Xylose dehydration in furfural using a continuous fix-bed reactor: Insights on phosphate addition to niobic acid performances

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Introduction

The transformation of hemicellulosic feedstock into chemicals such as furfural is of high interest. The current process for furfural production uses H_2SO_4 as catalyst in a batch reactor and gives 30-35% yield in furfural from the hemicelluloses part of raw biomass^[1].

C6-C5 sugars dehydration in water, in a monophasic system, is known to be unselective. However, this reaction medium should be privileged for environmental and economical reasons. For that, the design of solid acid catalysts, active, selective and stable in water is essential. Niobium based materials are known to be efficient for the catalytic dehydration of xylose into furfural^[2]. This concerns mainly crystallized Nb₂O₅ or niobium phosphate, while only few studies deals with amorphous NbOH^[3]. The present work compares the performances of crystallized Nb₂O₅ to amorphous NbOH and phosphate modified Nb₂O₅. The objectives of present study is to bring new insights on the superficial sites of Nb catalysts involved in xylose dehydration in fufural and their dependence with the bulk properties, together with their potential modification by the water medium.

Fix bed reactor is privileged in this study to perform reaction at short contact time in order to limit the degradation of furfural into humins and to control the evolution of the catalyst properties with time on stream.

Materials and Methods

In preliminary catalytic tests carried out in continuous reactor at different WHSV and temperatures, we observed that hot water itself enhances the xylose dehydration reaction, evolving as homogenous reactive media. In order to solely observe the impact of the acid solid, experimental conditions have been settled properly. Thus, using high input flow (0,6cc/min) for the sugar aqueous solution and mild temperature (150°C), furfural is not formed in pure water in absence of a solid catalyst placed into the reactor (as shown in **Figure 2**), and xylose conversion is limited to 9%.

 Nb_2O_5 is obtained from NbOH calcinated at 600°C for 2h. Nb oxide modified with phosphate is synthesized by anionic exchange between phosphoric acid with NbOH, the exchange levels were set to 25%, 50%, 75%, 100% and excess. Then, exchanged solids were calcined at 600°C for 6h. The acidic properties were measured by calorimetry of NH₃ adsorption and IR of pyridine adsorption.

Results and Discussion

Figure 1. a) XRD patterns and b) Calorimetry – NH₃ adsorption



We can clearly observe that NbOH calcined at 600°C is crystallized in Nb₂O₅ phase while NbOH is totally amorphous. On the Nb-P samples, the formation of crystallized Nb₂O₅ phase is progressively inhibited with the extent of the phosphate exchange. The presence of phosphate has also a positive effect on the BET surface: the NbP catalysts exhibit S(BET) between 50-76m²,g⁻¹ while Nb₂O₅ present only 11 m²,g⁻¹. The calorimetric curves in **Figure 1** show that all the samples have few sites with very high acid strength (Qdiff >200kJ). NbOH presents a significant higher amount of acids sites compared to Nb₂O₅, and Nb-P has intermediate acidity. IR of Pyridine adsorption gives evidence that phosphates have suppressed the Brønsted acidity of NbOH. All these catalysts have been evaluated in continuous reactor for the dehydration of xylose into furfural in conditions where the homogenous contribution of hot water is limited. Results giving xylose conversion (wt%) and furfural yield (mol%) are presented in Figure 2.



Figure 2. Xylose conversion (wt %) and Furfural yield (mol %): (a) NbOH, (b) Nb-P-50%, (c) Nb-P-75%, (d) Nb₂O₅, (e) none. Conditions: Continuous flow reactor, 0.6cc/min, 1wt% xylose, 1g catalyst, 150°C.

NbOH exhibits a significant higher activity compared to Nb₂O₅, probably accounting to its higher superficial acidity. Both solids are quite stable with TOS, and XRD pattern of used Nb₂O₅ does not show the formation of NbOH at the expense of Nb₂O₅. Phosphate entities lead to less active solids than NbOH but improve furfural selectivities: 32% on NbOH against 40% over NbP samples. Note that as regards to Nb₂O₅, improved activities are obtained with phosphate insertion, this might explain controversial results from the literature. Based on solids characterizations, this is tentatively explained by a "passivation" effect of phosphates which have suppress Brønsted sites of NbOH, probably involved in humins formation, combined to their positive impact on the textural features.

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