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Glycerol valorization: The effect of Cu on the HZSM5 catalyst structure and increased selectivity towards allyl alcohol

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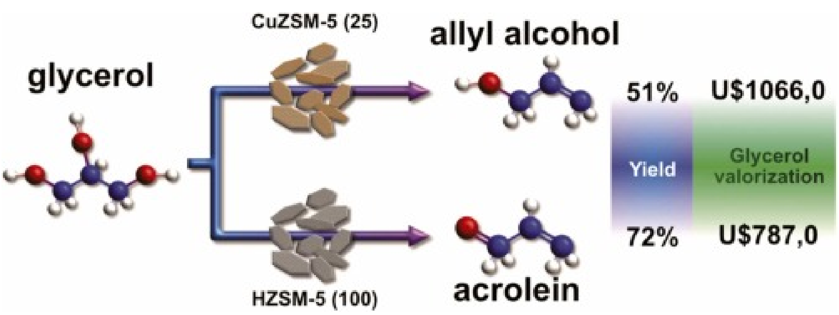
Abstract

The valorization of glycerol modified with impregnated Cu nanoparticles was investigated. Significant enhancement in the rate of formation and yield of the allyl alcohol and acrolein is observed in the gas-phase conversion of glycerol. Concerning characterization results, Cu showed low interaction with the ZSM-5 support, resulting in minor changes in the structure of materials. ZSM-5 samples showed higher selectivity to acrolein and the CuZSM-5 ones showed higher selectivity to allyl alcohol. Due to agglomeration of Cu clusters and, consequently, conversion of Cu^{2+} into Cu^{0} species during glycerol reaction, liquid product selectivity was shifted from acrolein to allyl alcohol. Analysis of the glycerol valorization of the studied processes shows that the CuZSM-5 zeolite catalyst has greater selectivity for allyl alcohol, also has better performance in terms of added value than HZSM-5 catalyst, since allyl alcohol has a higher market value than acrolein.

Graphical Abstract



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ZSM-5 catalyst modified with impregnated CuO nanoparticles for gas-phase conversion of glycerol to allyl alcohol. The glycerol conversion, allyl alcohol selectivity, and yield to the products reached 93%, 55%, and 51%. over CuZSM-5 zeolite. The CuZSM-5 zeolite catalyst has greater selectivity for allyl alcohol and has better performance in terms of added value than HZSM-5 catalyst, since allyl alcohol has a higher market value than acrolein.

Introduction

Along the past decades, several state initiatives, with emphasis on the directives of the Federal European Union, have encouraged the production of biodiesel as part of their policies to reduce greenhouse gas emissions (Zhou et al., 2008; Brehmer et al., 2009). Commonly known as the main residue of biodiesel production (Ravi et al. 2020), glycerol can be used to replace fossil resources in the production of important chemical intermediates in industry (Avasthi et al., 2020, Chong et al., 2020, Gujar and Modhera, 2023, Zhang et al., 2020).

The chemical transformation of glycerol has thus become a major point of interest for glycerol valorization. From glycerol, we can produce many commodity chemicals, polymer precursors, and solvents (i.e., acrolein, lactic acid, glyceric acid, propanol, propanediol, glycerol carbonate, solketal, acrylic acids, epichlorohydrin, and allyl alcohol, acetin, and oligomers, are highlighted) (Varma and Len, 2019). High added-value products can be obtained from glycerol through different pathways, such as oxidation, carbonylation, reforming, acetalyzation, etherification, esterification, dehydration, hydrogenolysis, etc. (Aroua et al., 2020, Manera et al., 2021).

Several studies of the use of glycerol as a precursor in chemical reactions of high industrial interest have been carried out (Kinage et al., 2010, Liu and Gao, 2018). According to some researchers, catalytic dehydration of glycerol is one of the most promising routes to value this compound (Wang et al., 2019; Katryniok et al., 2010; Chai et al., 2007; Kostyniuk et al., 2020; Kostyniuk et al., 2020a; Wang et al., 2023a, Wang et al., 2023b; Shan et al., 2023).

