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Zeolite-supported iron catalysts for allyl alcohol synthesis from glycerol

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a Priority Research Centre for Energy (PRCfE), The University of Newcastle, Callaghan, NSW 2308, Australia b School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia. *Corresponding author: michael.stockenhuber@newcastle.edu.au Dochead : Research paper Highlights Increased iron loading on MFI improved allyl alcohol yield; Alkaline preparation conditions engendered the zeolite with mesoporosity; Rubidium deposition enhanced allyl alcohol yield and decreased acrolein yield; Alkali post synthesis modification reduced the concentration of acid sites.

Abstract

Under most reaction conditions studied, acrolein is reported as the primary product in the conversion of glycerol over zeolites. In such processes, acrolein forms at relatively high yields, with negligible allyl alcohol selectivity. In this contribution, we report the development of ZSM5-supported iron catalysts, modified by rubidium deposition, as stable materials for production of allyl alcohol from glycerol. Our results demonstrate a reduced rate of formation of acrolein over modified catalysts. Both unmodified and modified catalysts were analysed by inductively coupled plasma optical emission spectrometry, nitrogen adsorption, scanning electron microscope, X-ray diffraction, ammonia temperature programmed desorption, X-ray photoelectron spectroscopy and ultraviolet-visible spectroscopy. These techniques revealed that differences in product distribution and catalyst performance are due to the combined effects of iron loading, catalyst acidity and changes in the porosity of the catalyst.

Keywords: Allyl Alcohol; glycerol conversion; transition metal zeolites;

acrolein; acidity; basicity

Graphical abstract



1. Introduction

The size and shape of zeolites pores are known to influence the product distribution in reactions such as the conversion of glucose to aromatics or the synthesis of glycerol monolaurate from glycerol and lauric acid [1, 2]. For "bulky" molecules, zeolitic channels control the rate of internal diffusion of reactants within the structure (based on steric effects), and limit product formation, usually as a function of their effective kinetic diameters. Pore size and shape are also known to favour certain transition states affecting, consequently, final product distribution [2]. In the conversion of glycerol to allyl alcohol, acrolein is one of the primary (and usually undesirable) by-products. When considering the influence of shape selectivity on glycerol conversion, a cursory analysis might suggest these factors would be irrelevant for species such as allyl alcohol and acrolein given that, in addition to being molecules of similar composition and conformation, they both have small molecular dimensions. However when converting glycerol over a variety of catalysts, oligomers of glycerol [3] as well as cyclic compounds and dimers are present as products from the reaction of glycerol, glycerol/acrolein and glycerol/acetaldehyde [4]. The presence of such compounds positions zeolites as potential catalysts for allyl alcohol production from glycerol, since the presence of well defined micropores can reduce (due to shape selectivity) the formation of those "bulky" molecules which appear to be involved with, and indeed facilitate, catalyst deactivation. Thus, zeolites have a major potential advantage over other commonly used supports (most notably alumina [5] and zirconia [6]). To the best of our knowledge, investigations aimed at the use of zeolites in the conversion of glycerol to allyl alcohol have not been reported.

The acid and base properties of catalysts are important features to consider in the conversion of glycerol to allyl alcohol. Catalyst acidity has been correlated with acrolein formation, while basicity was shown to drive the reaction towards allyl alcohol formation [5, 7]. Zeolite acidity can be typically reduced by dealumination [8, 9], modification with phosphorus [10], alkali treatment [11], alkali metal exchange [12] amongst other methods. In the present research, we have modified the acidity of an iron-exchanged zeolite via rubidium deposition, aiming to enhance the rate of formation of allyl alcohol from glycerol.

In most applications of zeolites to glycerol conversion, dehydration is found to occur. Consequently, a high selectivity towards acrolein is observed, whereas the rate of formation of allyl alcohol is negligible. The presence of C=C and C-OH groups in allyl alcohol promotes the occurrence of additions, substitutions, decompositions, oxidations, re-arrangements and polymerisation reactions which make of this commodity an important chemical intermediate [13]. Allyl alcohol derivatives are present in perfume, pharmaceutical and food formulations. In the chemical industry, allyl alcohol is required for the production of allyl diglycol carbonate, allyl glycidyl ether, allyl methacrylate, diallyl phthalate, 1,4-butanediol, 2-methyl-1,3-propanediol, poly(styrene-allyl alcohol), etc., which are used as lens, coupling agents, plasticisers, crosslinking agents and coating additives [14, 15]. This broad range of applications creates a market requirement for allyl alcohol which has a higher commercial value than other value-added glycerol products such as acrolein [16].

