



Research article

Hydrogenation of bio-oil into higher alcohols over Ru/Fe₃O₄-SiO₂ catalysts

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ABSTRACT

Liquid-phase hydrogenation of a solution of furfural, phenol and acetic acid has been studied in the 50–235 °C range over magnetic Ru/Fe₃O₄-SiO₂ catalyst targeting the renewable production of second generation biofuels with minimum hydrogen consumption. Phenol was fully hydrogenated to cyclohexanol in the entire temperature range. Below 150 °C, furfural was mainly hydrogenated to tetrahydrofurfuryl alcohol while hydrogenolysis to cyclopentanol was the main reaction pathway above 200 °C. The hydrogenation rate was doubled in an acidic solution (pH = 3) as compared to that at a pH 6. The spent catalyst was regenerated and reused in subsequent catalytic runs.

1. Introduction

Rising energy prices along with the depletion of fossil resources constitute one of the most important challenges of the modern world. To address the challenge, sustainable sources of energy, and in particular, fuels are required with the most promising source being biomass. There are several methods for fuel production from biomass such as conversion into syngas followed by synthesis of methanol, higher alcohols or hydrocarbons via the Fischer-Tropsch or methanol to gasoline processes [1,2]. A more targeted approach requires the growth of particular energy-rich organisms such as algae and their direct conversion into target fuels [3,4]. However, these processes require either long synthetic sequences or provide utilisation only of a very narrow range of biomass sources.

Fast pyrolysis is a particularly promising approach being simple and universal for various biomass sources. It occurs at moderate temperatures (480–520 °C), produces liquid oil product (convenient to handle) with yields up to 70 wt% (of dry feed basis), and holds the potential to supplement crude oil as a liquid hydrocarbon feedstock. However, raw bio-oil has a number of drawbacks such as (i) low heating value, (ii) incompatibility with conventional fuels due to high oxygen content, (iii) high solids content, (iv) high viscosity, and (v) chemical instability [5–9]. Because of these, bio-oil cannot be used as a liquid fuel in internal combustion engines.

Bio-oil is usually upgraded via hydrodeoxygenation, cracking, steam

reforming or other methods to overcome the problems [10–13]. Hydrodeoxygenation is considered to be a promising route for converting bio-oils to a traditional refinery-ready hydrocarbon feedstock. Given the multitude of C–O bond types in bio-oil, each with varying bond strength and thermodynamically preferred deoxygenation pathway, the term hydrodeoxygenation represents a complex network of many reactions. The process can be simplified by distinguishing reactions according to the hydrocarbon and oxygen elimination products using some model compounds present in the oil to understand the basic processes [14,15]. These studies are especially useful for comparison of the catalyst performance and essential for understanding of the reaction mechanisms and kinetics.

Phenol derivatives comprise up to 30 wt% of bio-oil [16]; therefore, phenol is widely used as a model molecule to study its hydrogenation or deoxygenation pathways [17]. A recent work was focussed on the hydrogenation of phenol in the aqueous phase through which the use of an organic solvent could be eliminated by its replacement with water identified as a ‘green’ solvent [18,19]. The analysis can then be extended further, for example, acetic or propionic acid can be co-fed with a phenolic model compound to investigate reactant interactions before feeding the whole bio-oil [14,20,21]. In the hydrogenation of acetic acid, it was found that a Ru/C catalyst showed the highest activity, followed by Ru/Al₂O₃, Pt/C, Pt/Al₂O₃, Pd/Al₂O₃, and Pd/C [21]. Furfural and its derivatives are another main class of molecules present in bio-oil in the amounts up to 30–40 wt% [8,13,16]. Its hydrogenation

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was extensively studied in literature. Nakagawa et al. [22] demonstrated that introduction of Ir into Pd nanoparticles increases TOF due to increased adsorption of C=O bond. Pang et al. [23,24] showed an increased aldehyde hydrogenation and hydrodeoxygenation selectivity with the introduction of thiols over Cu-based catalysts. O'Driscoll et al. [25] demonstrated an excellent selectivity towards furfuryl alcohol over Pt–Sn catalysts in a range of solvents. Xu et al. [26] investigated the effect of additives such as acetone or acetic acid on the hydrogenation of furfural over Ni Raney catalysts. They found that both selectivity and activity can be changed dramatically due to different adsorption modes of substrate molecules over the catalyst surface.

Supported noble metals are attractive because they are known to activate hydrogen and are less susceptible to deactivation by water. Thus, they hold the potential to exhibit suitable performance with longer catalyst lifetimes. A recent report by Wildschut et al. highlights the promising activity of supported Ru, Pd, and Pt catalysts compared to traditional transition metal sulphide catalysts for the bio-oil hydro-treatment [27]. Model compounds have been used to develop an understanding of the role and interaction of the metal, promoter, support, and process conditions in deoxygenation.

Heres et al. performed fundamental studies on hydrotreatment of bio-oils and model compounds using a Ru/C catalyst [28]. Different levels of upgrading were studied from stabilisation with low levels of oxygen removal through mild hydrotreatment to two-stage hydro-treatment with substantial oxygen removal. Lercher proposed a “one-pot” approach which is based on aqueous phase hydrodeoxygenation of phenolic monomers using bifunctional catalysis that couples precious metal catalysed hydrogenation and acid-catalysed hydrolysis and dehydration [29]. A more complex process involving hydrotreatment, esterification and cracking in supercritical ethanol on supported palladium catalysts has been reported [30]. This work demonstrated a significant improvement in a number of properties such as removal of aldehydes, a decomposition of macromolecules and a decrease in viscosity as well as an increased heating value.

