Enhanced acidity properties of KIT6_Zr as solid catalyst for the dehydration of sorbitol to isosorbide

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The modification of mesoporous silicas by incorporating heteroatoms (Zr, Al, Ti, among others) and / or treatment with mineral acids are an attractive strategy in heterogeneous catalysis for the preparation of solid acid catalysts for a variety of processes of industrial interest [1]. In this context, the architecture of the pores and the concentration and strength of acid sites are important factors, directly related to the catalytic performance in the dehydration of sorbitol to isosorbide [2]

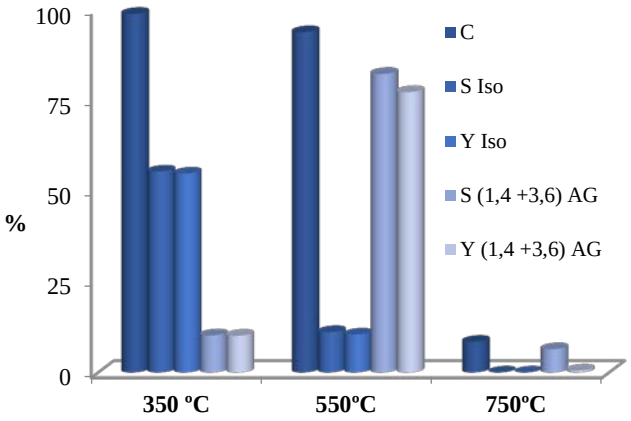

Figure 1. Catalytic performance of sulfated KIT-6 catalysts obtained by impregnation with zirconium sulphated and calcined at different temperatures, at 140ºC for 3 h, 10% sorbitol/catalyst.

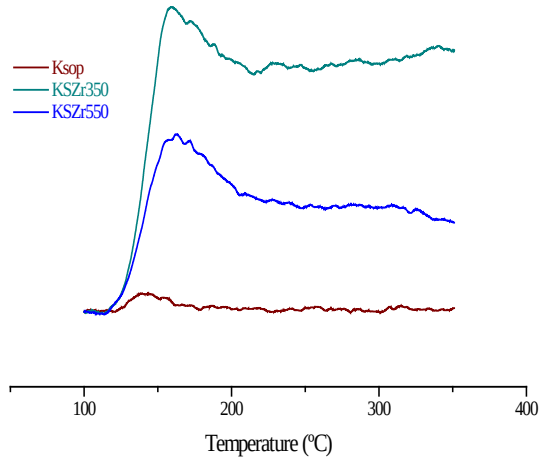

Figure 2. NH_3-TPD profiles of KIT_SZr calcined at different temperatures.

In order to modulate the surface acidity of a mesoporous KIT-6-type silica, the Si/Zr molar ratio has been varied using TEOS and iso-propoxide zirconium, as precursors. Besides, different sulfation treatments of the zirconium-doped KIT-6 catalyst were carried out: i) immersion in a concentrated sulfuric acid solution, under stirring, ii) impregnation at incipient volume with sulfuric acid and iii) impregnation of a KIT-6 silica with zirconium sulfate solution and varying the calcination temperature.

These catalysts were evaluated in the dehydration of sorbitol in a batch reactor, in molten medium, at different reaction times and temperatures. The zirconium sulfate-based catalyst calcined at 350ºC reaches an isosorbide yield of 55%, at only 140°C (Fig. 1), which can be explained by its higher concentration of acid sites (Fig. 2). Moreover, this catalyst possesses a high surface area and Brönsted acidity.

The physical-chemical characterization data and catalytic results demonstrate that the incorporation of zirconium reduces slightly the microporosity, although the presence of Brönsted acid sites allows attaining high selectivities to isosorbide. In addition, variations in textural properties are observed by modifying hydrolysis and aging times.

References

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[2] D. Yuan, N. Zhao, Y. Wang, K. Xuan, F. Li, Y. Pu, F. Wang, L. Li, F. Xiao, Appl Catal B-Environ., 240 (2019) 182–192.