Commercially available)* (0.2gm) was mixed with the solution of (5 gm) Nickel Chloride (in 80 ml of water) along with 1 gram of PVP and kept on sonication for 1 hour and then further Calcinated at 450 degree Celsius in the muffle furnace. The ratio of the catalyst is 1: 25.

Catalyst 4

Ruthenium on Carbon (10%) with 0.2 gm of amount was mixed with the solution of Nickel chloride (5 gram) in 80 ml of water along with 1 gram of PEG (polyethylene glycol) and then kept on sonication for 1 hour and further calcinated at 450 degree Celsius. The ratio of the Catalyst is 1:25.

Catalyst 5

Ruthenium chloride with quantity 0.5 gm was mixed with 30 ml of ethanol and the solution of Nickel chloride (0.5 gm)

was mixed with 80 ml of water. Now both the solutions were combined and further 9 gram of activated carbon was added along with 1 gram of PVP and sonicated for 1 hour [5]. The liquid sample was further heated at 110 degree Celsius till we obtain the powdered form of the catalyst. The ratio of the catalyst is 1: 10

1) Hydrogen Estimation, Dye Degradation & Overall Process Cost Result (for 1 gram of catalyst)

Figure 1: Hydrogen peroxide estimation, degradation and Overall cost for 1 gm of catalyst

Sample	*Content*	*Heating/ Calcination*	*Hydrogen peroxide Estimation*	*%age Degradation (50 ppm Congo Red)(1 hour Sonication)*	*Overall cost for synthesis, hydrogen peroxide estimation & degradation*
Catalyst 1	Ruthenium chloride and Nickel Oxide + PVP	Hot Air Oven at 110 degree Celsius	1.9125 mg	Time taken- 2 hours 100% degradation	Rs. 623.92
Catalyst 2	Ruthenium Chloride and Nickel Chloride + PVP	Calcination at 450 degree Celsius	1.65 mg	Time taken – 1 and a half hour 100% degradation	Rs. 216
Catalyst 3	Ruthenium on carbon(10%) and Nickel Chloride + PVP	Calcination at 450 degree Celsius	1.1475 mg	Time taken- 1 hour 45 minutes 100% degradation	Rs. 272.02
Catalyst 4	Ruthenium on carbon(10%) and Nickel Chloride + PEG	Calcination at 450 degree Celsius	1.02 mg	Time taken -3 hours 100 % degradation	Rs. 262.654
Catalyst 5	Ruthenium Chloride and Nickel Chloride with Activated Carbon + PVP	Hot Air Oven at 110 degree Celsius	1.02 mg	Time taken -2 hours 100% degradation	Rs. 81.626

References of cost for the chemicals have been taken from Sigma Aldrich Website. Here is the brief table for the cost per quantity.

Figure 2: Table for the Cost per Quantity (Ref- Sigma Aldrich)

Chemical/Instrument	Price in Rupees (Rs.)
Nickel Chloride /gram	Rs. 27
Ruthenium Chloride /gram	Rs. 820
Activated Carbon /Kg	Rs. 250
Nickel Oxide /gram	Rs. 354.12
Ruthenium on Carbon/gm	Rs. 488
PVP /gram	Rs. 13.17
PEG /gram	Rs. 3.804
Cost of Sonication(750 W) /hour	Rs. 3.75
Cost for Muffle furnace(1500W) / hour	Rs. 7.50
Cost for Hot Air Oven(600W) /hour	Rs. 3.00

The factors involving the overall cost [6] for the Synthesis, Hydrogen Peroxide Estimation and Degradation are:

1. Cost of the Catalyst (RuCl2 / NiCl2 / NiO / Ru on Carbon(10%)
2. Cost of the Stabilizing Agent (PVP /PEG)
3. Per hour electricity cost of the instrument (Sonicator / Muffle Furnace / Hot Air Oven)
4. Cost of the Activated Carbon (*if used)*

3. Results

Ruthenium being a very costly transition metal (*noble metal)* along with nickel, reducing the overall operating cost was kept into focus. To reduce the cost of catalyst synthesis, the bimetallic catalyst (Ru-NiO) was impregnated on Activated Carbon in the ratio 1: 10

4. Catalyst Activated Carbon

Catalyst 5 proved to the best among the other catalysts compared, though the degradation time is less than 30 minutes than the compared catalyst no. 2 but looking at the overall cost of the synthesis, hydrogen peroxide estimation and degradation, Catalyst 5 is 2.6 times cheaper than the catalyst 2.

