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The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol

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ABSTRACT

In this work the replacement of toxic chromium containing catalysts for the selective hydrogenation of furfural to furfuryl alcohol was investigated. The initial focus was on the synthesis of monometallic catalysts by wet impregnation and concentrated on the employment of metals such as platinum, palladium, copper and nickel. Experiments were conducted using ethanol as the solvent which was found to have a negative effect on the selectivity to the desired product, furfuryl alcohol, with high quantities of 2-Furaldehyde diethyl acetal and difurfuryl ether formed. Consequently, toluene was selected as an alternative solvent facilitating selectivity to furfuryl alcohol only. It was found that platinum was the most promising metal of those studied as it displayed higher selectivity to furfuryl alcohol and was subsequently employed for the synthesis of bimetallic catalysts. The bimetallic catalysts were synthesised by surface reactions using a variety of promoter metals selected according to their electronegativity. It was found that, while the selectivity of all catalysts to furfuryl alcohol was close to 100%, the conversion was influenced significantly by the second metal and followed the order tin > molybdenum > manganese > barium > iron > nickel. The purpose of the research was to produce an active catalyst for the liquid phase hydrogenation under suitable industrial conditions with the results presented here conducted at 100 °C and 20 bar hydrogen pressure. Furfural conversion of 47% and close to 100% selectivity to furfuryl alcohol was achieved using a 0.6%Pt0.4%Sn/SiO₂ catalyst.

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1. Introduction

Research to develop alternative liquid transport fuels has increased considerably in recent years influenced by the implementation of legislation and directives on alternative energy which sets targets for transposing members. Europe has set targets such as the Renewable Energy Directive to make renewable energy sources account for 20% of overall energy and 10% of transport energy by 2020 [1]. To achieve these targets in an ethical, environmentally sustainable and economical manner the use of lignocellulosic biomass or agri-waste for the production of second generation biofuels is proposed [2]. The production of biofuels from hemicellulose requires acid hydrolysis to open the biomass structure giving large quantities of xylose [3]. The synthesis of furfural (FF) as a by-product of this biofuel production process has developed an additional important research area.

Furfural, produced by the acid-catalysed dehydration or hydrolysis of xylose, is a versatile and renewable chemical with wide industrial applications [4–6]. These include uses in the agrochemical, fragrance and plastics industries while it is also a building block for the synthesis of various other chemicals and chemical products including nylons and adhesives [5,7,8]. The hydrogenation of furfural to furfuryl alcohol (FA) is a single step process and the most popular application of furfural conversion with approximately 60–62% of the furfural produced worldwide converted to furfuryl alcohol [9].

Furfuryl alcohol is formed from a simple hydrogenation reaction in the presence of a catalyst. The C=O of the aldehyde functional group in furfural breaks while the addition of hydrogen to the oxygen results in an alcohol group (O–H) with an additional hydrogen bonded to the exocyclic carbon of the furan based structure giving furfuryl alcohol. Furfuryl alcohol is used mainly in the polymer industry together with the production of synthetic fibres, rubbers, resins and farm chemicals. It is used in the manufacture of lysine, vitamin C and lubricants, the production of foundry sand binders in the metal casting industry and as a chemical building block for

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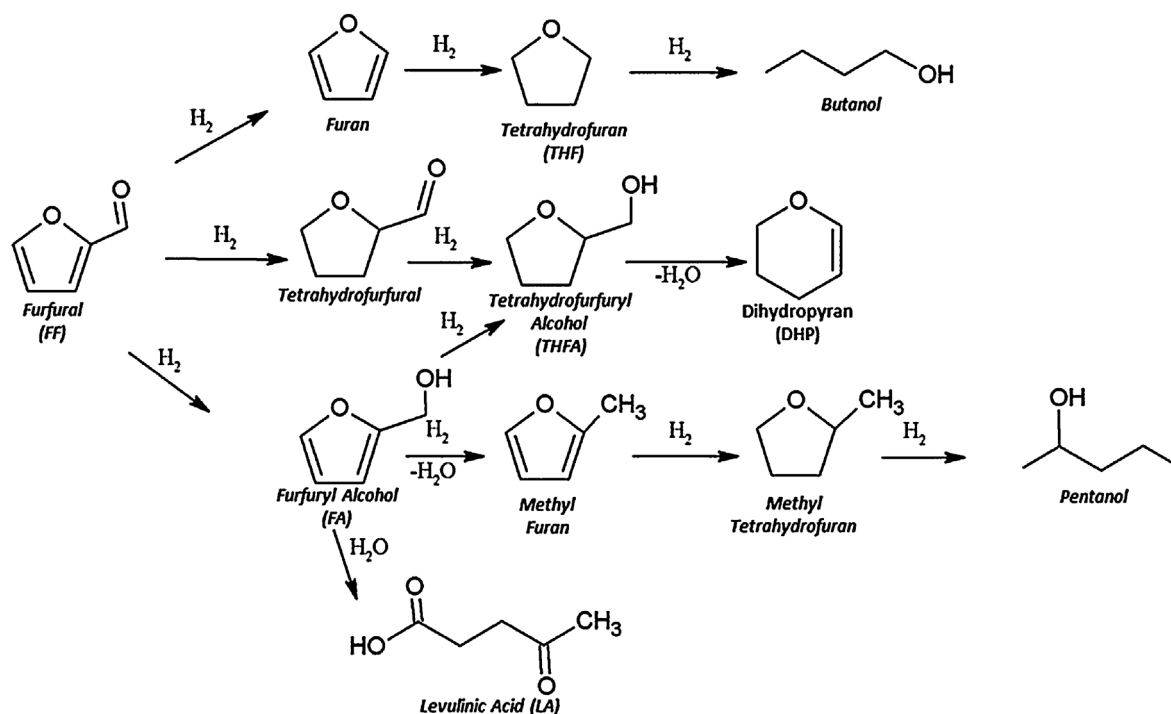


