

Catalytic Wet Air Oxidation of Aqueous Ammonia Over γ -Al₂O₃ Based Cu-Ru Bimetallic Catalysts



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Quaid-i-Azam University, Islamabad, in the partial
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in

Inorganic/ Analytical Chemistry

By

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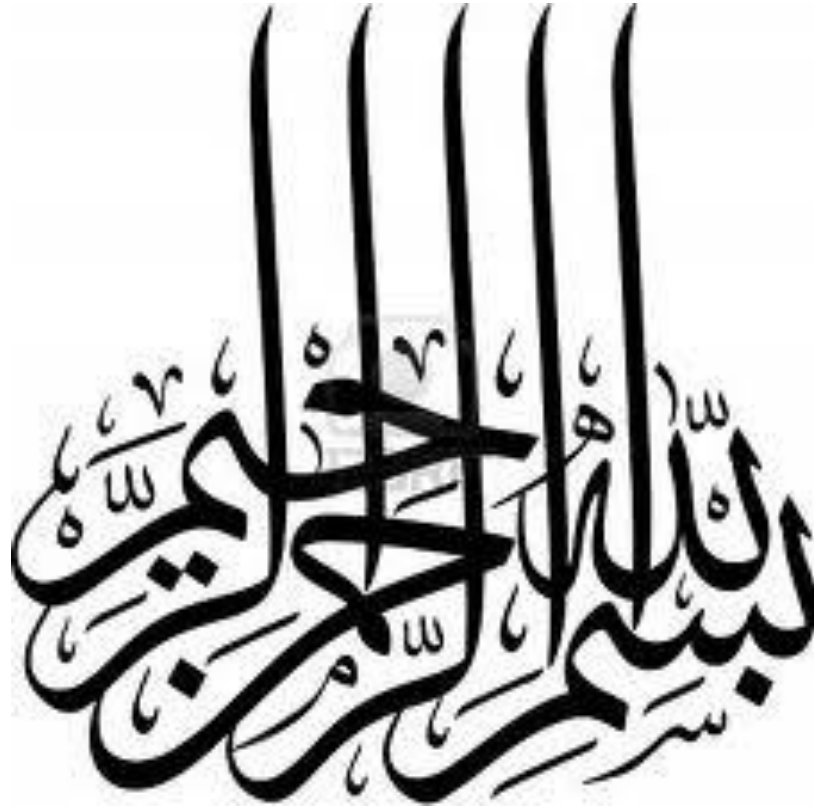
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**IN THE NAME OF ALLAH,
THE MOST BENEFICIENT, THE MOST MERCIFUL**

Dedicated to my family

DECLARATION

This is to certify that this dissertation entitled “*Catalytic Wet Air Oxidation of Aqueous Ammonia Over γ -Al₂O₃ Based Cu-Ru Bimetallic Catalysts*” submitted by *Mrs. Fatima Zahid*, is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, as satisfying the dissertation requirements for the degree of *Master of Philosophy in Inorganic/ Analytical Chemistry*.

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ABSTRACT

Due to the excessive use of ammonia in the industry it is one of the most important environmental issues. The presence of ammonia in the environment is harmful towards living organism. Therefore, removal of ammonia from waste water is very important in maintaining the aquatic environment. Catalytic wet air oxidation is one way of removing ammonia from the environment. Different catalysts have been used for ammonia removal. Ruthenium supported catalyst is very active towards ammonia decomposition. But due to the high cost and limited availability its industrial application is limited. Copper is also found to show some activity towards ammonia decomposition. In order to make the catalyst cost effective, the γ -Al₂O₃ supported Cu-Ru bimetallic catalysts with different metal loading have been successfully synthesized using impregnation method. The γ -Al₂O₃ was synthesized by sol-gel method. The catalysts were characterized by using different techniques including Atomic Absorption Spectrophotometry (AAS) , Surface Area Analysis, Powder X-ray diffraction (XRD), Fourier- Transformed Infra-Red Spectroscopy (FTIR), Thermal gravimetric analysis (TGA), and Field Emission Scanning Electron Microscopy (FE-SEM). The catalysts were successfully applied for catalytic wet air oxidation of aqueous ammonia. The ammonia decomposition activity was studied at three different temperatures i.e. 150 °C 200 °C 230 °C and it was found that catalytic activity increases with increase of temperature. Up to 99 % ammonia decomposition was achieved at 230 °C with catalyst containing 3% Ru loading over 10% copper. The promoting effect of Ru over catalytic activity of Cu was also studied and it was observed that activity of copper is enhanced by the addition of ruthenium. The selectivity of the catalyst towards different products was also calculated and it was found that selectivity towards nitrogen production was maximum with minimum production of nitrates. This was also confirmed by analysis of gaseous products which also indicated that no NO_x were present in the products. The ammonia to catalyst ratio was also optimized. The catalyst was recovered from the reaction mixture by filtration and it was found active for five cycles. The stability of catalyst in the reaction medium was confirmed by determination of dissolution degrees of the catalyst which was quite low.

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List of Abbreviations

| | |
|-----------|--|
| E_a | Activation Energy |
| Al_2O_3 | Aluminium oxide |
| Γ | Gamma |
| A | Alpha |
| Ru | Ruthenium |
| NP | Nanoparticle |
| Cu | Copper |
| CVD | Chemical vapor deposition |
| WAO | Wet air oxidation |
| CWAO | Catalytic wet air oxidation |
| AAS | Atomic Absorption Spectrophotometry |
| SAA | Surface Area Analysis |
| XRD | X-Ray Diffraction |
| FTIR | Fourier Transformed Infra-Red |
| TGA | Thermal Gravimetric Analysis |
| SEM | Scanning Electron Microscopy |
| SS | Stainless steel |
| HCl | Hydrochloric Acid |
| HPLC | High performance liquid chromatography |
| IC | Ion chromatography |
| MS | Mass spectrometry |
| TCD | Thermal Conductivity detector |
| BJH | Barrett-Joyner-Halenda |
| BET | Brunauer-Emmett-Teller |
| BDL | Below detection limit |
| EDX | Energy Dispersive X-ray Spectroscopy |

Chapter: 1

INTRODUCTION

1.1 Catalyst

A catalyst is a chemical substance which increases the rate of a chemical reaction by lowering the activation energy (E_a). The catalyst may change the reaction pathway but it does not influence the thermodynamic equilibrium of a reaction. It does not take part in a chemical reaction and can be recovered at the end of reaction. Only a very small amount of catalyst is required to speed up the reaction. The process in which the rate of a chemical reaction is increased in the presence of a catalyst is called as catalysis.

Catalysis may be homogeneous or heterogeneous. In homogeneous catalysis both reactant and catalyst are in one phase. They have single active site and low thermal stability. The main advantage of homogeneous catalysis is that reaction mechanism can be studied but their separation from reaction mixture is difficult and expensive.

In heterogeneous catalysis the catalyst is in a different phase than the reactant. Mostly they are solid and act on substrate in liquid or gaseous phase. They have multiple active sites and high thermal stability. The major advantage of heterogeneous catalysis is that the separation of catalysts from the reaction mixture is easy and cheap. The total surface area of the heterogeneous catalyst has an important effect on reaction rates. The smaller the size of particles higher will be the surface area.

Industrial productions of many important chemicals involve catalysts. Similarly most biochemical reactions are also catalyzed. Research into catalysis is one of the major fields in applied sciences. Catalytic reactions are preferred because they are environmentally friendly due to the reduction in the amount of waste generated as well as reduced cost.

The catalysts are generally characterized based on their activity, selectivity, thermal & mechanical properties, reusability, morphology and cost. A good catalyst must

have higher activity, selectivity, good thermal & mechanical properties, reusability and low cost.

1.2 Nano Catalysts, Their Advantages and Disadvantages

A nano catalyst is a substance or material with catalytic properties that has at least one nanoscale dimension, either externally or in terms of internal structures. Generally, catalysts that are able to function at atomic scale are called nano catalysts. Nano materials have attracted the researchers because of their novel properties like higher surface area and specific catalytic activities, greater stability, efficient recovery characteristics and cost effectiveness [1]. Nano materials constitute the important area of green chemistry and are reported in many applications.

Heterogeneous catalytic reactions take place at the active surface sites of bulk catalysts. So surface area of the catalyst is an important parameter for a catalytic reaction. Many efforts have been made to increase the surface area of heterogeneous catalysts which include the reduction in particle size or creating porosity in the material. Smaller the size of the catalyst higher will be the surface area and catalytic activity [1, 2]. Nano catalysts are produced by reducing the size of particles to nanoscale. For materials at the nanoscale, quantum-size effect is their basic characteristic.

The main advantage of nano catalysts is their high surface area. Due to very small particle size, the surface-to-volume ratio increases and more atoms are exposed on the surface hence the catalytic activity increases. Therefore, nano catalysts have novel physical and chemical properties that are different from bulk material [3, 4] .

Nano catalysts have applications in the field of H₂ generation, H₂ storage, fuel cell, organic synthesis and environmental remediation [1].

Major disadvantages of nano catalysts are that the agglomeration and sintering of small particles takes place which decreases their activity secondly their separation from reaction media is difficult [1]. To overcome these problem nanomaterial are usually dispersed on a suitable support [2] which reduces the agglomeration and sintering of particles leading to their easy separation. They can be separated out by filtration.

1.3 Supported Catalysts

Heterogeneous catalysts are normally dispersed on certain material which may increase their effectiveness or reduce their cost. Such catalysts are called supported catalysts. In heterogeneous and nanomaterial-based catalysts the reaction occurs at surface atoms. Therefore, great effort is made to maximize the surface area of a catalyst by distributing it over the support which affects the performance of the catalyst. This effect is due to the electronic interaction at the metal-support interface [5]. The catalyst support is normally a material which have good thermal and mechanical properties and high surface area. It may be inert or participate in the catalytic reactions. The support serves following purpose

- a. Improves the thermal and mechanical properties of catalyst
- b. Increase surface area of catalyst
- c. Reduces agglomeration and sintering of small particles of catalyst
- d. Stabilizes the crystallites of the catalyst

Most commonly used catalytic supports are alumina, zirconia, silica, titania and various forms of carbon including graphene, carbon nanotubes etc.

1.4 Alumina, a Catalytic Support

Aluminium oxide (Al_2O_3) is the amphoteric oxide of aluminium and is commonly referred as alumina. It has greater affinity for water as well as high thermal stability. It is the most common ceramic oxide used as active catalyst, catalyst support and adsorbent [6]. The most common crystalline forms of alumina are $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ which have high surface area and good mechanical, electrical and thermal properties [6]. Among these crystalline forms of alumina, $\gamma\text{-Al}_2\text{O}_3$ is mostly used as a catalyst support [6] because of high surface area, mesoporosity (i.e. pore size distribution) and acid base properties which are mainly related to surface chemical composition, structure and phase composition [7]. The $\gamma\text{-Al}_2\text{O}_3$ is formed upon dehydration of the aluminium hydroxide (boehmite) at temperatures ranging from 400°C to 700°C with controlled reproducible properties like particle size, morphology, surface area and pore size distribution. The $\gamma\text{-Al}_2\text{O}_3$ has BET surface area below $250\text{ m}^2/\text{g}$ and pore volume less than $0.50\text{ cm}^3/\text{g}$. Because of these textural properties the $\gamma\text{-Al}_2\text{O}_3$ has applications in the field of catalysis

and adsorption. It has high thermal and mechanical stability. It is insoluble in water and organic solvents but slightly soluble in strong acid and alkalis [8]. The $\gamma\text{-Al}_2\text{O}_3$ used as catalyst support is presented in Figure 1.



Figure 1: The $\gamma\text{-Al}_2\text{O}_3$ used as catalyst support

1.5 Supported Metal Catalysts

It is well known that metal nanomaterials have very good mechanical, electrical and electromagnetic properties, in addition to this such materials have applications in the field of catalysis, magnetic recording, sensing and medical diagnosis [9-11]. There are many industrial applications which involve transition metals and noble metals based catalyst [12]. The common example is Fe, which is used in Haber process for the production of ammonia. Hydrogenation of alkenes using Ni as catalyst and catalytic converters in car exhausts using Pd/ Pt as catalyst are some other examples.

1.6 Supported Bimetallic Catalyst

A catalyst in which two distinct metals are homogeneously distributed on a support material is called bimetallic catalyst [13]. Addition of second metal can tailor the

electronic and structural properties of nanomaterials which may enhance the catalytic activity and selectivity of the material [14]. Bimetallic nanomaterials have certain mixing pattern of two metals and definite geometric architecture which can perform specific actions [9, 13]. The physical and chemical properties of such catalysts show synergetic effect of both metals [9, 15, 16]. By changing the composition and morphology (like core shell, hollow structure, random alloyed structure) both physical and chemical properties of a bimetallic catalyst can be changed which can be exploited to catalyze a particular reaction [3, 9, 17, 18].

