

# Catalytic Functionalities of Ru Supported on Activated Carbons Prepared from Rice Straw for Glycerol Hydrogenolysis

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**ABSTRACT:** Activated carbons are prepared from Rice straw by using  $(\text{NH}_4)_2\text{HPO}_4$  as an activating agent. The effect of different conditions during pretreatment on textural properties like surface area, pore volume, average pore size diameter and catalytic functionalities are evaluated. These activated carbons are used as supports for Ruthenium metal and the catalysts UR-0, Ru/C-UR0-1, Ru/C-UR0-3, Ru/C-UR0-5, Ru/C-UR0-7 (end numerical indicates wt. percentage of Ru) are prepared. The activities of the catalysts are studied for glycerol hydrogenolysis. Maximum conversion of glycerol is observed at 5 wt. % of Ru, hence the same wt. % is loaded on other activated carbon supports and other catalysts Ru/C-UR1-5, Ru/C-UR2-5, Ru/C-UR3-5 are also prepared. All these catalysts are subjected for characterization of surface area, pore volume, X-ray diffraction, and TEM studies. Highest surface area shown by Ru/C-UR3-5. Among these catalysts maximum activity was found for Ru/C-UR3-5.

**KEYWORDS:** Rice Straw, Activated Carbon, Surface area, Glycerol Hydrogenolysis, Metal dispersion

## I. INTRODUCTION

Biomass is an abundant and renewable energy source derived from all organic materials produced by human and natural activities [1]. Biomass can be considered as one of the promising environment friendly renewable energy options and has attracted more and more interests [2]. Rice straw from the agricultural industries is an abundant biomass resource in India and China that has typically been treated using traditional methods such as composting and incineration. However, they are not suitable to process this solid waste as rice straw contains small concentrations of nitrogen for composting and a considerable amount of solid grains that would generate smoke into the environment during incineration [3]. As the rich in volatiles and combustible ingredients, the rice straw can be employed as a renewable energy source. How to reuse and recycle this valuable biomass resource is a very urgent significant, yet difficult job [4]. In recent years, the use of low cost waste, especially agricultural by-products as support materials to prepare activated carbons has attracted much attention due to the high cost in the production of commercial activated carbons from coal, wood and coconut shell. Rice straw is a by-product of rice production. In most of the Asian countries, increasing rice production has permitted production of a large amount of rice straw, which is mostly burned for the purpose of quick disposal and land clearing due to its lower heat value compared with other agricultural residue. Since past two decades, several researchers began to focus on developing porous activated carbons from rice straw for the removal of pollutants from wastewater. In 1990's Chinese researchers adopted chemical activation with  $\text{ZnCl}_2$  as activating agent to produce powdered activated carbons from rice straw for the purification of water. Recently, Basta et al. in 2009 applied a two-step process of carbonization followed by KOH activation to prepare activated carbons from rice

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straw.

Catalytic conversion of renewable biomass resources, as feed stocks for the chemical industry, becomes more and more important because of the worldwide serious energy and environmental problems. The use of renewable feedstock is essential for the sustainable development of society. The conversion of renewable feedstock into chemicals and fuels are important in the present scenario as the availability of fossil fuels is limited. Catalyst plays an important role to convert bio-renewable feedstock to commodity chemicals and clean fuels [5-10]. Some chemical functionalisation of glycerol is also carried out in industry. In future the glycerol will be a cost-effective raw material for the preparation of valuable chemicals and fuel additives. With a focus on recent developments in the conversion of glycerol into value-added chemicals, new chemistry of glycerol will be developed which plays a crucial role in future bio-refineries, as its derivatives find uses in sectors as diverse as fuels, chemicals, automotive, pharmaceutical, detergent, and building industries. Value-addition of glycerol will increase profitability of biodiesel industry [11,12]. A variety of reactions are used to produce valuable chemicals from glycerol. Maris et al. [13] used commercial carbon-supported Ru and Pt catalysts in the batch wise hydrogenolysis of glycerol in aqueous solution at 200 °C and 40 bar of H<sub>2</sub>, with and without added base. The presence of both 0.8 M NaOH and CaO enhanced the rate of glycerol hydrogenolysis over both catalysts. However, the extent of enhancement was greater over Pt/C than Ru/C. In the absence of base, Ru/C was more active than Pt/C for the hydrogenolysis of glycerol. Under neutral conditions, Ru favors the formation of ethylene glycol over propylene glycol. The same group [14] prepared bimetallic Pt-Ru and Au-Ru catalysts. Pt-Ru/C and Au-Ru/C favored the formation of ethylene glycol over propylene glycol during glycerol hydrogenolysis in neutral pH conditions. The product selectivities over the bimetallic catalysts at both high pH and neutral conditions were quantitatively similar to those observed over the monometallic Ru catalyst. Feng et al. [15] achieved very high selectivity at high conversion using Ru/TiO<sub>2</sub> as catalyst in basic aqueous solution. In our current study, the main focus is to develop high surface area carbon materials by using (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> as an activating agent. The main purpose of this work is to develop activated carbons from rice straw and to use them as support materials for impregnating with Ru active metal. Activity of these catalysts is studied for hydrogenolysis of glycerol.

