

Catalytic conversion of glycerol to solketal under mild and solvent-free conditions

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Introduction

Activated carbons prepared from agricultural waste (olive stones) were modified to introduce acid sites on the surface by treatment with HNO₃ or H₂SO₄. These acid-functionalized materials were studied as heterogeneous catalysts for the solvent-free acetalisation of acetone with glycerol to produce 2,2-dimethyl-1,3-dioxolane-4-methanol (solketal). This five-membered ring ketal presents an interesting range of potential applications as solvent, low-temperature heat-transfer fluid, surfactant and fuel additive (1).

Materials and Methods

Activated carbon (AC) was prepared by chemical activation of olive stone wastes from Rio Grande do Sul, Brazil. The olive stones were impregnated with a 73% aqueous solution of H₃PO₄ (v/v) at 357 K for 4 h. The activation was carried out under nitrogen at 723 K for 2 h. Then, the activating agent (H₃PO₄) was removed by washing with hot distilled water. The activated carbon was treated with HNO₃, either 6 M (AC-N-6M) or 15 M (AC-N-15M), and aqueous H₂SO₄, either 6 M (AC-S-6M) or 18 M (AC-S-18M). Acetalisation reactions of glycerol with acetone were performed in a high throughput reaction platform, equipped with a heating and stirring unit. In a typical catalytic test, 0.01 mol of glycerol (99%), 0.04 mol of acetone, and 0.0015 mol of 1,3-dioxane, as GC internal standard, were weighed in a 10 mL glass vial containing 25 mg of catalyst. The mixture was stirred at 800 rpm for 6 h in a capped vial at room temperature. The reaction products were analysed by gas chromatography.

Results and Discussion

Characterization data are given in **Table 1** for each catalyst.

Table 1. Textural properties and acidity of the parent and acid-treated activated carbons.

	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	Total acid sites (mmol g ⁻¹)	Stronger acid sites (mmol g ⁻¹)
AC-untreated	1550	0.94	0.55	0.60	0.17
AC-N-6M	1290	0.73	0.47	1.30	0.62
AC-N-15M	1240	0.64	0.44	6.52	1.0
AC-S-6M	1550	0.94	0.55	0.72	0.48
AC-S-18M	1495	0.83	0.53	1.88	0.90

Acid-functionalised activated carbons display extremely high specific surface area (1240 to 1550 m² g⁻¹) and a relevant population of surface acid sites of different strength. The

catalytic behaviour of the four acid-treated activated carbons was investigated further by performing a kinetic study of the acetalisation of acetone with glycerol at room temperature with a glycerol to acetone molar ratio of 1:4 and a catalyst loading of 2.7 wt% (Figure 1). With all tested catalysts, the conversion of glycerol tends to reach a plateau after 4 h of reaction. In line with the catalytic trends discussed above, AC-S-18M was remarkably more active than the other catalysts in the first 30 min of reaction, reaching a glycerol conversion of 36% that corresponds to a high turnover frequency (TOF = 153 h⁻¹, if calculated as mol of glycerol converted per mol of acid sites of the catalyst per hour; and TOF = 320 h⁻¹, if calculated as mol of glycerol converted per mol of stronger acid sites of the catalyst per hour). The heterogeneous nature of acid-treated activated carbon catalysts was investigated by means of leaching tests performed by removing the catalyst from the reaction mixture after 30 min by filtration at the reaction temperature, and by allowing the liquid phase to react for further 5 h 30 min under the same experimental conditions (2). In all cases, no or negligible increase in the glycerol conversion was observed after removal of the catalyst (Figure 1), indicating that the active species present on the activated carbons surface did not leach during the acetalisation reaction and thus proving the truly heterogeneous nature of these catalysts.

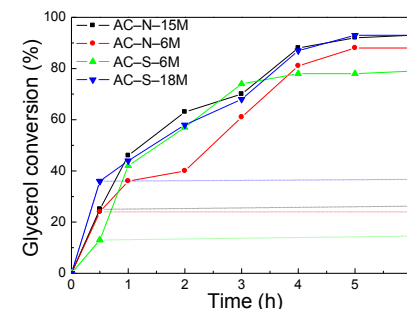


Figure 1. Kinetic study (solid lines) and leaching test (dashed lines) for the acetalisation of acetone with glycerol catalysed by acid-treated activated carbons.

Significance

The material prepared by treatment with H₂SO₄ 18 M displayed the best catalytic performance, achieving 97 % conversion of glycerol with high selectivity towards solketal under mild and environmental friendly conditions (solvent-free reaction at room temperature) and with a low catalyst loading compared to that used for state-of-the-art heterogeneous catalysts for this reaction. The excellent catalytic performance of this catalyst is attributed to its population of carboxylic and sulphonic acid sites, and to its lower hydrophilicity compared to the HNO₃-treated activated carbons.

References

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