Among the metals, the transition metals (like Fe, Ni, Co, Cu etc) having two 4s electrons and partially filled 3d electrons which show specific magnetic and catalytic properties [9, 19, 20] while noble metals (like, Ag, Ru & Pd, Au, Pt, Ir) have 4d and 5d electrons due to which they have more profound electronic structure and show high activity in catalysis compare to transition metals [21, 22]. But the industrial applications of noble metals based catalysts are limited due to their high cost.

Bimetallic nano catalysts can be produced by the combination of transition and noble metals having multifunctional structure and properties [16, 18, 23, 24]. In some cases the transition metals are taken as base metal and noble metals are added in small proportion. They show higher activity and selectivity for a particular reaction under environmental friendly conditions as well as they reduce the cost.

Like monometallic catalysts, the bimetallic catalysts also have wide range of applications for example in magnetic recording, sensing, medical diagnosis [10, 11, 25], catalytic reforming reactions, fuel cell, hydrogen generation, alcohol oxidation and environmental remediation etc. [25].

1.6.1 Synthesis of Bimetallic Supported Catalysts

The bimetallic supported catalysts can be synthesized by following the general methods which are used for synthesis of monometallic supported catalysts. In supported metal catalysts, the metal is distributed over the support by impregnation of a porous support (e.g. γ -Al₂O₃) with an aqueous solution of a metal salt (e.g. Ruthenium trichloride), followed by heating in air (calcination) and reduction in hydrogen

environment [26] which results in the dispersion of the metal particles over the internal surface of support [27]. The common steps involved in the preparation of such catalysts are given below.

- a. Selection of support
- b. Pretreatment of support
- c. Deposition of active metal on the surface of support
- d. Drying of material
- e. Calcination
- f. Reduction

The important step in synthesis of supported catalysts is the deposition of active metal on support material, which can be done by any of the following methods [26, 28].

- a. Co-precipitation
- b. Impregnation
- c. Precipitation deposition
- d. Adsorption
- e. Ion Exchange
- f. Chemical vapor deposition (CVD)

1.6.2 Impregnation Method

The commonly used method is the impregnation method which is simple and gives reproducible metal loading. In its essential features, this procedure requires that the support is contacted with a certain amount of solution of the metal precursor, usually a salt, and then it is aged, usually for a short time, dried and calcined. In this method active metal precursor is dissolved in some suitable solvent. The metal solution is then added on the support material followed by drying and calcinations. The impregnation is repeated to get the desired metal loading [11, 26, 28]. The resulting catalyst is then activated by reduction which is carried out either by co-reduction method or by sequential method. The co-reduction method is commonly employed in which the mixture of two kind of metal salts containing the desired composition are reduced by using a reducing agent [29, 30]. The concentration of the metal precursors on the support will depend on the

concentration of the solution as well as on the pore volume and number of pores on the surface of the support [28]. For bimetallic catalyst, alternate impregnations are carried out with two metal solutions [31].

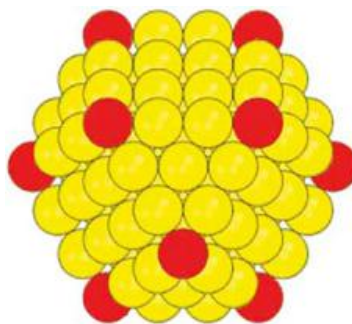
1.6.3 Metal Ratio in Bimetallic Catalysts

In bimetallic catalysts the addition of second metal can affect the properties of first metal so the mole ratios of two metals play an important role in catalytic performance of a catalyst. Only a suitable amount of second metal can enhance the properties of first metal which can be explained by their alloyed effect [32-35]. The metallic ratio is an important controlling factor which is adjusted in such a way that it shows maximum activity and selectivity for a particular reaction [3]. The catalytic composition is related to the structure of the catalyst. Any change in the mole ratio of metals can change the structure as well as surface distribution of two metals [36-39].

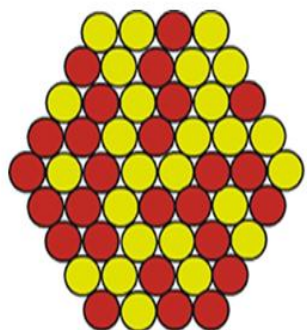
1.6.4 Structure of Bimetallic Catalysts

The bimetallic catalysts are synthesized with different morphologies and structures like crown jewel, core shell, alloyed, cluster and porous structure. In crown-jewel structure one metal atom (single atom) is controllably assembled at the special position on the surface of the other metal atoms. Generally, the ‘jewel’ metal is the more expensive metal with high catalytic activity. There are two advantages of such catalysts, one is the effective use of precious metal and second is the improved catalytic properties [3]. The Core-shell structures are formed when one type of metal is reduced first to form an inner core and another type of metal is deposited around the core to form a shell. In hetero structured NPs, individual nucleation and growth of two kinds of metal atoms occur with the sharing of a mixed interface during the growth process. Alloy structures have homogeneous distribution of two metals on the atomic level and can be distinguished owing to the formation of metal-metal bonds [14]. Among these bimetallic structures, the bimetallic alloy structures are very important because of their applications in numerous catalytic reactions, including catalytic reforming reactions, pollution control, and alcohol oxidation [25, 40-43].

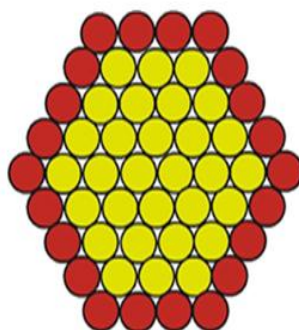
The morphology of a bimetallic catalyst depends upon its method of preparation [44]. For example, in the production of alloyed structures reaction conditions must be controlled in such a way that it can simultaneously reduce both metals, such as use of strong reducing agent, use of surfactant or counter ion and use of a metal ion that can facilitate reduction of both metals [3]. Common morphologies of bimetallic catalysts are presented in Figure 2.



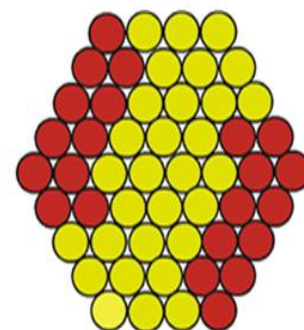
Crown Jewl Structure



Alloy



Core- Shell



Cluster

Figure 2: Common morphologies of bimetallic catalysts

1.7 Use of Bimetallic Catalysts for Environmental Remediation

1.7.1 Ammonia, an Industrial Chemical

Ammonia (NH_3), a compound of nitrogen and hydrogen, exists as colourless gas with characteristic pungent smell. It is lighter than air and its density is 0.589 times less than that of air. It can easily be liquefied due to strong hydrogen bonding. It is soluble in

water, alcohol, ether and chloroform. Some important physical properties of ammonia are listed in Table 1.

Table 1: Physical properties of ammonia

| Formula | NH₃ |
|------------------|--|
| Molar mass | 17 g/mol |
| Density | 0.682 g/cm ³ (at -33 °C) |
| Specific gravity | 0.77 at 0°C |
| Boiling point | -33.3 °C |
| Freezing point | -77.7 °C |

Ammonia is a useful industrial chemical having many applications, e.g. in agriculture as fertilizers [45], as refrigerant gas, in the manufacturing of plastics, pesticides, explosives, textile dyes, ammonium nitrate, livestock feed lots, petroleum refineries etc. [45-47]. The industrial consumption of ammonia is illustrated in Figure 3.

1.7.2 Ammonia, a Pollutant

Due to the excessive use of ammonia in the industry it is one of the most important environmental issue. It is discharged in the air as well as in the water from the industries [48]. The decomposition of protein based wastes and other biological processes are other sources of ammonia in air [49, 50]. In air the ammonia can cause odor problems as well as it can affect the breathing system, skin and eyes of living organism. Its concentration greater than 300 ppm can cause death of individual [49, 51].

The presence of ammonia in water is toxic for living organisms as well as it causes eutrophication in the aquatic environment [48] which results in the disturbance of aquatic life and disappearance of water bodies. Up to a certain limit ammonia is used as nutrient by the plants but beyond that its presence in water is harmful. It enters in a living body where it reacts with water to form ammonium hydroxide, which is corrosive and damages the cells. Even less than 10 ppm of ammonia is toxic for some fish species [52-

54]. Therefore, removal of ammonia from waste water is very important in maintaining the aquatic environment [55].

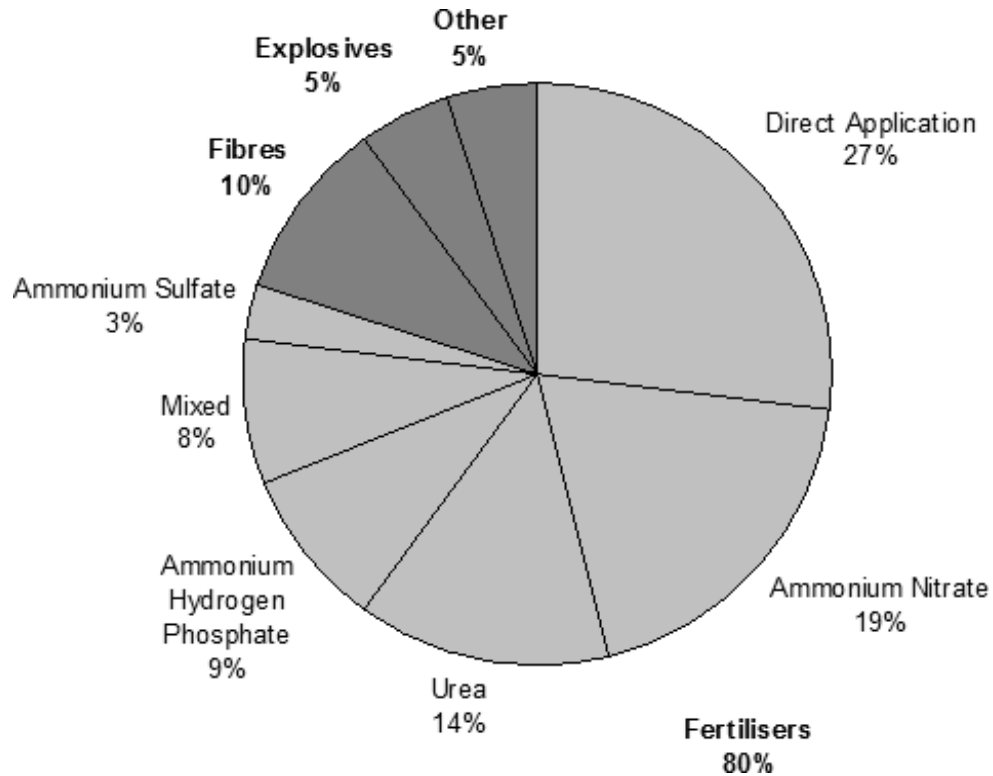


Figure 3: Industrial consumption of ammonia

1.8 Removal of Ammonia from Environment

The removal of ammonia from the environment is brought out either by gas phase decomposition or liquid phase decomposition [56].

1.8.1 Gas Phase Decomposition

The removal of ammonia from air is carried out by gas phase decomposition which includes wet air oxidation (WAO) and catalytic wet air oxidation (CWAO). These methods involve oxidation of ammonia at high temperature and pressure in the presence of suitable catalyst. This method is best suited for the treatment of high concentration of

ammonia. In this method no harmful byproducts are formed. The requirement of high temperature makes energy costs high [57].

1.8.2 Liquid Phase Decomposition

The common liquid phase decomposition methods used for ammonia removal include biological methods, stripping, chlorination, ion-exchange, activated carbon adsorption and catalytic wet air oxidation (CWAO) [47, 58-61]. Some of these methods may yield a contaminated sludge and adsorbent which require secondary treatment. Secondly they produce harmful byproducts which are hazardous for life. Their maintenance and operation costs are also high [47]. A brief comparison of different methods used for the removal of aqueous ammonia is presented in Table 2.

1.9 Catalytic Wet Air Oxidation (CWAO)

Among the methods used for the removal of ammonia from environment, catalytic wet air oxidation (CWAO) has been widely used for the treatment of waste water containing ammonia and other pollutants. In catalytic wet air oxidation (CWAO), the waste water containing ammonia is oxidized under high temperature and pressure in the presence of a suitable metal catalyst [45]. The efforts have been made for selective oxidation of ammonia to nitrogen and water which makes the process ideal as no harmful byproducts are formed [62].

