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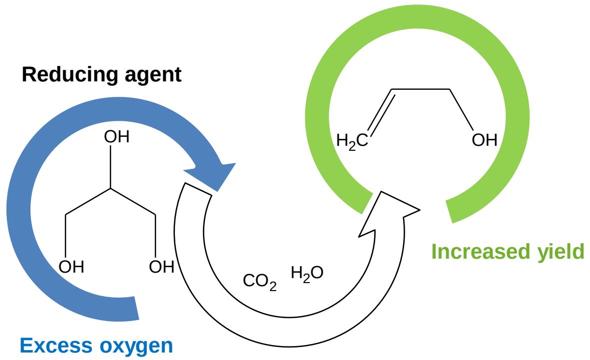
Significant enhancement on the yield of the allyl alcohol is obtained where a reductant is added to the glycerol feed.



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ARTICLE

Catalytic conversion of glycerol to allyl alcohol; effect of a sacrificial reductant on the product yield

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A continuous process for the conversion of glycerol to allyl alcohol, where ammonia or organic acids are added to the feed as sacrificial reductants, was investigated. Significant enhancement on the rate of formation and yield of the allyl alcohol is observed with some of the reducing agents examined over an alumina-supported iron catalyst. Optimising the molar ratio of the reductant relative to feed glycerol results in an increase in the yield of allyl alcohol from 9% (in the absence of additives) to 11.3% with ammonia, 15.1% with ammonium hydroxide, 17.8% with oxalic acid and 19.5% with formic acid. Moreover, the addition of other organic acids, which are produced in a typical glycerol conversion experiment, was studied. However, acetic and propanoic acid had little effect on the rate of formation of allyl alcohol. Analysis of the product distribution in the liquid and gas phases when oxalic and formic acid were added suggests a two-step process for the formation of allyl alcohol under the operating conditions of the reaction; the initial step involves the dehydration of glycerol while the second comprises the reduction of the species produced in step one.

Introduction

The variety of functional groups present in biomass engenders these materials as potentially valuable feedstocks for the production of useful chemicals, however, their high oxygen/carbon ratios tend to be detrimental to their use in many applications due to their polar and corrosive nature. For instance pyrolysis oil, a liquid formed from biomass by heating, has a pH of 3 and it separates into different phases on storage. While the conversion of pyrolysis oil and other bio-derived liquids such as glycerol into synthesis gas is common, transformations that result in selectively reducing the oxygen content of such feedstocks are attractive alternatives to their utilisation.

Deoxygenation of glycerol leads to the formation of 1-propanol and propane over a ruthenium complex [1]. Another reductive deoxygenation route is the conversion of glycerol into propanediols using synthesis gas with a tungsten catalyst in basic medium [2]. Carbonylation of glycerol with carbon monoxide was found to be catalysed by rhodium and iridium with methyl iodide or hydrogen iodide as co-catalysts. Products of this reaction comprise butyric acid, isobutyric acid, vinyl acetic acid, crotonic acid, allyl acetate, allyl iodide, isopropyl acetate and isopropyl iodide [3]. Carbon monoxide together with water was reported to selectively deoxygenate epoxides into alkenes where gold catalysts play a key role in the reductant activation [4].

One valuable product that can be produced from glycerol is allyl alcohol, a compound which has a significant market value [5] and very broad commercial applications [6]. Allyl alcohol is primarily a chemical intermediate, used in the synthesis of compounds such as epichlorohydrin, 1,4-butanediol, allyl diglycol carbonate, among others, which are processed further into epoxy resins, polymers and screens, respectively, as final applications [6]. Allyl alcohol is also a precursor of final products in the pharmaceutical and cosmetic industries. As reported by our group and others [7-9], the conversion of glycerol to allyl alcohol can be achieved over a number of iron-based catalysts. Based simply on stoichiometric analyses, a reducing agent is necessary for the formation of allyl alcohol from glycerol. Classical reducing agents such as $LiAlH_4$ were used in the synthesis of allylic alcohols from esters [10].

Ammonia is a very well-known sacrificial reductant industrially used since the 1970's in the selective catalytic reduction (SCR) of nitrogen oxides [11]. The use of ammonia is not uncommon in glycerol conversion, a variety of reactions have been documented. For example ammonia is utilised in the ammoxidation of glycerol into acrylonitrile, which occurs over alumina supported Sb, V and Nb catalysts [12] or on V-Sb mixed oxides with hydrogen peroxide [13]. As well as in the synthesis of propionitrile over an iron on alumina catalyst doped with potassium [14]. Other reactions are the hydrogenating amination of glycerol using hydrogen [15] and the reductive amination of the glycerol oxidation products (2,3-dihydroxypropanoic acid or dihydroxyacetone) that produces (±)-2-amino-3-hydroxypropanoic acid [16]. In this contribution we report for the first time the role of ammonia enhancing the rate of formation of allyl alcohol from glycerol.

Oxalic acid, another reductant, undergoes decomposition at approximately 160 °C resulting in the formation of formic acid and carbon dioxide. At higher temperatures carbon monoxide and water are also formed [17]. Kinetic studies of the reaction between glycerol and oxalic acid conducted at low temperatures (40-160 °C) concluded that in the presence of glycerol both decarboxylation and esterification of oxalic acid take place [18-20]. Methods for the synthesis of allyl alcohol from glycerol and oxalic acid at a laboratory scale have been noted in the literature for a hundred years [21-25]. We have established a heterogeneously catalysed process for the direct and continuous production of allyl alcohol based on those studies. Our focus is to optimise some of the engineering aspects of the process aiming at its potential scale up due to the commercial importance of the reaction.

It is well known that due to the its propensity to lose both hydrogens and form carbon dioxide, formic acid has been widely used as a reducing agent [26]. This is not the only decomposition reaction formic acid can undergo, over metal catalysts and at high temperatures it can form water and carbon monoxide [26]. The auto-reduction of formic acid produces formaldehyde which is unstable at high temperatures, and decomposes into carbon monoxide and hydrogen [27]. We argue in this communication that the *in situ* formation of reducing species from formic acid has a significant influence on the yield of allyl alcohol from glycerol through a reductive mechanism.

