Cascade Dehydrative Amination of Glycerol to Oxazoline

Rajan Pandya,[a] C. V. Rode[a]*

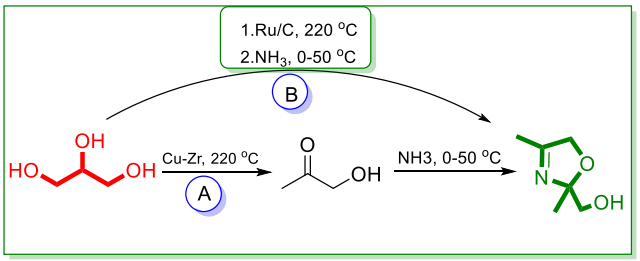
[a]*Chemical Engineering and Process Development Division, CSIR-National Chemical laboratory, Dr Homi Bhabha Road,Pashan, Pune-411008, India*

**Corresponding author: Fax: +9120 2590 2361, Phone: +9120 25902349, E-mail address cv. rode@ncl.res.in*

Abstract: Biomass Transformation into valuable nitrogen containing compounds is less explored yet. Here, we report direct conversion of bioglycerol to oxazoline involving glycerol dehydration followed by its amination using ammonia. For two step strategy a non-noble metal, Cu-Zr catalyst developed giving glycerol conversion of 78% to acetol followed by amination separately with 95% selectivity to oxazoline. Moreover, we have demonstrated a single pot process using Ru/AC to achieve 95% selectivity to oxazoline. XPS studies revealed the co-existence of multivalence Ru species RuO_2 and RuO_3 have synergistic effect for activation of carbonyl group whereas Ru^o is an active site for ammonia dissociation.

Keywords: Amination, bioglycerol, oxazoline.

1. Introduction - Oxazoline have been attractive targets for chemists owing to their immense applications in medicinal, polymer material, and food flavour research. In this context, a catalytic, single step, one pot process for oxazoline preparations using renewable, cheapest bio-glycerol feed stock has been demonstrated. We report here supported Cu and Ru catalysts for oxazoline synthesis which involves the amination in aqueous solution making the process environmentally benign. The use of aqueous medium makes the process energy efficient by avoiding separation step of glycerol from water. Other salient features of this process are i) use of inexpensive commodity chemical like ammonia for amination reaction, ii) elimination of the step of separation of intermediates and iii) leaching of the active metal in presence of ammonia. It was found that for the two-step reaction, increased yield of oxazoline (95% selectivity) was achieved by both Cu and noble metal Ru catalysts because acetol was continuously removed through distillation process which helped in shifting the equibrium towards right. Whereas, for a single pot reaction Cu-based catalysts gave lower glycerol conversion and very less oxazoline selectivity compared to that of Ru/AC catalysts. Further studies on the effect of support, solvent and process parameters on glycerol conversion and oxazoline selectivity were performed over the Ru/AC catalyst for a single pot reaction.



Scheme 1. Two pathways for glycerol amination to oxazoline

2. Experimental –The reaction was carried out in reactive distillation set up (Figure 1) in which round bottom flask having 100 mL capacity was taken to which 50 g of pure bio-glycerol and 0.8 g of Cu-Al catalyst were added. This reaction mixture was stirred by a magnetic stirrer at an agitation speed of 600 rpm and temperature was maintained at 220 °C by using silicon oil bath. The reaction was continued for about 2 h and acetol formed was continuously distilled out during the reaction.

The obtained distillate mainly containing acetol and 1, 2-propanediol, was analyzed by GC (Model Shimadzu GC-2025) equipped with an auto sampler (Model AOC-20i) and a capillary FFAP (Free Fatty Acid Phase) (30 m length 60.53 mm i.d.61mm film thickness) column connected to the flame ionization (FID) detector. The distillate was cooled to 0°C and then 30% aqueous ammonia solution (1:3 ratios) was

added drop wise with stirring in the presence of 0.01g Cu-Al catalyst, while the reaction temperature was maintained below RT. The reaction mixture was stirred for 2 h and reaction progress was monitored by GC.

3. Results and discussion

Table 1. Catalytic screening for dehydrative cyclised amination[a].

Entry No.	Catalysts	Glycerol to Acetol				Acetol to Oxazoline			
		Conc.	Acetol	1,2-PDO	other[b]	Conc.	Oxazoline	5-methyl imidazole	1,2-dimethyl imidazole
1	Cu-Al	75	77	13	10	99	95	3	2
2	Cu-Zr	78	80	12	8	99	95	3	2
3	Cu-Mg	80	68	20	12	99	95	3	2
4	3%Ru/AC	85	30	20	50	99	80	2	8

[a] Reaction conditions: Glycerol to Acetol- 20 g glycerol, 220 °C, 0.8 g catalyst, 3 h. Acetol to oxazoline- 5 g distillate, 15 mL 30% aq. NH_3, 50 °C, 0.05 g catalyst , 2 h. [b] Others comprised of solketol, ethylene glycol, ethanol and unknowns.

4. Conclusions- We have demonstrated amination of glycerol with ammonia in aqueous medium for the production of oxazoline for the first time, using inexpensive copper based catalyst. In a two step variation, Cu catalysts exhibited almost complete conversion of acetol with 95% selectivity to oxazoline. Interestingly, non-catalytic amination gave acetol conversion of 82% with decrease in oxazoline selectivity from 95 to 80% along with multiple side reactions. In a single step cascade process, supported Ru catalysts showed the excellent activity and most importantly, the stability against the poisoning by ammonia. XPS studies and several other characterization techniques confirmed the multivalence Ru association species functioned as a highly efficient catalyst which played a key role in the amination of glycerol. A high Brønsted acid density with moderate acid strength was a crucial factor for the high catalytic performance. Py-IR evidenced that increasing the B/L ratio led to better performance of Ru/AC with higher activity and oxazoline selectivity. Based on the catalyst characterization integrated with the activity results, a plausible reaction pathway was proposed. In the first step of the reaction glycerol dehydration although mainly catalyzed by acid sites, tautomerization to keto form takes place by abstraction of the proton by metallic Ru to give acetol. The subsequent amination of acetol furnishes imine, which undergoes cyclization with another molecule of acetol to obtain oxazoline. The effect of various reaction parameters such as temperature, metal and catalyst loadings, solvents on the conversion and oxazoline selectivity were also studied.

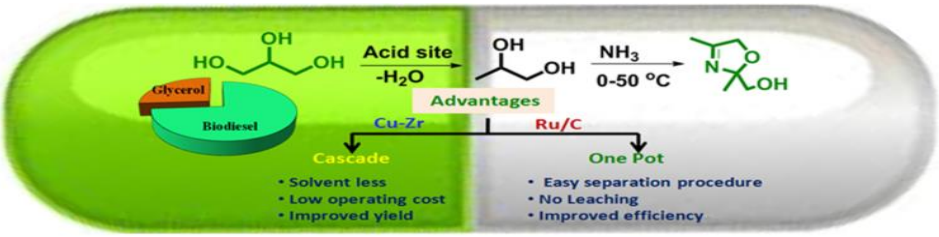


Fig. 1- Simple & environmentally benign process for bioglycerol to oxazoline synthesis is reported using aqueous ammonia.

References

1. C. V. Rode, R. Pandya and R. B. Mane, US20170240515A1.
2. R. B. Mane, A. Yamaguchi, A. Malawadkar, M. Shirai and C. V Rode, RSC Adv., 3, (2013), 16499–16508.
3. R. Mane, S. Patil, M. Shirai, S. Rayalu and C. Rode, *Appl. Catal. B Environ.*, 204, (2017), 134–146.