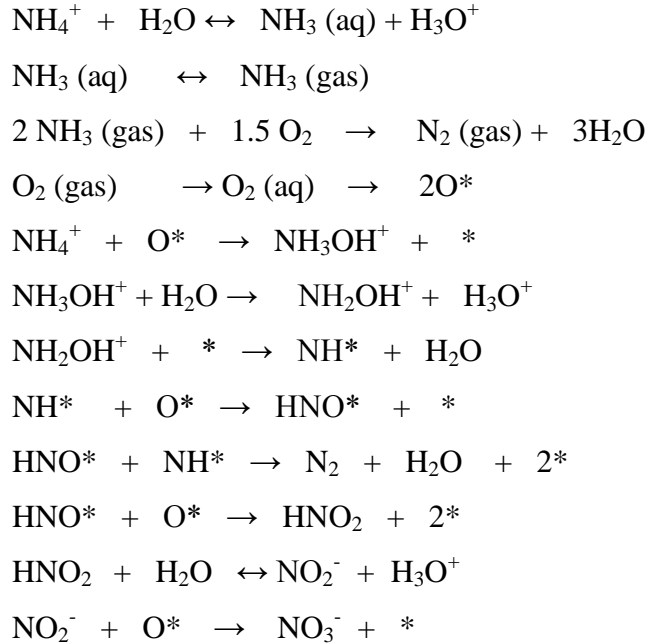
The main advantages of catalytic wet air oxidation (CWAO) are that ammonia can be transformed into nitrogen with minimum formation of NO_x [63]. As no harmful byproducts are formed so no secondary treatment is required. Secondly waste water containing high concentration of ammonia can be oxidized in short time which is difficult to be treated by conventional methods [45, 55, 64, 65].

Table 2: Comparison of methods used for ammonia decomposition

| Method | Advantages | Disadvantages | Ref |
|---|---|--|--------------|
| Biological Methods , Nitrification/ Denitrification | Simple, Cheap | Limited to low conc. (≤ 80 ppm), Long reaction time, Nitrites and nitrates are produced, Large sewage sludge, High cost. | [45, 47, 54] |
| Ammonia stripping | Low cost, Simple, reliable, Minimum addition of dissolved solids. | Poor efficiency in cold weather, Scaling problem with reactor. | [47, 48] |
| Chlorination | Low cost, High efficiency, No effect of temperature. | Chlorination | [48] |
| Ion exchange | High efficiency, Minimum addition of dissolved solids, No harmful products. | Limited to low conc., Secondary treatment is required, Complex process, High cost. | [66] |
| Activated carbon adsorption | Simple | Large sewage sludge, Secondary treatment is required, High cost. | [61] |
| CWAO | High concentration of ammonia can be treated, No harmful by products, No secondary treatment. | High temperature, High cost. | [45, 64, 65] |

1.9.1 Mechanism for Catalytic Wet Air Oxidation of Ammonia

In catalytic wet air oxidation (CWAO), ammonia is converted mainly to nitrogen and very low concentration of nitrates is also produced. The proposed reaction mechanism is as follow [50].



Where * indicates the catalytic active site. It has been reported that the catalyst plays an important role in selectivity towards nitrogen production. The nitrates and nitrites are undesirable as they are pollutants. The pictorial description of ammonia oxidation over the surface of catalyst is given in Figure 4.

1.9.2 Catalysts for Wet Air Oxidation of Ammonia

It has been observed that WAO is difficult under mild conditions in the absence of a catalyst [63]. Use of a suitable catalyst can make the reaction to take place under milder conditions. Several catalyst systems based on transition and noble metals are reported for ammonia oxidation e.g. Ni and other transition metals supported over $\gamma\text{-Al}_2\text{O}_3$ has been used for ammonia removal from aqueous stream at 257 °C but their efficiency was low [55]. Cobalt based catalysts have also been used for ammonia decomposition with high activity and selectivity but the reaction temperature was high i.e. 550°C [67].

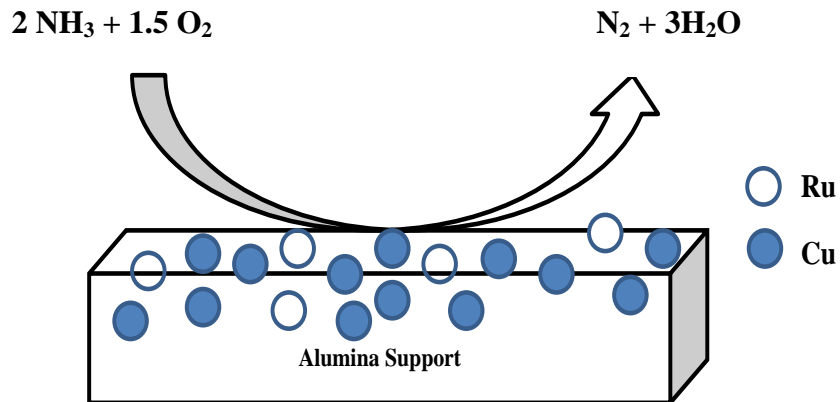


Figure 4: Oxidation of ammonia over catalyst surface

It has been found that noble metals like Ru, Ir, Pt, Pd and Rh show more activity towards ammonia decomposition [55, 63]. Noble metals supported over $\gamma\text{-Al}_2\text{O}_3$ show high activity and selectivity to nitrogen production in CWAO of ammonia as compared to transition metals [45, 48, 55, 68]. Pd, Ru, Rh supported over CeO_2 have also been used but selectivity to nitrogen was also low [50]. The Ru supported over activated carbon is the most active catalyst for ammonia decomposition reaction [67]. However, high cost and limited availability of Ru inhibits its use in the industry [46, 67].

In spite of having good activity, noble metal catalysts are mostly costly and some of them also lack the stability under reaction conditions [55, 63]. To reduce the cost of noble metal catalysts, bimetallic catalysts are getting attention of many researchers. Transition metal catalysts are doped with noble metals and promoting effects of noble metal in ammonia oxidation is studied by many researchers e.g. $\text{Ag-Cu}/\gamma\text{-Al}_2\text{O}_3$ has been used for gas phase decomposition of ammonia from air [49] at 150°C to 400°C whereas temperature can be lowered to 300°C using $\text{Pt-CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Similarly, Pt-Pd-Ru composite catalyst has also been used for ammonia decomposition but selectivity to nitrogen production was found low [46].

As mentioned before the supported ruthenium catalyst has widely been used for ammonia decomposition with high selectivity towards nitrogen production at low temperature. Due to the high cost of ruthenium researchers are trying to produce a catalyst which is highly active towards ammonia decomposition but at the same time it is cost effective. The copper metal supported over different supports also shows some

activity towards ammonia decomposition [55, 62, 63]. There is a need to develop a catalyst having high activity, selectivity, stability as well as low cost [63].

Some other examples of catalysts used for catalytic wet air oxidation (CWAO) of ammonia [67] are given in Table 3.

Table 3: Catalysts used for ammonia oxidation

| Initial concentration | Catalyst (weight) | Oxidizing Agent | Pressure | Temperature pH | Ref. |
|-------------------------|---|----------------------------------|-------------|---------------------------------|--------------|
| 1.9–6.9 -- 10-3 g mol/L | | O ₂ -H ₂ O | 24.6 MPa | 803–973 K | [69] |
| 1450–1800 ppm | M*/Al ₂ O ₃ (4 g) | Air | 2.0–4.1 MPa | 423–503 K, 12 | [51] |
| 50 m mol/L | M**/CeO ₂ Ru Pd/CeO ₂ (4 g/L) | O ₂ | 2 MPa | 393–473 K (acidic Condition) | [27] |
| 1000 ppm | Ru/TiO ₂ (0.5–2.0 g) | O ₂ | 0.5–1.6 MPa | 433–493 K, 5.5–12.3 | [70, 71] |
| 400–1000 mg/L | Cu/La/Ce(25 g) | O ₂ | 2.0 MPa | 423–503 K, 11.0 ± 0.2 | [72] |
| 400–1000 mg/L | Pt/Pd/Rh (25 g) | O ₂ | 2.0 MPa | 423–503 K, 11.0 ± 0.2 | [73] |
| 400 mg/L | Cu/La/Ce(25 g) | O ₂ | 4.0 MPa | 423–503 K, 11.5 ± 0.2 | [74] |
| 1870ppm | Cu-Ru/ γ-Al ₂ O ₃ 0.3g | Air | 0.2MPa | 423K-503K | Present work |

SCWO: supercritical water oxidation, CWO: catalytic wet oxidation, WO: wet oxidation. M*: Cr, Mn/CeO₂, Fe, Co, Ni, Mo, Ru, Rh, Pd, Pt., M**: Pt, Ru, Pd.

1.9.3 General Properties of Copper Metal

Copper is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; a freshly exposed surface has a reddish-orange color. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys. General properties of copper are listed here in Table 4.

Table 4: General properties of copper

| Physical Property | Value |
|--------------------------|---------------------------------------|
| Atomic No. | 29 |
| Atomic mass | 63.546 |
| Density | 8.9 g/cm ³ at 20 °C |
| Melting point | 1083 °C |
| Boiling point | 2595 °C |
| Electronic configuration | [Ar] 3d ¹⁰ 4s ¹ |

1.9.4 General Properties of Ruthenium Metal

Ruthenium is a noble metal which is inert to most chemicals. It is used for wear-resistant electrical contacts, production of thick-film resistors, in platinum alloys, and as a catalyst. General properties of ruthenium are listed in Table 5.

Table 5: General properties of ruthenium

| Physical Property | Value |
|--------------------------|--------------------------------------|
| Atomic No. | 44 |
| Atomic mass | 101.1 |
| Density | 12.2 g/cm ³ at 20 °C |
| Melting point | 2250 °C |
| Boiling point | 4150 °C |
| Electronic configuration | [Kr] 4d ⁷ 5s ¹ |

1.10 Plan of Work

As mentioned before the supported Ruthenium is very efficient catalyst in the decomposition of ammonia [67] but due its high cost its use on industrial scale is limited [46]. The copper metal supported over different supports also shows some activity towards ammonia decomposition. [49, 63]. The aim of present work is to synthesize a cost effective γ -Al₂O₃ supported Cu-Ru bimetallic catalyst with high surface area, high thermal and mechanical properties by impregnation method and to explore its application in the decomposition of aqueous ammonia. The focus is on low temperature decomposition of ammonia leading to harmless products with high selectivity towards N₂ production and low yield of Nitrates. For this purpose γ -Al₂O₃ supported Cu-Ru bimetallic catalysts with different metal loading were prepared. Amount of Copper was kept constant and Ru loading was changed in order to study the promoting effect of Ru in the activity of copper. For comparison monometallic Ru/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ were also prepared with 7% and 10% metal loading respectively. Promoting effect of Ru on the catalytic activity of Cu was also studied. Effects of different parameters on the ammonia decomposition were also studied. Reusability of the catalyst was studied by reusing the catalyst for five cycles.

Chapter 2

EXPERIMENTAL

2.1 Synthesis of Materials

2.1.1 Reagents and Chemicals

High purity reagents and chemicals were used in the preparation of catalysts. The precursor used for Ru and Cu were ruthenium chloride trihydrate, ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$), 40% by Ru (Sigma Aldrich) and copper sulphate pentahydrate, ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 99.9% pure (Merck). Hydrochloric acid (37%) was obtained from Labscan while ammonia (33%) was obtained from Analr. Aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) was obtained from Reidal-de-Haen. Deionized water was used as solvent for all the solution.

2.1.2 Synthesis of $\gamma\text{-Al}_2\text{O}_3$

Sol-gel method was used for the synthesis of $\gamma\text{-Al}_2\text{O}_3$. For this purpose 96.6 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 1000 ml of deionized water. 10 % ammonia solution was prepared by dissolving 150 ml of 33 % ammonia in 500 ml of deionized water. The carbon dioxide gas was passed through the ammonia solution to maintain the pH in the range of 7 to 9. The aluminium chloride solution was added slowly to the buffered ammonia solution till the pH is 8. The aging of prepared gel was done at 80 °C for four days followed by filtration and washing with water. After that gel was dried and converted to granular form. Heat treatment of the alumina gel was performed at 750°C for 10 hours to convert it into $\gamma\text{-Al}_2\text{O}_3$. The mesh size of the $\gamma\text{-Al}_2\text{O}_3$ was measured by passing it through the standard sieves. The mesh size of the $\gamma\text{-Al}_2\text{O}_3$ was in the range of 0.4 to 1.0 mm.

2.1.3 Preparation of Catalyst

For the preparation of solutions, 7.86 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 2.5 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were dissolved separately in 100 ml of deionized water to get 2% (w/v) Cu and 1% (w/v) Ru solution respectively. Few drops of hydrochloric acid (HCl) were added in both the solutions to maintain the pH value to 1.

Cu-Ru bimetallic catalysts supported over γ -Al₂O₃ were prepared by incipient wetness impregnation of Ru and Cu. For comparison monometallic Cu/ γ -Al₂O₃ and Ru/ γ -Al₂O₃ were also prepared. The proposed composition of the catalysts is given in Table 6.

