SYNERGIC EFFECT BETWEEN INORGANIC SALTS AND γ-Al_2O_3 FOR XYLOSE DEHYDRATION TO FURFURAL

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Introduction

Lignocellulosic biomass, with a high content of hemicellulose, is the main source of pentoses, from which biofuels and value-added chemicals can be produced. Amongst the latter, 2-Furfuraldehyde (furfural, FUR) is the only unsaturated organic compound prepared from carbohydrates, obtained by acid-catalyzed dehydration of xylose (XYL) [1]. Different acid solid catalysts have been studied as alternative to conventional mineral acids, which are employed in industry. Moreover, the addition of inorganic salts to improve furfural yield, especially in biphasic systems, has been previously reported in the literature [2]. In this work, the dehydration of XYL in a biphasic water:toluene system with a mesoporous γ-Al_2O_3 has been studied, and the effect of the presence of $CaCl_2$ or $MgCl_2$ in the reaction medium on the catalytic performance was evaluated.

Experimental

The catalytic dehydration was carried out under batch operations, by using a water:toluene biphasic system, in a glass reactor (Ace, 15 mL), with a thermostated bath and magnetic stirring, in the presence of γ-Al_2O_3 (Alfa-Aesar, 158 $m^2 \cdot g^{-1}$ y 478 µmol $NH_3 \cdot g^{-1}$) as catalyst. The experiments were carried out by mixing 50 mg of catalyst and 150 mg xylose in 1.5 ml of deionized water and 3.5 ml of toluene. The reaction products were analyzed by HPLC. Some preliminary results concerning the use of sugar liquors derived from the treatment of lignocellulosic biomass, as feedstock instead of commercial xylose, have been obtained.

Results and discussions.

The presence of $CaCl_2$ and the use of γ-Al_2O_3 in the reaction medium for xylose dehydration to furfural were studied and compared to the non-catalytic process, at 175 °C (Fig. 1A). In all cases, high conversion values were attained with respect to the non-catalytic process. γ-Al_2O_3 shows a high activity, with a XYL conversion of 96%, after 90 min of reaction, but the furfural yield was lower than expected due to alumina favored secondary reactions [3] (Fig. 1B). It has been previously demonstrated that alkaline earth cations, like Ca^{2+} interact with glucose molecules, accelerating considerably their dehydration, so it would be possible that they also exert a similar effect on the dehydration of xylose [4]. Thus, high furfural yields were achieved by using $CaCl_2$ even in absence of catalyst under these experimental conditions. However, considering that side reactions are favored at high temperatures, the catalytic process was studied with $CaCl_2$ and γ-Al_2O_3 at 150 °C (Fig. 2). At this lower temperature, a synergistic effect can be inferred between γ-Al_2O_3 and $CaCl_2$, reaching values of XYL conversion and FUR yield of 99% and 59%, respectively, after only 30 min of reaction.

Moreover, the effect of the addition of $CaCl_2$ and $MgCl_2$ was compared (Fig. 3), adding the same number of moles, corresponding to 0.65 and 0.39 $g_{salt} \cdot g_{aq.sol.}$, respectively. Although both salts improved the catalytic performance, $CaCl_2$ is more beneficial than $MgCl_2$. The reaction mechanism has been studied by ^{1}H NMR.

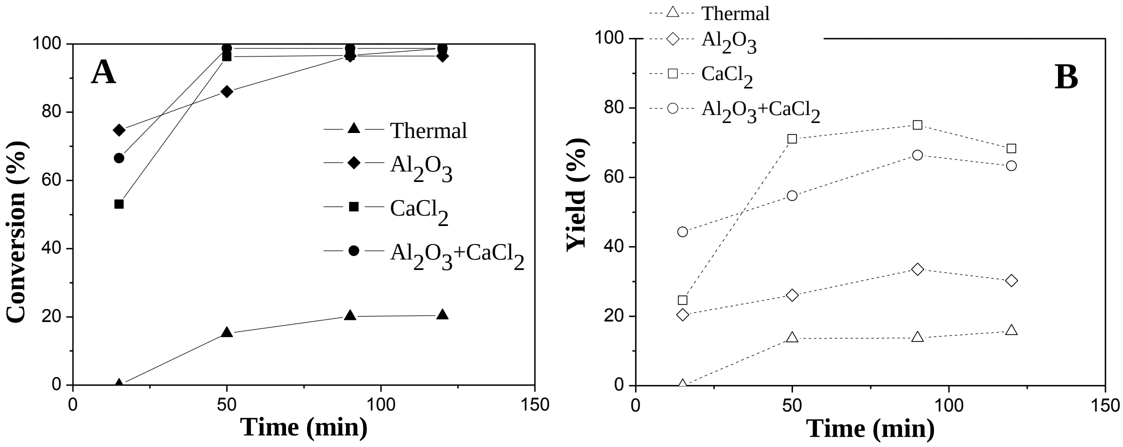

Figure 1. Xylose conversion (A) and furfural yield (B) as a function of reaction time in presence of γ-Al_2O_3 and/or $CaCl_2$ (175 °C and xylose:catalyst weight ratio = 3: 1).

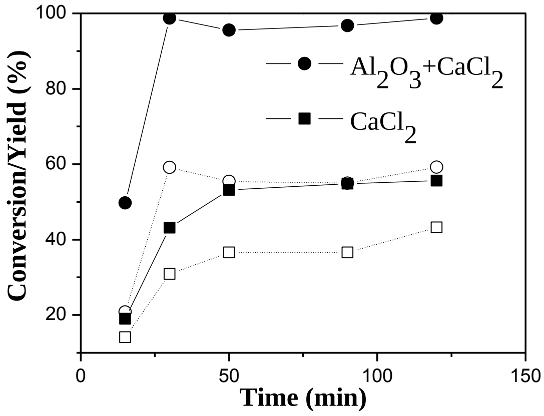

Figure 2. Evolution of XYL conversion (■, ●) and FUR yield (□, ○) with the time (150°C, xylose:catalyst weight ratio= 3:1).

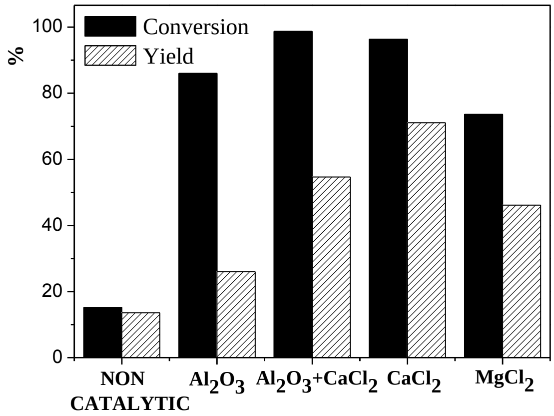

Figure 3. Influence of the addition of $CaCl_2$ and $MgCl_2$ to the reaction medium (175°C, 50 min and xylose: catalyst weight ratio= 3:1).

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