The reaction of glycerol and formic acid yielding allyl alcohol in a batch reactor was initially reported in 1921 [24], while a few years ago the reaction was carried out in the liquid phase in a semi-batch reactor [28]. Additional experiments were conducted very recently over a potassium supported zirconia-iron oxide catalyst [9]. As a result of these studies, different mechanisms for allyl alcohol formation from glycerol and formic acid were developed. Konaka et al. attributed the increased yield of alcohol to the transfer of hydrogen atoms resulting from the formic acid decomposition [9], whereas Arceo et al. found that formic acid was not acting as a hydride donor [28]. Batch or semi-batch reactors represent most common configurations for reported reactions of glycerol with either oxalic or formic acids [23, 28]. In the same studies, the temperature range (225 - 240 °C) seems to be critical for the selective formation of allyl alcohol [23, 28]. We have found that, it is possible to successfully produce the alcohol in a plug flow reactor from glycerol in the gas phase over an alumina-supported iron catalyst at 340 °C through a reductive mechanism.

The intention of this work is to communicate the development of a continuous process for enhancing the rate of formation of allyl alcohol from glycerol in the presence of formic and oxalic acids and to introduce the use of more practical and inexpensive reductants (i.e. ammonia and ammonium hydroxide (table S1 of the ESI)). Operation at conditions differing from those previously reported [23, 28] (atmospheric pressure and high temperatures in the current experiments) promote not only the dehydration of glycerol but also the decomposition of the additives into other readily available reductants. This suggests the formation of allyl alcohol takes place through a reductive mechanism following single dehydration of the glycerol molecule.

Experimental

An iron on alumina catalyst was prepared by modifying a recently developed non-aqueous impregnation method [7]. Using $Fe(NO_3)_3 \cdot 9H_2O$ (98% Sigma Aldrich) as source of iron, a solution in methanol was prepared. Excess $CaSO_4 \cdot 2H_2O$ (99% Sigma Aldrich) previously dried was used to pre-treat the iron solution. Alumina spheres (Sasol 1,8/210 (dehydrated)) were added to the methanol solution following filtration. The solvent was evaporated and the catalyst dried and then calcined in air with a heating rate of 1 °C min^{-1} for 4 hours at 400 °C. Modifications to the method described in [7] aimed at minimising the water content and accounted for methanol impurities.

The experimental setup was designed and constructed using tubing and fittings purchased from Swagelok. The vertical reactor consists of a stainless steel 1.9 cm O.D. x 60 cm tube fitted with an internal stainless steel 1.3 cm O.D. x 26 cm tube as a catalyst support. Preliminary tests revealed that there was no catalytic effect of the stainless steel tube. A quartz fritted disk (3 mm thick, pore sizes: 90–150 µm) purchased from Technical Glass Products, INC. was placed on top of the 1.3 cm tube (figure 1). The catalyst was loaded into the reactor tube, being retained in place by both the catalyst support and the quartz frit. Other details of the experimental setup have been provided elsewhere [7]. Catalytic tests were conducted at atmospheric pressure and at 340 °C using nitrogen as carrier gas. For each set of experiments, one additive was incorporated as a component of an aqueous solution consisting of glycerol (Merck AR grade). Glycerol concentration was constant at 35 wt %. The following additives were used: ammonia gas 99.5% from Coregas, ammonium hydroxide 28.0-30.0% ACS reagent NH_3 basis from Sigma Aldrich, formic acid 99.0% from Univar (Ajax finechem), oxalic acid dihydrate 99.0% from Sigma Aldrich, acetic acid glacial from Merck and propanoic acid 99.5% from Unilab. Additional tests were carried out using hydroxyacetone 90.0% (Sigma Aldrich). Reagents were used without further purification.

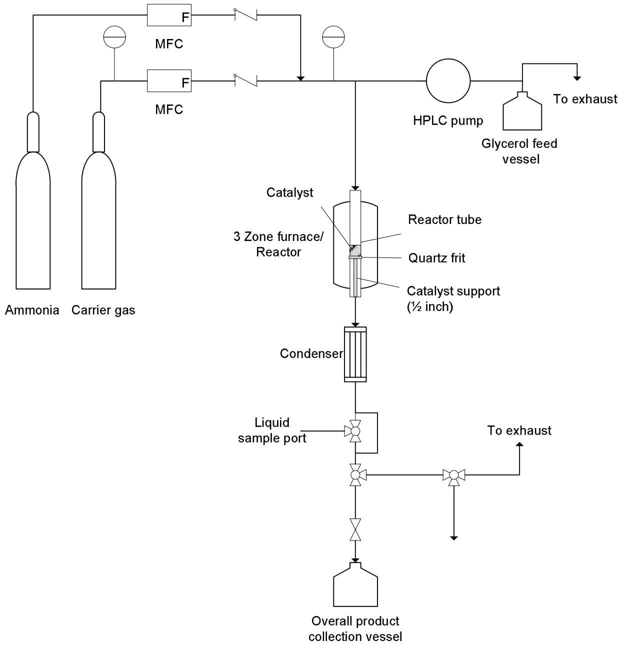

Figure 1. Experimental setup for the reaction of glycerol and ammonia over the alumina supported iron catalyst.

Liquid phase product analysis was carried out by gas chromatography following sample preparation in methanol adding cyclohexanone 99.8% (Sigma Aldrich) as internal standard. An Agilent 6890 Series GC System equipped with an Agilent 5973N Mass Selective Detector (MS) and a Restek Rtx-200 MS column (30 m × 0.25 mm ID × 0.5 µm film thickness) was employed for identification. A HP 5890A model GC, equipped with a flame ionization detector (FID) and a Restek Stabilwax column (30 m × 0.32 mm ID × 1 µm film thickness) was used for quantification of identified species. Details on GC-FID analyses are listed in table 1.

Organic acids were analysed by Ion Chromatography (IC) using a Suppressed Conductivity Detector on a Dionex DX-100 equipped with an Ionpac CS12 analytical column. For the gas phase an IR Prestige 21 Shimadzu FTIR QP 5000 apparatus in conjunction with QASoft software were employed for identification. A Varian 490-GC micro gas chromatograph was used for quantification.

