

Catalytic conversion of glycerol to phenylacetaldehyde cyclic acetals

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Introduction

Aldehyde acetalization can be promoted by several solid acid catalysts, as zeolites, aluminas and cation exchange resins, with good results. Activated carbons can also be used, due to the variable surface chemistry and high degree of surface reactivity [1]. Acid treatments with a strong oxidizing agent such as HNO₃ and H₂SO₄ result in the formation of oxygenated functional groups. In addition, the treatment with H₂SO₄ can insert sulfonated groups on the carbon surface. These groups are responsible for the acidic character of the activated carbon and their enhancement typically provides an increase in the catalytic activity.

Since typical polyols acetalization involve materials modified by processes that increase their acidity, such as sulfonation, in this work we evaluated the possibility of enhances the acidity of an activated carbon by treatment with nitric acid and sulfuric acid, in order to prepare catalysts active in the acetalization of glycerol. Phenylacetaldehyde cyclic acetals obtained in this reaction can be used as hyacinth fragrance [2].

Materials and Methods

Commercial Darco activated carbon (AC) was submitted to oxidation and sulfonation processes by treatment with a 20% aqueous nitric acid solution and/or fuming sulfuric acid (20% free SO₃). Nitric acid treatment was carried out under stirring at ambient temperature for 6 h. The sulfonation process was performed by treatment with fuming sulfuric acid under reflux for 10 h. The catalysts were identified as AC-N (activated carbon treated with nitric acid), AC-S (activated carbon treated with fuming sulfuric acid) and AC-NS (activated carbon treated with both nitric acid and fuming sulfuric acid). Glycerol acetalization with phenylacetaldehyde was carried out in a two neck round-bottom flask coupled to a condenser and a Dean-Stark apparatus. The experiments were performed typically with 7.5 wt glycerol% of catalyst, PA:glycerol molar ratio of 1:2 and 40 mL of toluene, under reflux for 6 h. Samples were analyzed by GC/FID, using decane as internal standard.

Results and Discussion

AC and AC-N samples have by far fewer carboxylic + sulfonic groups than the sulfuric acid treated carbons (0.15 and 0.18 mmol g⁻¹, respectively). The amount of strong acidic groups after sulfonation process increased to 0.62 mmol g⁻¹, while sample AC-NS presented the highest acidity, 0.79 mmol g⁻¹.

In order to test the activity and selectivity of treated activated carbons, amount of catalyst was evaluated maintaining the PA:glycerol ratio of 1:2 and the temperature at 383 K (Figure 1). The results indicate that conversion increases with increase in the catalyst loading as well as the surface acidity. Maximum PA conversion of 94% was achieved by AC-NS. All

the systems showed selectivity for the production of dioxolane higher than 85%. The catalyst with the higher amount of carboxylic + sulfonic groups, AC-NS, allowed reaching the maximum conversion in the range 7.5 – 12.5 wt%. Even when the amount of AC-NS was reduced to 2.5 wt%, the conversion remained high (84%), while the AC and AC-N catalysts showed conversion values lower than 80% with 10 wt% catalyst. The role of catalyst and the influence of surface acidity in this reaction are thus clearly evident. Indeed, the proposed mechanism for aldehydes acetalization using acid involves protonation of carbonyl group which needs Brønsted acidity [3]. The catalytic performance of the carbons submitted to different pre-treatments was compared to commercial resin Amberlyst-36. Although the acidity of this resin is much higher, it was less active which may be related to the presence of water in the reaction medium.

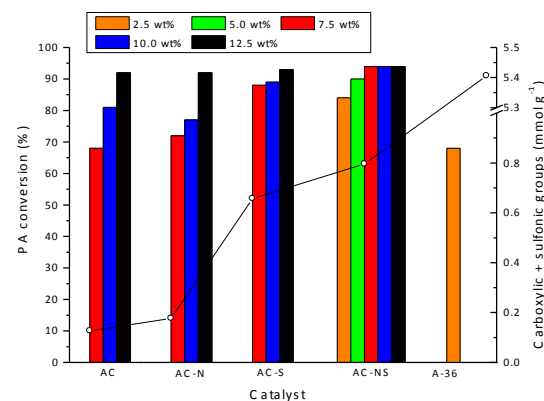


Figure 1. Influence of the catalyst amount and pre-treatment in glycerol acetalization (PA:glycerol molar ratio 1:2, 383 K, 2 h).

Significance

The flexible carbon bulk has increased its hydrophilicity after the oxidation process, what allows the conservation of acid sites activity even in the presence of excess water. The high catalytic performance of carbon-based solid acid is attributed to the incorporation of hydrophilic functional groups on the hydrophobic carbon surface. Oxidized carbons can incorporate large amounts of hydrophilic molecules into the carbon bulk, due to the high density of hydrophilic functional groups bound to the carbon sheets. This incorporation provides good access by reactants from solution to the acidic sites in the carbon material, giving rise to high catalytic performance.

References

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