RESEARCH PAPER

Preparation and Performance Analysis of γ-Al₂O₃ Supported Cu-Ru Bimetallic Catalysts for the Selective Wet Air Oxidation of Aqueous Ammonia to Nitrogen

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ABSTRACT

Series of Copper Ruthenium (Cu-Ru) bimetallic catalysts supported on γ-Al₂O₃ with different metal loading are prepared and investigated for catalytic wet air oxidation of ammonia to nitrogen. The ammonia decomposition activity was studied at three different temperatures i.e. 150, 200 and 230 °C. it is found that catalytic activity increases with the increase in temperature along with the high selectivity towards nitrogen production. The results also revealed that the bimetallic Cu-Ru/ γ-Al₂O₃ are much more efficient and stable than the corresponding monometallic Cu and Ru catalysts. Up to 99 % ammonia decomposed to N_2 without any undesirable nitrites and nitrates at 230 °C at optimized catalysts to ammonia ratio. So, it can be considered as a potential method to remove a large amount of ammonia from wastewater. Furthermore, the catalysts characterization results strongly suggested that there is a strong relationship between catalytic activity and Ru and Cu contents in bimetallic catalysts. The presences of both metals (Cu and Ru) affect the reactivity and coverage of oxygen species, as well as protecting each other from leaching. The combination of all effects including the strong interaction between metals, synergistic effect, proper oxygen coverage and resistance against leaching could be attributed to the enhancement of the catalytic activity of Cu-Ru/ γ-Al₂O₃ catalyst.

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INTRODUCTION

Excessive use of ammonia in the industry leads to ammonia pollution which has become a worldwide issue. It is discharged in the air and water from the industries [1]. The decomposition of protein-based wastes and other biological processes are its other sources [2, 3]. In the air, the ammonia can cause odor problems and it can also affect the breathing system, skin, and eyes of a living organism. It has been reported that its higher concentration of 300 ppm can cause the death of an individual [3, 4]. The presence of ammonia in water can cause eutrophication [1], which results in the disturbance of aquatic life and disappearance of water bodies. Up to a certain limit ammonia is used as a nutrient by the plants but beyond that its presence in water is harmful. It enters 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 [5, 6]. Therefore, removal of ammonia from wastewater is very important in maintaining the aquatic environment [7].

Among the methods used for the removal of ammonia from the environment catalytic wet air oxidation (CWAO) has been widely employed for the treatment of wastewater containing ammonia and other pollutants. In catalytic wet air oxidation

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(CWAO), the wastewater containing ammonia is oxidized under high temperature and pressure in the presence of a suitable metal catalyst [8]. The efforts have been made for selective oxidation of ammonia to nitrogen and water which makes the process ideal as no harmful by-products are formed [9].

Wet air oxidation (WAO) is difficult under mild conditions in the absence of a catalyst [10] but the use of a suitable catalyst can make the reaction to take place under milder condition. Several catalyst systems based on transition and noble metals are reported for ammonia oxidation [7, 8, 11-16] e.g. Ni and other transition metals like CuO supported over γ-Al$_2$O$_3$ have been used for ammonia removal from the aqueous stream at 257 °C but their efficiency was low [7, 17, 18]. Cobalt-based catalysts have also been reported for ammonia decomposition with high activity and selectivity but it required high reaction temperature i.e. 550°C [11].

However, noble metals like Ru, Ir, Pt, Pd, and Rh supported over γ-Al$_2$O$_3$ show high activity and selectivity to nitrogen production in CWAO of ammonia as compared to transition metals [7, 10]. In spite of having good activity, some noble metal catalysts do not show stability under given reaction conditions [7, 10]. Among all the supported noble metal catalysts, the Ru supported over activated carbon is the most active catalyst for ammonia decomposition reaction [3]. However, high cost and limited availability of Ru limits its use in the industry [11, 19]

To reduce the cost of Nobel metal catalysts, bimetallic catalysts are getting the 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. Ag-Cu/γ-Al$_2$O$_3$ has been used for gas phase decomposition of ammonia from the air [2] at 150 to 400°C whereas temperature can be lowered to 300 °C using Pt-CuO/γ-Al$_2$O$_3$ catalyst. Similarly, Pt-Pd-Ru composite catalyst has also been used for ammonia decomposition but selectivity to nitrogen production was found low [19]. Recently Cu-Ru bimetallic catalyst supported on carbon is reported for decomposition of ammonia [15].

The present work describes a study of developing a cost-effective catalyst for CWAO of ammonia under relatively mild conditions. Attention is given to the synthesis of γ-Al$_2$O$_3$

supported Cu-Ru bimetallic catalyst with the high surface area and stability with much lower Ru contents using simple impregnation method. The focus is on the low-temperature decomposition of ammonia leading to harmless products with high selectivity towards N$_2$ production and low yield of nitrates. We compared our results with the same results already reported in literature. The results are listed in Table S1.