Table 6: Proposed composition of catalysts

| Sr. No | Catalyst ID | Catalyst composition | |
|--------|-------------|----------------------|----------|
| | | Cu w/w % | Ru w/w % |
| C-1 | Cu-10 | 10 | 0 |
| C-2 | Cu-Ru-1 | 10 | 1 |
| C-3 | Cu-Ru-3 | 10 | 3 |
| C-4 | Cu-Ru-5 | 10 | 5 |
| C-5 | Ru-7 | 0 | 7 |

For the preparation of catalyst, γ -Al₂O₃ (mesh size 0.4 to 1.0 mm) was dried at 200°C in a drying oven for two hours in order to remove any adsorbed moisture and gases and then cooled in a desiccator. 5.0 gram of γ -Al₂O₃ was taken in a 100 cm³ china dish marked as C-1 – C-5. 5.0 cm³ of 2% copper solution was added to C-1 to C-4 and 5.0 cm³ of 1% ruthenium solution to C-5 in order to wet the alumina. All the catalysts were placed at room temperature for two hours for maximum absorption. Any extra solution was then decanted and samples were dried in a drying oven at 120 °C for two hours. Calcination of the samples was then carried out at 550 °C for 5 hours in a programmable muffle furnace (Naber Model No-280). Weight gain for each catalyst was noted. For C-1 next impregnation was repeated with 2.0% copper solution. For C-2 to C-5 impregnation was repeated with 1% Ruthenium solution. Alternate impregnations with copper and ruthenium were performed to get the desired metal loading on each catalyst. Activation of the catalyst was done by reduction in a continuous flow of 99.99 % pure H₂ gas at 550 °C for 5 hours. The catalysts were identified by their weight percentage of metals as given in Table 6. The pictorial description of catalyst preparation is presented below in Figure 5.

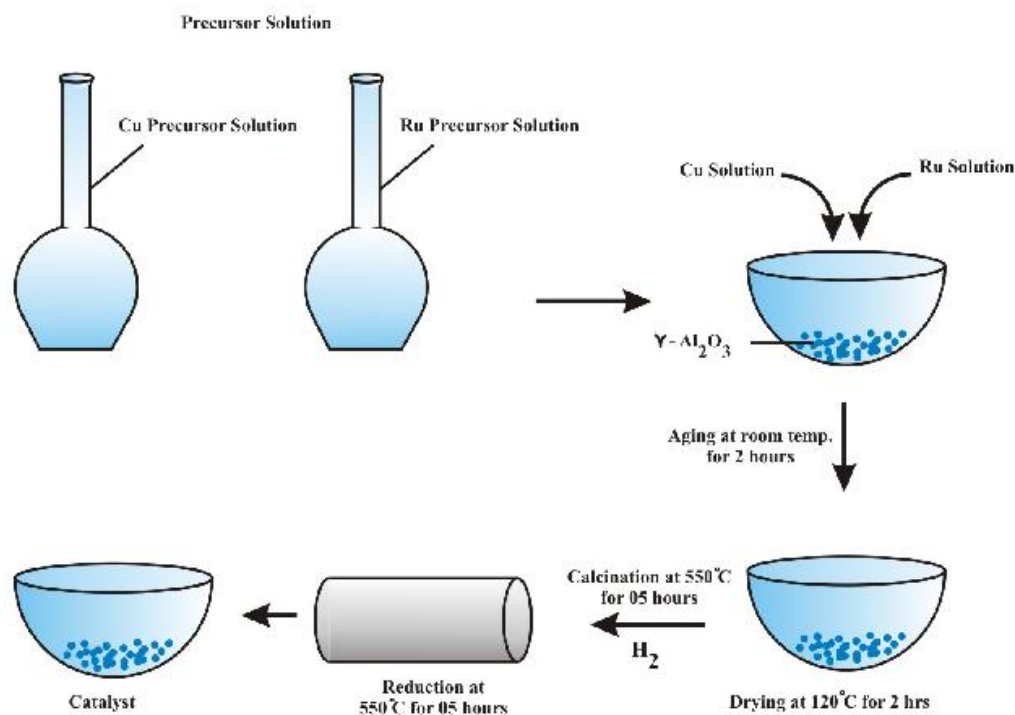


Figure 5: Pictorial description of catalyst preparation

2.2 Characterization of Materials

The characterization of selected catalyst was performed by using following techniques.

2.2.1 Atomic Absorption Spectrophotometry (AAS)

Composition of prepared catalysts was confirmed by Atomic absorption spectrophotometer. Alkaline oxidizing fusion method was used for sample preparation in which metallic ruthenium is oxidized to soluble sodium ruthenate, Na₂RuO₄ by treatment with NaOH and Na₂O₂ at 450- 600 °C [75, 76] . 0.1 g of each catalyst sample was fused with a fusion mixture of Na₂O₂: NaOH (1:1 ratio). The ratio of catalyst and fusion mixture was 1: 10 for each sample. Samples were fused at 600 °C for one hour and then dissolved in aqua regia. Analysis of copper and ruthenium was performed by using Flame Atomic Absorption Spectrophotometer Perkin Elmer AAnalyst 400. Hollow cathode

lamps of copper and ruthenium were used as light source. Results of atomic absorption spectrophotometric analysis are given in Table 7.

2.2.2 Surface Area Analysis

In order to study the textural properties of catalysts, surface area analysis was performed to determine the Brunauer-Emmett-Teller (BET) Area, Langmuir Area and micro pore volume of the prepared catalysts [77]. For this purpose surface area analyzer KELVIN 1042, Costech International, Italy was used. The instrument works on the principle of adsorption of nitrogen gas at liquid nitrogen temperature while helium was used as a carrier gas. Thermal conductivity detector is used to measure the adsorbed gas volume, which in turn gives the surface area. In order to remove any trapped gases and moisture samples were degassed at 250 °C for two hours before analysis. The surface area was obtained using Brunauer-Emmett-Teller (BET) equation for adsorption of N₂ in the relative pressure (p/p₀) range of 0.05 to 0.20. Complete isotherm and pore size distribution analysis were also performed for the selected catalyst from the series. Results of surface area analysis are tabulated in Table 8 whereas isotherm and pore size distribution are given in Figure 7 and 8 respectively.

2.2.3 Powder X-Ray Diffraction Analysis (XRD)

In order to identify the crystal structures and crystallite size of prepared catalysts, Powder X-rays Diffraction (XRD) analysis was carried out. In this technique a beam of incident X-Rays is focused on a crystal which causes diffraction. By measuring the angle and intensities of diffracted beams crystal structures of the catalyst can be measured. Panalytical, X-Ray Powder Diffractometer, Model 3040/60-X-Pert Pro, was used for crystal structure studies of the catalyst. Cu K α_1 was used as light source. X-Ray Diffractograms of bare γ -Al₂O₃ and catalysts are presented in Figure 9.

The average crystallite size of the samples was calculated by using Debye Scherer formula.

$$D_{av} = \frac{57.3 \text{ K } \lambda}{\beta \cos \theta} \text{ (nm).....(Equation.1)}$$

Where

D = Crystallite size

β = Broadening of diffraction line measured at half of its maximum intensity

θ = Diffraction angle

K = Particle shape factor (0.9 in case of cubic system)

λ = Wavelength of X-Ray beam (0.154 nm)

Average crystallite size of γ -Al₂O₃ and prepared catalysts are summarized in Table 9.

2.2.4 Fourier Transformed Infra-Red (FT-IR) Spectroscopy

Fourier Transformed Infra-Red (FT-IR) Spectroscopy is an important analytical technique used for the identification of materials. FT-IR analysis of γ -Al₂O₃ and the prepared catalysts was carried out by using Perkin Elmer FT-IR Spectrophotometer, Spectrum –II, USA. Small amount of sample was mixed with KBr and pressed into pallette form and then subjected to the FT-IR analysis. The frequency range was 4000 cm⁻¹ to 400 cm⁻¹. The FT-IR spectra are presented in Figure 10.

2.2.5 Thermal Gravimetric Analysis (TGA)

Thermal properties of γ -Al₂O₃ and catalysts were studied by measuring the weight loss of material with increase in temperature. Thermal gravimetric analysis was carried out by using TGA/DSC1 STAR-System, Model No. D-09123, Mettler Toledo Switzerland. For TGA analysis 2.0 to 3.0 milligrams of the samples were analyzed in nitrogen atmosphere with a flow rate of 60 ml/min. Samples were analyzed in a temperature range of 0 °C to 600 °C with temperature increase at the rate of 10 °C/ min. Results of thermal gravimetric analysis are presented in Figure 11.

2.2.6 Scanning Electron Microscopy (SEM)

In order to study the microstructure of the catalyst Scanning Electron Microscopy (SEM) analysis of selected bimetallic catalyst was undertaken. In this technique a beam of electron is focused on a spot of analyte material and textural properties of a localized area are studied. Scanning Electron Microscopic study was carried out by using field

emission scanning electron microscope (FE-SEM), TESCAN, Czech Republic. Samples were coated with carbon prior to analysis. EDX mapping was performed with the same instrument. SEM micrographs are presented in Figure 12 whereas EDX analyses are presented in Figure 13-15.

2.3 Application of Catalysts for Decomposition of Ammonia

The catalyst testing for ammonia decomposition was carried out in a homemade reactor made up of stainless steel (SS-316 Grade). The experimental setup for ammonia decomposition is presented in Figure 6.

2.3.1 Blank Experiment

The blank experiment was carried out in the absence of any catalyst at three different temperatures i.e. 150 °C, 200 °C and 230 °C under 2 bar pressure of argon gas for three hour reaction time. Another test was carried out using bare γ -Al₂O₃ and change in ammonia concentration was measured. The results are discussed in the next section.

2.3.2 Ammonia Decomposition Experiment

For catalyst testing 20 cm³ of aqueous solution of ammonium hydroxide 0.11 moldm⁻³ solution (pH value =11) was taken in the reaction vessel. For each experiment, 0.3 gram of the catalyst was weighed and transferred in the reaction vessel. In order to remove adsorbed moisture and gases the catalysts were heated at 120°C for two hours in a drying oven before the reaction. Reactor was then closed and reaction mixture was stirred for 30 minutes at room temperature to achieve adsorption equilibrium. The compressed air was introduced into the reactor up to an internal pressure of 2 bar at 25°C. All the valves were then closed. Outlet was dipped in the trapper containing 50 cm³ of 0.01 moldm⁻³ HCl solution. Reaction mixture was then heated to 150 °C and maintained at that temperature for 3 hours. After 3 hours of reaction time the mixture was cooled to room temperature and gas was allowed to enter into the trapper by opening the valve in order to trap any gaseous ammonia and oxides of nitrogen produced. The reaction mixture was filtered to recover the catalyst.

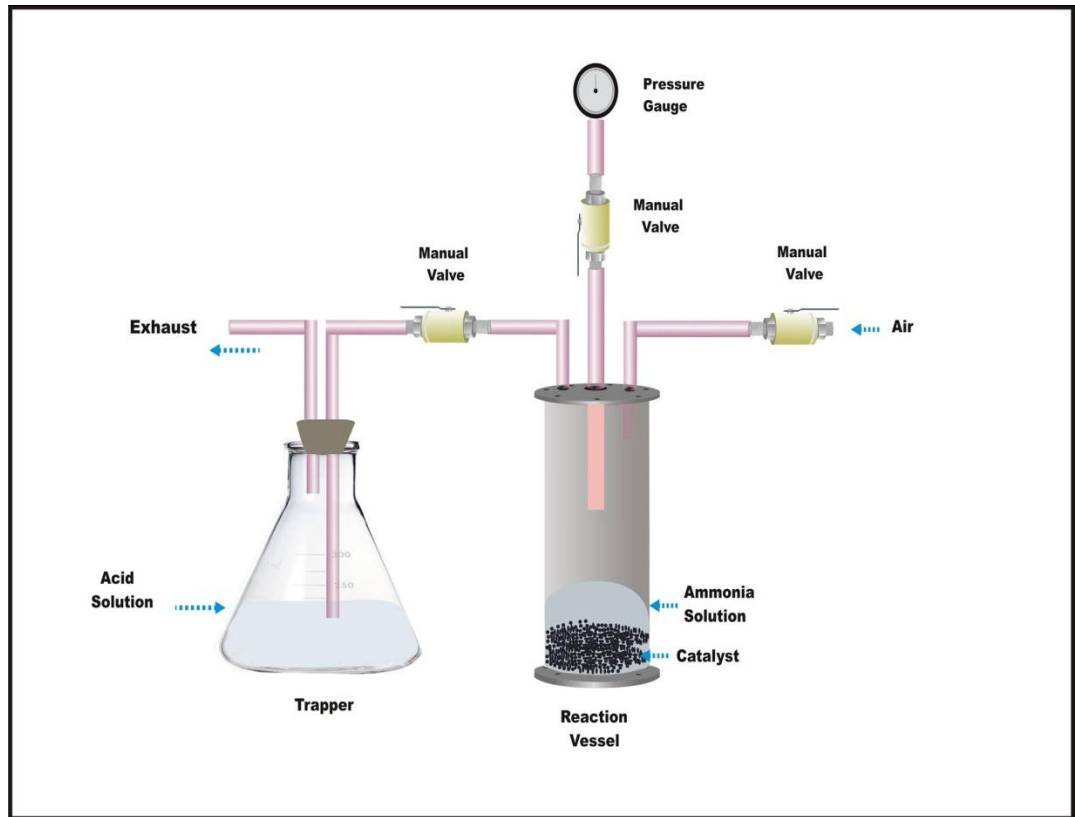


Figure 6: Experimental setup for ammonia decomposition

The liquid was analyzed for ammonia concentration by titration and the concentration of ions (nitrate & nitrites) was determined by ion chromatography. The pH of the reaction mixture and the trapper was also measured before and after the reaction. Gaseous samples of ammonia decomposition over a selected catalyst were also analyzed by Mass Spectrometer to detect any oxides of nitrogen produced as result decomposition. Ammonia decomposition was calculated using following formula [53, 56, 63]

$$\text{Ammonia decomposition (\%)} = \frac{C_o - C_t}{C_o} \times 100 \dots \dots \dots \text{Equation. 2)}$$

Where

C_o =Initial concentration of ammonia

C_t = Concentration of ammonia after the reaction

The selectivity of the products was calculated using equation .3 which is given below [53, 63].

$$\text{Selectivity to NO}_3^- = \frac{\text{Moles of NO}_3^{-1} \text{ formed in term of N}_2}{\text{Moles of ammonia decomposed in term of N}_2} \times 100$$

$$\text{Selectivity to N}_2 = 100 - \text{Selectivity to NO}_3^- \dots\dots\dots \text{(Equation.4)}$$

Total yield of nitrates can be calculated by using following formula [53, 56, 63].

$$\text{Yield of Nitrates (\%)} = \frac{\text{Moles of Nitrates formed}}{\text{Moles of ammonia initially present}} \times 100 \dots \text{(Equation.5)}$$

2.4 Analysis of the Decomposition Products

Following analytical techniques were used for the analysis of ammonia and its decomposition products.