Table 1. Variables for GC-FID analyses

Split ratio	100:1
Injector temperature	300 °C
Detector temperature	320 °C
Oven initial temperature	35 °C
Oven final temperature	200 °C

Results and discussion

Effect of ammonia/ammonium hydroxide addition on glycerol conversion

An initial test in the absence of additives with a solution of 35 wt % glycerol in water and nitrogen as carrier gas over an alumina-supported iron catalyst was used as control experiment. X-ray photoelectron spectroscopy analyses confirmed the presence of ferric ions in the synthesised iron catalyst [7]. This was in agreement with the X-ray diffraction analysis, which revealed a haematite structure [7]. Inductively coupled plasma spectroscopy was used to assess the efficacy of the non-aqueous impregnation of the support which resulted in a catalyst with an iron content of approximately 14 wt %. Based on these characterisation techniques the chemical formula of the catalyst was determined as γ-$Al_2O_3/(Fe_2O_3)_{0.16}$.

The products of glycerol conversion over the iron catalyst in the absence of additives have been listed in table 2. With these species, 55% of the carbon balance was accounted for. Similar results, when estimating the carbon balan, were obtained in the work of Liu et al. [8], that reported a procedure which assigns (in the absence of calibration data) a relative response factor of 1 to every species detected by GC-MS. For the current reaction, the sum of the areas of identified and unidentified peaks to the area of the peak corresponding to glycerol in the feed were compared. This rough approximation of the carbon balance (assumption of the same FID response for reactants and products) was found to be 90%.

Table 2. Product distribution for glycerol conversion over the alumina-supported iron catalyst, carbon yield basis

Species	Yield (%)
Allyl alcohol	8.5
Acrolein	2.5
Hydroxyacetone	7.8
Acetaldehyde	6.9
Acetic acid	5.0
Propanoic acid	6.7
Carbon dioxide	3.3
Carbon monoxide	0.9
Acrolein (gas phase)	5.2
Acetaldehyde (gas phase)	5.0
Unconverted glycerol	3.0
Sum of all unknown products [a]	36.4

[a] Determined as described by Liu et. al. [8]

Experiments were conducted to study the effect of ammonia on glycerol conversion. The reactant gas (3% ammonia in nitrogen balance) was fed under the same conditions for a molar ratio additive relative to glycerol equal to 0.14:1. In presence of ammonia, the rate of formation of allyl alcohol increased by 20% (figure 2.a.). The use of ammonium hydroxide with the same molar ratio as for NH_3 (0.14:1, 4.9 wt % ammonium hydroxide and 35 wt % glycerol in water) did not affect the rate of formation of allyl alcohol.

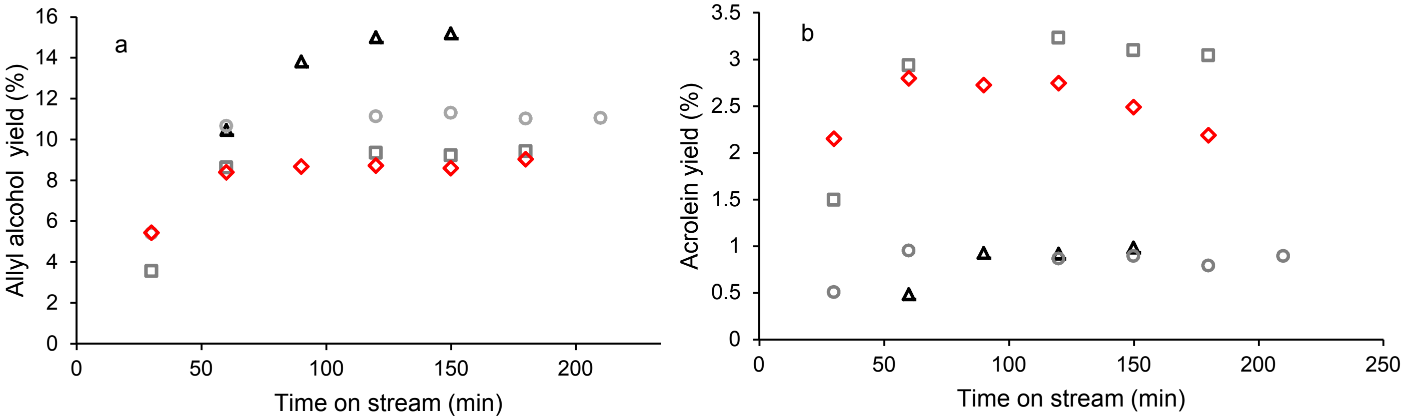

Fig. 2.a Effect of ammonia and ammonium hydroxide addition on allyl alcohol yield as a function of time on stream over the iron on alumina catalyst. b Effect of ammonia and ammonium hydroxide addition on acrolein yield as a function of time on stream over the iron on alumina catalyst. (◇) No additives, (□) ammonium hydroxide: additive/glycerol ratio = 0.14:1, (△) ammonium hydroxide: additive/glycerol ratio = 0.75:1, (○) ammonia: additive/glycerol ratio = 0.14:1. Temperature: 340 °C. GHSV: 1,190 h^{-1}.

A dependency of product yield on the concentration of additive has been observed, as the yield of allyl alcohol increased by 78% at 150 min of time on stream for molar ratios ammonium hydroxide to glycerol as high as 0.75:1. Ammonia concentration has been found to influence product distribution when converting diols and polyols as reviewed by Fischer *et al.*[29]. While cyclic products are favoured at low molar ratios, high concentration has been associated with catalyst deactivation [29]. The presence of the additive at a reductant/glycerol ratio of 0.75:1 was detrimental to the rate of formation of acrolein, ethanal, hydroxyacetone, acetic and propanoic acid (table 3). Similar concentrations of these species were found when co-feeding ammonia at a lower molar ratio. Reactions of polyols and ammonia often involve an initial dehydration step. For example, over solid acidic catalysts, the amination of ethylene glycol and 1,4-butanediol initially results in the formation of an olefin or an ether, both precursors of the amines [29]. Moreover for the conversion of glycerol into acrylonitrile an initial dehydration of the glycerol feed followed by nitrogen insertion was proposed [12].