MATERIALS AND METHODS
Preparation of Catalyst

Cu-Ru bimetallic catalysts supported over γ-Al$_2$O$_3$ were prepared by incipient wetness impregnation method (See Fig. 1) using (CuSO$_4$. 5H$_2$O) and (RuCl$_3$. 3H$_2$O) as a precursor for Cu and Ru respectively. For the preparation of the catalyst γ-Al$_2$O$_3$ (mesh size 0.4 to 1.0 mm) was dried at 200°C in a drying oven for two hours to remove any adsorbed moisture and gases and then cooled in a desiccator. 5.0 gram of γ-Al$_2$O$_3$ was taken in a 100 cm^3 china dish marked as C-1 – C-5. 5.0 cm^{3}of 2% copper solution was added to C-1 to C-4 and 5.0 cm^3 of 1% ruthenium solution to C-5 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-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 the reduction in a continuous flow of 99.99 % pure H$_2$ gas at 550 °C for 5 hours. γ- Al$_2$O$_3$ was synthesized by sol-gel method using AlCl$_3$.6H$_2$O and ammonia solution at pH 8 followed by drying and heat treatment at 750°C for 10 hours. The mesh size of the γ- Al$_2$O$_3$ was in the range of 0.4 to 1.0 mm.

Characterizations

The composition of prepared catalysts was confirmed by Flame Atomic Absorption Spectrophotometer Perkin Elmer AAnalyst 400. Alkaline oxidizing fusion method was used for sample preparation. [20, 21]. For textural properties of catalysts including Brunauer-Emmett-
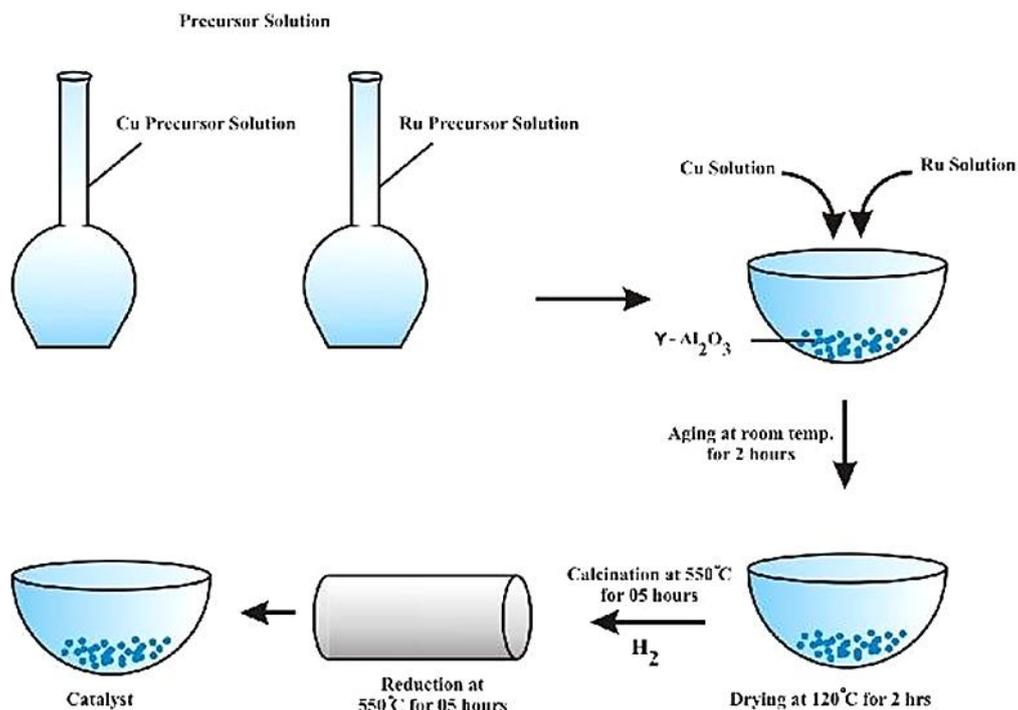
Fig.1. Schematic representation of catalyst preparation (impregnation method)

Teller (BET) Area, Langmuir Area and micropore volume, surface area analysis were performed [22] (surface area analyzer KELVIN 1042, Costech International, Italy). Panalytical, X-Ray Powder Diffractometer (Model 3040/60-X-Pert Pro) was used to determine crystal structures and crystallite size of prepared catalysts using Cu Kα_1 as a light source. Thermal properties were investigated by measuring the weight loss of material with an increase in temperature by using TGA/DSC1 (STAR-System, D-09123, Mettler Toledo Switzerland). Catalyst Microstructure was determined using Scanning Electron Microscopy (SEM) analysis (FE-SEM, TESCAN, Czech Republic). For H_2-temperature programmed reduction (TPR) 50.0 mg sample was placed in quartz reactor followed by heating at 150°C in pure oxygen and cooling to room temperature. After the gas was switched to 7.0% H_2/Ar, the temperature was increased to 400 °C at the rate of 10°C/ min.

Catalytic Wet Air Oxidation of Ammonia

The catalyst testing for ammonia decomposition was carried out in a self-made reactor made up of stainless steel (SS-316 Grade) equipped with a magnetically driven stirrer (Supplementary information, Fig. S1). In a typical run, 20 cm³ of an aqueous solution of ammonium hydroxide (0.11M) solution (pH value = 4, 11) was taken in the reaction vessel. For each experiment, 0.3 gram of the catalyst was weighed and transferred to the reaction vessel. To remove adsorbed moisture and gases, the catalyst was pre-heated at 120°C for two hours in a drying oven before the reaction. The reactor was then closed, and the 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. The outlet was dipped in the trapper containing 50 cm³ of 0.01M HCl solution. The reaction mixture was then subsequently heated to 150 °C for 3 hours. After 3 hours mixture was cooled to room temperature before analysis. The catalyst was recovered by filtering the reaction mixture.