5. Characterization Of Catalyst 5

5.1 XRD OF CATALYST 5

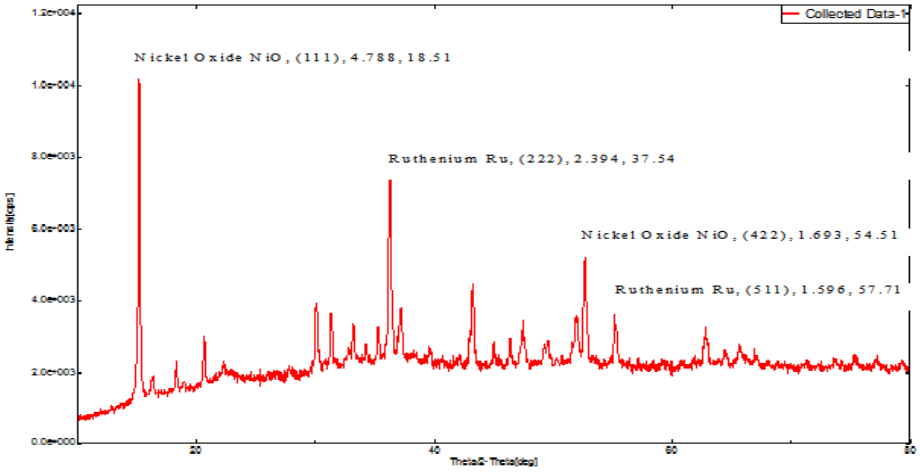


Figure 3: X-Ray Diffraction of Catalyst 5 (Ru- NiO)

5.2) SEM OF CATALYST 5

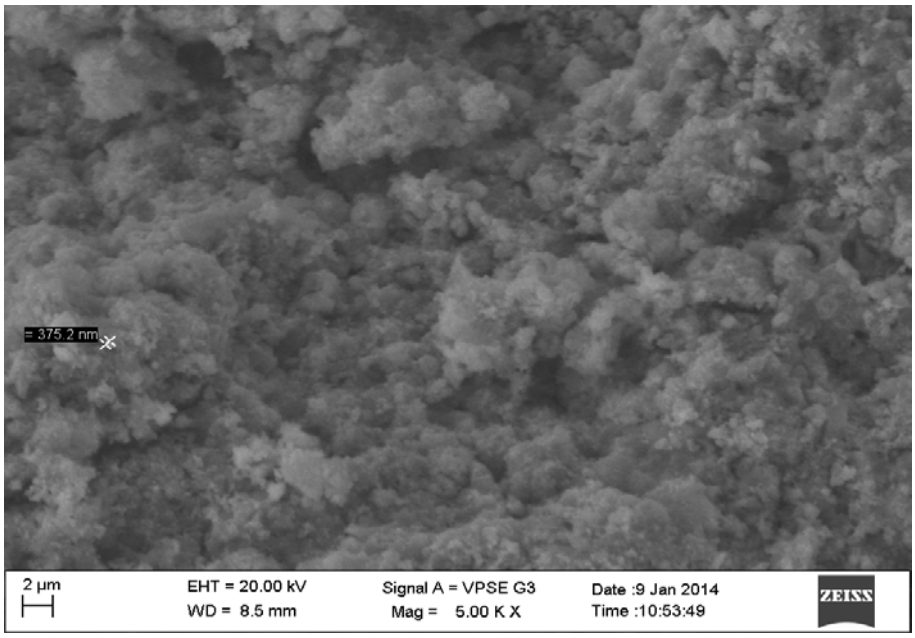
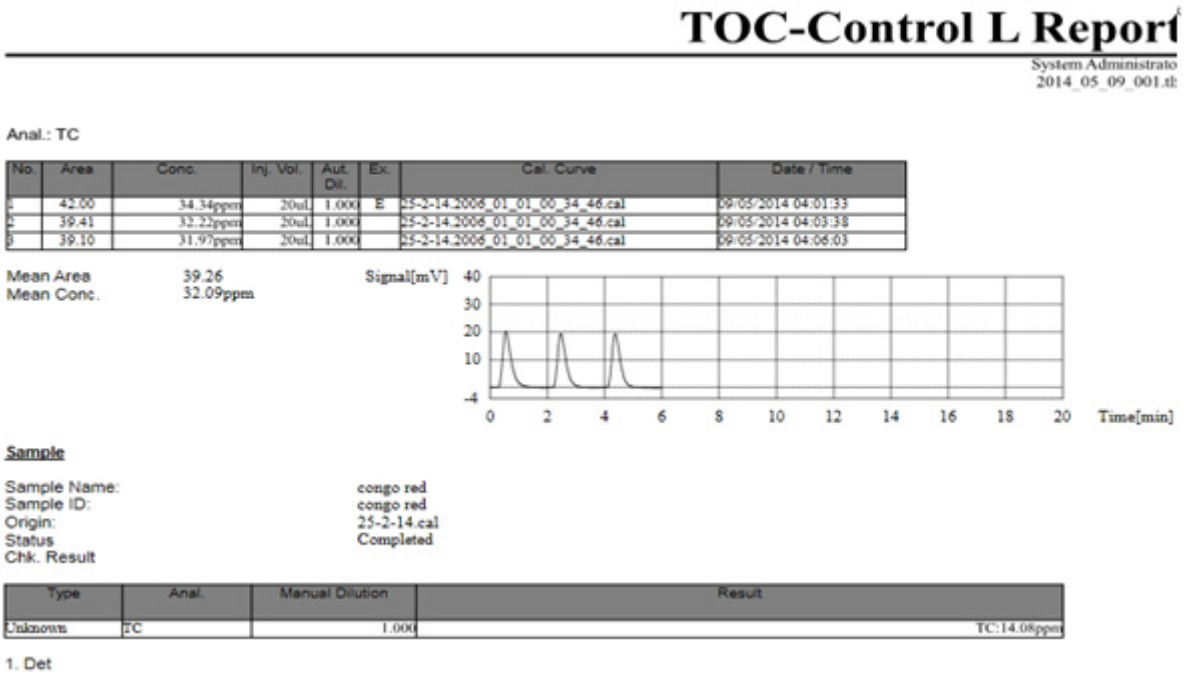