Two valuable products that can be produced from glycerol are acrolein and allyl alcohol, a compound which has a significant market value and very broad commercial applications. The average sale price of glycerol is $350 USD/ton (Oleoline, 2021) while its derivatives reach a price of acrolein $1400 USD/ton (Marketizer, 2021), and allyl alcohol (CAS nº. 107–18–6) $2900 USD/ton (CommoPrices, 2021) according to the market references.

Acrolein is a product of glycerol with high aggregate value because is used primarily as an intermediate component in the manufacture of chemical substances. Acrolein is a useful intermediate to the production of various compounds including methionine, methionine hydroxy analog, 1, 3 propanediol, and glutaraldehyde (MarketWatch, 2021). The global acrolein market by type includes glycerol dehydration method and propylene oxidation method of the total market revenue in 2021. Acrolein is produced by a non-renewable route, by propylene oxidation method accounted for over 50% share of the total revenue generated (Deleplanque et al., 2010a, Jia et al., 2010) by this segment, followed by glycerol dehydration method with over 40%, a renewable route (IndustryGrowthInsights, 2021).

Furthermore, allyl alcohol, which is commercially obtained from allyl chloride hydrolysis, is also an alternative to value glycerol. Allyl alcohol is used as a precursor to many specialized compounds such as drying oils, flame resistant materials, and plasticizers (Krähling et al., 2000). Allyl alcohol is primarily a chemical intermediate, used in the synthesis of compounds such as epichlorohydrin, 1,4-butanediol, allyl diglycol carbonate, among others (DataInteloReport, 2021). In the industry the 90% of allyl alcohol are obtained by allyl acetate hydrolysis method and propylene oxidation method. Other methods of obtaining allyl alcohol include catalytic hydrogenation of acrolein in vapor phase (TransparencyMarketResearch, 2021). Rise in demand of chemical industries, pesticide, water treatment agent and polymer-based products is boosting the market for allyl alcohol and acrolein.

An increase in commercial interest to obtain better yields has encouraged researchers to prepare catalyst zeolites of the type ZSM-5 (Wu et al., 2021; Zhou et al., 2020; Zhokh and Strizhak, 2017), that has been successfully applied to the glycerol dehydration reaction, mainly because it may generate active sites within its cavities and channels (Corma, 1995).

Apart from the economic advantages, the direct conversion of glycerol to allyl alcohol and acrolein, which represents an environmentally friendly and renewable route, makes allyl alcohol and acrolein production to become independent from crude oil, thus less straining for the environment in terms of global warming.

Previous studies showed that a larger number of Brönsted acid sites, by comparison with Lewis sites, may favor acrolein production (Jia et al., 2010, Chai et al., 2007). The ratio between both types of acid sites can be controlled by the Si/Al ratio in the catalyst, which affects reaction selectivity (Kim et al., 2010). The gas-phase dehydration of glycerol was already studied by our research group (Neves et al., 2019), with the use of ZSM-5 with low Si/Al ratios (from 25 to 75). The zeolite with Si/Al of 25 showed the best catalytic performance, with selectivity to acrolein around 70% at 300°C. However, there was considerable drop of glycerol conversion over time, mainly due to coke formation on the catalyst surface. Coke deposition, which is a common occurrence in dehydration reactions involving zeolites at high temperatures, is a determining factor in catalyst performance. Thus, performing reactions at low temperatures may favor decrease in coke deposition (Kim et al., 2010).