Analysis

The liquid samples were analyzed for ammonia concentration 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. 0.05M standard solution of HCl was added dropwise till

the appearance of light pink color.

The concentration of ions (nitrate & nitrites) was determined by ion chromatography (High-Performance Liquid Chromatograph, HPLC 10 AVP) equipped with conductivity detector CDD 6AVP, while the gaseous samples of ammonia decomposition (oxides of nitrogen) were also analyzed using Mass Spectrometer (GC-MS BALZER Company Model No. QMG-420).

As decomposition product is mainly nitrogen-containing compounds (like N_2, NH_4^+, NO_3^-, NO_2^-), the conversion of ammonia and selectivity of nitrogen can be calculated by following formula.

$$X_{NH_3} = \left(C_{NH_3}^0 \times \frac{C_{NH_3}}{C_{NH_3}^0} \right) \times 100 \qquad (1)$$

Whereas

Percentage of ammonia decomposition was calculated using Eq. 2 [18, 19, 20]:

$$Ammonia\, decomposition\, (\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

Where

C_o =Initial concentration of ammonia

C_t = Concentration of ammonia after the reaction

The selectivity of the products was calculated using Eq. 3 [18, 20]:

$$Selectivity\, to\, NO_3^- = \frac{Moles\, of\, NO_3^-\, formed\, in\, term\, of\, N_2}{Moles\, of\, ammonia\, decomposed\, in\, term\, of\, N_2} \times 100 \qquad (3)$$

$$Selectivity\, to\, N_2 = (100 - Selectivity\, to\, NO_3^-) \qquad (4)$$

Total yield of nitrates can be calculated by using following formula [23, 24].

$$Yields\, of\, Nitrates\, (\%) = \frac{Moles\, of\, Nitrates\, formed}{Moles\, of\, ammonia\, initially\, present} \times 100 \qquad (5)$$

RESULTS AND DISCUSSIONS
Bimetallic effect on catalytic performance
Bimetallic catalysts exhibit high catalytic performance due to its interaction and the synergistic effect of different active metals. Cu/Al₂O₃, Ru/Al₂O₃ and Cu-Ru/Al₂O₃ with different metal contents were prepared and tested in the present study for catalytic Wet Air Oxidation (CWAO) of aqueous ammonia at three different temperatures (150 °C, 200 °C, 230 °C) and pH (4, 11). A blank experiment was also performed in the absence of a catalyst to detect the change in the ammonia concentration under given reaction conditions. There is no detectable change in ammonia concentration after the experiment, which indicated that the ammonia cannot oxidize under the given reaction conditions. An additional test was also performed in the presence of bare γ-Al₂O₃ in order to evaluate its potential catalytic activity. But ammonia concentration remains unchanged, indicated that the bare γ-Al₂O₃ is inactive towards ammonia decomposition [8].

The effect of temperature, Ru contents, and the selectivity of monometallic (Cu/ Al₂O₃, Ru/Al₂O₃) and bimetallic (Cu-Ru/Al₂O₃) catalysts for ammonia decomposition were investigated first. The Cu contents were kept constant in the present study (i.e. 10%) while Ru contents were varied from 1-7%. The pH of the reaction mixture is kept at 11.0. The performance of catalysts (with different Ru) at three different temperatures i.e. 150, 200 and 230°C are shown in Fig. 2(a). As revealed from Fig. 2(a), the catalyst with 3% Ru and 10% Cu labeled as Cu-Ru-3/ γ-Al₂O₃ was the best catalyst in terms of activity and selectivity towards ammonia decomposition. It was observed that with the increase in temperature from 150 to 230 °C, the NH₃ decomposition for Cu-Ru-3/ γ-Al₂O₃ was also increased from 43.6 to 98.2 %. The monometallic catalysts i.e. Ru/ γ-Al₂O₃ (containing 7% Ru) showed comparable conversion efficiency with the Cu-Ru-3/γ-Al₂O₃ but its high cost put a limit in its use. In case of Cu/γ-Al₂O₃ catalyst, only 32.2% ammonia was decomposed at 150°C, although the temperature has a positive effect on the activity, the decomposition increased only up to 55.1% even at 230°C.

