

Acetalization of Glycerol over Solid Acid Catalysts

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Introduction

Glycerol is formed as a byproduct in the biodiesel production from vegetable oils and animal fat. In recent years, many reviews on glycerol chemistry have appeared in the literature [1,2]. The major reactions of interest were etherification, hydrogenation, oxidation, and dehydration. By contrast, glycerol acetals and ketals have received considerably less attention. They can find applications as fuel additives, surfactants and flavors. The acetals produced in the reaction of glycerol with formaldehyde, finds applications as disinfectant and solvent for cosmetics and medical usage [3]. A drawback in the glycerol acetalization is the formation of water, which weakens the acid strength of the catalyst and favors the reversibility of the reaction. The use of solvents to distill off the water formed is a common practice, but most of them, such as dichloromethane, benzene and chloroform, are hazards to humans. In this contribution we report the use of heterogeneous acid catalysts for the acetalization of glycerol with aldehydes and ketones.

Materials and Methods

All the reagents were analytical grade. The reactions were carried out in batch conditions. Typically, 54.3 mmol of glycerol was stirred with 65.5 mmol of ketone (acetone, butanone) or 65.5 mmol of aldehydes (formaldehyde solution, butanal, pentanal, hexanal, octanal and decanal) at 70 °C. The molar ratio of glycerol to ketone or aldehyde was 1:1.2. The weight of the catalysts (HBeta, Amberlyst-15, K-10, HZSM-5, PTSA) was adjusted to provide 1.5 mmol of acid sites in every reaction. The kinetics of glycerol conversion was estimated by withdrawing samples at specific time intervals, followed by gas chromatography coupled with mass spectrometry analysis. In all experiments, 1,4-dioxane or dimethylformamide was used as internal standard. In the reactions with the aldehydes, except formaldehyde, dimethylsulfoxide was used as solvent, to allow proper stirring and homogeneity of the liquid phase.

Results and Discussion

Figure 1 shows the conversion for the acid-catalyzed reactions of glycerol with acetone and formaldehyde. Only one product is formed in the reaction with acetone (five-membered ring ketal), whereas two acetal isomers (five and six-membered ring acetals) are present in the reaction with formaldehyde. The reactions with acetone were significantly faster than the reactions with formaldehyde, achieving more that 90% conversion within 40 minutes of reaction for all heterogeneous catalysts, except HZSM-5, which may present shape selectivity properties. The homogeneous catalyst, p-toluene-sulfonic acid (PTSA) showed an inferior performance, yielding a conversion of 80% after 40 minutes. The acetalization of glycerol with formaldehyde solution showed a complete different behavior. All the catalysts, except the zeolite HBeta, showed conversion below 80% within 60 minutes of reaction time.

These results might be explained in terms of the excess of water present in the medium, due to the use of an aqueous solution of formaldehyde. The high conversion (over 90%) achieved with zeolite HBeta after 60 minutes of reaction might be explained in terms of the Si/Al ratio (16) of this zeolite catalyst, which infers a hydrophobic character to its pore structure. This avoids the diffusion of water to the interior of the pores and expels the water formed upon acetalization, preserving the strength of the acid sites.

For the study of glycerol acetalization with aldehydes of different hydrocarbon chain, Amberlyst-15 was chosen as catalyst. The conversion decreased with the size of the chain, but this is not related with diffusion or accessibility problems. In control experiments, without using catalysts, the same trend was observed. The reaction with butanal showed the highest glycerol conversion, whereas the reaction with decanal the lowest (table 1). These results can be explained in terms of the aggregation (micelization) of the aldehyde in the reaction medium to minimize the repulsive interactions between the apolar hydrocarbon chain and the polar reaction medium.

Table 1. Acetalization of glycerol. Conversion after 120 minutes.

Catalyst	Butanal	Pentanal	Hexanal	Octanal	Decanal
Amberlyst-15	75	70	68	48	10
None	20	15	10	6	4

Significance

The results show that glycerol acetals and ketals can be effectively formed with use of heterogeneous acid catalysts, avoiding the use of hazard solvents. They can be relevant for the development of new processes to transform glycerol into value-added products.

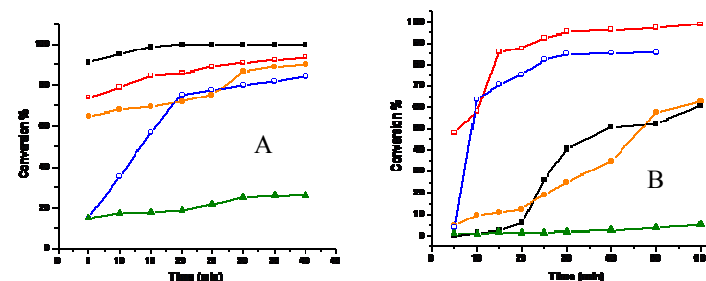


Figure 1. Kinetics of the glycerol reaction with acetone (A) and formaldehyde (B) at 70 °C over various acid catalysts. (■) Amberlyst-15, (□) zeolite Beta, (●) argila K-10, (○) APTS, (▲) zeolite ZSM-5.

References

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