Microwave-assisted synthesis of SAPOs to be used as catalysts for glycerine revalorization

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1. Introduction – The catalytic acetalization of glycerol with furfural is becoming an attractive process for the production of dioxolane and dioxane, which can be used as fuel additives revalorizing glycerine. The use of microwaves for the synthesis or modification of catalysts considerably decreased the preparation times, with the subsequent energy saving. The aim of this work was to study the effect of using microwaves vs conventional heating for the preparation and acid-functionalization of SAPO-5 and SAPO-34 catalysts on the acetalization of glycerol with furfural**.**

2. Experimental – SAPO-5 and SAPO-34 were prepared following the method reported elsewhere [1] in conventional autoclave at 180 ºC for 24 h and 48 h, respectively, and at 180ºC for 2 h and 6 h, respectively, using microwaves (SAPO-5-Mw and SAPO-34-Mw). SAPO-5 and SAPO-34 were acid-functionalized with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane solution using conventional heating at 120 ºC for 6 h (SAPO-5-SC and SAPO-34-SC) and microwaves at 120ºC for 2 h (SAPO-5-SMw and SAPO-34-SMw). Catalysts were characterized by different techniques. The catalytic reaction was carried out in a batch reactor with glycerol: furfural ratio 1:1, 40ºC, 2 h, and 5 wt % of catalyst.

3. Results and Discussion – X-Ray Diffraction of the catalysts confirmed the presence of the corresponding pure crystalline phases. SAPOs synthesized with microwaves were achieved in significant less time than those synthesized by conventional heating. N_2 physisorption showed the micropore structure of the catalysts. The incorporation of sulfonic groups was higher for the SAPOs sulfonated by conventional heating, as confirmed by titration, probably due to the higher time used for sulfonation. Higher conversion was observed for sulfonated catalysts due to the presence of the sulfonic groups (Figure 1). The differences between catalysts in the selectivity to the products of interest were low.

Figure 1. Catalytic activity results. Green column: Conversion; Orange column: Selectivity to dioxolane; Blue column: selectivity to dioxane.

4. Conclusions – The use of microwaves allowed us to decrease the synthesis time for both SAPOs. All catalysts showed moderate conversion and high selectivity to the products of interest.

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6. References

[1] S. H. Newland, W. Sinkler, T. Mezza, S. R. Bare, M. Carravetta, I. M. Haies, A. Levy, S. Keenan y R. Raja. *ACS Catal.*, **5** (2015), p. 6587.