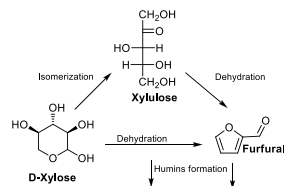


SiO₂Al₂O₃: an efficient, stable and reusable catalyst for furfural production from xylose

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Introduction

Worldwide agricultural activity produces high volume of waste, which become an interesting renewable resource for valuable chemicals production. Hemicellulose, amorphous polymer whose main component is D-xylose, corresponds to 25-40% w/w of agricultural waste. Furfural, which is intermediary in the production of valuable products such as furfuryl alcohol and furoic acid and its esters, can be obtained by triple dehydration of D-xylose. Currently, furfural is produced by treatment of rich in pentosans agricultural waste with sulfuric acid with a maximum yield of 50%. Toxic waste generation and corrosion are the main drawbacks of process using homogeneous catalysis. The replacement by an environmental friendly process using solid acids such as zeolites, γ -Al₂O₃, Zr-(W, Al) mixed oxides and resins, among others has been studied [1-3]. The dehydration of xylose to furfural is accompanied by undesirable side reactions like condensation or “resinification” of furfural that form humins (Scheme 1) besides xylose isomerization to xylulose and subsequent dehydration to furfural. In this work, we have analyzed the influence of operating conditions with the aim to optimize furfural production using SiO₂Al₂O₃ as catalyst. Moreover, further studies about stability of catalysts in reaction conditions are needed in order to develop a commercial process. Therefore, we have studied the stability of this catalyst by performing successive catalytic runs.



Scheme 1: Xylose dehydration

Materials and Methods

The catalyst employed in this work, SiO₂-Al₂O₃ (Grade 135 Sigma-Aldrich), was calcined in air flow before reaction. The Xylose dehydration was carried out in a high pressure stainless steel batch reactor. The reactor was loaded with 50 cm³ of solvents and 1 g of catalyst, purged with N₂ and heated to reaction temperature. In order to start the reaction, the reactant (1.5 g of xylose) was incorporated. Reactant and products were analyzed by HPLC (Shimadzu Prominence UFLC) with IR and UV-VIS coupled detectors and GC (Agilent 6850) equipped with FID detector.

Results and Discussion

In the biphasic system, toluene is used as extractor solvent to stabilize the furfural formed. In this sense, we have carried out additional experiment to analyze the furfural stability in both solvents. At 413 K, in absence of catalyst, 78% of furfural is converted to no detected products in water, 24% in a water-toluene mixture, while only 11% of furfural disappeared when toluene is used as solvent. The catalyst was tested on xylose dehydration using water and a mixture of toluene and water (50%-50%) at 413 K and 433 K. Main products

were xylulose, from xylose isomerization, and furfural. When the reaction was carried out in the biphasic system at 413 K, although the xylose conversion was 87%, the xylulose and furfural yields (η_{xylulose} and η_{furfural}) were only 10 and 26%, respectively. A large part of xylose (or products) was converted in non-detectable compounds, probably humins. At higher temperature, 433 K, maximum yield of furfural obtained was 76% corresponding at 99% of xylose conversion, indicating that the rate of dehydration is more affected by temperature than the humins formation what has been reported previously [4]. As expected, using water as solvent, the furfural yield was considerably lower, only 32%, indicating that the use of the second solvent is essential to avoid humins formation and thereby obtain high yield of furfural.

Table 1. Catalytic Results of Xylose dehydration on SiO₂Al₂O₃

Solvent	Temperature [K]	X _{xylose} [%]	η_{xylulose} [%]	η_{furfural} [%]
Water	433	97	1.4	32
Water-toluene (50-50%)	413	84	10	26
Water-toluene (50-50%)	433	99	1.8	76

In order to study the stability and reutilization of the catalyst, we have performed three consecutive runs, washing with water and treating in air flow the catalyst after the first and second reaction. Results in Figure 1 showed that almost same values of yields were reached for 1st and 2nd run, and slightly lower yield in the last run. Before the last run, the color of catalyst was darker indicating the presence of carbonaceous deposits that were not totally eliminated during the pre-treatment. In conclusion, we found the conditions and catalyst suitable for the selective synthesis of furfural from D-xylose, and we demonstrated that catalyst can be re-used.

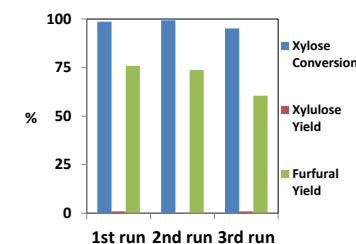


Figure 1: Xylose conversion and yields in consecutive runs. Conditions: water-toluene (50%-50%), T= 433 K, Catalyst: SiO₂-Al₂O₃

Significance

We reported here furfural yield of 76% on SiO₂-Al₂O₃ at 433 K and using water-toluene as solvent. This catalyst is stable and it can be re-used becoming an alternative to homogenous catalysts..

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