



Synthesis of furan derivatives via cascade-type reactions catalyzed by solid acids



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ABSTRACT

The 2-methylfuran (2-MF), easily obtained from furfural as a lignocellulosic biomass derivative, can be converted in good yields (70%) into 5,5-bis(5-methyl-2-furyl)pentan-2-one by condensation in the presence of mineral acids. This molecule is an important precursor for various interesting industrial products, such as benzofuranics with physiological activity and hydrocarbon mixtures useful as fuel components. In this work, the synthesis of 5,5-bis(5-methyl-2-furyl)pentan-2-one was successfully achieved (yield = 80%) via hydrolysis/condensation of 2-methylfuran, by using ethanol/water as solvent and Amberlyst® 15 as a solid catalyst under moderate reaction conditions. Different polymeric ionic exchange resins were tested, conversion of 2-MF and product performances during reaction showed a proportional dependence to the capacity of proton exchange of resins. Amberlyst® 15 presented the best results, and the resin can be regenerated and reused several times arriving to a constant product yield after the 3rd–4th reuse. Results attained for different zeolites tested indicate that 2-MF conversion appears to be function of pore size and channels structure of zeolite. These catalysts produced low yields of desired product mainly due to deactivation by the retention of intermediate reactions and products on the surface and inside pores. The use of H-Beta (F⁻) catalyst presenting a more hydrophobic surface could partially minimize catalytic deactivation.

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1. Introduction

A wide range of renewable raw materials can be easily obtained from lignocellulosic biomass in both polymeric (i.e. cellulose, starch, lignin) and monomeric (i.e. sugars, polyols, phenols) forms [1]. These bio-based platform compounds could be converted in a large variety of chemical products (specialities and fine chemicals) to replace non-renewable fossil raw materials (oil, coal, natural gas) [1–3]. Up to now, the bio-based products are more eco-friendly than the fossil-derived ones, but in most of the cases they are more expensive due to the lack of practical and efficient synthetic processes [4,5]. Thus, the development of new catalytic processes to competitively and efficiently produce these biomass-derived chemicals is largely needed. In this sense, bio-based platform compounds, such as sugars, polyols, furfural, succinic acid, among others, can be transformed into valuable chemicals via new

eco-friendly processes in which the number of steps in synthesis are reduced by performing cascade type catalytic reactions [6–9].

One of these biomass derivatives of great interest is furfural, which can be produced via acid medium dehydration from lignocellulosic type biomass with high content of cellulose and hemi-cellulose (and also inulin) [10]. Furfural can be used as platform chemical for the production of several interesting compounds, such as furfuryl alcohol [11], 2-methylfuran (2-MF) [12], tetrahydrofuran (THF) [13], among others. In recent years, furfural and its derivatives have received a growing interest from both academic [14–16] and industrial [17–19] research communities due to the numerous possibilities that these furan derivatives offer to synthesize different organic compounds useful as intermediates and final products for chemical and petro-chemical industries.

The 2-methylfuran (2-MF) can be easily attained by means of vapor-phase hydrogenation of furfural [12]. Depending on the type of catalyst used, hydrogenation of furfural can give a variety of products such as furfuryl alcohol, 2-methylfuran (2-MF), and tetrahydrofurfuryl alcohol (THFA) [12]. In the past century, copper chromite has been the most successful commercial catalyst used in

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the furfural hydrogenation in liquid and gas phases. More recently, many attempts have been made to develop new and environmentally friendly catalysts to overcome toxicity problem of CuCr-based catalysts, which causes severe environmental pollution [1].

The 2-MF can be transformed mainly into 5,5-bis(5-methyl-2-furyl)pentan-2-one via condensation reaction in the presence of mineral acids (with aqueous H_2SO_4 at 336 K under reflux during 2 h); thus achieving conversion and yield levels of 87% and 70%, respectively [20,21]. This compound is used as precursor for the synthesis of benzofuranic derivatives with interesting physiologic activities and employed in pharmaceutical products [22]. In addition, it has been recently described that a catalytic process is able to produce the condensation of three molecules of 2-MF to obtain the 5,5-bis(5-methyl-2-furyl)pentan-2-one in good yields (80% yield at 16 h of reaction), which is then submitted to a dehydration/hydrogenation reaction step to attain aliphatic hydrocarbons useful as components of high quality fuel for transportation [23,24].

All the above-mentioned indicates that the 5,5-bis(5-methyl-2-furyl)pentan-2-one becomes an important platform chemical for obtaining different products with industrial interest. Up to now, its effective synthesis has only been described by using homogeneous catalytic systems with mineral acids, with all the problems and disadvantages associated to this type of processes concerning the ulterior steps of product separation and effluents neutralization, among others. In this sense, it would be interesting to develop an alternative catalytic route to synthesize this compound by using a heterogeneous acid catalyst, thus avoiding all the troubles associated to the use of mineral acids in homogeneous phase. In this work, the use of different solid acids, such as proton exchanged polymeric resins (i.e. Amberlyst[®] 15 and different commercially available Dowex-type resins) and zeolites (i.e. H-Beta, H-USY, H-MOR) in their protonic forms as catalysts for the synthesis of 5,5-bis(5-methyl-2-furyl)pentan-2-one will be investigated. Selection of these materials obeys to their well-known properties when used as catalysts in acid-type reactions. On one hand, ion-exchange polymeric resins, and particularly Amberlyst[®] 15, have largely been used as acid catalysts in a wide range of organic reactions, such as esterifications [25,26], acetal formations [27], etherifications [28], and also olefin condensations [29]. On the other hand, zeolitic materials have extensively been used for several years in different acid-catalyzed reactions, such as hydrocarbons cracking, alkylations, acylations, among others [30–32]. It will be here demonstrated that Amberlyst[®] 15 effectively catalyzes the hydrolysis/condensation of 2-MF to the desired product, offering better results than the zeolitic materials. Further studies on operational conditions allow us to optimize product yield, and more importantly catalytic results and recycling of the catalyst. Finally, a reaction mechanism is proposed based on kinetic studies of the hydrolysis/condensation process in the presence of Amberlyst[®] 15 as catalyst.