Table 3. Effect of different sacrificial reductants/glycerol co-feeding ratios on liquid phase product distribution of glycerol conversion over the Fe/alumina catalyst

Additive	Ammonia	Ammonium hydroxide	
Molar ratio additive/glycerol	0.14:1	0.14:1	0.75:1
Allyl alcohol yield (%)	11.3	8.0	15.1
Acrolein selectivity (%)	0.82	2.8	0.9
Ethanal selectivity (%)	3.5	7.8	2.5
Hydroxyacetone selectivity (%)	2.3	4.5	2.3
Acetic acid (%)	3.5	4.8	2.8
Propanoic acid (%)	5.2	7.2	4.9
Conversion (%)	98.5	99.1	99.7

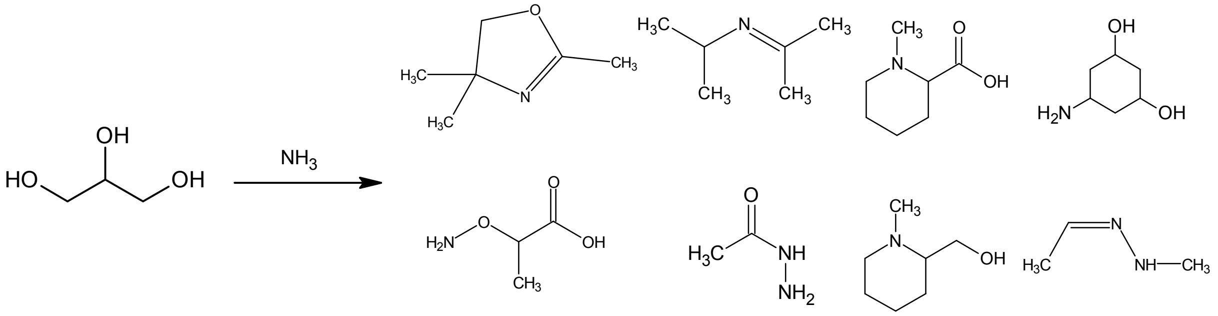

Fig. 3 Scheme for the reaction of glycerol and ammonia

Since at high temperatures one expects the dehydration of glycerol [30], this possibility cannot be ruled out under our reactions conditions. Experiments that enhanced the yield of allyl alcohol also generated lower concentration of acrolein (figures 2.a and 2.b). The dehydration of glycerol into acrolein followed by the hydrogenation of the aldehyde in the presence of glycerol or other alcohols has been previously reported [8]. The mechanism through which the use of ammonia enhances the yield of allyl alcohol is not yet clear and studies are currently being undertaken in our laboratory to examine this phenomenon. Nevertheless we hypothesise that, following glycerol dehydration, acrolein could have been hydrogenated due to the reducing character of ammonia.

The reaction of ammonia with glycerol also resulted in the formation of 2,4-dimethyl-2-oxazoline-4-methanol, 2-(aminooxy)propanoic acid; 2-propanamine, N-(1-methylethylidene); acetaldehyde, methylhydrazone and acetic acid, hydrazide (figure 3), which is consistent with the common products (imines and enamines) reported in the amination of diols and polyols [29]. Derivatives of piperazine have been formed in the hydrogenating amination of glycerol [15]. Even though hydrogen was not available in our experiments, species such as 1-methyl-2-piperidinemethanol and 1-methylpyrrolidine-2-carboxylic acid were identified in the liquid phase. Moreover 3,5-dihydroxycyclohexanamine was produced over the alumina-supported iron catalyst. As reported in the literature, zeolites are known to prevent the formation of cyclic amines [29].

Effect of oxalic acid addition on glycerol conversion

Studies were conducted under standard conditions, varying the composition of the reactant mixture (solution of 7 wt % oxalic acid and 35 wt % glycerol in water). The addition of organic acid effectively doubled the yield of allyl alcohol, as shown in figure 5.a. This result corresponds with a higher yield of carbon dioxide (8.3%) compared with 3.3% obtained in experiments conducted in the absence of additives over the same catalyst. An increase in the average allyl alcohol to hydroxyacetone yield ratio from 1.5 to 4.8 was observed in the presence of the additive. With oxalic acid, acrolein was also produced at an increased rate (figure 5.b.) as previously reported [24, 25]. These studies ([24, 25]) and others ([21-23]) are uncatalysed reactions. Table 4 summarises a comparison of the current experimental conditions to the work of Coffey and Ward [23]. The use of the iron catalyst reduced by 74 % the required amount of oxalic acid respect to the uncatalysed process.

Table 4. Operating conditions for the reaction of glycerol and oxalic acid

	Coffey and Ward [23]	This work
Reactor configuration	Batch	Plug flow reactor
Temperature (°C)	240	340
Catalyst	-	ɣ-alumina/Fe
Mass of glycerol (g)	400	35.6
Mass of oxalic acid (g)	275	7.1
Mass of allyl alcohol produced (g)	40	3.9
Molar ratio glycerol/oxalic acid	0.70:1	0.14:1
Mass ratio allyl alcohol/oxalic acid	0.1	0.1
Allyl alcohol yield (%)	15.9	17.5

In our experiments with oxalic acid over the alumina-supported iron catalyst, the rate of catalyst deactivation was reduced in comparison with the rate of deactivation of the same catalyst in the absence of additives. While glycerol conversion was found to be 93.9% following three hours time on stream in the absence of additives, with oxalic acid glycerol conversion remained constant at 99.8% (figure 5.c.). Oxalic acid could not be detected using GC-FID, nevertheless, complete conversion was confirmed through liquid sample analyses by ion chromatography.

