

Base-free oxidation of 5-Hydroxymethylfurfural catalyzed by a titanossilicate-encapsulated AuPd catalyst

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Abstract

The use of metal nanoparticles in the selective oxidation of 5-hydroxymethylfurfural (HMF), a derivative from fructose possesses great applicability in fine chemistry industry with an unexploited potential. A novel bimetallic AuPd catalyst was synthesized, wherein the AuPd nanoparticles were encapsulated in titanossilicate matrix. The catalyst was applied for the aerobic oxidation of HMF in water in the absence of any base.

Introdução

Due to environmental and economic issues, more sustainable alternatives to petroleum have been studied.^{1,2} The current utilization of renewable biomass - carbohydrates in general, and sugars in particular, as feedstock for the chemical industry is modest when considering their ready availability at low cost and the huge as yet unexploited potential. HMF has emerged as a key precursor for the synthesis of derivatives with application in pharmaceutical and polymer industries.^{1,2}

The use of metal nanoparticles offers excellent chance for the development of viable industrial processes for conversion of renewable biomass into bio-based chemicals. Gold catalysis has attracted much attention in recent years, mainly due to its high selectivity and better resistance to water and O₂. The alloying of another metal (e.g., Pd and Pt) with Au to form bimetallic alloy catalysts may combine the advantages (functions) of different components in the atomic level and may enhance the activity and stability for the aerobic oxidation of organic compounds in water.^{1,2}

We have prepared a bimetallic AuPd catalyst, wherein AuPd nanoparticles were encapsulated in a titanossilicate matrix. The catalyst was applied for the aerobic oxidation of HMF in water in the absence of any base.

Resultados e Discussão

The catalyst was characterized (Figure 1 and Table 1). FDCA is a promising renewable alternative to petroleum-derived terephthalic acid. Typically, a base is required as promoter to produce 2,5-furandicarboxylic acid (FDCA). The aerobic oxidation of HMF to FDCA requires several tandem oxidation steps. Another serious problem is the requirement of an excess amount of a base additive such as NaOH.

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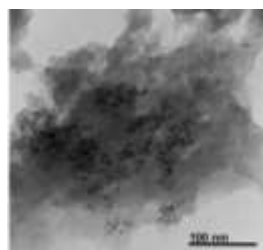


Table 1. Caracterization of titanossilicate-encapsulated AuPd catalyst.

Pd (%)	Au (%)	Size (nm)
1.4	2.3	4.1

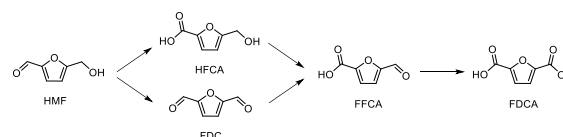
Figura 1. TEM micrograph.

However, the base-free oxidation can be performed taking into account the basicity of the support.

The results performed under base-free conditions (Table 2) show positive effect of the increase of pressure and reaction time over conversion and selectivity for FDCA. with up to 50% conversion.

During the initial times, the concentration of FDC is high, but decreases within 24h forming FFCA. This is an indicative of the reaction pathway through FDC. This agrees with the literature which suggests that under base-free condition, FFCA is formed from FDC, while under basic conditions HFCA is the intermediate.¹

Tabela 1. Aqueous oxidation of HMF.



P (bar)	t (h)	Conv. (%)	Selectivity			
			HFCA	FDC	FFCA	FDCA
6	2	9	19	54	25	2
4	2	9	21	43	34	2
1	2	6	20	46	33	1
6	24	50	12	15	56	17
4	24	45	15	18	56	11
1	24	39	15	19	55	11

^aReaction conditions: 5 mg cat, substrate:catalyst = 18, T = 90 °C.

Conclusões

A novel bimetallic TiSiNH₂-AuPd catalyst was synthesized and successfully applied for the aerobic oxidation of HMF in water in the absence of any base. The increase of pressure and reaction time boosted the conversion to 50%.

Agradecimentos

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