## II. RELATED WORK

- i. Earlier commercial samples of activated carbons were used for glycerol hydrogenolysis by using Rh, Pt, Pd, Ru as metal precursors.
- ii. The main objective of the work is to use low cost Bio-waste, especially agricultural by-products like Rice Straw for preparation of activated carbons.
- iii. The surface properties of carbons were modified by using (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> as an activating agent.
- iv. The prepared activated carbons are used as support materials for Ru metal catalysts.
- v. Ru/C catalysts are implied to study the conversion of Glycerol into 1,2 PDO, 1,3 PDO, Ethylene glycol etc. through hydrogenolysis reactions.

## III. EXPERIMENTAL

### 3.1 Materials

Rice straw was collected from Krishna district, Andhra Pradesh, India, was trimmed in to small pieces. These pieces were soaked in 2 wt. % NaOH solution for 24 hr. to remove ash and water soluble substances. The straw was then washed with distilled water until the pH is neutral and then dried at 110°C overnight.

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## 3.2 Preparation of Activated Carbons

A tubular furnace for carbonization provided with temperature programmer was used to prepare activated carbons. 10 gr. of dried rice straw was heated in the furnace under nitrogen atmosphere at 100c/min. from room temperature to a 600<sup>0</sup>C and maintained for an hour. After carbonization, the furnace was cooled to room temperature under continuous flow of nitrogen to avoid post oxidation process. Thus produced solids were washed with 1 M HCl acid followed by thorough washing with hot distilled water to remove chloride ions and other residues until the pH became neutral. The purified solids were dried at 110<sup>0</sup>C for 10 hr. This samples is designated as UR-0. This sample was further activated by using diammonium hydrogen phosphate and from this three other samples are prepared under varied conditions. i) 5 gr. of UR-0 was calcined at 250<sup>0</sup>C for 2hr for oxidation under air. Then the sample is impregnated with 30wt. % (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solution using an impregnation mass ratio of 1:5 (straw/ (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>). This sample is designated as UR-1. ii) 5 gr. of UR-0 is first impregnated with 30 wt. % (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and then heated at 600<sup>0</sup>C under nitrogen atmosphere. This sample is named as UR-2 iii) 5 gr. of UR-0 is first impregnated with 30 wt. % (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and then heated at 250<sup>0</sup>C under air for 2 hr. Then the same sample is subjected to heating at 600<sup>0</sup>C under nitrogen atmosphere for activation. This sample is named as UR-3.

## 3.3 Preparation of supported ruthenium catalysts by impregnation

Activated carbons prepared from rice straw are used as support for Ru catalysts. The catalysts were prepared by conventional impregnation using aqueous solution of RuCl<sub>3</sub>.nH<sub>2</sub>O. In the conventional method, calculated amounts of aqueous metal precursor solution was added to activated carbons UR-0, UR-1, UR-2, UR-3 and after allowing overnight adsorption the excess solution was first evaporated to near dryness on a water bath and then the partially dried material was further dried in air oven at 120 <sup>0</sup>C for 12 h. The catalysts were reduced in H<sub>2</sub> flow at 300 °C for 2 h before its use for glycerol hydrogenolysis.