Under the same conditions, a 35 wt % glycerol solution in water in the absence of additives was examined and subsequently a 7 wt % oxalic acid, 35 wt % glycerol solution in water was used. The substitution of the standard feed was carried out once the yield of allyl alcohol reached a constant value (following 200 minutes of time on stream). An enhancement of approximately 60% in the yield of allyl alcohol was observed at the end of the experiment (figure 6) despite the expected influence of catalyst deactivation following three hours of time on stream. Differences with the results presented in figure 5.a. were attributed to the pre-coking of the catalyst. The addition of oxalic acid has a deleterious influence on the yield of hydroxyacetone, which decreased from 7.7% (reached at 180 minutes of time on stream) to 6.8% (100 minutes after the addition of oxalic acid to the feed). Relatively stable conversion levels were observed following the alteration of the feed composition in contrast to a trend of decreased conversion from 98 to 93% in the first three hours of the test (figure 6). In the gas phase, increased quantities of carbon dioxide concurred following the introduction of the additive.

For glycerol conversion in the absence of additives over the iron catalyst, a positive correlation between the rate of formation of allyl alcohol and hydroxyacetone were observed. This suggests that iron was active for the formation of both species. Since the addition of oxalic acid significantly increases the selectivity ratio of allyl alcohol/hydroxyacetone, when compared with the same ratio in the absence of additives (figure 4), studies were conducted to rule out the possibility of consecutive reactions.

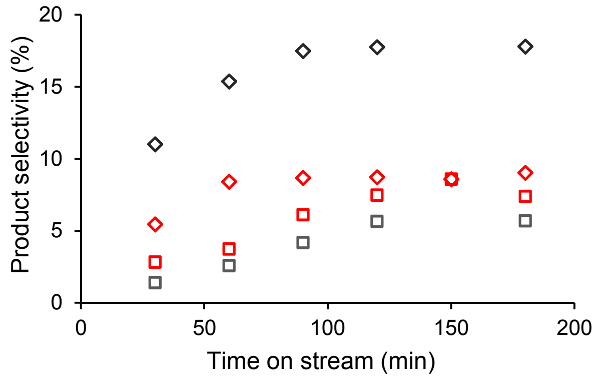

Figure 4. Selectivity towards allyl alcohol and hydroxyacetone in the absence of additives and co-feeding oxalic acid as a function of time on stream over the iron on alumina catalyst. No additives: (◇) Allyl alcohol, (□) hydroxyacetone. Oxalic acid: (◇) Allyl alcohol, (□) hydroxyacetone. Oxalic acid/glycerol ratio: 0.14:1. Temperature: 340 °C. Reactants: 7 wt % Oxalic acid, 35 wt % Glycerol. GHSV: 1,190 h^{-1}.

A solution of 10 wt % hydroxyacetone and 10 wt % oxalic acid in water was mixed with nitrogen gas at 340 ° C and reacted over the catalysts under standard reaction conditions. The major products formed (acrolein and acetaldehyde) appear to be the result of the carbon-carbon cleavage in hydroxyacetone as previously reported [31]. Low selectivity to allyl alcohol was obtained, excluding the likelihood of hydroxyacetone being an intermediate for allyl alcohol formation in the absence of glycerol (table 5).

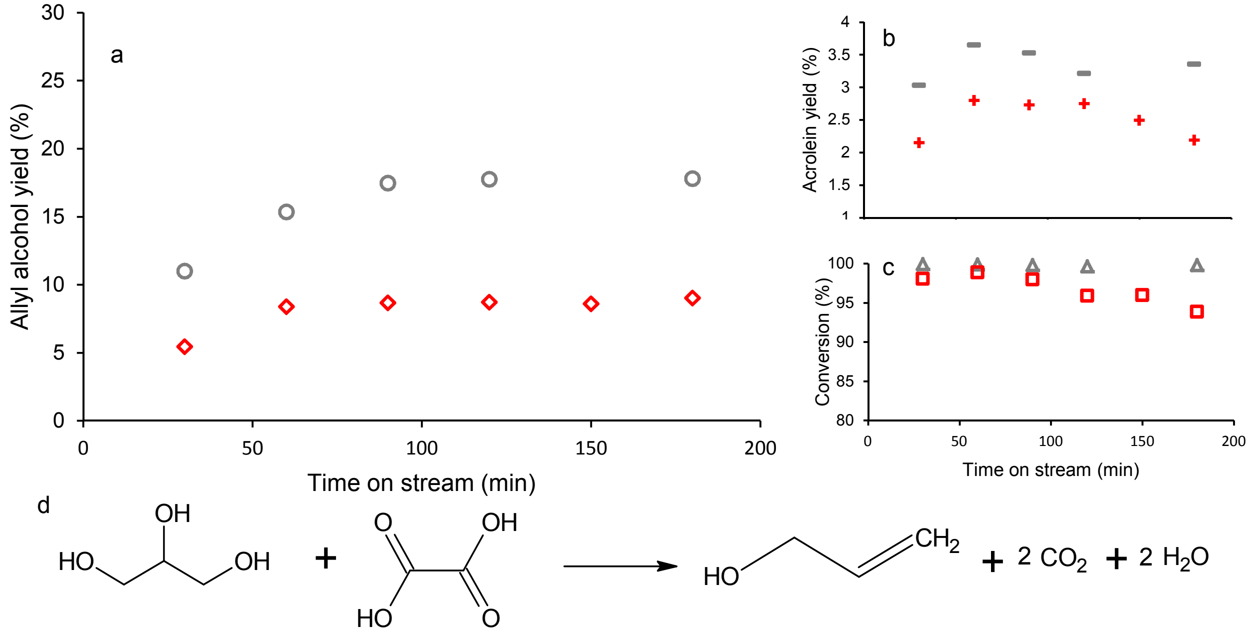

Fig. 5.a Effect of oxalic acid addition on allyl alcohol yield as a function of time on stream over iron supported on alumina catalysts. (◇) No additives, (○) oxalic acid. b Effect of oxalic acid addition on acrolein yield as a function of time on stream over iron supported on alumina catalysts. (✚) No additives, (–) oxalic acid. c Effect of oxalic acid addition on glycerol conversion as a function of time on stream. (□) no additives, (△) oxalic acid over iron supported on alumina catalysts. Oxalic acid/glycerol ratio: 0.14:1. Temperature: 340 °C. Reactants: 7 wt % Oxalic acid, 35 wt % Glycerol. GHSV: 1,190 h^{-1}. d Balanced equation for the reaction of glycerol and oxalic acid.