Fig. 1. The hydrogenation pathway of the platform chemical, furfural.

drug synthesis. Furfuryl alcohol is also used in the production of other products in the fine chemical industry [10–13].

The derivatives of furfural, some of which are outlined in Fig. 1, include furfuryl alcohol, tetrahydrofuran, 2-methylfuran, furoic acid, hydroxymethylfurfural, furylidene, furan and resins [14–17]. Many of these products are formed via furfural hydrogenation with a variety of additional reactions including furfural decarbonylation and oxidation also possible. It is therefore of great importance to choose a catalyst which is selective to the desired reaction route.

The industrial catalyst for the hydrogenation of furfural to furfuryl alcohol is copper chromite and is well known to be environmentally toxic, promoting extensive research to develop suitable alternatives [18]. The necessity to produce an alternative has increased the interest in heterogeneous catalysts for the synthesis of fine chemicals.

A wide variety of chromium free catalysts exist in literature employing an extensive selection of support and metal combinations. Catalysts investigated for liquid phase research were examined as a basis for metal selections applied in this work. Metals frequently selected include copper [19–22] and nickel [23–26] while metals such as platinum [27–29] and palladium [30–32] are sparsely reported with publications limited to dedicated research groups. Overall, no trends between metal selection and catalyst activity are evident from the literature although bimetallic catalysts are generally more active than monometallic catalysts for the desired reaction.

Furfural may be hydrogenated to furfuryl alcohol in the liquid or gas phase with the industrial process utilising high temperature and pressure although the chromium containing catalyst used in industry achieves only moderate activity for this reaction [29,33,34]. Vapour phase is often favoured over liquid phase due to the uneconomic outcome of large-scale batch processes. However, vapour phase also has issues relating to the production of undesired derivatives at high furfural conversion together with deactivation of the catalyst [35]. A wide variety of catalyst synthesis techniques have been investigated for this reaction from techniques such as impregnation [30,34] and co-precipitation [19,26] to

complex techniques including surface reactions together with synthesising supported and encapsulated metal nanoparticle catalysts [29,36–38].

This work focuses on the synthesis of a catalyst that is active for the hydrogenation of furfural to furfuryl alcohol. The selectivity to furfuryl alcohol is crucial which is the emphasis for the selection of the primary metal. An analytical approach regarding the electronegativity of metals is applied to the selection of a second metal in order to increase furfural conversion. The solvent used for the reaction is also scrutinised to ensure the selection does not have a negative effect on the desired reaction.

2. Materials and methods

Furfural, furfuryl alcohol, ethanol, toluene, hydrofluoric acid, hexanol, 1-propanol and *n*-heptane, all of analytical reagent quality, were obtained from Sigma-Aldrich. Metal salts for catalyst preparation; copper (II) nitrate hydrate, nickel (II) nitrate hexahydrate, platinum (II) acetylacetonate, tetraaminepalladium (II) chloride monohydrate, tetrabutyl tin, iron (II) chloride tetrahydrate, manganese (II) acetate tetrahydrate, nickel (II) nitrate heptahydrate, barium acetate molybdenum acetate together with lanthanum (III) chloride heptahydrate, aluminium isopropoxide, pleuronic® P-123 (P123) and tetraethyl orthosilicate (TEOS) were also obtained from Sigma-Aldrich. Metal standards were obtained from Lennox Dublin. Commercial palladium catalysts and catalyst supports, SiO₂ and TiO₂ were obtained from Sigma-Aldrich while β -Zeolite was obtained from Zeolyst International.

3. Experimental

3.1. Catalyst preparation

All monometallic catalysts were produced using wet impregnation. The required amount of a precursor salt was added to 50 ml of ethanol followed by the addition of the support. The suspen-

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