2. Experimental procedure

2.1. Materials

The 2-methylfuran (98%), tert-butyl alcohol (99.7%), methyl-tert-butyl ether (99.8%), and chlorobenzene (99%) were purchased from Sigma–Aldrich and used as received. Ethanol (99.9%), acetonitrile (99.98%), and acetone (analytical grade, 99.5%) supplied by Scharlau, and water (Milli-Q quality, Millipore) were used as solvents. For catalysts synthesis the following reactants were used: tetraethyl-ammonium hydroxide (TEAOH, Aldrich, 35 wt% in water), tetraethyl-orthosilicate (TEOS, Merck, >98%), HF (Aldrich, 48 wt% in water), silica gel (Aerosil 200, DEGUSSA), pseudobohemite (60 wt% de Al_2O_3), $\gamma\text{-Al}_2\text{O}_3$ (Aldrich), and aluminum *iso*-propoxide (Aldrich, 99%). Samples of Amberlyst[®] 15, Nafion[®] SAC-13, Dowex[®] 50WX2-200, Dowex[®] 50WX4-100, and Dowex[®]

50WX8-200 proton exchange polymeric resins were purchased from Sigma–Aldrich and used in experiments without any pre-treatment.

2.2. Catalysts preparation

2.2.1. Synthesis of zeolite microporous materials

Mordenite zeolite in its protonic form (H-MOR) with Si/Al molar ratio = 10 was prepared following the methodology described in ref. [33], through hydrothermal synthesis at 413 K in Teflon-lined stainless-steel autoclaves.

Samples of H-USY (CBV 720, protonic form, Si/Al = 15) and H-ZSM-5 (CBV 3024E, protonic form, Si/Al = 15) zeolites were purchased from Zeolyst International.

All zeolitic samples were calcined at 773 K during 3 h under air atmosphere prior to their use in catalytic experiments.

2.2.2. Synthesis of Beta zeolites microporous materials

H-Beta(OH^-) with different Si to Al molar ratios (Si/Al = 20 to ≈ 80) were synthesized in alkaline (OH^-) media by following the methodology described in ref. [34], through hydrothermal synthesis at 413 K in Teflon-lined stainless-steel autoclaves with rotation (60 rpm). After the required crystallization time, the autoclaves were cooled and the solids were filtered and extensively washed with distilled water.

H-Beta(F^-) hydrophobic materials with two different Si/Al molar ratios of 20 and 100 were synthesized in fluoride (F^-) media following the methodology described in ref. [35], through hydrothermal synthesis at 413 K in Teflon-lined stainless-steel autoclaves with rotation (60 rpm). Typically, H-Beta(F^-) was synthesized by mixing the adequate amounts of TEOS, TEAOH (35 wt% in water), aluminum *iso*-propoxide, and water. The mixtures were kept under stirring until the complete evaporation of the ethanol formed upon hydrolysis of TEOS. Finally, HF (48 wt% in water) and, optionally, dealuminated zeolite Beta seeds were added, thus obtaining the final gels. Then the gels were putted into the autoclaves to proceed with the hydrothermal treatment. After the required crystallization time, the autoclaves were cooled and the solids were filtered and extensively washed with distilled water.

In both H-Beta(OH^-) and H-Beta(F^-) cases, the Si/Al molar ratios were determined by chemical analysis (ICP). The solids were dried at 373 K and calcined at 853 K during 3 h prior to their use in catalytic experiments. The resultant materials were analyzed by XRD showing from moderate ($\approx 75\%$ for H-Beta- OH^-) to high (>92–93% for H-Beta- F^-) crystallinity. The samples were also characterized by other available techniques, such as SEM (crystal size $\approx 0.15\text{--}1.00\ \mu\text{m}$) and N_2 adsorption isotherms (BET method, and micropore volume = $0.21\text{--}0.23\ \text{cm}^3/\text{g}$ by *t*-plot method), among others.

The main physico-chemical and textural properties of the different zeolitic samples used in this work are detailed in Table 1, while additional information is also given in Supplementary Information (Figs. S7 and S8).

2.3. Catalysts characterization

Phase purity of the catalysts was determined by X-ray diffraction (XRD) in a Philips X'Pert MPD diffractometer equipped with a PW3050 goniometer (CuK α radiation, graphite monochromator), provided with a variable divergence slit and working in the fixed irradiated area mode. Infrared spectra were obtained in a Nicolet 710 FTIR spectrometer using self-supported wafers of $10\ \text{mg}/\text{cm}^2$ outgassed overnight at 653 K and $10^{-3}\ \text{Pa}$.

Thermogravimetric and differential thermal analyses (TGA–DTA) were performed in a Netzsch STA 409 EP thermal analyzer with about 20 mg of sample and a heating rate of

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