Current industrial processes for the production of allyl alcohol are fossil fuel-based routes that involve converting propylene. The oxidation of propylene to acrolein, followed by subsequent reduction is one example. A second approach involves propylene oxide isomerisation over a lithium phosphate catalyst at 300 °C with subsequent purification. Moreover, when allyl chloride undergoes alkaline hydrolysis, allyl alcohol is synthesised in yields of 92 - 93 %. Likewise, allyl alcohol can also be produced by further processing the liquid effluents of the

palladium catalysed acetoxylation of propylene [17]. Propylene is conventionally obtained from refining processes or by cracking of heavy liquids and its supply has historically satisfied the global market. However, recently in the US, the production of propylene has decreased due to the wide use of shale gas and the simultaneous production of ethane, propane and butane that are cracked instead of heavy hydrocarbons. This together with liquid petroleum gas (LPG) cracking in Europe has promoted an increase in global propylene prices [18] since propylene is highly demanded in the manufacture of several chemicals [19]. Considering that conventional methods for allyl alcohol production use fossil fuel-based propylene as feedstock and that besides propylene high prices, environmental and fuel security aspects are important limitations of these processes, investigating bio-routes for the synthesis of allyl alcohol have recently gained significant interest in the industrial context. In a continuous flow system, the active phases for the selective formation of allyl alcohol previously reported are iron [5, 7, 20] and MoO₃ - WO₃ [21]. In this contribution, we report, for the first time, the synthesis and modification (in terms of mesoporosity and acidity) of stable exchanged iron zeolites for direct conversion of glycerol to allyl alcohol in a flow reactor configuration under relatively mild reaction conditions.

2. Experimental

2.1 Catalyst preparation

Zeolites (NH₄-ZSM5 SiO₂/Al₂O₃ = 30) were obtained from Zeolyst and calcined for 5 hours in air flow at a rate of 5 °C min⁻¹ in order to generate the proton form of the zeolite. Iron was deposited on the zeolite using various methods. Approximately 10 g of the support and 3.97 g of 98 % Fe(NO₃)₃·9H₂O (Sigma Aldrich) crystals were mixed and then milled using a mortar and pestle as part of a standard solid state ion exchange (SSE). A second catalyst was synthetised by non-aqueous ion exchange (non-aqueous IE), where 3.97 g of the iron salt was

dissolved in methanol and the solution dried using CaSO₄ (previously dehydrated at 220 °C for two hours). Following vacuum filtration, 10 g of HZSM-5 was added to the filtrate and continuously stirred overnight. The third catalyst was prepared adopting an alkaline ion exchange method described elsewhere [22]. Approximately 10 g of HZSM-5 was added to an aqueous Fe(NO₃)₃·9H₂O solution (3.97 g of the salt in 100 g of water) and stirred at 50 °C for 12 h. The pH was controlled (pH = 8) by dropwise addition of ammonium hydroxide (28 – 30 wt % NH₃ basis, Sigma Aldrich) as previously reported [23]. The mixture was filtered and the exchange repeated three times. Following preparation, the catalysts were heated at a rate of 5 °C min⁻¹ to 550 °C and calcined for 5 hours in air.

The calcined alkaline ion exchanged catalyst underwent additional treatment using a solution of 0.147 g of rubidium nitrate in 100 mL of water. The treatment consisted in washing the catalyst with the alkali solution, followed by filtration. The filter cake was then dried and calcined on air. All catalysts were sieved between 250 and 600 μ m following calcination.

2.2 Catalyst characterisation

The Fe, Si and Al content of the catalysts as prepared was determined using a Varian Radial 715-ES Inductively Coupled Plasma – Optical Emission Spectrometer with a Sturman-Masters spray chamber, quartz torch and an SPS 3 autosampler. Sample digestion took place in a Milestone Start D microwave digestion system with acids in concentrations detailed elsewhere [24], and thulium was used as internal standard. Surface area measurements were carried out in a Micromeritics Gemini surface area analyser at -196 °C. A degassing step using a Micromeritics Vac Prep 061 sample preparation device proceeded nitrogen adsorption at liquid nitrogen temperature. The *t*-plot and Barrett-Joyner-Halenda (BJH) models were used to estimate micro and mesopore volume, as well as pore size distribution. SEM images were

captured using a Zeiss Sigma VP FESEM with a secondary detector (SE). Simultaneously, elemental analysis was conducted with a Bruker light element SSD Energy-dispersive X-ray spectroscopy (EDS) detector. The crystal structure of fresh and used catalyst was determined by means of a Phillips X'pert Pro diffractometer using Cu Kα radiation. Measurements were conducted in the 2θ range of 5° to 109°. Catalyst acidity was studied by temperature programmed desorption (TPD) of ammonia, in an apparatus described elsewhere [25]. Activation took place at 550 °C under high vacuum which was followed by ammonia adsorption at 150 °C. Desorption data was collected between 30 °C and 550 °C at a heating rate of 5 °C min⁻¹ where the ion current used for analysis was *m/z* = 16. Catalysts were analysed through X-ray photoelectron spectroscopy (XPS) in a Thermo Scientific ESCALAB250Xi instrument with a spot size of 500 µm using a mono-chromated Al K alpha source (energy 1486.68 eV). UV-visible spectra were recorded by means of a Cary 6000i UV-Vis-NIR spectrophotometer (Varian) coupled with a Praying Mantis accessory. Kubelka-Munk function conversions were applied to all the measurements. Total organic carbon determination in used catalysts samples was conducted in a LECO TruSpec CN Analyser.

