ISGC 2019 May 13rd - 17th

N°488 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Alternative technologies

SEMI-CONTINUOUS TWO-STEP CATALYTIC PROCESS FOR THE PRODUCTION OF 2-METHYLPIPERAZINE BY USING GLYCEROL AS STARTING RAW MATERIAL

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PURPOSE OF THE ABSTRACT

In the last years, due to the constrains imposed on the use of agricultural land for fuel industry, biodiesel production has started to be focused on the transformation and upgrading of unconventional raw materials (i.e. animal fats, cooked oils, etc) [1]. However, even in these novel cases, glycerol is obtained as by-product and its transformation into high added value products becomes essential to make the overall process profitable [2]. Specifically, a path seldom explored so far is the use of glycerol as a carbon source to produce nitrogenated compounds. In this work, the objective is to develop a catalytic route to obtain N-heterocycles of piperazine type out of a glycerol selective dehydration product, hydroxiacetone (or acetol), where just a few studies using continuous processes can be found [3]. The piperazine ring is used itself as an anthelmintic and can be also found in many drugs. Moreover, piperazines are intermediates for organic synthesis products, and they are also used in CO2 scavenging [4]. To produce the 2-methylpiperazine (2-MP) a semi-continuous two-step process was considered, involving a first selective dehydration of glycerol into acetol and a consecutive reductive amination with ethylenediamine [5]. The study aimed to optimize each single reaction step separately, to later linking the two processes. This work offers new insights into the production of nitrogenated compounds from this bio-based raw material.

As for the first step, different CuO-supported on metal oxides materials (ZrO2, Al2O3, TiO2 and MgO) were prepared, well characterized by different techniques (i.e. XRD, ICP, TPD analysis and N2 adsorption, among others), and tested for the selective dehydration of glycerol. Catalytic experiments were carried out in a stainless fixed-bed reactor with the catalyst diluted with SiC. A liquid mixture of glycerol and MeOH (20:80 weight ratio) was fed into the reactor at 240 ºC during 9h. Figure 1A shows the average catalytic performance of the selected materials together with their physicochemical properties. 5.0wt%CuO/ZrO2 catalyst offered the best compromise between both glycerol conversion and acetol selectivity, and also an excellent catalytic stability during 9h of reaction with practically no variation in the selectivity (c.a. 70%). Further experiments were done to evaluate the effect on the catalytic performance of i) the regeneration process in-between catalytic cycles, and ii) the inclusion of water in the feed, among others; all these results will be discussed and presented in the congress.

On the other hand, and based in previous works [5], materials based on Pd nanoparticles supported on simple (i.e. TiO2, Al2O3) and mixed metallic oxides (i.e. TiO2-Al2O3) were prepared for the selective reductive amination to yield the desired 2-methylpiperazine (2-MP). The Pd-catalysts were well characterized by ICP, TPR, XRD, NH3-TPD and HR-TEM. The best results were attained with Pd/TiO2-Al2O3, with 2-MP yields higher than 80%, also showing very high stability after several reuses (Figure 1B).

In general, results indicate that a waste by-product glycerol from biodiesel can be transformed into acetol by using environmentally friendly Cu-based oxides in a continuous flow fix-bed reaction system, which could be scaled up from an industrial point of view. Further reaction of this acetol with ethylenediamine in the presence of hydrogen

would yield the desired 2-methylpiperazine (2-MP), our currently work being focused on optimising the overall process described in Scheme 1.

FIGURES

(A) STEP 1

Catalyst	Cu content (wt%)[a]	Surface area (m^2/g)[b]	Glycerol conversion (%Mol.)	Yield to Liquids (%Mol.)	Selectivity to Acetol (%Mol.)
CuO/Al_2O_3	4.5	130	76	53	66
CuO/TiO_2	5.5	20	82	62	70
CuO/ZrO_2	4.5	136	100	90	70
CuO/MgO	5.0	172	50	26	43

a: Values measured by ICP. b: Values calculated from N_2 adsorption isotherms (BET method). Reaction conditions: feed = methanol/glycerol (80/20 in weight), flow = 2 ml/h, with 0.5 g of catalyst at 240 ºC, average results from TOS = 1-9h.

(B) STEP 2

Catalyst	2-MP yield (mol. %)
1wt.%Pd/TiO_2-Al_2O_3	82
1wt.%Pd/TiO_2	76
1wt.%Pd/Al_2O_3	74

Reaction conditions: 0.325 g acetol (slow addition), 0.227 g amine, 0.055 g cat., at 90 ºC and P_{H_2} = 13 bar during 3h.

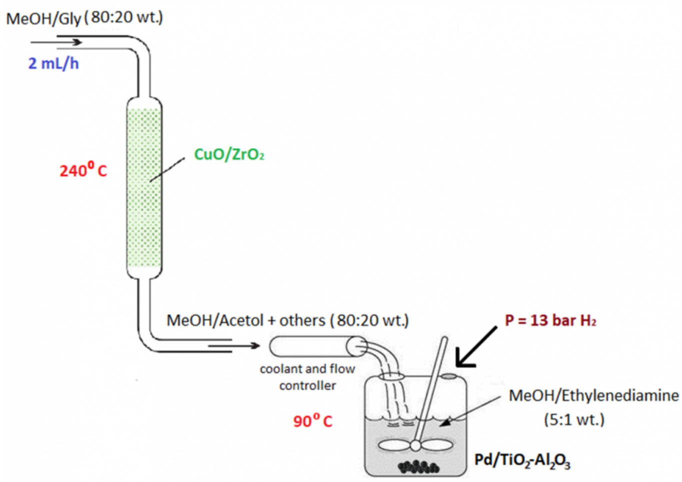

FIGURE 1

Figure 1.

(A) Step 1: Catalytic performance of CuO-supported materials in glycerol dehydration, and (B) Step 2: Yields to 2-MP in the consecutive reductive amination over Pd-catalysts.

FIGURE 2

Figure 2

Scheme of the overall process to produce 2-methylpiperazine starting from glycerol.

KEYWORDS

glycerol dehydration | Cu-based material | piperazine synthesis | Pd supported nanoparticles

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