2.4.1 Ion Chromatographic Studies (IC)

The catalytic wet oxidation of ammonia yields nitrate and nitrite ions which were analyzed by ion chromatographic (IC) method. For this purpose Shimadzu High Performance Liquid Chromatograph, HPLC 10 AVP equipped with conductivity detector CDD 6AVP was used. Analytical conditions are given below.

Detector: CDD 6AVP

Column: Shimadzu A-1 (Anion column)

Mobile Phase: 1.2 mM Potassium Hydrogen Phthalate

Flow Rate: 1.5 ml/min

Oven Temperature: 40 °C

The results are summarized in Table 10-12.

2.4.2 Mass Spectrometric Studies (MS)

In order to analyze the products in the gaseous state mass spectrometric analysis was carried out. The gaseous sample for ammonia decomposition over a selected catalyst was collected and then subjected to mass spectrometric analysis. For this purpose GC-MS

BALZER Company Model No. QMG-420 was used. Mass spectrum is presented in Figure 18.

2.4.3 pH Measurement

The pH of the solutions was measured using pH meter CP-500L, ISTEK Korea. The pH meter was calibrated with buffer solution of 4, 7 and 9 before each pH measurement. Results are given in Table 10-12.

2.4.4 Determination of Ammonia Concentration

The ammonia concentration was determined by direct titration against 0.05M standard HCl solution. 5.0 cm³ of ammonia solution was taken in an Erlenmeyer flask and few drops of methyl orange indicator were added. 0.05 moldm⁻³ standard solution of HCl was added drop wise till the appearance of light pink colour. The concentration of ammonia was calculated by using equation.6 and results are shown in Table 10 - 12.

$$\text{NH}_3 (\text{moldm}^{-3}) = \frac{A \times B}{C} \dots \text{Equation.6}$$

Where

A= Concentration of standard HCl solution (moldm⁻³)

B= Volume of HCl used, cm³

C= Volume of ammonia sample taken, cm³

2.5 Effect of Different Physical Parameters on Ammonia Decomposition

In order to optimize the reaction conditions the effects of different physical parameters on ammonia decomposition were studied.

2.5.1 Effect of Temperature

Three different temperature i.e. 150 °C, 200 °C and 230 °C were selected to study the effect of temperature over ammonia decomposition. Promoting effect of ruthenium over catalytic activity of copper was also studied at these temperatures. The results are presented in Figure 16 and tabulated in Table 10-12.

2.5.2 Effect of NH₃ to Catalyst Ratio

Ammonia decomposition experiments were carried out at three ammonia to catalyst ratios i.e. 8:1, 6:1 and 4:1 to explore its effect on decomposition. The results are given in Table 13.

2.5.3 Effect of Initial pH

Effect of pH for the selected catalyst was studied by keeping all other parameters constant. Experiments were carried out at two different pH values i.e. 11.0 and 4.01. For this purpose the pH of the ammonia solution was brought from 11.0 to 4.01 by adding few drops of 0.1 M HCl solution. The results are tabulated in Table 14.

2.6 Stability of Catalyst

2.6.1 Catalyst Reusability

The stability and reusability of the selected catalyst was checked by repeating the experiments five times. Each time catalyst was separated from the reaction mixture by filtration followed by washing with distilled water. The catalyst was then dried in a drying oven at 120°C for six hours and then cooled in a desiccator. After that it was weighed and used again. The results of catalyst reusability are presented in Figure 19.

2.6.2 Dissolution Degree of Catalyst

The dissolution degree of catalyst is an important parameter for catalyst characterization. Beside good activity and high selectivity catalyst should be insoluble in the reaction medium [53]. The dissolution degree of the catalysts during the reaction was also measured at 200 °C. For this purpose, concentration of copper and ruthenium was determined in the reaction mixture using Atomic Absorption Spectrophotometer Perkin Elmer AAnalyst 400. Dissolution degree of the catalysts was calculated by using following formula [53] and the results are tabulated in Table 15.

$$\text{Dissolution Degree (\%)} = \frac{W_{\text{dissolved}}}{W_{\text{initial}}} \times 100 \dots \dots \text{(Equation.7)}$$

Where

$W_{\text{dissolved}}$ = Weight of metals dissolved in the reaction mixture

W_{initial} = Weight of metal initially present in the catalyst

Chapter: 3

RESULTS AND DISCUSSION

3.1 Characterization of Material

In this study γ -Al₂O₃ supported Cu-Ru bimetallic catalysts with different metal loading were prepared by impregnation method. The prepared catalysts were characterized by using different techniques which are discussed in the next section.

3.1.1 Atomic Absorption Spectrophotometric Analysis (AAS)

The composition of prepared catalysts was confirmed by Atomic absorption spectrophotometer. The concentration of copper and ruthenium were determined using Perkin Elmer AAnalyst 400 Flame Atomic Absorption Spectrophotometer. Hollow cathode lamps of copper and ruthenium were used as light source. The results of atomic absorption spectrophotometric analysis are given in Table 7 which show that composition of catalysts was very close to the prepared composition.

Table 7: Composition of prepared catalysts

| Catalyst ID | Catalyst composition | |
|-------------|----------------------|----------|
| | Cu w/w % | Ru w/w % |
| Cu-10 | 10.18 | 0 |
| Cu-Ru-1 | 9.41 | 1.33 |
| Cu-Ru-3 | 9.74 | 2.87 |
| Cu-Ru-5 | 9.20 | 5.27 |
| Ru-7 | Nil | 7.42 |

3.1.2 Surface Area Analysis

In order to study the textural properties of the catalysts surface area analysis was carried out [77] by using SORPTOMETER KELVIN 1042, Costech Instrument Italy. In order to remove any adsorbed moistures and air all the samples were initially degassed at 250°C for two hours prior to analysis. Surface area analysis was

carried by adsorption of N₂ gas at -193 °C. Thermal conductivity detector (TCD) was used to measure the adsorbed gas volume. From the adsorbed gas volume surface area of the sample was calculated. Results of the surface area analysis are given in the Table 8. The results indicated that bare γ -Al₂O₃ has highest surface area 173.26 m²/g showing highest porosity and meso-porous structure [78]. BET Surface area decreased with the increase of metal loading showing that pores were filled with metal particles resulting in the decrease of surfaces area.

Table 8: Surface area analysis results

| Catalyst ID | BET Area (m ² /g) | Langmuir Area (m ² /g) | Micropore Volume (mm ³ /g) |
|--|------------------------------|-----------------------------------|---------------------------------------|
| γ -Al ₂ O ₃ | 173.26 | 233.59 | 14.17 |
| Cu-10 | 111.0 | 150.04 | 7.60 |
| Cu-Ru-1 | 116.72 | 157.80 | 7.37 |
| Cu-Ru-3 | 114.87 | 156.02 | 3.49 |
| Cu-Ru-5 | 100.85 | 135.59 | 9.26 |
| Ru-7 | 133.21 | 179.93 | 8.64 |

3.1.3 Isotherm and Pore Size Distribution Analysis

The isotherm analysis and pore size distribution analysis were carried out by employing surface area analyzer SORPTOMETER KELVIN 1042, Costech Instrument Italy. Isotherm analysis of selected catalyst (Cu-Ru-3/ γ -Al₂O₃) was carried out by adsorption of N₂ gas at P/P₀ values in the ranges of 0.05- 0.95, the resulting isotherm plot is presented in Figure 7. The isotherm is Type-II type isotherm which shows physical adsorption of N₂ over the mesoporous surface of the catalyst [49, 79].

Barrett-Joyner-Halenda (BJH) pore size distribution analysis of the same catalyst was also performed. The important finding is that the catalyst has very narrow pore size

distribution and maximum number of pores have pore diameter in the range of 2-20 nm which confirms the mesoporous structure of the catalyst [49, 80]. The BJH pore size distribution of the catalyst is presented in Figure 8.

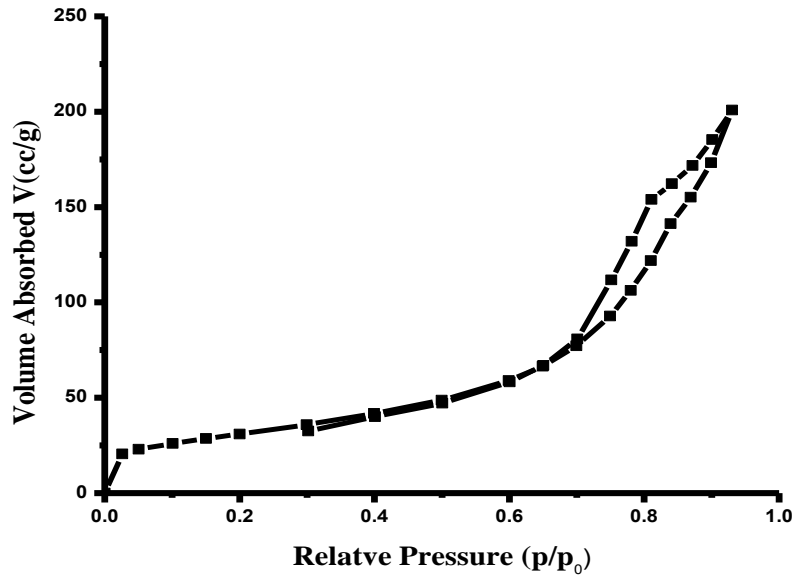


Figure 7: Isotherm plot of bimetallic catalyst

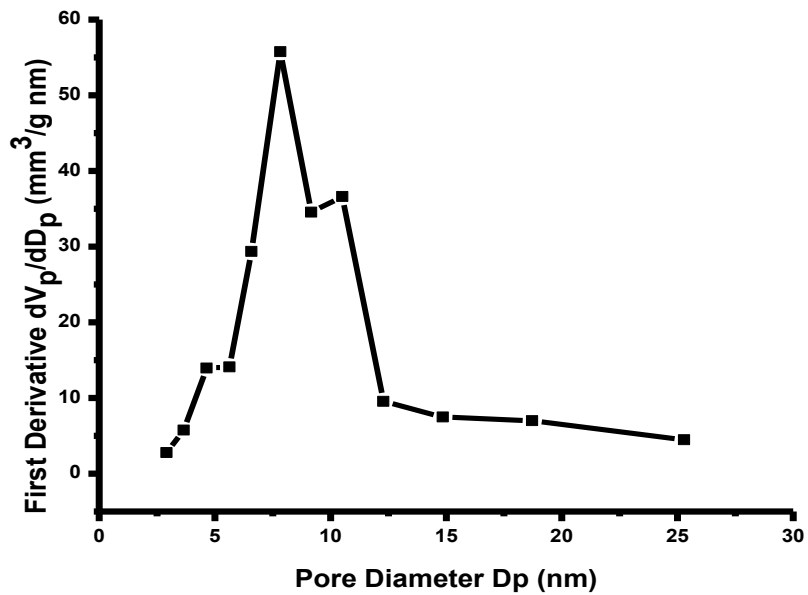


Figure 8: Pore size distribution plot of bimetallic catalyst

3.1.4 Powder X-Ray Diffraction Analysis (XRD)

XRD is the basic technique for the determination of crystal structure and crystallite size of the particles. The XRD Pattern of γ - Al_2O_3 and prepared catalyst are presented in the Figure 9. The γ - Al_2O_3 showed dominant peak in the entire XRD patterns at 2θ values of 31° , 33° , 38° , 39° , 43° , 46° and 68° [49, 81]. In the diffraction pattern of monometallic Cu catalyst, the diffraction peaks appeared at 43° and 54° which correspond to the crystalline Cu phase.