## 3.4 Activity measurements

Hydrogenolysis of glycerol was carried out in an autoclave. In this experiment, the required quantities of glycerol diluted with de- ionized water and catalyst were taken. Prior to the experiment, the catalysts were reduced at suitable temperature for 3 h with H<sub>2</sub> flow (30 ml/min). In a typical run, 50 g of the aqueous glycerol solution and required quantity of the catalyst were loaded into the reactor. The autoclave purged with H<sub>2</sub> flow to drive off the air present in autoclave. After the purge, the reaction temperature and hydrogen pressure raised to required temperature and pressure. During the reaction the decrease in hydrogen pressure and was made up to maintain the pressure constant. After the reaction, the autoclave was cooled, the gas products were collected in a Teflon bag, and the liquid products were separated from the catalyst by filtration.

## 3.5 Product analysis

After the reaction the system was allowed to cool down to room temperature and the gas products were collected in a gas bag and the liquid phase products were separated from the catalyst by filtration. These products were analyzed using a gas chromatograph equipped with a flame ionization detector (FID). The GC column used was an Inno wax capillary column (30 m X 0.32 mm X 0.5 mm). The Products were also identified by using GC-MS. The gas phase products were analyzed by a gas chromatograph equipped with Porapak Q column and thermal conductivity detector. The products identified during glycerol hydrogenolysis are 1,2- propanediol (1,2-PD), acetol, 1-propanol (1-PO), and 2-propanol (2-PO) as hydrogenolysis products and ethylene glycol (EG), ethanol, methanol, ethane and methane are as degradation products.

## IV. RESULTS AND DISCUSSIONS

### 4.1 Surface area and Pore volume

The surface area of pure activated carbon prepared from rice straw UR-0 is 376 m<sup>2</sup> g<sup>-1</sup>. As the wt.% of Ru increases from 1 to 7, the surface area and pore volumes gradually decreases which is shown in Table-1. The change in pore volume and average pore diameter is marginal. Based on the activity studies the highest activity is shown on Ru/C-

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UR0-5 catalyst, the same wt.% of Ru metal is loaded on other supports and their physico-chemical characteristics are presented in Table-2.

**Table: 1 Surface are and Pore volume of Ru/C catalysts**

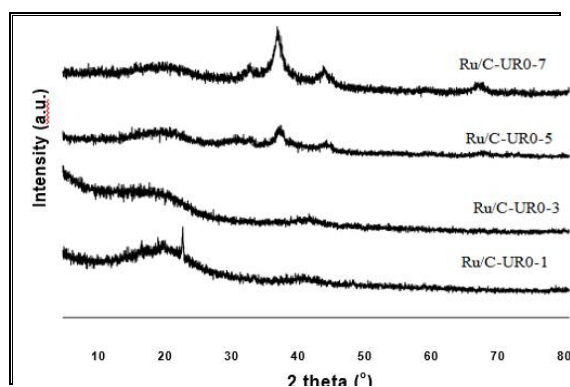
Catalyst	Ru Wt.%	S.A (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> /g)	Av.Pore diameter (nm)
UR-0	0	376	0.31	2.2
Ru/C-UR0-1	1	352	0.30	2.2
Ru/C-UR0-3	3	311.0	0.26	2.18
Ru/C-UR0-5	5	301.3	0.27	2.15
Ru/C-UR0-7	7	265.2	0.271	2.2

**Table: 2 Surface are and Pore volume of Ru/C catalysts**

Catalyst	S.A (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> /g)	Av.Pore diameter (nm)
Ru/C-UR0-5	301.3	0.27	2.15
Ru/C-UR1-5	542.2	0.29	2.21
Ru/C-UR2-5	865.6	0.41	2.35
Ru/C-UR3-5	1102.5	0.40	2.09