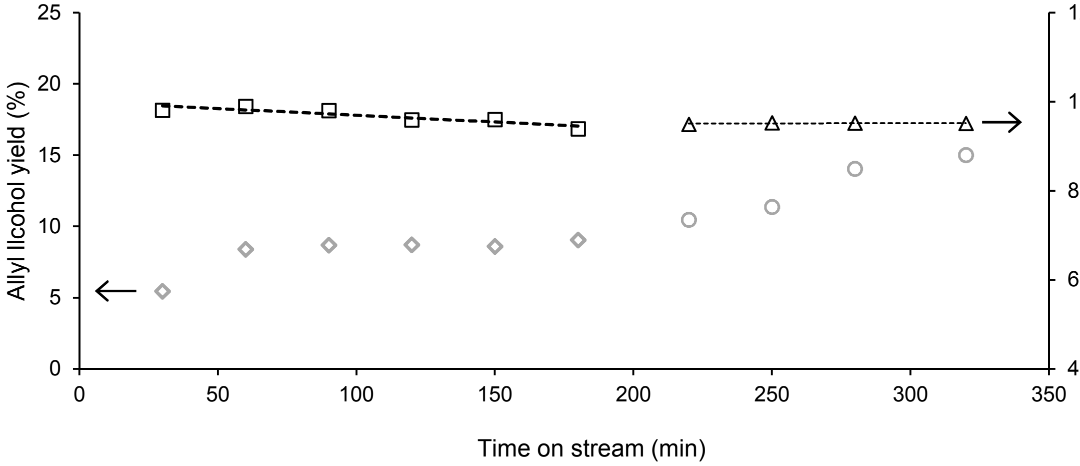

Fig. 6 Allyl alcohol yield and glycerol conversion over the iron on alumina catalyst in composition variation experiments. (◇,□) No additives, (○,△) oxalic acid. Oxalic acid/glycerol ratio: 0.14:1. Temperature: 340 °C. Reactants: 7 wt % Oxalic acid, 35 wt % glycerol. GHSV: 1,190 h^{-1}.

Table 5. Liquid phase product distribution over the iron on alumina catalyst. Reactants: 10 wt % hydroxyacetone and 10 wt % oxalic acid. GHSV: 6848.96 h^{-1}.

Time on stream	Allyl alcohol yield (%)	Acrolein selectivity (%)	Acetaldehyde selectivity (%)	Glycerol selectivity (%)	Hydroxyacetone conversion (%)
180 min	4.2	8.3	17.6	0.0	97.6
210 min	4.8	8.6	16.6	0.0	96.4

Previous studies on the reaction of glycerol and oxalic acid suggested that allyl alcohol was formed by the decomposition of 5-(hydroxymethyl)-1,4-dioxane-2,3-dione, with carbon dioxide as a major by-product [22]. In the same work, allyl formate was either produced by the reaction of formic acid 2,3-dihydroxypropyl ester with oxalic acid or in aqueous media when an acid oxalate was formed [22]. However, allyl formate was not detected in the current experiments even though 58 wt % water was present in the reactant mixture. Free formic acid (observed in the same reaction [23]) was also not identified in the product. These results contrast with the pathway proposed by Chattaway at least under the reaction conditions used in the present study (higher temperatures and pressures compared to the work of Chattaway [22]). Higher temperatures, for example, favour the dehydration of glycerol [30] which would prevent the formation of the dione product (5-(hydroxymethyl)-1,4- dioxane-2,3-dione). Catalyst acidity also promotes the dehydration of glycerol [32, 33]. As determined by the position in the carbon chain where the dehydration reaction occurs, formaldehyde/acetaldehyde, hydroxyacetone and acrolein are formed [30].

In the presence of oxalic acid, formaldehyde, acetaldehyde, ethyl acetate and acetic acid were detected in the liquid phase product stream. These products are a result of a carbon-carbon cleavage in the glycerol molecule and suggest 1,3-dehydration of glycerol. Due to the relatively low temperature of the reaction, dehydration of glycerol has not been considered in the mechanism reported by other authors when oxalic acid is present. In addition to 1,3 dehydration, 1,2 dehydration, either with central or terminal hydroxyl groups, is expected to occur at 340 °C over an iron catalyst [8]. The 1,2 dehydration with terminal hydroxyl yields 2,3-dihydroxypropene, which can tautomerise to form hydroxyacetone [30, 34]. However, in the presence of oxalic acid, a reduced rate in the formation of hydroxyacetone was observed, which is coincident with an increased yield of allyl alcohol. As discussed previously, oxalic acid readily decomposes into carbon dioxide and formic acid which then decomposes to carbon monoxide and water. As shown with experiments conducted with hydroxyacetone, the presence of glycerol seems to be crucial for carbon monoxide to induce the elimination of an oxygen atom in the hydroxyacetone molecule. Deoxygenation reactions involving $Re_2(CO)_{10}$ and $BrRe(CO)_5$ catalysts require secondary alcohols as solvents or/and reductants [35]. Another possibility is the abstraction of an oxygen atom from 2,3-dihydroxypropene preventing its tautomerisation as reported before over iron catalysts [36]. Evidence of these reduction reactions can be found in both the decrease in the yield of hydroxyacetone and the increase in the yield of carbon dioxide. The reductions require redox active sites such as highly dispersed iron species. A similar general reaction scheme has been suggested by Shiramizu et al. using 3-octanol as reducing agent [37].

Effect of formic acid addition on glycerol conversion

In a similar fashion to oxalic acid, the addition of excess formic acid (formic acid to glycerol molar ratio 1.90:1) doubled the yield of allyl alcohol and increased the yield of carbon dioxide up to 16.8%. Complete conversion of the added formic acid was observed.

