Mixed WO_x/ZrO_2 materials as acid catalysts for benzaldehyde acetalization

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Tungstated zirconia materials are known by their acidic properties that are dependent on the type of synergism between both metal, the loading of the dopant species (W) and also by the calcination temperature that can lead to different crystalline phases[1]. The combination of these different properties is already explored in catalytic process of isomerization of alkanes, dehydration of alcohols and esterification of fatty acids[2]. Our research group have developed previously a series of zirconia solids containing different loadings of tungsten oxide (12, 15, 19 and 22 wt%) treated at 500, 600, 700 and 800 ºC with full characterization of chemical composition and acid properties[2]. They were employed as catalysts for esterification reaction and the highest activities were noticed to solids treated at 800 ºC and also for those that presented the greater Bronstd:Lewis acid site ratio. In this way, this series of catalysts was tested towards the benzaldehyde (Bz) acetalization with triethyl orthoformate (TEOF), a remarkable step on fine chemical manufacturing since aldehydes are reactive compounds and often need to be protected from some reaction media[3]. All the catalyst solids tested showed activity on this reaction (Fig. 1a) with a first order exponential-like profile, suggesting a first-order reaction mechanism. Acidity is also a key property for this reaction and it is straightly linked to the initial rate for each catalyst (Fig. 1b), showing that it is not necessary a great amount of tungsten on zirconia to achieve great conversion for the reaction. It makes the process more economic and also indicates that synergism can be the driving force on the application of this family of materials as acid catalysts on fine chemical processes.

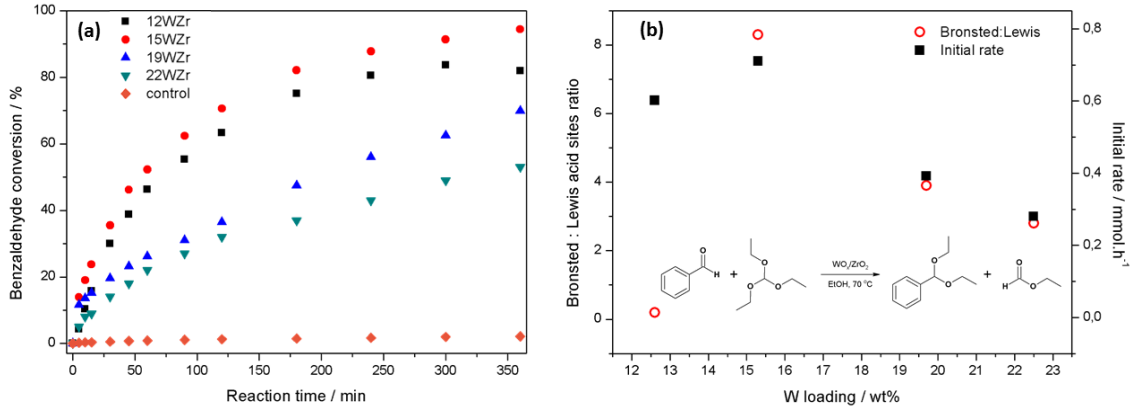

Fig 1. a) Reaction profiles for kinetic data from benzaldehyde conversion to diethyl acetal in function of time for catalysts with different loadings of tungsten species; b) correlation between initial rate and Bronsted:Lewis acidity and their dependence of tungsten loading. Inset shows the representation of acetalization of Bz with TEOF – Bz/TEOF molar ratio: 1:3, 10 wt% catalyst at 70 ºC in EtOH. Product quantification by GC and area normalization.

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The authors are thankful to financial support from CAPES, CNPq, UFPR and Fundação Araucária.