However, traditional bio-oil hydrodeoxygenation requires high-pressure H₂ in large excess, which significantly increases the cost of upgrading [31]. Bridgwater has estimated that 62 kg of H₂ is required to deoxygenate one tonne of bio-oil [34]. Moreover, a large number of by-products such as methane is usually formed resulting in the liquid fuel yield of only about 25% [32]. Therefore, significant economy can be achieved via minimization of the amount of H₂ required for deoxygenation by targeting only the most problematic substances.

An additional challenge posed by bio-oil is catalyst recovery which is difficult to do via filtering due to high particulate content, high viscosity and instability of bio-oil. In this respect, magnetic recovery of the catalysts seems particularly promising [33]. Magnetic catalyst recovery generates more environmentally friendly processes, cheaper products, and conserved energy for a range of processes [34–37]. In the majority of cases, catalytic complexes or nanoparticles (NPs) are placed on the surface of magnetic NPs [33,38,39], but for efficient magnetic separation, the NP aggregation is required [40,41]. In addition, NP based catalysts are normally synthesized in microgram amounts making scaling up a difficult task. Composite materials consisting of magnetite NPs and silica received considerable attention as catalytic supports. Well-defined and monodisperse core-shell NPs with a magnetic core and silica shell can be prepared using a microemulsion approach [42], but again scaling up and fast magnetic separation are problematic. When SiO₂ filled with Fe₃O₄ NPs bearing catalytic species are prepared in one-pot procedure [43] or with subsequent addition of corresponding species [44], larger amounts of catalysts can be obtained and NPs are aggregated, allowing easy magnetic separation. However, some catalytic species could be buried within these aggregates.

Many researchers performed hydrogenation of model bio-oil components such as furan and derivatives of phenol [8,29,45–47]; however, far less attention have been devoted to the study of the hydrogenation of more complex mixtures. Recently, substantial solvent effects on

hydrogenation rates were identified, which are expected to play a major role in bio-oil hydrogenation [48]. In the current work, we have studied hydrogenation of mock bio-oil containing three major components of the real oil such as phenol, furfural and acetic acid. The catalyst recycling which is essential for successful industrial applications is usually not performed, because recycling of conventional supported catalysts requires an aggressive oxidative treatment which leads to deactivation via sintering. To avoid this problem, we used magnetically-recoverable Ru catalysts deposited on a composite Fe₃O₄-SiO₂ support.

2. Experimental procedures

2.1. Materials

Ruthenium (III) acetylacetonate (Ru(acac)₃, 97 wt%), iron (III) nitrate (98 wt%), mesoporous silica gel 425 mesh, furfural (98 wt%), phenol (98 wt%), acetic acid (98 wt%) and calcium carbonate (99 wt%) were used as purchased from Sigma-Aldrich. Ethylene glycol (99 wt%) and tetrahydrofuran (THF, 99 wt%) were supplied by Macron Fine Chemicals. Ethanol (95 vol%) purchased from EMD was used without purification. Deionized water was used through the study.

2.2. Synthesis of Fe₃O₄-SiO₂

The Fe₃O₄-SiO₂ material was obtained using a procedure described in ref. [49]. The solution of Fe(NO₃)₃, 2 g in 10 mL of ethanol was prepared, mixed with 2.5 g of silica gel and left stirring overnight in air for solvent evaporation. The material obtained was dried at room temperature in a vacuum oven for 2 h. Afterwards, approximately 0.2 mL ethylene glycol was added and mixed with a spatula. The Fe₃O₄-SiO₂ formation was carried out in a tube furnace at a temperature of 250 °C (heating rate of 2 °C min⁻¹) for 5 h in a flow of argon.

2.3. Synthesis of Ru/Fe₃O₄-SiO₂

Impregnation of the magnetic support with Ru compound was performed by adding 0.5 g of Fe₃O₄-SiO₂ prepared in the previous step into a solution of 0.099 g of Ru(acac)₃ in 2.5 mL of tetrahydrofuran (THF). The solvent was evaporated by stirring in air overnight followed by drying for 2 h at room temperature in a vacuum oven. Ethylene glycol, 0.2 mL, was added to the powder which became red. Reduction and decomposition of Ru precursor were performed by placing the samples into a quartz tube furnace and heating at 2 °C min⁻¹ under a flow of argon at 300 °C. Prior to the catalytic reaction, the catalyst was reduced at 300 °C in the flow of 10 mL min⁻¹ (STP) 5 vol% H₂/N₂ for 4 h, cooled to room temperature and passivated in the flow of 10 mL min⁻¹ (STP) 1 vol% O₂/N₂. The catalyst was stored in sealed vials under nitrogen atmosphere. Ru nominal loading was 5 wt% and the catalyst was referred to as 5 wt% Ru/Fe₃O₄-SiO₂. The reference 5 wt% Ru/SiO₂ catalyst was obtained in the same way skipping the introduction of the magnetic nanoparticles.

2.4. Catalytic activity measurements

Acetic acid (120 mg), furfural (180 mg, distilled before experiment) or phenol (180 mg) were dissolved in 25.0 mL of water. Then 10.0 mL of the solution was transferred into a 25 mL vessel and purged ten times with 5 bar H₂ to remove dissolved air. The catalyst (10–500 mg) was placed in a 160 mL high-pressure stainless steel reactor (Parr Instruments). The reactor was filled with water (100 mL) and flushed five times under stirring with N₂ (40 bar) to remove dissolved air. The reactor was heated to the desired temperature. Below 150 °C, the reaction mixture was fed into the reactor after it reached the desired temperature. At higher reaction temperatures the reaction mixture was fed into the reactor at 150 °C and the reactor was further heated under a

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