### 4.2 X-Ray Diffraction studies

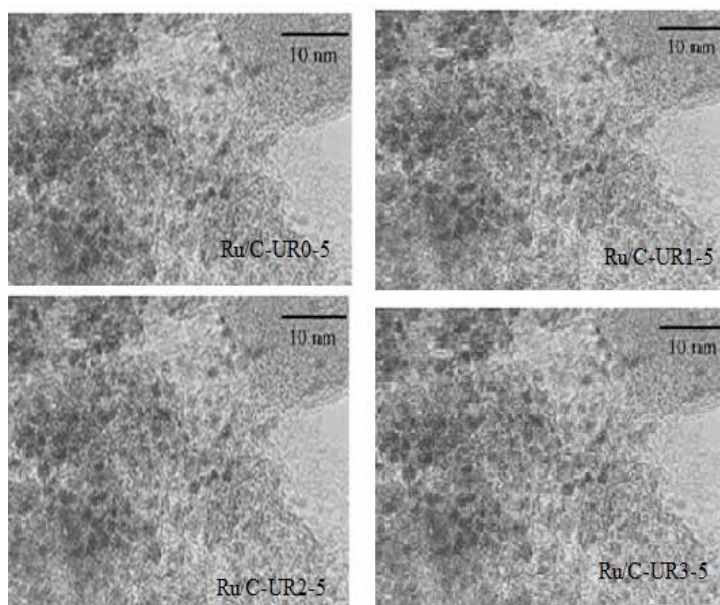
Fig.-1 shows the XRD patterns of activated carbon prepared from rice straw which is used as support for Ruthenium catalysts. A small broad-based diffraction peak appearing around 25.2 can be assigned to diffraction of the poorly crystalline graphite phase of carbon. This suggests that the metal particles on the graphite phase can have a high level of dispersion. The peaks around  $2\theta = 39.76, 41.5^\circ, 45.24$  and  $66.45^\circ$  is assigned to Ru metal for Ru/C catalysts. All the diffraction peaks of Ru metal catalysts displayed the presence of oxides indicating their co-existence in the catalysts. There is no obvious shift in an of the diffraction peaks of Ru metal which is in agreement with other noble metals [16].



**Fig.-1 XRD patterns of the Ru/C catalysts**

### 4.3 Transmission electron microscopy studies(TEM)

Fig.-2 shows TEM images of the fresh Ru/C catalysts. The average particle size of the catalysts was estimated to be about 2.5, 3.7, 2.9 and 3.5 nm, respectively for Ru/C-UR0-5, Ru/C-UR1-5, Ru/C-UR2-5 and Ru/C-UR3-5 catalysts. Maximum metal dispersion was seen for the Ru/C-UR3-5 catalyst. In addition, the TEM images of these catalysts used in the glycerol reaction showed that the metal particle size of catalysts was almost equal to that of the reduced catalysts before the activity test indicating that high dispersion was maintained.



**Fig.-2 TEM images of noble metal catalysts**

(a) Ru/C-UR0-5 (b) Ru/C-UR1-5 (c) Ru/C-UR2-5 (d) Ru/C-UR3-5

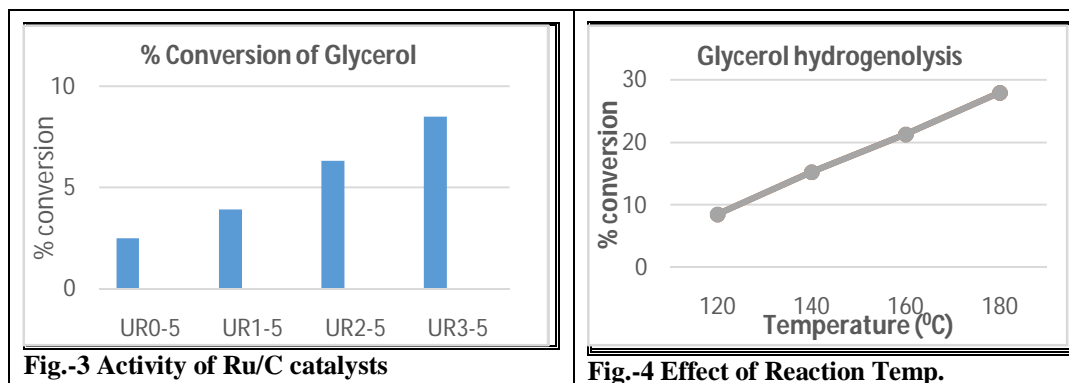
#### 4.4 Evaluation of metal functionality of carbon supported Ru metal catalysts