The diffraction peak at 35.5° and 38.8° are due to the presence of CuO which indicated the presence of metal oxide clusters having strong interaction with the support resulting in the formation of CuAl_2O_4 [78, 81]. It has been reported that interaction between CuO and Al_2O_3 occurs readily at calcination temperatures close to 600°C , yielding CuAl_2O_4 [81]. No peak is observed for the Ru metal which indicated that Ru is very well distributed over the support [31]. The average crystallite size of the catalysts was also calculated using Debye Scherer Equation which is tabulated in Table 9. The results indicated that particle size of monometallic catalysts is higher than the support while bimetallic catalysts have particle size less than monometallic catalysts showing high dispersion of metals over the support surface [82].

Table 9: Average crystallite size of catalysts

| Catalyst ID | Average Particle Size (nm) |
|------------------------------------|----------------------------|
| γ - Al_2O_3 | 11.06 |
| Cu-10 | 5.42 |
| Cu-Ru-1 | 7.34 |
| Cu-Ru-3 | 6.41 |
| Cu-Ru-5 | 9.19 |
| Ru-7 | 13.23 |

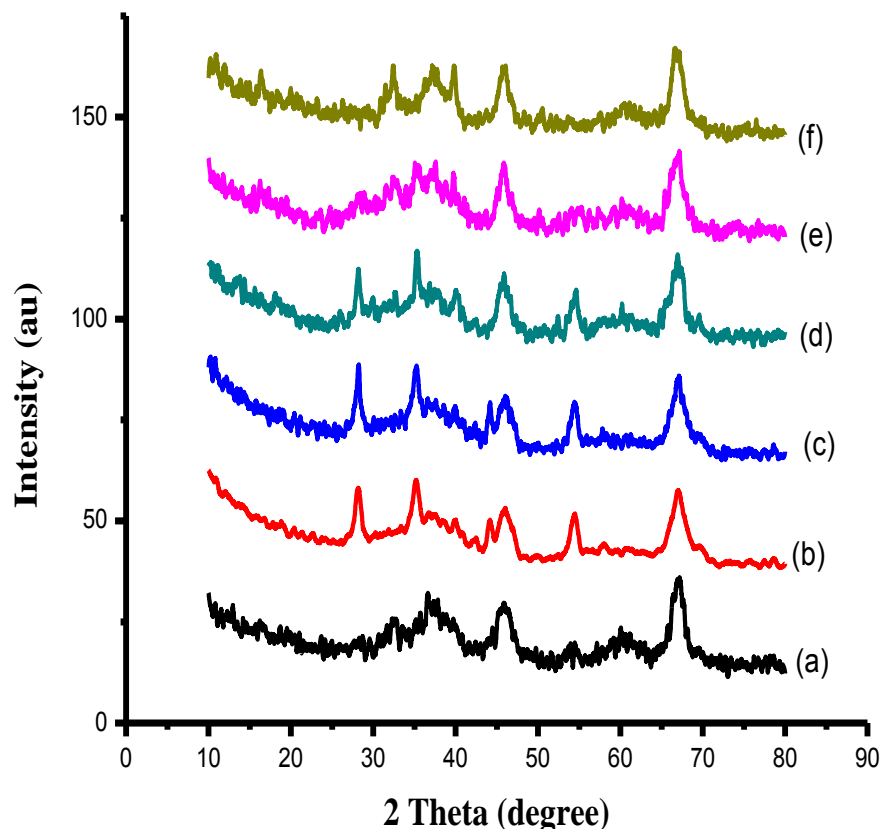


Figure 9: XRD Pattern of catalysts
 (a) γ -Al₂O₃ (b) Cu/ γ -Al₂O₃ (c) Cu-Ru-1/ γ -Al₂O₃
 (d) Cu-Ru-3/ γ -Al₂O₃ (e) Cu-Ru-5/ γ -Al₂O₃ (f) Ru-7/ γ -Al₂O₃

3.1.5 Fourier Transform Infra-Red Analysis (FT-IR)

Fourier Transform Infra-Red (FT-IR) Analysis of the γ -Al₂O₃ and prepared catalysts were carried out by using Perkin Elmer FT-IR Spectrophotometer Spectrum –II, USA. The FT-IR spectra are presented in Figure 10. In the FT-IR spectrum of γ -Al₂O₃, the peaks in the range of 500 to 800 cm⁻¹ were due to the stretching modes of Al-O bond of aluminium oxide [6, 80]. The strong and broad band above 3000 cm⁻¹ is due to the stretching vibration of adsorbed water molecules [6, 80, 83]. The peak at 1640 cm⁻¹ is attributed to the bending vibration of weakly bounded water molecules whereas a peak at 1384 cm⁻¹ is assigned to the O-H bending vibrations [80]. A peak below 3000 cm⁻¹ is due to

the boehmite phase of alumina. After the addition of the metal particles no new peaks appear in the FT-IR spectra of both monometallic and bimetallic catalysts.

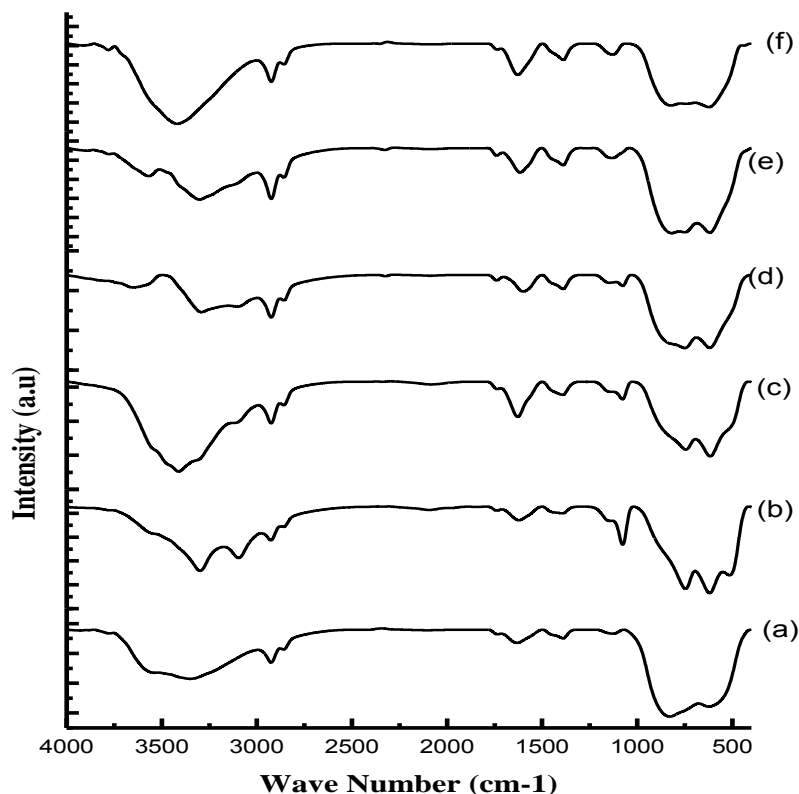


Figure 10: FT-IR Spectra of catalysts
(a) $\gamma\text{-Al}_2\text{O}_3$ (b) $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ (c) $\text{Cu-Ru-1}/\gamma\text{-Al}_2\text{O}_3$
(d) $\text{Cu-Ru-3}/\gamma\text{-Al}_2\text{O}_3$ (e) $\text{Cu-Ru-5}/\gamma\text{-Al}_2\text{O}_3$ (f) $\text{Ru-7}/\gamma\text{-Al}_2\text{O}_3$

3.1.6 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) of the $\gamma\text{-Al}_2\text{O}_3$ and prepared catalysts was performed to study their thermal behavior. The resulting thermograms are presented in the Figure 11 which indicated a single weight loss below 100°C which is due to the loss of physically adsorbed water from the samples [6, 80]. There is no further weight loss at higher temperature which confirms that catalysts are thermally stable up to 600°C .

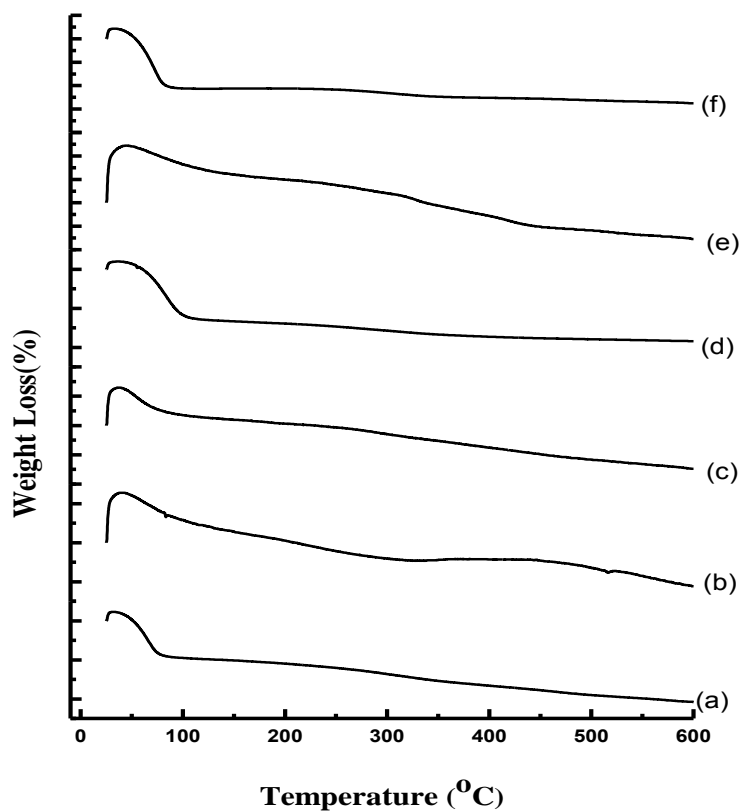


Figure 11: Thermal Gravimetric Analysis plot

(a) $\gamma\text{-Al}_2\text{O}_3$ (b) $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ (c) $\text{Cu-Ru-1}/\gamma\text{-Al}_2\text{O}_3$ (d) $\text{Cu-Ru-3}/\gamma\text{-Al}_2\text{O}_3$ (e) $\text{Cu-Ru-5}/\gamma\text{-Al}_2\text{O}_3$
 (f) $\text{Ru-7}/\gamma\text{-Al}_2\text{O}_3$

3.1.7 Scanning Electron Microscopy Analysis (SEM)

The Scanning Electron Microscopy (SEM) analysis of selected catalyst ($\text{Cu-Ru-3}/\gamma\text{-Al}_2\text{O}_3$) was performed to study the external morphology of the catalyst [21]. The resulting SEM micrographs are presented in the Figure 12 which indicates that metal particles are spherical in shape and they are uniformly distributed over the surface of the support. No agglomeration of the metal particles is observed in the Scanning Electron Microscopy (SEM) images. EDX analysis of a bimetallic and a monometallic catalyst also indicated that pure metal particles are well distributed over the support which is presented in Figure 13 whereas the Figure 14 and 15 represents the EDX mapping of

bimetallic and monometallic catalysts which also confirmed that metal particles are homogenously distributed over the support.