A synergistic effect of Cu and Ru metals on catalytic behavior was observed in this case. In comparison to monometallic catalysts, high activity and high selectivity were found for bimetallic catalysts. It is illustrated in Fig. 2(a) that the catalytic activity of monometallic Cu/γ-Al₂O₃ catalyst is minimum. The incorporation of Ru in the system has remarkably improved the catalytic performance. Even low Ru content i.e. 1% in Ru-Cu/γ-Al₂O₃ bimetallic catalysts exhibited the higher activity (upto 70% ammonia decomposition).
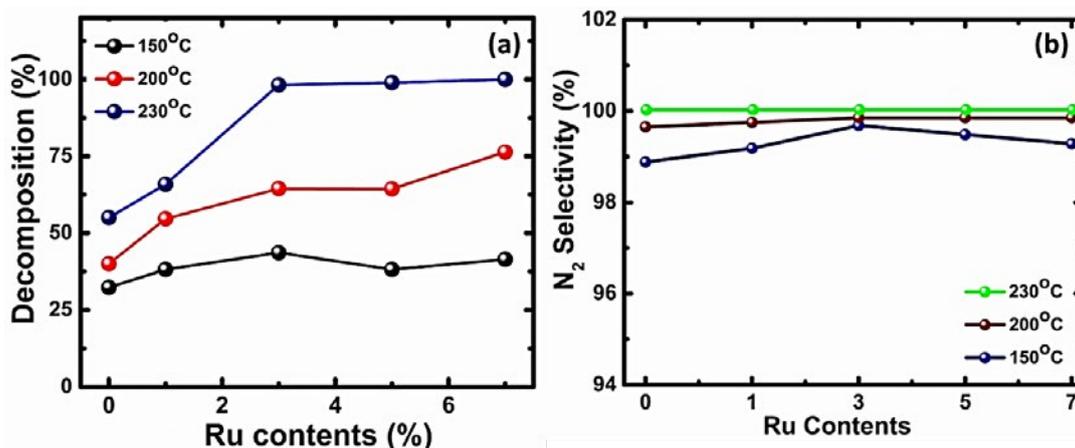
Fig. 2. (a) Ammonia decomposition at a different temperature, (b) Selectivity of each catalyst toward nitrogen production.

Table 1. Effect of pH on ammonia decomposition

Weight of Ammonia (g)	Weight of Catalyst (g)	Initial pH	Ammonia Decomposition (%)
20.5	0.3	4.0	95.1
20.5	0.3	11.0	98.2

Further enhancement in activity was observed for catalyst system having 3% Ru at given reaction conditions, but at higher contents of Ru (more than 3%) there is decreased in catalytic activity, which can be correlated to the reduced surface area of the catalyst as shown in Table 2.

The selectivity of each catalyst at three different temperatures i.e. 150, 200 and 230 °C is shown in Fig. 2(b) and summarized in Table S2-S4 (supplementary information). It is clear from Fig. 2(b) that at high temperatures i-e. 200 and 230°C selectivity towards nitrogen was 100% for each catalyst system. Furthermore, all the possible products of ammonia oxidation were analyzed, both in gaseous and liquid phase quantitatively using ion chromatography and mass spectrometric

analysis. (see experimental section). The results are shown in Fig. 3(a) and Table S2-S4. The results revealed that the treated water contains small amount of nitrates (less than 1%) and nitrites (below detection limit) (Table S2-S4). The mass spectrometric analysis of gaseous samples also indicated that the gaseous samples mainly consist of nitrogen and oxygen as clear from the Fig. 3(a).

The stability of catalysts is an important parameter in their practical applications, conceivably more important than active CWAO of ammonia to nitrogen. The stability of the catalyst was also explored in terms of reusability of the catalyst as well as the degree of metal dissolution in the reaction medium. The recycling operations were applied for used catalysts to examine the stability of Cu-Ru-3/ γ-Al₂O₃ under mild conditions (at 150°C and at pH=11.0). After the first run, the catalyst was recovered, followed by washing with deionized water and drying at 120°C for 12h. To recompense the loss of catalysts, the first experiment was repeated two times to ensure the same amount of catalysts used in recycling experiment (300 mg). The conversion of ammonia after 5 recycling experiment is shown in Fig. 3(b),

Table 2. Textural properties and percentage of metals in given catalyst series

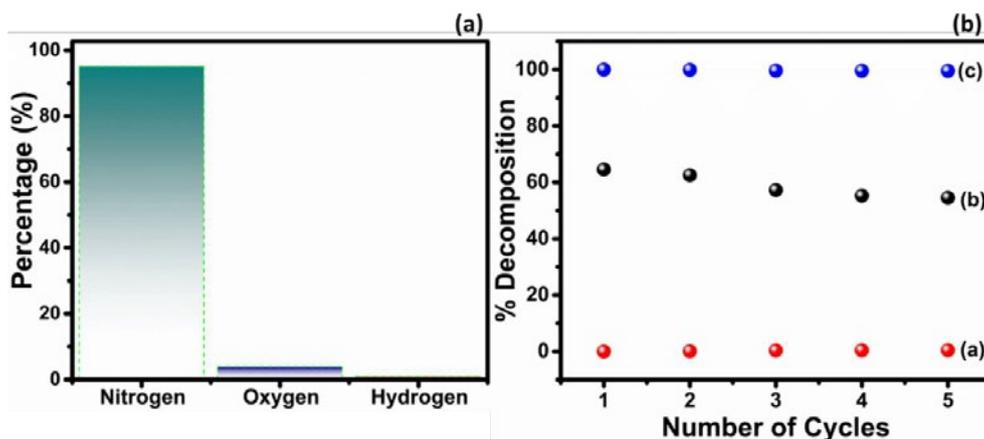| Catalyst ID	BET Area (m²/g)	Langmuir Area (m²/g)	Micropore Volume (mm³/g)	Crystallite Size of Cu (nm)	Cu w/w %	Ru w/w %
γ-Al₂O₃	173.2	233.5	14.2	/	0	0
Cu-10	111.0	150.0	7.6	15.4	10.2	0
Cu-Ru-1	116.7	157.8	7.4	7.3	9.4	1.3
Cu-Ru-3	114.8	156.0	3.5	6.4	9.7	2.9
Cu-Ru-5	100.8	135.5	9.3	6.2	9.2	5.3
Ru-7	133.2	179.9	8.7	/	0	7.4