The hydrogenolysis reaction was carried out at temperature of 120<sup>o</sup>C, hydrogen pressure of 60 bar, catalyst weight of 0.3 g and a reaction time of 8h using 50 ml of 20% glycerol aqueous solution as the feed. All reactions were carried out under identical conditions. Propylene glycol (PG) (1,2-propanediol (1,2-PDO)), 1,3-propanediol (1,3-PDO), 1-propanol (1PO), 2-propanol (2PO), acetol, methanol, ethanol and ethylene glycol (EG) are formed during the reaction. 1,2-PDO and 1,3-PDO are the desirable products of glycerol hydrogenolysis. 1-propanol and 2-propanol are known as over-hydrogenated products. Methanol, ethanol and ethylene glycol are formed during the reaction by cleavage of C-C bond of glycerol. Ethylene glycol can be identified as a by-product of reaction. Acetol or hydroxyl acetone is a reaction intermediate. Only selectivity to 1,2-PDO, 1,3-PDO and EG were discussed in this study in view of their commercial importance and the relative large amounts detected in the products. The activity results of glycerol hydrogenolysis are listed in Table-3. Highest conversion of glycerol is observed for Ru/C-UR3-5 catalyst which is shown in Fig.-3.

**Table-3 Glycerol hydrogenolysis activity of different noble metal catalysts**

Catalyst	Conv %	Selectivity				
		1,2-PDO	EG	1,3-PDO	Acetol	Others
Ru/C-UR0-5	2.5	20.3	65.4	3.2	0.9	8.1
Ru/C-UR1-5	3.9	21.2	52.1	10.4	0.4	12.4
Ru/C-UR2-5	6.3	19.5	57.2	4.8	0.2	12.7
Ru/C-UR3-5	8.5	18.4	64.1	0.5	0.1	10.2

**Reaction conditions: 20 wt % Glycerol aqueous solution: 50 ml; H<sub>2</sub> Pressure: 60 bar; Reaction Time: 8 h; Catalyst Weight: 0.3 g (5%); Reaction Temperature: 120° C.**



#### 4.5 Effect of reaction temperature on glycerol hydrogenolysis

Reaction temperature is an important parameter for selective hydrogenolysis of glycerol. Therefore, the effect of temperature was studied over Ru/C-UR3-5. The obtained results are listed in Table-4. Reaction temperature showed a positive impact on glycerol conversions. Fig-4 shows that as the temperature increases, the glycerol conversion increased. The glycerol conversion increased from 8.5 to 27.9 % when the temperature varied from 120 to 180 °C for Ru/C. The selectivity towards 1, 2-PDO decreased upon increasing of the reaction temperature mainly due to the formation of ethylene glycol and other gaseous products.

**Table-4 Effect of reaction temperature on glycerol hydrogenolysis activity using Ru/C-UR3-5 catalyst**

Catalyst	Temp. (°C)	Conv %	Selectivity			
			1,2-PDO	EG	1,3-PDO	Others
Ru/C-UR3-5	120	8.5	23.4	58.1	0.5	10.2
Ru/C-UR3-5	140	15.2	19.2	55.3	1.2	9.2
Ru/C-UR3-5	160	21.3	16.7	56.2	1.5	5.6
Ru/C-UR3-5	180	27.9	20.1	49.1	0.9	2.7

Ru/C-UR3-5 catalyst gave the highest glycerol conversion at 180°C than at lower temperatures. However, the main product was derived from cleavage of C-C bond leading to the degradation product ethylene glycol [17]. On the other hand, the remaining catalysts showed low glycerol conversion with high 1, 2 propane diol selectivity than Ru/C-UR3-5 catalyst.

#### V. CONCLUSIONS

- Among all the activated carbons prepared from rice straw, UR-3 shows maximum surface area. This may be attributed to the yield of highest percentage of activated carbon due to formation of higher thermally stable substances from the interaction of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> with carbon containing compounds in the rice straw.
- Activation temperature and atmosphere has great effect on the yields of activated carbons prepared from rice straw. The high surface area of UR-3 support may be due to release of volatile matters through pore opening and biomass gasification during activation.
- Among all Ruthenium catalysts, Ru/C-UR3-5 is identified as the best catalyst. But the catalyst activity can be further enhanced by using acid co-catalyst for glycerol hydrogenolysis, which is our future plan of action.
- Hydrogenolysis of glycerol follows single step mechanism when Ru/C catalysts are used alone.
- The catalytic system gives better selectivity with good conversion when the temperature is increased gradually.

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