

Hydrogenation of furfural over supported Pd catalysts

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Introduction

Modern society demands the development of integrated and energy-efficient processes for the sustainable production of chemicals and fuels. This objective has been prompted by the depletion of fossil fuels and increasing pollution of environment. Lignocellulosic biomass is the most abundant and economical non-fossil carbon source. Furthermore, it is not competitive with the food chain, coming from lignocellulosic wastes including agricultural and food processing, local urban solid and forestry wastes. However, these are made up of complex carbohydrates (mainly, cellulose and hemicellulose), which require to be broken down in their respective monomers. The hemicellulose is mainly composed of pentosans, which, after an initial hydrolysis step, are dehydrated to furfural.

Furfural is an important chemical with an annual production of 280,000 Tm,¹ which is considered as a platform molecule of great interest, since it has a wide range of applications, being considered the main chemical, aside from bioethanol, obtained from the sugar platform for the synthesis of chemicals, for plastics, agrochemical and pharmaceutical industries.^{2,3} Furthermore, furfural is considered as one of the most important building block molecule due to its versatility for the synthesis of a variety of chemicals, such as linear alkanes, furoic acid, furan, 2-methylfuran, and mainly furfuryl alcohol, among others.⁴

In the present work, the hydrogenation of furfural in gas phase has been studied by using Pd as active phase, and different metal oxides as support, in order to elucidate the influence of the support on the catalytic performance.

Experimental

Supported Pd-based catalysts (1 wt%) were prepared by wetness impregnation methodology of some selected oxidic supports. The supports were synthesized by the precipitation method, using a 0.3 M aqueous solution of metal precursor and a 0.3 M NaOH_{aq} solution, which was dropwise to rise the pH of the solution to 10-11. The resulting precipitates were aged under continuous stirring at 323 K for 4 h. After cooling, they were filtrated and dried for 3 h at 353 K, followed by calcination at 723 K for 2 h. For the sake of comparison, analogous commercial supports have been also employed.

The vapour-phase hydrogenation of furfural was performed in a tubular quartz reactor with a diameter of 6.35 mm ($\frac{1}{4}$ "). The pelletized catalyst (325-400 μ m) was plugged between two layers of glass beads and quartz wool and the temperature was controlled by a thermocouple in direct contact with the catalyst bed. The temperature of reaction was 463 K, and a H₂ flow of 10 ml min⁻¹ was set. When this temperature was reached, a flow of 3.87 ml h⁻¹ of a furfural solution in cyclopentylmethyl ether (CPME) (2.5 vol.%) was continuously injected using a HPLC pump. The reaction products were analysed by gas chromatography equipped with a Flame Ionization Detector and a CP-Wax 52 CB capillary column.

Results and Discussion

Furfural can be converted into chemicals with important applications in many different industrial fields (Fig. 1). Thus, reduction of furfural can proceed through different pathways depending on the experimental conditions, where the nature of the catalysts plays a key role. In the case of Pd-based catalysts, the main products come from the decarbonylation of furfural.

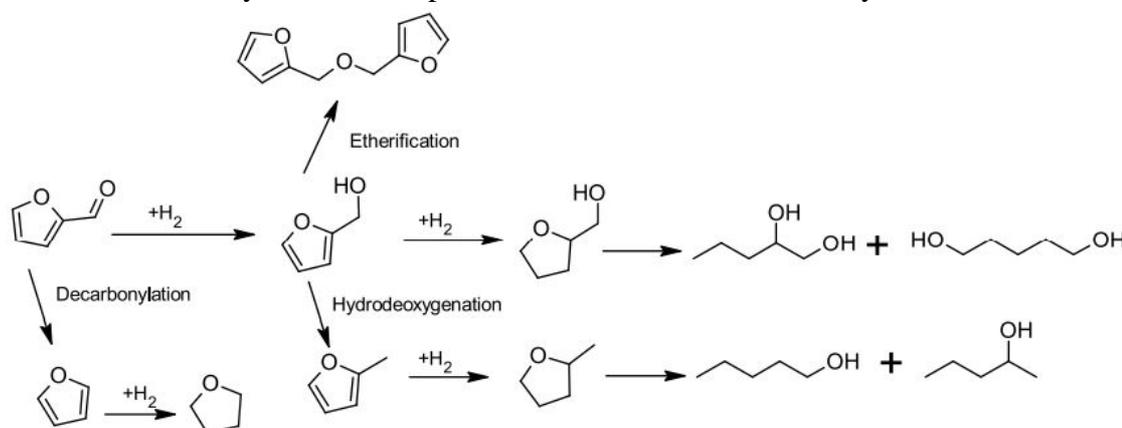


Figure 1. Reaction mechanism of furfural hydrogenation

The catalytic results reveals that the nature of the support exerts an important influence on furfural conversion and yield (Figs. 2 and 3). The highest conversion (92% after 5 h of TOS at 463 K) was attained with a Pd-SiO₂ catalyst, with a furan yield close to 70 mol%. This catalyst is more selective than the others to furan and it is only observed a moderate deactivation after 5 h reaction. The catalytic performance demonstrates that decarbonylation reaction was the main pathway, although the formation of furfuryl alcohol and 2-methylfuran also suggests that the hydrogenation of the carbonyl group of furfural takes place.

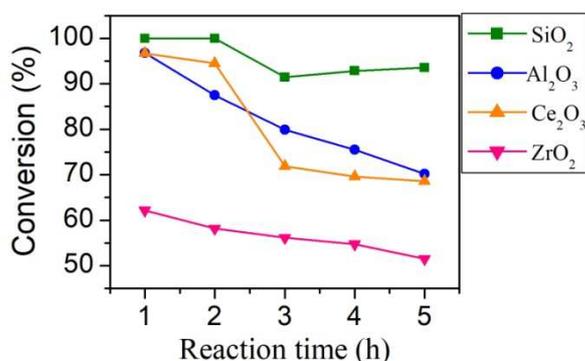


Figure 2. Evolution of furfural conversion with TOS at 463 K

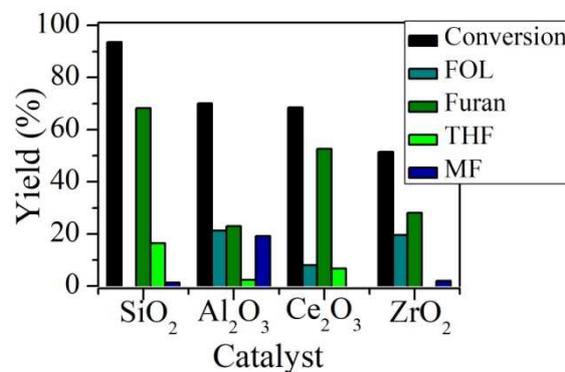


Figure 3. Conversion and yield values at 463 K

Acknowledgements

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