Unveiling the deactivation process of Amberlyst-15 in the etherification reaction of glycerol with ethanol

Mario SAMPERI[1], Giuseppe BONURA[1], Mariarita SANTORO[1], Serena TODARO[1], Alessandro CAJUMI[2],
Mauro FAILLA[1], Francesco ARENA[2], Catia CANNILLA[1]
[1]Institute of Advanced Technology for Energy CNR-ITAE, S. Lucia sopra Contesse 5, 98126 Messina, Italy.
Institution, Dept., address, city, country.
[2]University of Messina, Dept. of Engineering, c.da Papardo, 98166 Messina, Italy.
**mario.samperi@itae.cnr.it*

Significance and Relevance

This work discloses the operating limits and the critical aspects associated with the use of Amberlyst-15 as heterogeneous catalyst for the etherification of glycerol with ethanol to oxygenated additives for biodiesel. Although this strongly acidic resin is widely recognized in the literature as an effective catalyst for this reaction, its lifetime and stability has been generally overlooked. Our findings demonstrate that although elevated temperatures (≅200°C) enhance conversion and yield to *poly*-ethers, A significant deactivation occurs after the first catalytic run. An in-depth physicochemical characterization of the used catalyst provides valuable insights into the deactivation process.

Fundamental advances in understanding catalysis
Oral preferred or Short Oral

Introduction and Motivations

Biofuels are increasingly recognized as an important renewable energy source, particularly for their potential in reducing greenhouse gas emissions and dependence on fossil fuels. The valorization of glycerol, the main by-product of biodiesel production, has emerged as a significant area of research to enhance biofuel quality, efficiency and environmental sustainability[1]. One promising approach is the etherification reaction, through which glycerol can be converted into oxygenated poly-substituted ethers. These compounds improve combustion properties, enhance fuel stability, lower viscosity, and facilitate blending with petroleum diesel. The glycerol etherification reaction involves the use of various *O*-alkylating agents, such as alkenes or alcohols, in the presence of solid catalysts like sulfonic resins or acidic zeolites[2]. The choice of catalysts and reactants significantly affects the efficiency, selectivity, and yield of glycerol ethers, as well as the overall cost of large-scale production[3]. This study explores the etherification of glycerol using ethanol, a widely available and cost-effective alcohol, to promote sustainability in biofuel production. However, the use of primary alcohols presents a notable challenge due to the more stringent reaction conditions required for their activation.

Materials and Methods

The etherification of glycerol with ethanol was carried out in a stainless-steel batch reactor under autogenous pressure in inert atmosphere. The products and catalyst were easily separated by filtration and then analyzed. The etherification reaction was carried out within a temperature range of 140–220 °C, varying the reaction time (R_t) from 1 to 24 hours, the ethanol-glycerol molar ratio ($R_{EtOH/Gly}$) ranging from 4:1 to 15:1, and the catalyst amount between 3 and 30 wt.% with respect to glycerol. The reaction mixture was analyzed offline by gas chromatography (GC), while compounds identification was carried out by GC–Mass analysis. A detailed catalyst characterization of both fresh and spent catalysts was performed by hyphenated thermogravimetric analysis-mass spectroscopy (TGA-MS). Finally, X-ray photoelectron spectroscopy (XPS) was employed for additional structural investigation.

Results and Discussion

Glycerol conversion, selectivity and yield of *di*- and *tri*-ethers (DEGs and TEG) are strongly dependent on temperature and reaction time. At low temperatures, glycerol conversion (χ_{Gly}) varies significantly with the reaction time, while selectivity and yield of DEGs/TEG values result to be similar.