Fig. 3. Mass Spectrophotometric analysis of gaseous products, (b) Catalyst reusability for five repeated experiments with, (a) Selectivity to nitrates (b) % Ammonia decomposition (c) Selectivity to nitrogen production.

which indicates that bimetallic Cu-Ru-3/ γ-Al₂O₃ exhibited excellent stability. No deactivation was observed, and conversion of ammonia was sustained at a level higher than 60% for 5 consecutive cycles. These results revealed that the synergetic effect between Ru and Cu not only improves activity but also leads to good stability. Furthermore, a synergetic effect between Ru and Cu could help to maintain the surface area of catalysts. For fresh Cu-Ru-3/ γ-Al₂O₃ samples surface area based on BET measurement was 114.8 m²/g. After third run a bit decreased in surface area is observed (98.2 m²/g), it remains almost constant during rest of runs. This is consistent with the stable activity of catalyst as shown in Fig. 3(b).

The effect of initial pH over ammonia oxidation to nitrogen for Cu-Ru-3/ γ-Al₂O₃ catalyst was also investigated and results are tabulated in Table 1. For convenience, the experiment was performed at two different pH values i.e. 11 and 4.01. Ammonia conversion is strongly affected by Initial pH as reported in the literature. The higher pH the more ammonia is converted to products. Table 1 specified that there is no significant effect of pH on ammonia decomposition but in acidic conditions, corrosion was observed in the reactor.

Characterization of γ-Al₂O₃ and supported catalysts

The synthesized catalysts with different metal loading were characterized by employing different techniques. Results of atomic absorption spectrophotometric analysis are presented in Table 2 which showed that the composition of prepared catalysts is very close to the expected

values. Surface area measurements (Table 2) indicated that bare γ-Al₂O₃ have a highest surface area (173.2 m²/g) showing high porosity and mesoporous structure [25]. However, BET surface area decreased with the increase of metal loading, showing that the pores are filled with metal particles resulting in a decrease in surfaces area.

To further confirm the porous nature of synthesized bimetallic catalysts gas adsorption-desorption studies was carried out for the selective catalyst that showed highest ammonia decomposition (i.e.Cu-Ru-3/ γ-Al₂O₃) and results are presented in Fig. 4(a) as an isothermal plot. This is of Type-II isotherm which shows physical adsorption of N₂ over the mesoporous surface of the catalyst [26]. The Barrett-Joyner-Halenda (BJH) pore size distribution of the catalyst (Fig. 4(b)) showed that the bimetallic catalysts have narrow pore size distribution with the pore diameter in the range of 2-20 nm.[2, 27].

X-ray diffraction (XRD) study was used to analyze the crystal structure of the prepared catalysts. XRD pattern of γ-Al₂O₃ was also shown for comparison in Fig. 5(a). In XRD pattern of γ-Al₂O₃ (Fig. 5(a)) and prepared catalyst, γ-Al₂O₃ showed dominant peaks at 2θ values of 31°, 33°, 38°, 39°, 43°, 46° and 68° [2, 28]. Typical diffraction peaks due to metallic Cu appeared at 43° and 54° corresponding to (111) and (200) plane for all catalysts containing Cu. The diffraction peak at 35.5° and 38.8° are due to the presence of Cu. The appearance of these peaks indicates the presence of metal oxide clusters having a strong interaction with the support [25, 28]. It has been reported
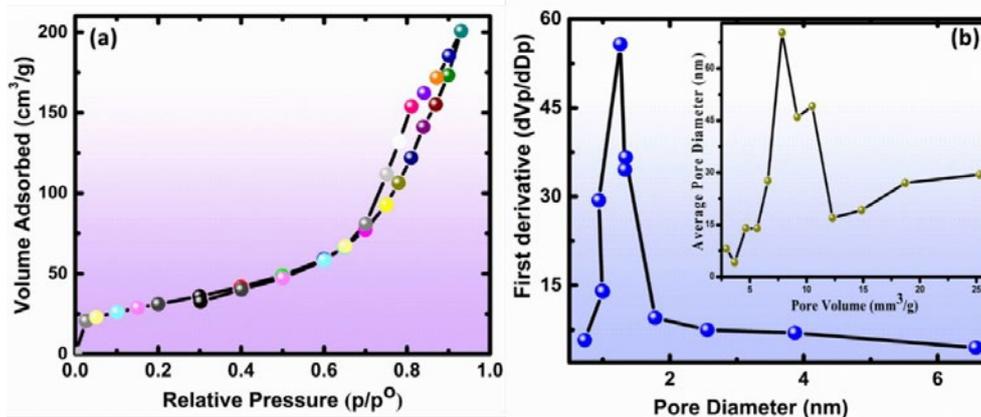
Fig. 4. (a) Isotherm plot of bimetallic catalyst (Cu-Ru-3/ γ-Al₂O₃) with relative pressure range of 0.05 to 0.20, (b) Pore size distribution plot of bimetallic catalyst (Cu-Ru-3/ γ-Al₂O₃)
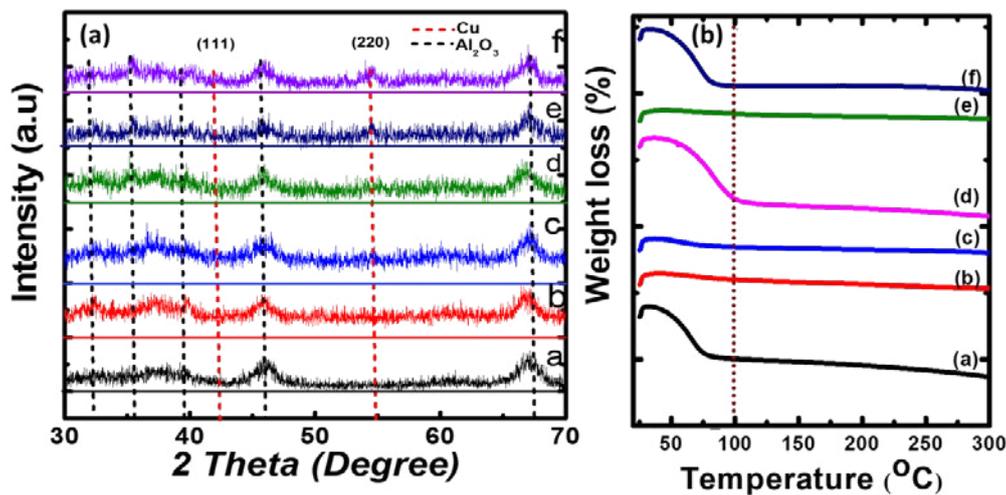

