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On the process for furfural and HMF oxidative esterification over Au/ZrO_2

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ABSTRACT

The process for the oxidative esterification of furfural and HMF on Au/ZrO_2 catalyst has been deeply investigated. Many variables, such as reaction time, temperature, pressure, and nature of the oxidant, have been optimised. For both processes, a considerable effect of the reaction temperature has been evidenced in the range here investigated (60–140 °C). As regards furfural, oxygen pressure can be lowered from 6 to 1 bar without significant changes in the catalytic performances. Molecular oxygen can be replaced by the more economic air, still at very low relative pressure (0.5 bar). In the case of HMF, oxygen pressure can be lowered from 6 to 1 bar without significant changes in the catalytic performances. Data on the reaction mechanism have been also verified by FTIR spectroscopy measurements taken in opportune experimental conditions in order to mimic reaction conditions.

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1. Introduction

Bio-renewable fuels and chemicals are becoming increasingly important as we continue to deplete our finite petroleum resources. A great effort is being expended in industry and academia to develop processes to produce chemical intermediates from bio-based sources that can replace petrochemicals in existing products [1].

Currently, there is an intensive research on the use of lignocellulosic raw material as a biomass source for producing chemicals and fuels. Plant biomass consists mainly of carbohydrates, lignin, protein and fats. Out of an estimated 170 billion metric tons of biomass produced every year, roughly 75% are in the form of carbohydrates which makes biomass carbohydrates the most abundant renewable resource [2]. This makes carbohydrates the centre of attention when looking for new and greener feed stocks to replace petroleum for producing commodity. It is therefore important to continue to develop processes that can economically convert lignocelluloses into chemicals. 2-Furaldehyde (furfural) is a C5 compound and it is industrially manufactured for a long time through hydrolysis of pentose which comes from agricultural raw materials (see upper part of Scheme 1).

Actually furfural has many different uses, but additional transformations are highly desired [3]. Furfural can be transformed in alkyl furoates, which find applications as flavour and fragrance components in the fine chemical industry.

On the other hand, 5-hydroxymethyl furfural (HMF) is considered an important and renewable platform chemical in the bio-based renaissance as a dehydration product of hexoses. HMF plays an important role, because it can be obtained not only from fructose, sucrose and inulin but also, more recently, from glucose *via* isomerisation to fructose, as well as directly from cellulose [4]. HMF is an important versatile intermediate that can be further transformed into a wide variety of high performance and high value-added chemicals [5]. In particular, HMF can be oxidised to 2,5-furandicarboxylic acid (FDCA), that is a monomer for the synthesis of polymers alternative to those obtained from terephthalic acid. For instance, polyethylene terephthalate (PET) is a polymer commonly made into fibres, resins, films, etc., and it is one of the highest tonnage and fastest growing plastic materials [6]. Actually, PET is mainly manufactured by the purified terephthalic acid whose process, jointly developed by Scientific Design and Amoco [7,8], is based on the liquid-phase oxidation of p-xylene. However, the harmful effects of bioaccumulation in living organisms of both phthalates and derived polymers have been known for a long time. Besides being obtained from a bio-derived, renewable raw material, the polymer got from FDCA (PEF), is more easily degradable

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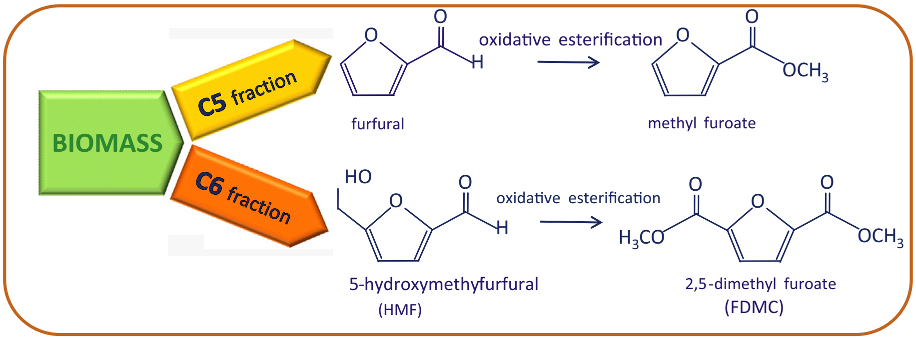

Scheme 1.

and above all, it does not present problems of bioaccumulation. A study commissioned by the U.S. Department of Energy identified FDCA as one of the 12 potentially useful building blocks for value-added chemicals from biomass [9]. Unfortunately, FDCA is practically insoluble in most of the solvents industrially used. HMF can be transformed by oxidative esterification into the corresponding furan-2,5-dimethylcarboxylate (FDMC) as reported in Scheme 1, lower part. The latter molecule is easily purified by low-temperature sublimation to give high purity FDMC, which is readily soluble in the most common solvents and therefore it could be even more suitable than FDCA as monomer for the replacement of terephthalic acid in plastics [10,11].

