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The effect of catalyst modification on the conversion of glycerol to allyl alcohol



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ABSTRACT

Conversion of glycerol to allyl alcohol was carried out over an iron on alumina catalyst. With the aim of enhancing selectivity towards the desired product and to reduce acrolein formation (a detrimental impurity in the subsequent epoxidation of allyl alcohol) the supported iron catalyst was modified using alkali metals. It was found that lithium, sodium, potassium, rubidium and caesium deposition on the catalyst surface increased allyl alcohol yield and reduced the rate of catalyst deactivation. Coincidently, acrolein selectivity decreased by up to 75% following treatment with the alkali salt.

Changes in the product distribution were determined to be associated with altering the acid/base properties of the catalyst, as confirmed by isopropanol dehydration/dehydrogenation, ammonia and carbon dioxide temperature programmed desorption. The treatment was also found to influence the physical properties of the catalyst surface. A correlation between acid to basic site concentration and allyl alcohol selectivity was established. A reduction in the former value results in an enhancement in the rate of allyl alcohol formation. A reaction mechanism was developed based on the effect of iron and alkali metals catalysing the conversion of glycerol into allyl alcohol. The proposed catalyst modification technique is a straightforward method, readily applicable at a larger scale due to the simplicity of the alkali inclusion and its striking influence on the reaction selectivity.

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1. Introduction

Global concern over carbon dioxide emissions and the exhaustion of fossil fuel resources make the development of synthetic fuels a field of intense study, facilitating the development of industrial applications of reactions such as the transesterification of triglycerides [1,2]. Although the transesterification of triglycerides is the most widely adopted biodiesel production method, it invokes the necessity to deal with glycerol, a by-product formed during the reaction [1]. In biodiesel production through transesterification, glycerol formation has serious implications for manufacturers, accounting for approximately 10 wt% of the product generated [3]. Despite its multiple uses, the purification of the fatty-acid methyl esters (FAME) by-product (containing from 30 to 60 wt% of the trivalent alcohol [4]) to the level of purity required for sale entails costly and specialised techniques. Additionally, markets for glycerol are considered to be saturated and therefore unable to accommodate the large quantities of crude glycerol being produced. In

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http://dx.doi.org/10.1016/j.apcatb.2014.01.019 0926-3373/© 2014 Published by Elsevier B.V. 2005, 200,000 tonnes of glycerol were generated as part of the biodiesel manufacturing process, while demand for refined glycerol was roughly 900,000 tonnes. In 2008, the rate of glycerol generated from transesterification increased to 1.224 million tonnes, with no reported parallel growth in glycerol markets [5]. Consequently, the commercial value of glycerol has dropped, adding significant cost to biodiesel manufacturers for storage and appropriate disposal. Clearly, finding a suitable glycerol derivative, with a significant market demand and price is essential, with glycerol valorisation to enhance the viability of the biodiesel manufacturing process.

Crude glycerol currently represents a waste (and therefore a financial liability) for the biodiesel industry, however it is a low cost reactant for which a number of technological options are currently being explored. While one of these options is the production of acrolein [6], a more valuable conversion product is allyl alcohol, which has a 36% higher market value [7]. Allyl alcohol global production was estimated to be 136,000 tonnes in 2005 [8]. It is also possible to convert allyl alcohol to products of higher value such as glycidol, which has a current market price of US\$546 per kilogram [7]. This potential opportunity makes pathways towards allyl alcohol production of considerable interest. Due to the bi-functionality (hydroxyl group and carbon–carbon double bond) of the molecule,

allyl alcohol is often used as a chemical intermediate. As reported by others [9], conversion of glycerol to allyl alcohol can be achieved over iron catalysts in a two-step process (acrolein formation followed by the selective hydrogenation of the double bond in acrolein promoted by glycerol or/and other alcohols). The role of iron in the process remains uncertain.

The direct conversion of glycerol to allyl alcohol has been reported over bimetallic catalysts (zirconia-iron surfaces) [10] or using formic acid as a reactant, which causes glycerol to undergo a double dehydroxylation [11]. Other catalysts such as a MoO_3-WO_3/TiO_2 [12] and methyltrioxorhenium (MTO) [13] have also been found to selectively catalyse allyl alcohol formation from glycerol.

Glycerol conversion to acrolein was achieved over acidic zeolites, with selectivities of up to 70% being reported [14]. Catalyst acidity influences both selectivity and conversion. A Hammett acidity value between -8.2 and -3.0 [15,16] was suggested to be ideal for the conversion of glycerol into the aldehyde. Low selectivity or accelerated deactivation were observed over catalysts with acid strengths outside this range [3]. Conversely, allyl alcohol as main product has been obtained using surfaces of very weak acidity, such as zirconia-supported iron oxide [10]. Clearly the product distribution of the converted glycerol is expected to be strongly dependent on the acid and base properties of the catalyst and or support.