Fig. 5. (a) XRD Pattern of catalysts, (a) γ-Al₂O₃ (b) Cu/ γ-Al₂O₃ (C) Cu-Ru-1/ γ-Al₂O₃(Cd) Cu-Ru-3/ γ-Al₂O₃ (e) Cu-Ru-5/ γ-Al₂O₃ (f) Ru-7/ γ-Al₂O₃, (b) Thermal Gravimetric Analysis plot (a) γ-Al₂O₃ (b) Cu/ γ-Al₂O₃ (c) Cu-Ru-1/ γ-Al₂O₃ (d) Cu-Ru-3/ γ-Al₂O₃ (e) Cu-Ru-5/ γ- Al₂O₃ (f) Ru-7/ γ-Al₂O₃

earlier that interaction between CuO and Al₂O₃ occurs readily at calcination temperatures close to 600°C, yielding CuAl₂O₄ [25]. No peak is observed for the Ru metal which indicated that either the Ru concentration is very low or Ru was dispersed on support much better than copper [29]. The average crystallite size of the Cu is also calculated using Debye Scherer equation and results are tabulated in Table 2. The results showed that the crystallite size of Cu in monometallic catalysts is higher than bimetallic catalysts The possible reason is the strong interaction between Ru and Cu wich results in effective dispersion of metals over support surface [30].

The stability of catalysts with temperature is also an important parameter, as decomposition of

ammonia is carried out at high temperature (150, 200, 230 °C). Therefore, the thermal gravimetric analysis (TGA) of the catalyst was carried out up to 300°C. The thermograms (Fig. 5(b)) indicated a single weight loss below 100°C which is due to the loss of physically adsorbed water from the samples [27, 31]. There is no further weight loss at a higher temperature which confirms that catalysts are thermally stable up to 300 °C.

The surface morphology of prepared catalysts was further studied by Scanning electron microscopy (SEM). The SEM images of bare alumina and supported catalysts are shown in Fig. 6(a-d). For bare alumina (Fig. 6(a, b)) particle size is quite larger and morphology is cylindrical, while for bimetallic catalysts (Fig. 6(c, d)) Cu
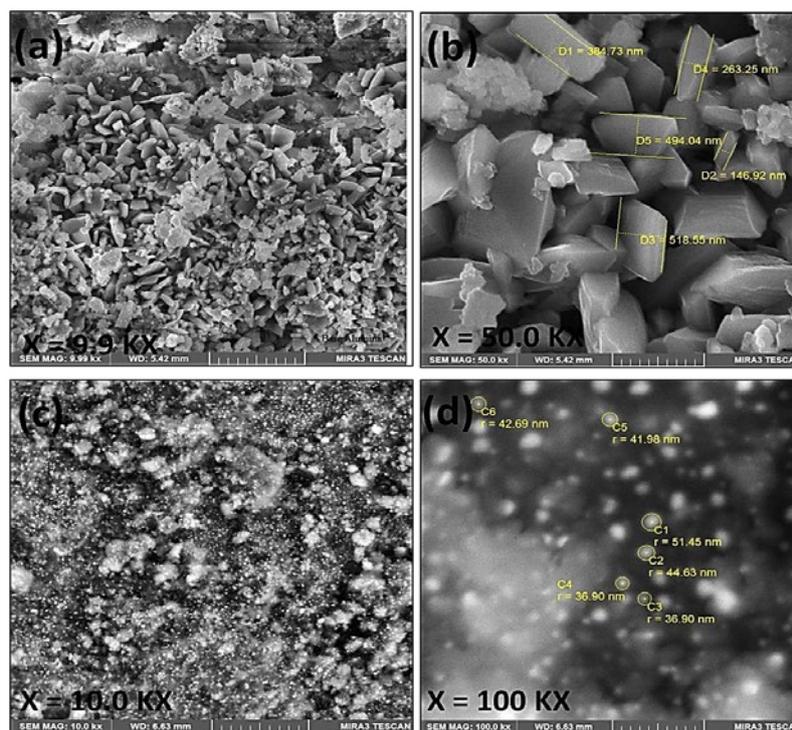
Fig. 6. SEM micrographs of γ-Al$_2$O$_3$. (a, b) without metal loading, (c-d) with bimetallic loading (Cu-Ru-3/ γ-Al$_2$O$_3$).