Impregnation with different metals can generate new active sites for glycerol transformation and act as a complementary way to the catalytic features of the support. Sánchez et al. studied ZSM-5 zeolites impregnated with iron to dehydrate glycerol. According to the authors, the sample with 13 wt% Fe showed selectivity toward allyl alcohol of 61.8%, after a 5-h reaction at 340°C; however, glycerol conversion was only 1.7% (Sánchez et al., 2016). Almeida et al. have used vanadium catalysts supported on beta zeolites to convert glycerol into allyl alcohol (Almeida et al., 2019). The authors proposed a reaction pathway which was similar to the one that had already been reported by Chai et al. (2007), in which formation of allyl alcohol occurs through a series of consecutive reactions, where glycerol is dehydrated to acrolein in zeolite acid sites, followed by selective reduction through a hydrogen transfer mechanism enabled by metallic sites.

The use of copper (Cu) as a promoter in catalytic reactions has great potential, especially due to its characteristic of dehydrogenation of different alcohols (Rioux and Vannice, 2003, Sato et al., 2008, Yuan et al., 2011). Sato et al. (2008) impregnated different amounts of Cu in alumina supports, the sample with 30% wt of CuO showed the highest glycerol conversion; values were close to 100% after 5 h on stream. In another study, Freitas et al. tested a series of catalysts with Cu and Ni impregnated in ZSM-5, in the glycerol dehydration at 250°C and 40 bar (Freitas et al., 2018). Results showed acetol production and its subsequent hydrogenation to propylene glycol, without any external hydrogen source.

Although the use of metals, such as Cu, impregnated in ZSM-5 for conversion reactions of glycerol, has already been studied. The way the zeolite framework behaves when this metal is added has not been properly understood yet. Thus, characterization techniques, such as the Rietveld Refinement method, can be applied to elucidate this issue. Moreover, the role of Cu impregnated in ZSM-5 on the gas-phase glycerol conversion has not been thoroughly discussed in the literature. Therefore, this study aims to understand how the Cu impregnation affects the ZSM-5 zeolite structure, and its consequences on the performance of this catalyst in the gas-phase glycerol conversion reaction.

Section snippets

Catalyst syntheses

ZSM-5 zeolites with different morphologies [ZSM-5(25) and ZSM-5(100) nanoparticles] were synthesized by a chemical method, and the detailed process is described by Frantz et al., 2016, Hu et al., 2015, Nandiwale et al., 2015.

ZSM-5 zeolites in two distinct Si/Al molar ratios, 25 and 100, were prepared in this work because Wei and Smirniotis showed that Si/Al ratios between 25 and 100 in ZSM-5 are ideal for the development of uniform intracrystalline mesoporosity by means of desilication and…

Characterization of fresh catalysts

Fig. 1(a-f) shows the SEM images of ZSM-5 zeolites prepared with different Si/Al ratios. The Si/Al ratio of 25 showed small spherical particles, consisting of smaller disk-like ZSM-5 crystals, formed with an average size of 105 nm as shown on the image, Fig. 1a and c.

The diameters of the ZSM-5 (25) can be attributed to the higher alumina concentration. Since the Brønsted acid site is generated by the substitution of silicon with aluminum in the framework, the acidity of HZSM- 5 is associated…

Conclusions

The valorization of glycerol by selective production of allyl alcohol and acrolein from glycerol over zeolite catalysts was studied. All catalyst samples were active in the gas-phase conversion of glycerol at 250 ^{o}C with the ZSM-5 samples showing higher selectivity to acrolein during the 6-hour reaction and the CuZSM-5 ones showing higher selectivity to allyl alcohol after 2 h of reaction. In contrast, glycerol conversion values decreased with a decrease in Si/Al ratio from 100 to 25 in HZSM-5…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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> In memory of Professor Juliano Rosa de Menezes Vicenti, a remarkable professor and scientist whose life was cut short, we express our deep gratitude for his invaluable contributions and unwavering dedication to this work. Despite his time being limited, he left an indelible mark and inspired countless individuals with his knowledge, passion, and commitment. His legacy will continue to resonate within the scientific community and serve as a reminder of the profound impact one person can make in…

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