On the other hand, irrespective of the reaction time, high temperatures have a minor influence on glycerol conversion, whereas selectivity and yield are significantly affected. The most relevant results were obtained at 220°C after 24h, with a glycerol conversion of 88.7% and DEGs/TEG yield of 46.8%. However, these experimental conditions deeply affect the catalyst stability. The activity is quite low at 140°C (χ_{Gly}=12.3%), but the catalyst remains stable over five catalytic runs, whereas at 180°C, the remarkable activity recorded after the first run (χ_{Gly}=56.9%) is followed by an abrupt catalyst deactivation. TGA/MS analyses carried out on both fresh and used catalyst were useful to obtain important information on the structure of Amberlyst-15 and to define the main reasons behind the loss of catalytic activity. Specifically, the thermal stability of the fresh catalyst at 180°C indicates that the reason behind its deactivation after the reaction is to be found on the chemical modification of the active sites. TGA/MS measurements allowed observing the presence of both physisorbed and chemisorbed products on the catalyst surface, whose formation is driven by temperature (Figure 1A). This evidence has been confirmed by XPS measurements (Figure 1B), which highlight a complex *sulfur* structure consisting of sulfonic and sulfynil groups, together with disulfide bonds on the backbone of the polymeric structure. On the whole, the characterizations on used catalysts suggest the occurrence of a covalent bond involving sulfonic groups and the reaction products, which represents the main path of deactivation.

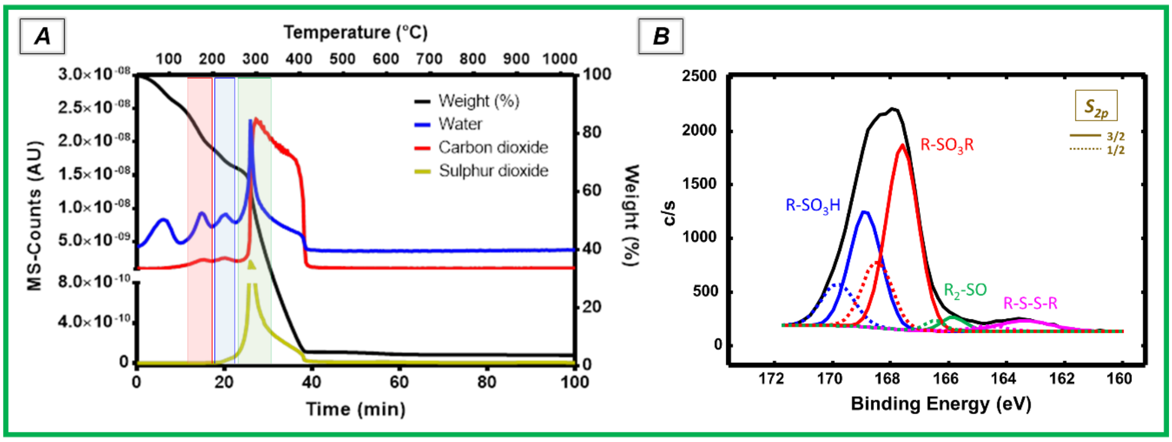

Figure 1 (A) TGA/MS of used Amberlyst-15 at 160°C (1 run). XPS spectrum S_{2p} of Amberlyst-15 used at 180°C (1 run). (B) Experimental conditions: $R_{EtOH/Gly}$=9 mol/mol, R_t=6h, Amberlyst-15=10%wt to glycerol.

References

1. N. Yadav, G. Yadav, M. Ahmaruzzaman, *Industrial Crops and Products* **2024**, *210*, 117999.
2. C. Cannilla, G. Bonura, S. Maisano, L. Frusteri, M. Migliori, G. Giordano, S. Todaro, F. Frusteri, *Journal of Energy Chemistry* **2020**, *48*, 136-144.
3. C. Cannilla, G. Giacoppo, L. Frusteri, S. Todaro, G. Bonura, F. Frusteri, *Journal of Industrial and Engineering Chemistry* **2021**, *98*, 413-424.

Acknowledgements

This research was funded by the EU – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA, the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.4 - Call for tender No. 3138 of December 16, 2021 of Italian Ministry of University and Research funded by the European Union – NextGeneration EU (CN-MOST-SP14).