metal is poorly dispersed and aggregated into large particles, while Ru metal showed a better distribution over the support. For Cu-Ru-3/ γ-Al$_2$O$_3$ bimetallic catalysts average particles size of metal particles are found to be approximately 42.2 nm. The presence of Cu and Ru in samples is furtehr confirmed by the EDX analysis of a bimetallic and a monometallic catalyst as shown in Fig. 7 (a-d).

The redox property of oxygen species over Cu/ γ-Al$_2$O$_3$, Ru/ γ-Al$_2$O$_3$ and Ru-Cu-3/ γ-Al$_2$O$_3$ were investigated by H$_2$-TPR experiments, as it was essential for both NH$_3$ conversion and nitrogen selectivity. Prior to the H$_2$-TPR experiment, the sample was treated with the oxygen at 150°C for 2h to generate the oxygen species. As illustrated in Fig. 8(a), Cu/ γ-Al$_2$O$_3$ catalyst presented the main reduction peak at 262.21 and hydrogen consumption was extended up to 300 °C, indicating that reactivity of oxygen species over Cu/ γ-Al$_2$O$_3$ is much lower. For Ru/ γ-Al$_2$O$_3$ the main reduction peak appeared at 186.91 with a shoulder at 203.0°C and no hydrogen peak was observed at a temperature higher than 250°C. These results suggested that oxygen species possesses much higher reactivity over Ru/ γ-Al$_2$O$_3$. However, in case of Cu-Ru-3/ γ-Al$_2$O$_3$, oxygen species exhibited

the moderate reactivity and main reduction peak appeared at 270.89°C, much closer to the average value of those of Cu/ γ-Al$_2$O$_3$ and Ru/ γ-Al$_2$O$_3$. Obviously, the presence of Ru and Cu can effectively tune the reactivity of oxygen species over catalysts surface. Not only reactivity but also surface coverage of oxygen species can also be modified by the co-existence of Ru and Cu. It is cleared from Fig. 8(a) that the area of hydrogen consumption peak is much higher in case of Cu-Ru-3/ γ-Al$_2$O$_3$ as compared to the Ru/ γ-Al$_2$O$_3$ and Cu/ γ-Al$_2$O$_3$. Mild activity and proper coverage of oxygen species are the probable reason for enhancement in catalytic activity of bimetallic Cu-Ru-3/ γ-Al$_2$O$_3$ for ammonia decomposition.