However, the use of formic acid in the same molar ratio as for oxalic acid (formic acid to glycerol molar ratio 1:0.14) had no quantifiable effect on the yield of allyl alcohol (figure 7) or carbon dioxide. While selectivity towards hydroxyacetone was reduced at high additive/glycerol ratios compared to the absence of additives, no effect on the yield of hydroxyacetone was observed at low concentrations of formic acid (table 6). Differences in the amount of oxalic and formic acid required to produce similar effects on the yield of allyl alcohol were not stoichiometric. Formic acid (from oxalic acid) increases the rate of decomposition of oxalic acid [18] which may have favoured the formation of allyl alcohol respect to a slower decomposition rate of the added formic acid. Moreover products such as cyclohexane, 1,1-dimethoxy; cyclohexane, 1-methoxy and 1,1-dimethoxy-cyclopentane were formed in significant quantities in the presence of formic acid but were absent with the use of oxalic acid. The formation of those species at the expense of formic acid was thought to explain the large amount of additive required.

Table 6. Effect of different formic acid/glycerol co-feeding ratios on liquid phase product distribution over the Fe/alumina catalyst

	Formic acid	
Molar ratio additive/glycerol	0.14:1	1.90:1
Allyl alcohol yield (%)	9.5	19.5
Acrolein selectivity (%)	2.7	2.5
Ethanal selectivity (%)	5.2	4.7
Hydroxyacetone selectivity (%)	7.0	5.5
Acetic acid (%)	4.1	4.9
Propanoic acid (%)	5.2	7.4
Conversion (%)	99	97.9

At lower temperatures, an acid-mediated double removal of hydroxyl groups in the glycerol molecule yielding allyl alcohol, has been reported previously [28]. Under the conditions used in the paper (235 °C) the final products were allyl alcohol, carbon dioxide, allyl formate and formic acid [28]. However, in the experiments in the present investigation, the excess formic acid was completely converted and allyl formate was not detected suggesting that the production of allyl alcohol follows a different pathway.

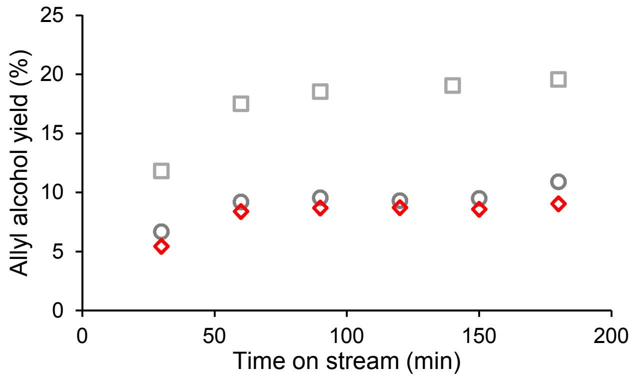

Fig. 7 Effect of oxalic acid and formic acid addition on allyl alcohol yield as a function of time on stream over the iron on alumina catalyst. (◇) No additives, (○) formic acid/glycerol molar ratio: 0.14:1, (□) formic acid/glycerol molar ratio: 2:1. Reactants: 2.53 wt % formic acid, 33.3 wt % formic acid, 35 wt % glycerol, aqueous solution. GHSV: 1 190 h^{-1}.

Equivalent to oxalic acid, changes in product distribution following the addition of formic acid to the feed are suggested to result from a reductive deoxygenation of the intermediate species leading to the formation of hydroxyacetone. This pathway is an alternative to a pathway reported by Arceo et al. and does not contradict their isotopic experiments, but considers both the dehydration of glycerol and the decomposition of formic acid into carbon monoxide, water, hydrogen, and carbon dioxide at the higher reaction temperature.

Effect of other additives on glycerol conversion

As propanoic and acetic acid are produced in the conversion of glycerol to allyl alcohol, their influence on glycerol conversion is of significant interest when considering the viability of product recycle. The molar ratio of both additives to glycerol was approximately 1:1, resulting in aqueous solutions of 22.8 wt % acetic acid and 28.1 wt % propanoic acid in 35 wt % glycerol. In acetic acid/glycerol/water systems, glycerol undergoes acetylation [3] which explains the presence of 1,2,3-propanetriol, 1-acetate in the liquid phase, as confirmed by GC-MS. However the addition of acetic acid did not promote allyl alcohol formation nor did it appear to influence catalyst deactivation (figure 8). These results are in agreement with the work of other authors when introducing acetic acid (20 wt %) to a 30 wt % glycerol solution at 350 °C and atmospheric pressure over an zirconia-iron oxide catalyst [9]. The presence of propanoic acid in the feed did not produce a significant change in the rate of allyl alcohol formation, as shown in figure 8. The observed effect for both acetic and propanoic acid can be explained by the decomposition of carboxylates formed on metal surfaces at the reaction temperature (340 °C). Whereas formate decomposed primarily into a reductive species (carbon monoxide), ketene and acrolein were the main products observed in the decomposition of acetic acid and propionic acid at elevated temperatures [38]. Therefore, a reductive process was not observed with propanoic and acetic acids, in turn providing further evidence for involvement of this route in the conversion of glycerol to allyl alcohol using oxalic and formic acid.

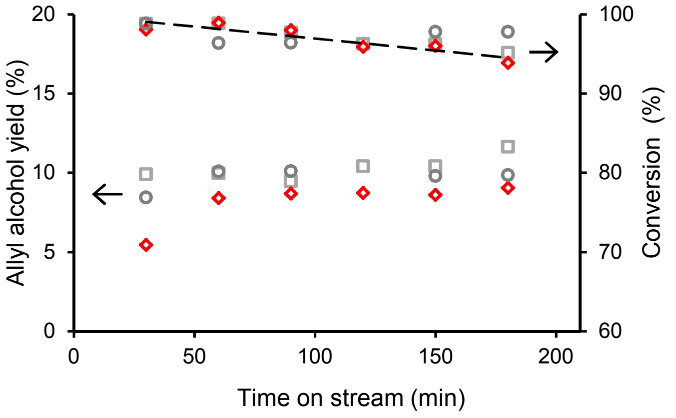

Fig 8 Effect of acetic and propanoic acids addition on glycerol conversion and allyl alcohol yield as a function of time on stream over supported alumina iron catalysts. (◇) No additives, (○) propanoic acid/glycerol molar ratio: 1.14:1, (□) acetic acid/glycerol molar ratio: 1.14:1. Temperature: 340 °C. Reactants: 22.8 wt % acetic acid, 28.1 wt % propanoic acid, 35 wt % glycerol. GHSV: 1,190 h^{-1}.