Porous alumina is extensively used as a catalyst support in industrial processes due to its high surface area and minimal transport limitations. The γ phase of alumina is slightly acidic but it is possible to neutralise it through deposition of alkali metals [17]. In addition to the influence on surface acidity, alkali metals were reported to induce structural alterations on the catalyst, and thus improving iron dispersion for supported iron catalysts [18]. The electronic effects of alkali metals also can influence the catalyst activity [18]. This has been attributed to either ion exchange of alkali cations with protons from surface hydroxyl groups present in γ alumina, or the interaction of the introduced cation and anion with the Lewis acidic aluminium sites [19]. Various characterisation techniques, including IR spectroscopy, indicators with different pK_a , X-ray photoelectron spectroscopy and temperature programmed desorption, have been applied to determine the nature and distribution of the active sites being modified. While implications on the effect of total surface acidity have been observed, some authors attribute changes to the removal of Lewis sites, others to the replacement of Brønsted acidity or even a combination of the two [20]. The catalytic activity/selectivity is said to be related to the ionic radii of the modifier [21]. However, the catalyst modification is not necessarily straightforward, as under some conditions the effect on acid concentration or strength is unexpected. Furthermore, not only the nature of the alkali cation is important for the acid base properties but also the concentration of the solution used to treat the support [19]. Structural properties were also altered by alkali metal modification as indicated by inhibition of iron cluster formation due to Rb. Rubidium was used to modify iron oxide on silica catalysts, and inhibited cluster modification by parallel ion exchange between the iron and the added alkali cation [18]. Alkali metal-supported zirconia-iron oxide catalysts were reported to improve allyl alcohol production and reduce the concentration of some reaction by-products [22].

In this work, we aim to use alkali metal deposition techniques to modify iron surfaces prepared by a novel non-aqueous impregnation method and study its effect on the direct catalytic conversion of glycerol to allyl alcohol. It was the intention to increase selectivity to allyl alcohol, and minimise the formation of acrolein in the conversion of glycerol, since in the course of the allyl alcohol epoxidation to glycidol, acrolein competes with the alcohol, consuming peroxide and forming other species instead of the desired glycidol [23]. Reduction of acrolein formation in the upstream process is clearly preferred to purification in a separate step. Alkali metals are present in crude glycerol from biodiesel manufacturing [24] (when the reaction is base catalysed, present in the resultant mixture as waste catalyst up to 10% or as low as 0.05% after purification [25]), and thus could potentially aid the process through improved selectivity/yield. A detailed understanding of alkali metal modification is necessary to determine the economically most viable process conditions of glycerol conversion to value added products.

2. Experimental

2.1. Catalyst preparation

All materials were synthesised by a recently developed nonaqueous impregnation method. High purity alumina spheres (Sasol 1,8/210) were dehydrated for 1 h at 120 °C. Similarly, CaSO₄·2H₂O (99% Sigma Aldrich) was heated at 220 °C for 2 h to obtain the anhydrous form. The precursor salt, Fe(NO₃)₃·9H₂O (98% Sigma Aldrich), was dissolved in methanol and the solution was dried using CaSO₄. The resultant suspension was filtered under vacuum and the spheres added to the filtrate. After allowing the solvent to evaporate under continuous stirring, the catalyst was calcined in air for 4 h at 400 °C. The alkali metal treatment was accomplished following calcination.

Different methods were implemented for rubidium deposition on the iron oxide catalyst surface. Catalysts were modified by rinsing the spheres (washing), impregnation or ion exchange with RbNO₃. Impregnation consisted in adding the iron catalyst to a 0.1 M solution of rubidium nitrate in water, allowing the solution to evaporate under continuous stirring. For ion exchange, the iron on alumina catalyst was added to a fresh solution of rubidium nitrate in water stirring it overnight at 50 °C. The catalyst was then filtered and the treatment was repeated two more times. All the techniques investigated showed advantages and disadvantages, with impregnation and ion exchange allowing greater control of the quantity of modifier, while washing did not allow accurate control of modifier concentration in the solid product. Inductively coupled plasma atomic emission spectroscopy was used to determine the final catalyst composition. The influence of the sequence of metal impregnation on catalyst properties was also studied. "Inverse treatment" is described as the impregnation of rubidium (by ion exchange) being conducted prior to addition of active iron phase. In order to investigate the effect of the modifiers, Li, Na, K, Rb and Cs modified catalysts were prepared. Solutions of sodium nitrate and potassium nitrate (0.1 M) in methanol and lithium nitrate and caesium nitrate (0.1 M) in water were used to wash the spheres. The catalysts were then dried at room temperature.

2.2. Catalyst characterisation

Surface areas of used and fresh catalysts, both treated and untreated, were determined by nitrogen adsorption. The materials were first degassed overnight under vacuum and at 150 °C using a Micromeritics Vac Prep 061 sample preparation device. Tests were carried out in a Micromeritics Gemini surface area analyser at -196 °C and based on these data, Langmuir surface areas were calculated. X-ray diffraction measurements were conducted on unmodified and modified catalysts fresh and used using a Phillips X'pert Pro diffractometer with Cu K α incident radiation (λ = 1.54060 Å). Thermogravimetric studies were carried out for unmodified and rubidium modified iron catalyst using a Metter Toledo TGA/DSC 1 apparatus. Data was collected using 8.0 mg of sample at a heating rate of 5 °C min⁻¹ with a nitrogen flow of approximately 20 cm³ min⁻¹. XPS spectra were obtained by means of a Thermo Scientific ESCALAB 250Xi electron Download English Version:

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