PEF has some better physical properties than PET, such as higher gas impermeability (10 times compared to oxygen, 4 times compared to carbon dioxide and 2 times compared to water) and higher glass transition temperature (for the PEF = 86 °C while for the PET = 74 °C). Finally, PEF production could be made in the same facilities used for PET [12]. As a demonstration of the importance of this polymer, the “Coca Cola” company has recently signed a trade agreement with “Avantium” for the development and production on industrial scale of this polymer in order to replace PET bottles with PEF bottles [12].

Christensen et al. [10] have firstly demonstrated that good yields in the oxidative esterification of furfural and HMF can be obtained with a commercial Au/TiO_2 catalyst provided by the World Gold Council in the presence of a base (8% CH_3ONa). However, the use of the base makes the process less green and less advantageous from an economic point of view [11]. Subsequently, Corma et al. [11] tested these reactions over gold-based catalysts on different supports, but without using the base. However, only one catalyst dispersed on ceria nanoparticles showed satisfactory performances for HMF oxidative esterification, while Au/C, Au/CeO_2, Au/TiO_2, Au/Fe_2O_3 samples require reaction times ranging from 24 to 72 h to get still very low yields. Very recently, we investigated gold catalysts supported on zirconia [13,14], ceria and titania [15] for a base-free esterification of furfural. In particular, we identified the physico-chemical properties that render gold supported on zirconia an active, selective and recyclable catalyst [14,15].

In the last years, some reviews [16–18] have been published on the selective oxidation of furan derivates meaning that a great attention has been paid to these reactions. From literature studies, it is possible to affirm that the choice of gold nanoparticles is advantageous for the oxidative esterification reactions. However, it would be advantageous to optimise the operating conditions in order to make the process environmentally friendly and industrially feasible. Basing on these premises, the goals of the present work are:

(1) to prove the effective mechanism of the oxidative esterification performed over gold supported on zirconia under our reaction conditions;
(2) to find the best process conditions, in terms of pressure, temperature, nature of the oxidising agent and reaction time, in order to yield a greener, safer, economic and sustainable process.

2. Experimental

2.1. Catalyst preparation

$Zr(OH)_4$ was prepared by precipitation from $ZrOCl_2{\cdot}8H_2O$ at constant pH = 8.6 and then aged for 20 h at 90 °C. The hydroxide was sulphated with $(NH_4)_2SO_4$ (Merck) by incipient wetness impregnation in order to obtain a 2 wt% amount of sulphates on the final support. Then, sulphated zirconium hydroxides (SZ2) were calcined in air (30 ml/min STP) at 650 °C for 3 h.

2 wt% of gold was added by deposition–precipitation (DP) at pH = 8.6: The oxide was suspended in an aqueous solution of $HAuCl_4{\cdot}3H_2O$ for 3 h and the pH was controlled by the addition of NaOH (0.5 M). After filtration, the sample was dried at 35 °C overnight and finally calcined in air for 1 h at 400 °C. 2 wt% of SO_4^{2-} was found on the calcined support before DP. On the contrary, no sulphates are present in the final AuZ catalyst anymore. This is due to the detachment of sulphate groups during the DP at pH = 8.6 [19]. The Au/TiO_2 catalyst provided by the World Gold Council (WGC) was also studied as a reference. Table 1 summarises the characterisation data of the examined gold catalysts.

2.2. Methods

The sulphate content was determined by ion chromatography (IC). Sulphate concentration was calculated as the average of two independent analyses, each including two chromatographic determinations.

The gold amount was determined by atomic adsorption spectroscopy after microwave destruction of the samples (100 mg).

CO pulse chemisorption measurements were taken at −116 °C in a lab-made equipment. Before the analysis, the following pretreatment was applied: The sample (200 mg) was reduced in a H_2 flow (40 ml/min) at 150 °C for 60 min, cooled in H_2 to room temperature, purged in He flow and finally hydrated at room temperature. The hydration treatment was performed by contacting the sample with a He flow (10 ml/min) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption (−116 °C) [20].

FTIR measurements of adsorbed molecules were carried out on the samples in self-supporting pellets introduced in a cell allowing thermal treatments in controlled atmospheres and spectrum scanning at controlled temperatures (from −196 °C to 25 °C). The FTIR spectra were taken on a PerkinElmer 1700 spectrometer (equipped with a cryogenic MCT detector). From each spectrum, the spectrum of the sample before the inlet of the molecule was subtracted. The

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