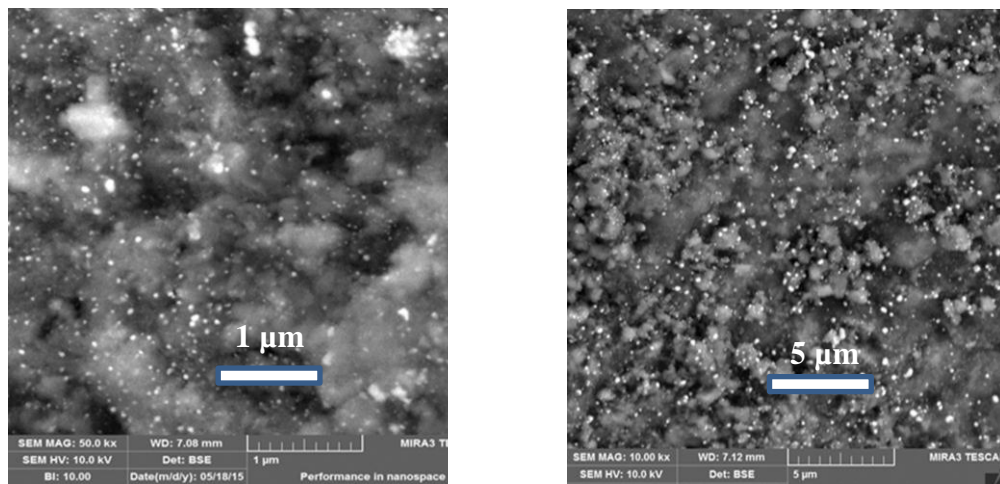
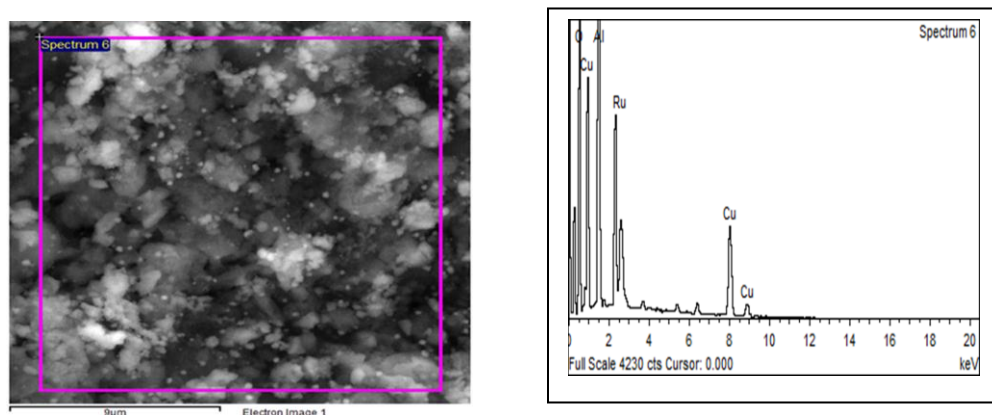


Figure 12 : SEM micrographs of Cu-Ru-3/ γ -Al₂O₃ bimetallic catalyst



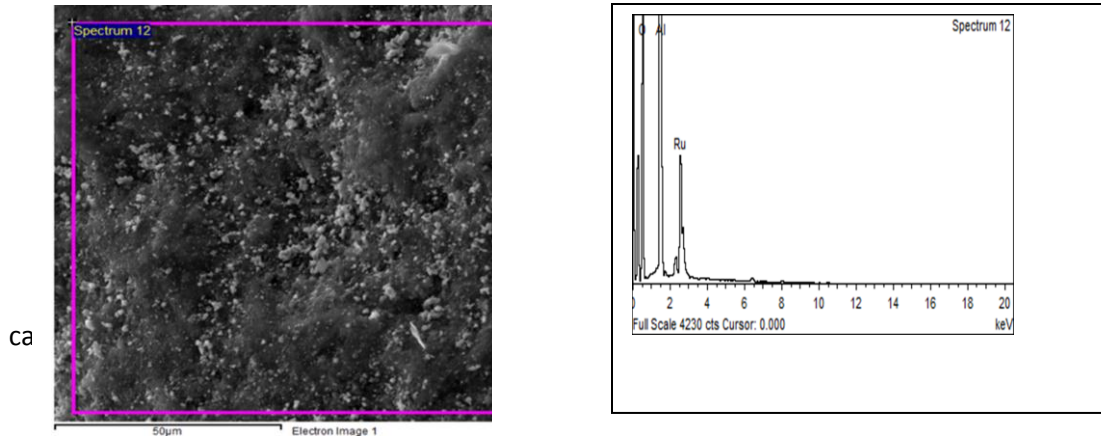


Figure 13: EDX analysis of catalysts

(a) Cu-Ru/ γ -Al₂O₃ bimetallic catalyst (b) monometallic Ru/ γ -Al₂O₃ catalyst

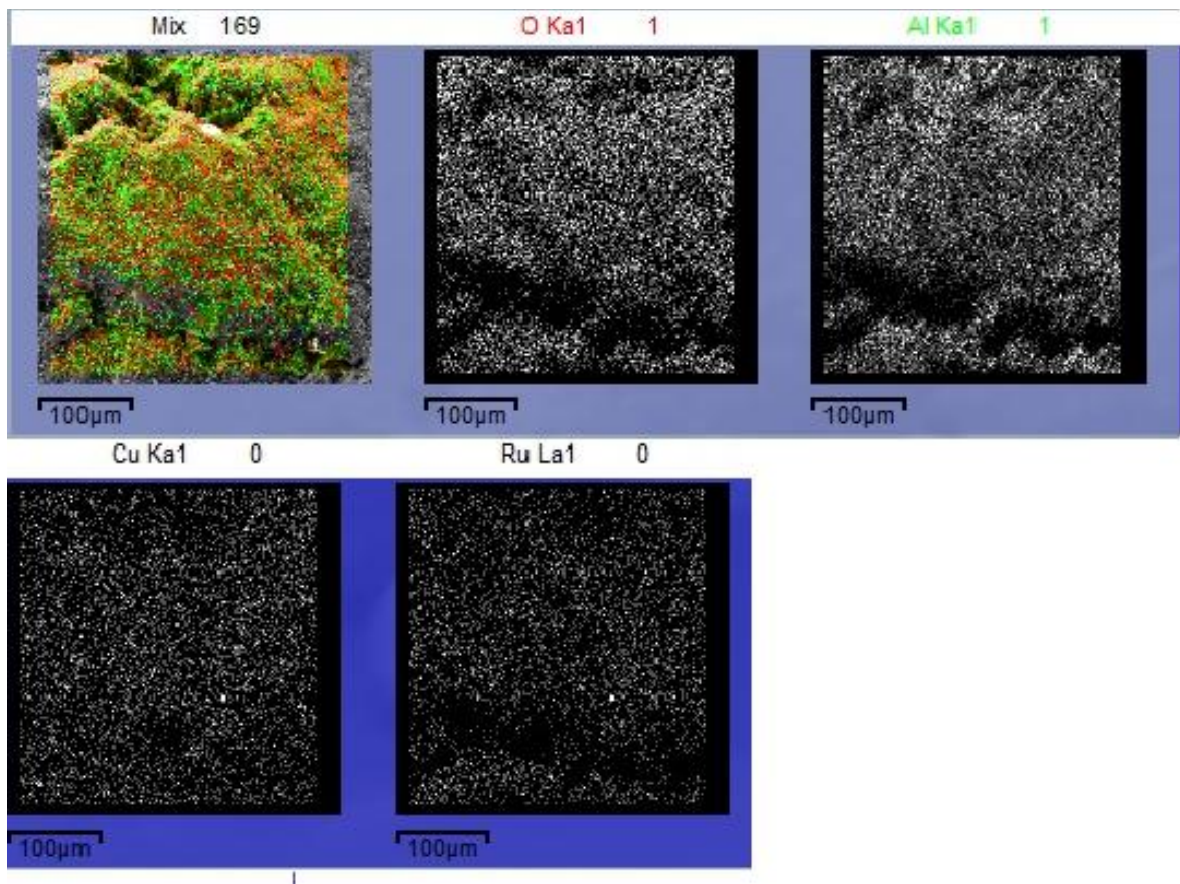


Figure 14: EDX mapping of a bimetallic catalyst

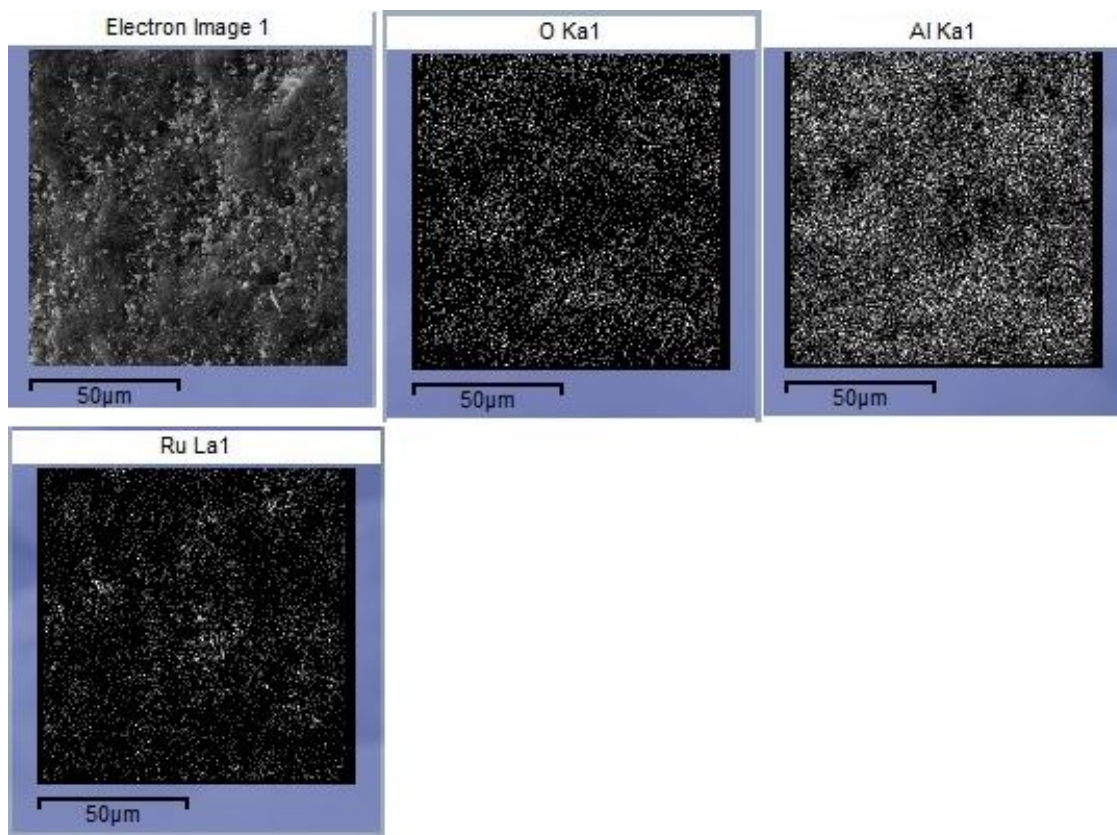


Figure 15: EDX mapping of monometallic catalyst

3.2 Application of Catalyst for Catalytic Wet Air Oxidation (CWAO) of Ammonia

Catalytic Wet Air Oxidation (CWAO) of aqueous ammonia solution was performed in the presence of prepared catalysts at three temperatures i.e. 150°C, 200°C and 230 °C. Blank experiments were also performed in the absence of catalyst and no change in the ammonia concentration was observed which indicated that ammonia did not get oxidized under the given reaction conditions. Similarly the ammonia concentration remained same in the presence of bare γ -Al₂O₃ indicating that it is inactive towards ammonia oxidation [45]. The pH of the trapper remained the same before and after the reaction which indicated that ammonia remained in the liquid state. The catalytic activities towards ammonia decomposition were calculated by using equation.2. The graphical representation of catalytic activities is given in Figure 16.

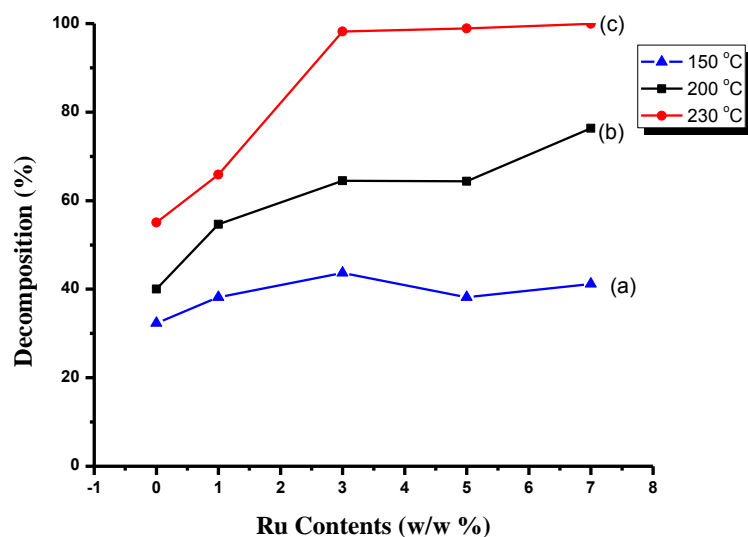


Figure 16: Ammonia decomposition at different temperature
 (a) At 150°C (b) 200 °C (c) 230 °C

3.2.1 Promoting Effect of Ruthenium

It is clear from the figure 16 that catalytic activity of monometallic Cu/ γ -Al₂O₃ catalyst at 150°C activity was minimum. With the addition of 1% Ru to the Cu the activity increases. The catalyst having 3% Ru exhibited further enhanced activity. Further addition of Ru does not increase the activity but it decreases which is due to the decrease in the surface area of the catalyst as shown in Table 8. Activity of monometallic Ru/ γ -Al₂O₃ towards ammonia decomposition was less than bimetallic catalyst at this temperature. At higher temperature ammonia decomposition increases and best activity was observed for bimetallic catalyst containing 3% Ru. Promoting effect of Ru over the catalytic activity of Cu was observed at all temperatures. Results indicated that Cu-Ru-3/ γ -Al₂O₃ was the best catalyst in term of activity towards ammonia decomposition. Although the activity of monometallic Ru/ γ -Al₂O₃ (containing 7% Ru) towards ammonia decomposition was higher than bimetallic catalysts at higher temperature but the cost is also high. Liquid samples were also analyzed for the presence of nitrite and nitrates (products of ammonia decomposition) by ion chromatography. Only nitrates were detected in very low concentration showing that

most of the ammonia was converted to molecular nitrogen which is the desired product. The promoting effect of Ru over catalytic activity of Cu is presented in Figure 16.