Conclusions

The effect of additives on the yield of allyl alcohol from glycerol is dependent on the concentration of the reducing agent. While an increase of 100% in the yield of allyl alcohol was obtained with an oxalic acid to glycerol ratio as low as 0.14:1, similar results were observed with a formic acid to glycerol ratio of 1.90:1. Enhancement of allyl alcohol yield concurred with an increase in the rate of formation of carbon dioxide and a decrease in the yield of hydroxyacetone. Both results are evidence of a reductive process where an oxygen atom is removed from the feed to form a reduced species and carbon dioxide.

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Notes

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References

1. D. Taher, M. E. Thibault, D. Di Mondo, M. Jennings and M. Schlaf, *Chemistry – A European Journal*, 2009, **15**, 10132-10143.
2. *United States Pat.*, 1985.
3. T. Coskun, C. M. Conifer, L. C. Stevenson and G. J. P. Britovsek, *Chemistry – A European Journal*, 2013, **19**, 6840-6844.
4. J. Ni, L. He, Y. Liu, Y. Cao, H. He and K. Fan, *ChemComm*, 2011, **47**, 812–814.
5. D. T. Johnson and K. A. Taconi, *Environmental Progress*, 2007, **26**, 338-348.
6. Lyondell, *Data Review and Assessment for Allyl Alcohol*, 2005.
7. G. Sánchez, J. Friggieri, C. Keast, M. Drewery, B. Z. Dlugogorski, E. Kennedy and M. Stockenhuber, *Applied Catalysis B: Environmental*, 2014, **152–153**, 117-128.
8. Y. Liu, H. Tüysüz, C.-J. Jia, M. Schwickardi, R. Rinaldi, A.-H. Lu, W. Schmidt and F. Schüth, *Chemical Communications*, 2010, **46**, 1238-1240.
9. A. Konaka, T. Tago, T. Yoshikawa, A. Nakamura and T. Masuda, *Applied Catalysis B: Environmental*, 2014, **146**, 267-273.
10. X. Wang, X. Li, J. Xue, Y. Zhao and Y. Zhang, *Tetrahedron Letters*, 2009, **50**, 413-415.
11. G. Busca, L. Lietti, G. Ramis and F. Berti, *Applied Catalysis B: Environmental*, 1998, **18**, 1-36.
12. M. Guerrero-Pérez and M. Bañares, *ChemSusChem.*, 2008, **1**, 511-513.
13. V. Calvino-Casilda, M. O. Guerrero-Perez and M. A. Banares, *Green Chemistry*, 2009, **11**, 939-941.
14. Y. Zhang, T. Ma and J. Zhao, *Journal of Catalysis*, 2014, **313**, 92-103.
15. *United States Pat.*, 2010.
16. H. Kimura and K. Tsuto, *J Am Oil Chem Soc*, 1993, **70**, 1027-1030.
17. J. Higgins, X. Zhou, R. Liu and T. T. S. Huang, *The Journal of Physical Chemistry A*, 1997, **101**, 2702-2708.
18. M. A. Haleem and P. E. Yankwich, *The Journal of Physical Chemistry*, 1965, **69**, 1729-1731.
19. I. V. Gruzin, A. F. Alksnis and Y. A. Surna, *Polymer Science U.S.S.R.*, 1975, **17**, 1887-1891.
20. L. W. Clark, *Journal of the American Chemical Society*, 1955, **77**, 6191-6192.
21. F. D. Chattaway, *Journal of the Chemical Society, Transactions*, 1914, **105**, 151-156.
22. F. D. Chattaway, *Journal of the Chemical Society, Transactions*, 1915, **107**, 407-410.
23. S. Coffey and C. F. Ward, *Jounal of the Chemical Society*, 1921, 1301-1306.
24. O. Kamm and C. S. Marvel, *Organic Syntheses*, 1921, **1**, 15.
25. O. Kamm and C. S. Marvel, *Organic Syntheses*, 1941, **1**, 42.
26. H. W. Gibson, *Chemical Reviews*, 1969, **69**, 673-692.
27. M. H. Haider, N. F. Dummer, D. Zhang, P. Miedziak, T. E. Davies, S. H. Taylor, D. J. Willock, D. W. Knight, D. Chadwick and G. J. Hutchings, *Journal of Catalysis*, 2012, **286**, 206-213.
28. E. Arceo, P. Marsden, R. G. Bergman and J. A. Ellman, *Chemical Communications*, 2009, 3357-3359.
29. A. Fischer, T. Mallat and A. Baiker, *Catalysis Today*, 1997, **37**, 167-189.
30. M. R. Nimlos, S. J. Blanksby, X. Qian, M. E. Himmel and D. K. Johnson, *The Journal of Physical Chemistry A*, 2006, **110**, 6145-6156.
31. W. Suprun, M. Lutecki, T. Haber and H. Papp, *Journal of Molecular Catalysis A: Chemical*, 2009, **309**, 71-78.
32. B. Katryniok, S. Paul, V. Belliere-Baca, P. Rey and F. Dumeignil, *Green Chemistry*, 2010, **12**, 2079-2098.
33. K. Kongpatpanich, T. Nanok, B. Boekfa, M. Probst and J. Limtrakul, *Physical Chemistry Chemical Physics*, 2011, **13**, 6462-6470.
34. Ü. Arda, RWTH Aachen University, 2009.
35. E. Arceo, J. A. Ellman and R. G. Bergman, *Journal of the American Chemical Society*, 2010, **132**, 11408-11409.
36. L. S. Glebov, A. I. Mikaya, A. E. Yatsenko, V. G. Zaikin, G. A. Kliger and S. M. Loktev, *Tetrahedron Letters*, 1985, **26**, 3373-3376.
37. M. Shiramizu and F. D. Toste, *Angewandte Chemie International Edition*, 2012, **51**, 8082-8086.
38. K. S. K. M. A. Barteau, *Langmuir*, 1988, 945-953.