



Aldol-condensation of furfural by activated dolomite catalyst



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ABSTRACT

Aldol-condensation of furfural with acetone catalysed by activated dolomite was investigated at temperatures from 306 to 413 K. The process of activation by calcination and hydration produced catalytically active calcium and magnesium hydroxides with improved surface area and surface basicity. The aldol-condensation mechanism began with a deprotonation of acetone forming a carbanion intermediate by hydroxyl ions, which then reacted with the carbonyl group of furfural to form a water soluble C₈ monomer (4-(furan-2-yl)-4-hydroxybutan-2-one). This C₈ monomer readily dehydrated to form selectively α,β -unsaturated ketone (4-(2-furyl)-3-buten-2-one), which in turn, reacted with furfural forming a C₁₃ dimer (1,4-pentadien-3-one,1,5-di-2-furanyl). Compared with conventional sodium hydroxide catalyst, activated dolomite was less selective towards lumped C₈ monomers and C₁₃ dimers owing to carbon losses and deactivation, particularly at high temperatures. Activated dolomite was more selective to C₁₃ dimer owing to higher adsorption enthalpy of C₈ monomer compared with acetone competitor. Activated dolomite is therefore a promising catalyst to produce C₁₃ dimers which can be transformed upon hydrogenation and deep hydrodeoxygenation in high-quality diesel fuels. The first-order kinetic model with respect to furfural and acetone fitted well with actual experimental results with an average normalised standard deviation of 6.2%.

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1. Introduction

The development of usable renewable energy is a major challenge in the twenty-first century owing to the finite nature of fossil fuels and their environmentally damaging effects. Burning of fossil fuels, for instance, is the anthropogenic activity which contributes the most to increasing levels of carbon dioxide in the atmosphere with an inevitable consequence on global warming [1]. Bio-refineries are cited as a good option to respond to humanity's concerns about sustainable energy as they integrate multiple biomass conversion processes to produce fuels, power, heat, and value added chemicals, with reduced waste and energy usage [2]. The key goal of a bio-refinery process is to transform this captured energy into usable energy. Liquid fuels represented by bio-alkanes have been synthesised by the hydrodeoxygenation of sugar derivatives which comprises dehydration of associated aldehydes, followed by hydrogenation and condensation to produce long chain alkanes [3]. It has previously been shown that furfural can be produced from xylose with high yields using aqueous phase dehydration [4]. Furfural is a highly versatile intermediate which

can be transformed into a variety of chemicals by hydrogenation, oxidation, reductive amination, decarbonylation, nitration and condensation. Processes of aldol-condensation, hydrogenation and hydrodeoxygenation are seen as effective integration steps towards the production chain of liquid fuels and industrial production is anticipated [4–9].

The reaction of aldol-condensation is base catalysed, bonds two carbon molecules together to produce longer hydrocarbon chains and ultimately produces low volatile and easy to transport fuels. Base catalysed aldol-condensation proceeds through a nucleophilic attack of the enolate ion on the C^{δ+} atom of the C=O group [6,10–12]. The reaction may occur between two ketones, two aldehydes or an aldehyde and a ketone, provided that one member of each pair possesses an α -H-atom. The missing α -H-atom in furfural does not allow, therefore, its self-condensation. As shown in Fig. 1, a proton is abstracted from the α -carbon, herein the acetone carbonyl function, creating a carbanion and leading to the formation of C₈ monomer, 4-(2-furyl)-3-buten-2-one (FAC). Due to the symmetry of the acetone molecule, the FAC monomer is, in turn, susceptible to a second attack by furfural leading to a double condensation C₁₃ dimer, 1,4-pentadien-3-one,1,5-di-2-furanyl (FFAC) [7]. Fakhfakh et al. [8] successfully used sodium hydroxide to catalyse the aldol-condensation reaction of furfural and acetone at temperatures between 293 and 313 K in homogeneous

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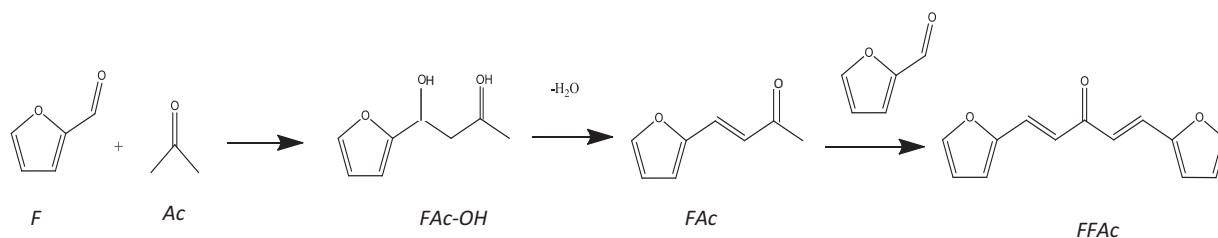


Fig. 1. Proposed reaction pathway for aldol-condensation of furfural with acetone. *F*: Furfural, *Ac*: Acetone, *FAC-OH*: 4-(furan-2-yl)-4-hydroxybutan-2-one, *FAC*: 4-(2-furyl)-3-buten-2-one and *FFAc*: 1,4-pentadien-3-one,1,5-di-2-furanyl [7].