3.2.3 Product Selectivity

All the possible products of ammonia oxidation, both in gaseous and liquid phase were identified and analyzed quantitatively. The results revealed that treated water contains only small amount of nitrates and no nitrites were detected. The mass spectrometric analysis also indicated that gaseous samples mainly consist of nitrogen and oxygen. It is clear from the Figure 18 that traces of hydrogen were also detected. At the end of reaction, the selectivity of each catalyst towards nitrates and nitrogen as well as the yield of nitrates was calculated by using equation 3, 4 and 5 respectively.

The selectivity at three different temperatures i.e. 150 °C, 200 °C and 230 °C are summarized in Table 10-12 whereas the graphical representation of selectivity at 150 °C is depicted in Figure 17. The results indicated that selectivity towards nitrogen production was greater than 99% whereas selectivity to nitrates was less than 1% for all the catalysts. No nitrites were detected for any catalyst. At higher temperatures i.e. 200°C and 230°C no nitrates were produced and selectivity towards nitrogen was 100%.

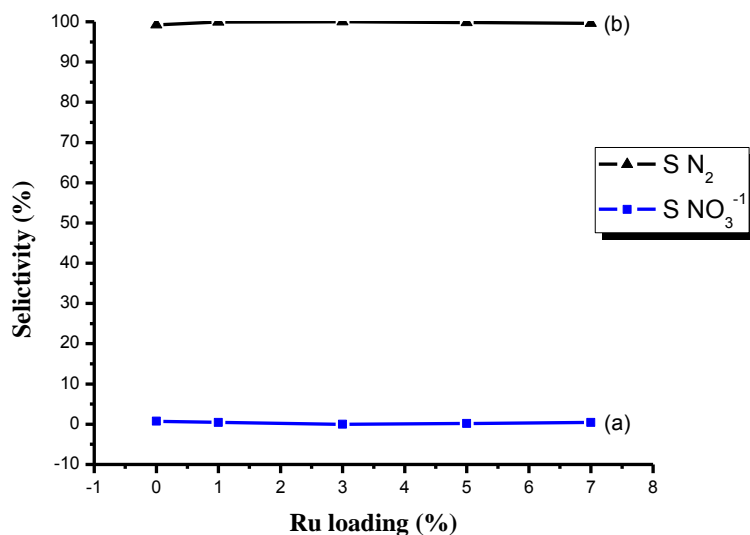


Figure 17: Selectivity of catalysts
(a) Selectivity to Nitrates (b) Selectivity to Nitrogen

Table 10: Selectivity at 150 °C

| Catalyst ID | Ammonia Decomposition (%) | Yield of NO₃⁻(%) | Selectivity to NO₃⁻(%) | Selectivity to N₂(%) | pH |
|--------------------|----------------------------------|---|---|--|-----------|
| Cu-10 | 32.32 | 0.253 | 0.78 | 99.22 | 8.6 |
| Cu- Ru-1 | 38.18 | 0.381 | 0.463 | 99.54 | 8.5 |
| Cu- Ru-3 | 43.64 | Nil | Nil | 100 | 8.5 |
| Cu- Ru-5 | 38.18 | 0.077 | 0.201 | 99.80 | 8.6 |
| Ru-7 | 41.44 | 0.177 | 0.402 | 99.60 | 8.5 |

Table 11: Selectivity at 200 °C

| Catalyst ID | Ammonia Decomposition (%) | Yield of NO₃⁻(%) | Selectivity to NO₃⁻(%) | Selectivity to N₂(%) | pH |
|--------------------|----------------------------------|---|---|--|-----------|
| Cu-10 | 40.00 | 1.423×10 ⁻² | 0.196 | 99.80 | 8.2 |
| Cu- Ru-1 | 54.64 | 0.05 | 0.092 | 99.91 | 8.2 |
| Cu- Ru-3 | 64.46 | Nil | 0.0 | 100 | 8.1 |
| Cu- Ru-5 | 64.36 | Nil | 0.0 | 100 | 8.0 |
| Ru-7 | 76.36 | Nil | 0.0 | 100 | 8.1 |

Table 12: Selectivity at 230 °C

| Catalyst ID | Ammonia Decomposition (%) | Yield of NO ₃ ⁻ (%) | Selectivity to NO ₃ ⁻ (%) | Selectivity to N ₂ (%) | pH |
|-------------|---------------------------|---|---|-----------------------------------|-----|
| Cu-10 | 55.05 | Nil | Nil | 100 | 8.3 |
| Cu- Ru-1 | 65.87 | Nil | Nil | 100 | 8.2 |
| Cu- Ru-3 | 98.18 | Nil | Nil | 100 | 8.0 |
| Cu- Ru-5 | 98.91 | Nil | Nil | 100 | 8.1 |
| Ru-7 | 99.97 | Nil | Nil | 100 | 8.1 |

3.2.4 Mass spectrometric studies

Gaseous sample for ammonia decomposition over Cu-Ru-3/ γ -Al₂O₃ was analyzed by mass spectrophotometer and the results are presented in Figure 18.

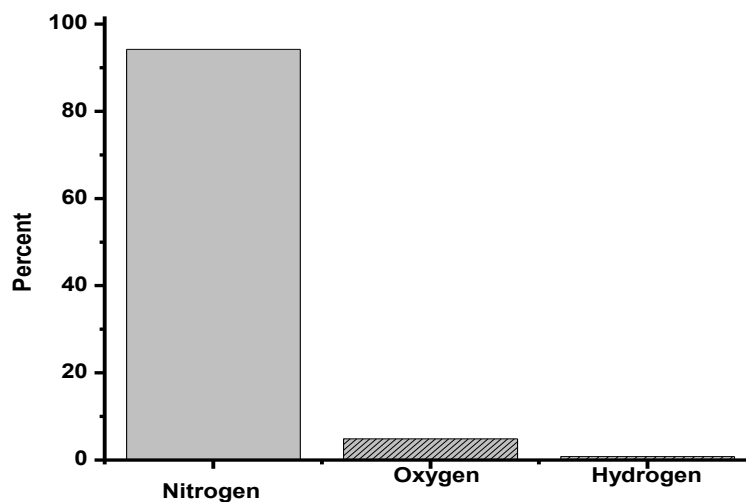


Figure 18: Mass Spectrophotometric analysis of gaseous products

The figure indicated that only nitrogen, oxygen and hydrogen were present while no NO_x were detected which also confirms that ammonia is decomposed to nitrogen.

3.3 Effect of Different Physical Parameters on Ammonia Decomposition

The effects of different parameters on ammonia decomposition were also studied. All these experiments were performed with Cu-Ru-3/γ-Al₂O₃ catalyst, which was selected because of high of activity as well as cost effectiveness.

3.3.1 Effect of Temperature

Catalytic Wet Air Oxidation (CWAO) of aqueous ammonia was studied at three temperatures i.e. 150°C, 200 °C and 230 °C. The results are presented in figure 16 which indicated that catalytic activity increases with increase of temperature.

3.3.2 Effect of Ammonia to Catalyst Ratio

The effect of ammonia to catalyst ratio over ammonia decomposition was also explored with three different ratios i.e. 8:1, 6:1 and 4:1. The results are summarized in Table 13 which indicated that ammonia decomposition was maximum with ammonia to catalyst ratio 4:1 whereas for other ratios the decomposition was low.

Table 13: Effect of ammonia: catalyst ratio on ammonia decomposition

| Weight of Ammonia (g) | Initial Ammonia Conc. (M) | Weight of catalyst (g) | Ammonia: Catalyst Ratio | Ammonia Decomposition (%) |
|-----------------------|---------------------------|------------------------|-------------------------|---------------------------|
| 20.88 | 0.11 | 0.155 | 8:1 | 33.63 |
| 20.11 | 0.18 | 0.315 | 6:1 | 46.11 |
| 20.50 | 0.11 | 0.312 | 4:1 | 98.18 |

3.3.2 Effect of Initial pH

The effect of initial pH over ammonia oxidation was also studied. The experiments were performed at two different pH values i.e. at pH 11 and 4.01. The results are tabulated in table 14 which indicated that there is no significant effect of pH in ammonia decomposition but in acidic conditions corrosion were observed in the reactor.

Table 14: Effect of pH on ammonia decomposition

| Weight of Ammonia (g) | Weight of Catalyst (g) | Initial pH | Ammonia Decomposition (%) |
|-----------------------|------------------------|------------|---------------------------|
| 20.50 | 0.334 | 4.01 | 95.09 |
| 20.50 | 0.312 | 11.0 | 98.18 |

3.4 Stability of Catalyst

The stability of the catalyst was also explored in term of reusability of the catalyst as well as the dissolution degree of the metals in reaction medium.

3.4.1 Reusability of Catalysts

In order to study the reusability of the catalyst, the experiments were repeated five times with the selected catalyst. The results are presented in figure 19 which indicated that catalyst was stable for five different cycles and a slight decrease in ammonia decomposition was observed. For all cycles the selectivity towards nitrogen production was maximum.

3.4.2 Dissolution Degree of Metals

The Dissolution degree of catalyst is an important parameter for catalyst characterization. Dissolution degree of the catalysts during the reaction was calculated at 200°C by using equation 6. For this purpose concentration of Cu and Ru was determined in the reaction mixture using Atomic Absorption Spectrophotometer [53]. Dissolution degrees of the catalyst and final pH of the reaction are given in table 15. Result indicated

that only copper dissolved in the reaction medium but ruthenium did not dissolve in the reaction medium.

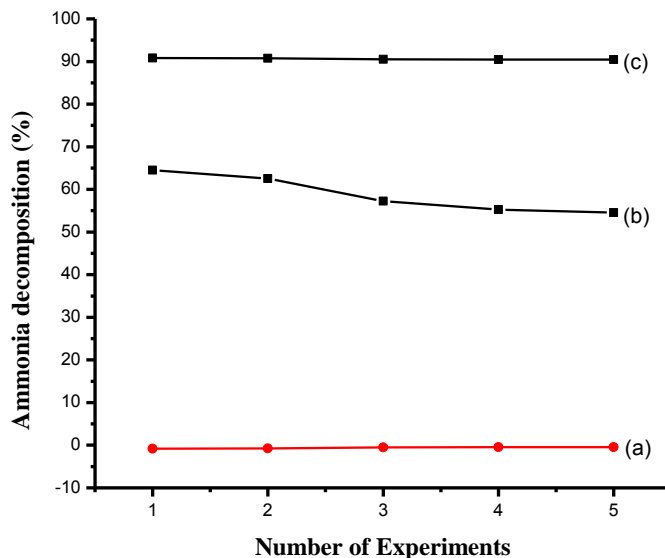


Figure 19: Catalyst reusability for five repeated experiments
 (a) Selectivity to nitrates (b) % Ammonia decomposition (c) Selectivity to nitrogen production

Table 15: Dissolution degree of metals

| Catalyst ID | Dissolution Degree of Cu (%) | Dissolution Degree of Ru (%) | pH after reaction |
|-------------|------------------------------|------------------------------|-------------------|
| Cu-10 | 2.956 | BDL | 8.8 |
| Cu-Ru-1 | 7.656 | BDL | 8.6 |
| Cu-Ru-3 | 8.14 | BDL | 8.3 |
| Cu-Ru-5 | 2.063 | BDL | 8.5 |
| Ru-7 | BDL | BDL | 8.3 |

3.5 Conclusions

Bimetallic γ -Al₂O₃ supported Cu-Ru catalysts with different metal loading were successfully prepared by impregnation method. The prepared catalysts were characterized by different techniques. The prepared catalysts were successfully applied for wet air oxidation of ammonia. The ammonia decomposition was achieved up to 99 % with high selectivity towards nitrogen production and minimum nitrate production. The catalyst can able to decompose high concentration of ammonia which was 0.11 molL⁻¹ (1870 ppm) in the present study.

The promoting effect of ruthenium over catalytic activity of copper was also studied and enhancement in catalytic activity was observed with the addition of Ru metal. The catalyst with 3% Ru loading over 10% Cu showed maximum activity which is due to the alloying effect as well as high surface area. The Effect of different parameters on ammonia decomposition was studied. It was found that under 2 bar air pressure best activity can be achieved with initial pH value=11.0 while keeping ammonia catalyst ratio 4:1. The stability of the catalyst was checked by repeated experiments and catalyst was found active for five cycles with minimum dissolution of metals in the reaction media.

3.6 Future Perspective

Discovery of bimetallic catalysts has a potential to revolutionize the world of science and technology. Due to its synergistic effect of second metal the properties of the catalysts can be tailored for a particular application. Bimetallic catalysts have enhanced properties as well as low cost.

In the present study bimetallic catalysts with different metal loading were synthesized and applied for catalytic wet air oxidation of ammonia. It is proposed to synthesize bimetallic catalysts, with some other metallic ratio using the same metals and apply these materials for ammonia decomposition reaction. It is also proposed to use the same catalyst for ammonia decomposition by using some other oxidant like oxygen or hydrogen peroxide. The same catalyst can be used for catalytic wet air oxidation of phenol.

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