To study the relationship between the properties of oxygen species and catalytic behavior of bimetallic and monometallic catalysts, the variation of reduction peak with the composition is plotted in Fig. 8(b) accompanied by ammonia decomposition and N$_2$ yield. It can be seen that NH$_3$ decomposition increased from 55.1 to 98.2% with the increased in reduction temperature, which might be due to the increased in the surface coverage of oxygen. Since the ammonia is activated over the surface of oxygen,
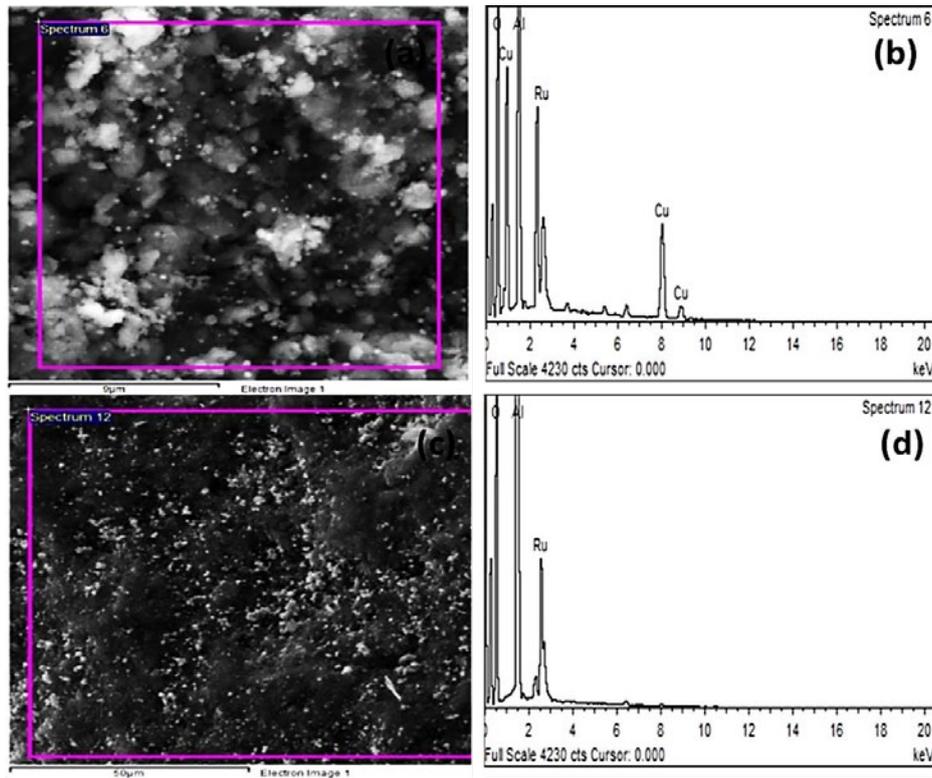
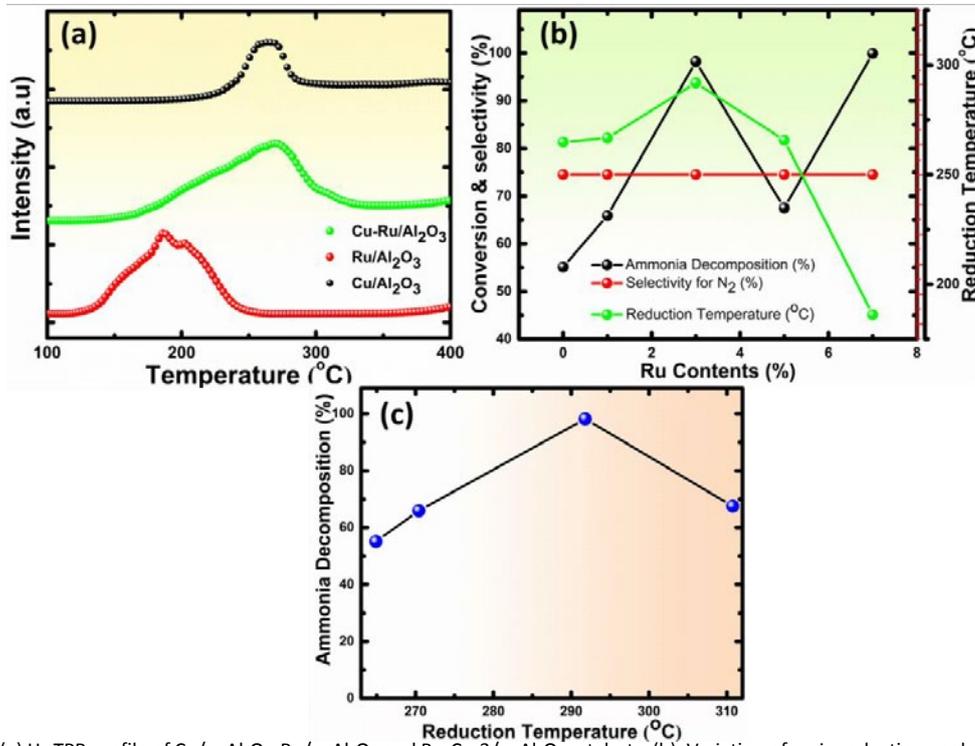Fig. 7. EDX analysis of catalysts (a,b) Cu-Ru-3/γ-Al₂O₃ bimetallic catalyst (c,d) monometallic Ru/ γ-Al₂O₃ catalyst.

Fig. 8. (a) H₂-TPR profile of Cu/ γ-Al₂O₃, Ru/ γ-Al₂O₃ and Ru-Cu-3/ γ-Al₂O₃ catalysts, (b): Variation of main reduction peak and catalytic performance as function of composition of catalyst. Reaction conditions: 230°C, pH =11.0, (c): Variation of ammonia decomposition with reduction temperature as function of composition of catalyst. Reaction conditions: 230°C, pH =11.0

Cu-Ru-3/ γ-Al$_2$O$_3$ catalysts showed relatively higher ammonia decomposition due to the high reactivity of oxygen. It is cleared from Fig. 8(c) that the ammonia decomposition is first increased with increasing of Ru loading due to the increasing amount of active oxygen over catalysts. However, when Ru loading was above 3% the main reduction temperature was shifted toward a value higher than 250°C. The low reactivity of oxygen results in decreased decomposition. The selectivity of each catalyst toward N$_2$ remains almost 100%.

The leaching of metals in the reaction medium is a major problem, resulted in the deactivation of CWAO catalysts. For this purpose, we analyzed the catalysts after reaction using Atomic Absorption spectrophotometer for leaching of Ru and Cu and results are presented in Table S5. In the case of monometallic Ru/ γ-Al$_2$O$_3$ and Cu/ γ-Al$_2$O$_3$, metal loading was decreased with the increase in several cycles. However bimetallic Cu-Ru-3/ γ-Al$_2$O$_3$ exhibited excellent stability even after five cycles of testing. Less than 1% losses are observed after five cycles in weight of both Ru and Cu metals. The probable reason for very low leakage is the strong interaction between Ru and Cu, which prohibited the leeching of both metals, resulted in remarkably improved catalytic stability. Any support from the literature

CONCLUSIONS

γ-Al$_2$O$_3$ supported Cu-Ru bimetallic catalysts with different metal loading were successfully prepared by impregnation method. The designed catalysts were characterized by different techniques and were successfully applied for wet air oxidation of ammonia. Up to 99 % ammonia decomposition was achieved with high selectivity towards nitrogen production and minimum nitrate production. 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. Catalyst with 3% Ru loading over 10% Cu showed maximum activity which is due to the alloying effect as well as the high surface area. By considering the effect of different parameters on ammonia decomposition it was observed 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 the minimum dissolution of metals in the reaction media.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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