ethanol–water solvent. Yields of around 50% were achieved. Similarly, West et al. [9] investigated aldol-condensation using biomass derived furans such as furfural, methyl furfural and HMF along with ketones such as acetone, acetol, dihydroxyacetone, 2-hexanone and 3-hexanone. A reactive aqueous phase was used including a homogeneous base NaOH catalyst and a salt in a biphasic system to reach high product yields by phase transfer separation. Although sodium hydroxide is a cost effective base, it completely dissociates in water and raises therefore some downstream processing issues such as energy intensive separation, product neutralisation, waste disposal and potential regeneration [10–19]. Recently, there has been a shift towards heterogeneous base catalysts such as alkali and alkaline earth oxides, phosphates and molecular sieves, i.e. mobile crystalline material (MCM-41) and hydrotalcites. Guida et al. [20] who investigated the Claisen-Schmidt condensation of benzaldehyde with excess acetone using calcined hydrotalcites as catalyst, recognised the catalytic effect of basic hydroxyls. Uncalcined hydrotalcites were initially found to be totally inactive, but once thermally treated and hydrated, were found to be active, implying that the reaction was catalysed specifically by hydroxyl sites. Yoosuk et al. [21] used activated dolomite as heterogeneous catalyst for the reaction of palm oil transesterification with methanol. The most effective catalyst was the dolomite sample which was subject to calcination, hydration and second calcination. The initial calcination transformed the non-porous structure of natural dolomite to a mesoporous structure of CaO–MgO resulting from the expulsion of carbon dioxide from the dolomite's core. Upon exposure to water, the oxide part became swollen and was transformed to a hydroxide surface. Upon a second calcination, the hydroxide structure was reversed back to an oxide coincident with the release of a molecule of water, the production of a higher surface area along with a lower crystalline size. After hydration–dehydration, the strong basic sites were considerably enhanced. Wilson et al. [22] used dolomite for transesterification of C₄ and C₈ triglycerides and olive oil for biodiesel applications. The active sites were thought to be the calcium oxide portion of the dolomite which was produced by calcination and decomposition of the dolomite structure.

The aim of this work is to investigate the aldol-condensation of furfural with acetone at relatively low temperatures using calcined and hydrated dolomite as base catalyst. Dolomite was selected because it presents high green credentials owing to its abundance and low toxicity [21]. Dolomite is an abundant sedimentary carbonate rock containing alternating plane structures of Ca²⁺ and Mg²⁺ cations forming a non-ideal chemical composition of basic CaMg(CO₃)₂. The work focuses on experimental validation of the mechanism involved in a monophasic system. An activated dolomite by calcination and fully hydration is used as it offers a constant number of fully developed Brønsted hydroxyl sites for the kinetic modelling. These hydroxyl sites were found more effective than relevant Lewis sites of mixed oxides [10–18,23]. The kinetic modelling of furfural as biomass derivative compound model provides a promising option to produce, under controlled

operating conditions, the desired route towards product oxygenates FAC monomer, 1,4-pentadien-3-one or FFAc dimer which are sources of the desired alkanes in bio-refinery processing. A reaction mechanism is proposed and the kinetic parameters normalised to hydroxyl base sites are estimated and compared with those of sodium hydroxide catalyst.

2. Experimental

2.1. Catalyst preparation and characterisation

A natural dolomitic rock was mined from a deposit in Fermanagh, (Northern Ireland), ground on site and supplied in its powdered and brownish form. Dolomite was calcined using a tubular furnace at 1073 K. A range of methods were used to characterise the chemical and structural changes occurring within the dolomite. The basicity strength of dolomite was carried out by Hammett indicators (bromothymol blue, phenolphthalein, and 2,4-dinitroaniline) in anhydrous methanol and volumetric titration using acetic acid. X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert Pro X-Ray Diffractometer with Cu K_α radiation. The 2θ range was scanned between angles of 5° and 60° and the detector was set at 40 kV and 40 mA. Scanning electron microscopy (SEM) was carried out using a Jeol JSM-6500F Field Emission working at 0.5–30 kV and giving a resolution of 1.5 nm. The surface area analysis was carried out using a BET Micromeritics ASAP 2010. Thermogravimetric analysis was carried out using Mettler Toledo using a 5 mg dolomite sample that was heated to a temperature of 1273 K. Spent dolomite was analysed by temperature-programmed desorption (TPD) using Krypton as reference gas and temperature-programmed oxidation (TPO) using a mixture of krypton, argon and oxygen (40:50:10 mol.%), at a heating rate of 5 K/min. Soluble dolomite ions in water were analysed by inductively coupled plasma/atomic emission spectrometer (ICP/AES).

2.2. Batch reactor

The reactor was a 316L stainless steel, 100 mL four ports Parr reactor. An on/off controlled heating jacket was used ensuring a liquid phase temperature within a 2 K deviation from the set-point. The heating jacket and the agitator were controlled using an Autoclave Engineers Sentinel Series control box. A sampling valve was attached to a threaded piece of 1/8 in. tubing that was immersed inside the liquid phase of the reactor. The reactor also included a 50 mL stainless steel sampling vessel which was connected to a supply of helium at 20 bars pressure. This additional setup allowed furfural to be held at room temperature and charged to the reactor at the desired temperature. This procedure minimised degradation of furfural before the start of the reaction.

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