Figure 4: Scanning Electron Microscope Result with 375.2 nm of particle size

5.3 TOC Result


TOC-Control L Report

System Administrato
2014_05_09_001.tl

Anal.: TC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	42.00	34.34ppm	20ul	1.000	E	25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:01:33
2	39.41	32.22ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:03:38
3	39.10	31.97ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:06:03

Mean Area 39.26
Mean Conc. 32.09ppm

Signal[mV] 40 30 20 10 -4
0 2 4 6 8 10 12 14 16 18 20 Time[min]

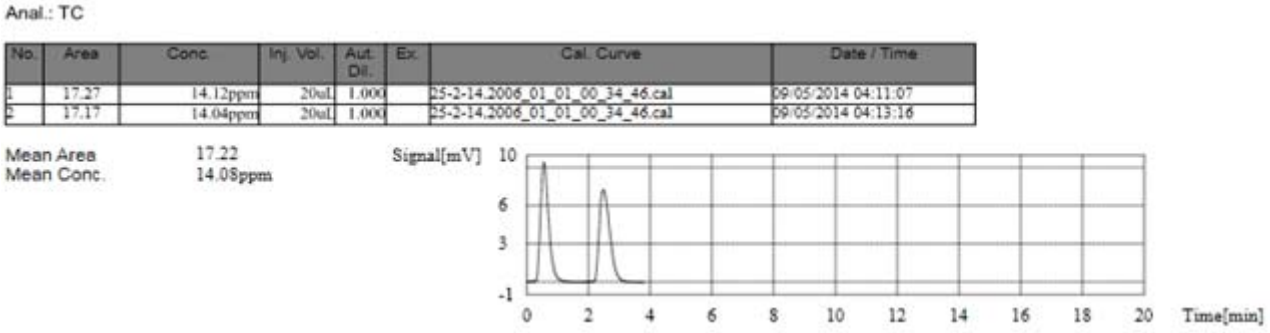
Sample

Sample Name: congo red
Sample ID: congo red
Origin: 25-2-14.cal
Status Completed
Chk. Result

Type	Anal.	Manual Dilution	Result
Unknown	TC	1.000	TC:14.08ppm

1. Det

Figure 5: Initial report of TOC for Congo Red Dye Degradation


Anal.: TC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	17.27	14.12ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:11:07
2	17.17	14.04ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:13:16

Mean Area 17.22
Mean Conc. 14.08ppm

Signal[mV] 10 6 3 -1
0 2 4 6 8 10 12 14 16 18 20 Time[min]

Figure 6: Final report of TOC for Congo Red Dye Degradation

6. Discussion and Conclusion

The mechanism involved in the synthesis of bimetallic catalyst is the ultrasound wave passing through the liquid media causing supercritical conditions to the environment with high temperature, high pressure and turbidity. During the synthesis of catalyst, its cost management was kept in focus so as to achieve a process which can degrade the dye in an appropriate time & in a cost effective way. The overall cost of the catalyst 5 (Ru-NiO) was brought down by impregnating it with activated carbon which is very cheap as compared to noble transition metals like Ruthenium. In the end, we synthesized a catalyst which can degrade 50 ppm of Congo Red Dye in 2 hours in 81.626 which is too much cheaper than any other catalyst synthesized.

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