Synthesis and characterization of bimetallic catalysts Pd-Ru and Pt-Ru supported on γ-alumina and zeolite FAU for the catalytic transformation of HMF

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Introduction

According to the global network of renewable energy policies for the 21st century (REN21), by 2016 fossil fuels such as natural gas, coal and oil dominate approximately 80% of the world's primary energy consumption [1], fact that generates great worries motivated by the diminution of the reserves of fossil resources and the increase of its price, as well as the in-creasing considerations on the environmental contamination and the global warming. Fuels derived from biomass are emerging as a widely attractive alternative energy [2]. The catalytic conversion of biomass rich in hexoses gives rise to a bioproduct of crucial interest in the field of biofuels: 5-hydroxymethylfurfural (HMF), which is particularly attractive because it can be transformed into many promising chemicals in the area of biofuels, such as 2,5-dimethylfuran (2,5-DMF) or 2,5-dimethyltetrahydrofuran (2,5-DMTHF). Additionally, the HMF is not only a platform for obtaining biofuels, it is also a compound from which high added-value furan derivatives can be obtained, such as 2,5-DFF, which has a wide application in the pharmaceutical and insecticide industry [3]. 5-Acetoxymethyl-2-furaldehyde (5-A-2-F) is another value-added compound that can be obtained from HMF, it is used as a flavoring in the food industry, particularly to modulate the sweet taste of some beverages [4].

Materials and Methods

Bimetallic catalysts Pd-Ru and Pt-Ru with low metal content (0.5%), supported on commercial gamma alumina and synthetized FAU zeolite, were prepared and characterized for the catalytic transformation of HMF in valuable furan derivatives. The reactions were carried out at 70 ºC and 24 hours in a batch reactor, with HMF in THF, formic acid as hydrogen donor and HCl as co-catalyst. The determination of the products was made by GC-MS, using an HP-5 column.

Results and Discussion

Table 1 shows the catalytic activity of the bimetallic and monometallic catalysts. Bimetallic catalysts supported on zeolite FAU are more active in the catalytic transformation of HMF than alumina catalysts. This behavior may correspond to the high quantity of acid sites of the zeolites compared with other materials like γ-Al_2O_3 [5]. However, for both supports the combination of Pd-Ru metals was much more selective for the formation of biofuels or added-value products such as 5-MF, 2,5-DMF and 2,5-DFF than the Pt-Ru combination. It is also important to highlight the lower production of chlorinated byproducts such as 1,4-dichlorobutane and 1-chloro-1-butene, when the Pd-Ru combination is used rather than Pt-Ru. This enhanced selectivity for added-value furan compounds may suggest a better synergy of the Pd and Ru metals, attributable to the fact that the two separately have good capacity for the formation of biofuels of interest. All bimetallic catalysts produce a significant amount of an interesting furan derivative such as 5-A-2-F.

Table 1. Catalytic activity of bimetallic and monometallic catalysts

Catalyst	HMF Conversion (%)	Selectivity (%)					
		5-MF	2,5-DMF	2,5-DFF	5-A-2-F	1,4-dichlorobutane	1-chloro-1-butene
Pd-Ru/γ-Al_2O_3	18.51	3.76	0.0035	2.31	50.98	5.50	11.87
Pt-Ru/γ-Al_2O_3	45.07	0.13	-	2.32	59.04	2.65	16.44
Pd-Ru/FAU	61.72	0.14	0.0036	1.13	41.59	7.31	0.85
Pt-Ru/FAU	89.75	0.08	-	-	61.85	9.24	18.26
Ru/γ-Al_2O_3	25.72	0.22	0.0036	4.53	6.97	0.72	2.78
Pd/γ-Al_2O_3	39.23	0.85	0.0025	1.22	24.20	7.80	23.54
Pt/γ-Al_2O_3	4.60	2.85	-	1.23	9.94	3.55	5.14

HMF: 5-hydroxymethylfurfural; 5-MF: 5-methyl furfural; 2,5-DMF: 2,5-dimethylfuran; 2,5-DFF: 2,5-diformylfuran; 5-A-2-F: 5-Acetoxymethyl-2-furaldehyde

Significance

A variety of added-value furan derivatives can be obtained form HMF under mild reaction conditions, using bimetallic Pd-Ru and Pt-Ru catalysts.

References

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