2.3 Catalytic measurements

For each experiment, 5 g of catalyst was charged into the reactor equipped with a catalyst support (stainless steel) and a fritted disk (quartz). Dimensions are reported in previously published work [5]. Experiments were conducted at atmospheric pressure and 340 °C in continuous operation with nitrogen as carrier gas and a constant supply of a 35 wt % glycerol aqueous solution. Details on mass flow controllers, furnaces and pumps are described elsewhere [26]. Sampling took place at hourly intervals, and product analyses were off-line. Liquid samples were collected using a syringe. Methanol was used as solvent for GC-MS analyses, performed in an Agilent 6890 series GC with an Agilent 5973N detector and a Restek

Rtx-200 MS column: 30 m × 0.25 mm ID × 0.5 μ m. Helium was used as carrier gas with a sample injection (1 μ l) split ratio of 10:1 applied for all analyses. Injector and detector were maintained at 220 °C and 285 °C respectively, while the oven initial temperature (45 °C) was held for 5 min, increasing to 115 °C in 15 min and then ramping up to 285 °C at a rate of 10 °C · min⁻¹. Filament and detector were turned off during the elution of the injection solvent (i.e. methanol). For quantification, cyclohexanone was used as internal standard and GC-FID analyses were conducted in a 5890A model GC, fitted with a Restek Stabilwax column: 30 m × 0.32 mm ID × 1 μ m, using air, hydrogen and helium with a split ratio of 100:1. Injector and detector were kept at 300 °C and 320 °C respectively, while an initial temperature of 35 °C was held for 5 min, ramping to 200 °C at a rate of 10 °C · min⁻¹, holding at this temperature for 20 min. Gas samples were collected in a gas bag and analysed using a Varian 490-GC micro gas chromatograph and an IR Prestige 21 Shimadzu FTIR QP 5000 apparatus. IR spectra were processed using QASoft software.

3. Results and discussion

3.1 Catalyst characterisation

The various methods employed to synthesise iron zeolites for glycerol conversion were found to have a significant influence on the eventual iron loading on the zeolite support, as determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Catalysts of low iron content (significantly below the theoretical exchange capacity of H-ZSM5 with silica to alumina ratio equal to 30) were obtained by ion exchange in the methanol procedure as evident from Table 1. Higher iron containing materials were prepared by solid state exchange. Interestingly, using the alkaline solution (NH₄OH in water, pH 8) as a solvent instead of methanol to conduct the ion exchange caused a three-fold increase in the mass of iron present

in the resulting iron-loaded zeolite with respect to the latter catalyst. Iwamoto et al. found that controlling the pH of the solution with NH₄OH, KOH, NaOH, Ca(OH)₂, Mg(OH)₂, Ba(OH)₂ or pyridine resulted in the preparation of over-exchanged zeolites [27]. More recently, Tsikoza et al. synthesised Cu-ZSM5 catalysts, with copper content that exceeded the ion exchange capacity of the zeolite, in aqueous ammonia solutions of a copper salt with pH of approximately 10 [28]. Repeated ion exchange processes have been associated as well to highly exchanged materials [29]. In these preparation methods, the zeolite undergoes ion exchange several times (the catalyst is filtrated following the first ion exchange treatment and the filter cake is placed again in a fresh solution to repeat the exchange) [29]. While an exchange between metal ions and countercations on aluminium sites have been reported to occur at low pH, electrostatic adsorption is suggested to take place at high pH on silanol groups when tetra ammine complexes are formed reported for platinum and cooper [30]. Under our conditions Fe(OH)₃ is likely to form as opposed to the ammine complex, for which such adsorption on silanol groups was not thought to occur.

The alkaline medium in which the ion exchange was conducted promotes partial dissolution of both framework silicon and aluminium, as measured by ICP-OES which revealed a composition of 30.2 wt % silicon and 1.8 wt % aluminium for the alkaline, iron-exchanged catalysts. Similar observations have been reported when desilicating various MFI zeolites with NaOH [31]. Melian et al. desilicated ZSM5 with NaOH to prepare fully exchanged Fe-ZSM5 [32]. When the Si/Al ratio decreases following catalyst treatment as reported elsewhere [32], an increase in the exchange capacity of the material is observed. For the current experiments this is not applicable due to simultaneous reduction of the aluminium content.

The degree of the exchange (given by the molar ratios H/Al and Fe/Al) has been calculated adopting a procedure described elsewhere [33]. Results from ammonia TPD experiments (Figure S1 ESI) were employed to quantify the remaining protons in the catalyst following iron

exchange. It was assumed that high temperature peaks are a measure of the number of residual protons as previously reported [34]. When considering trivalent cations to be exchanged with H-ZSM5 $SiO_2/Al_2O_3 = 30$, the maximum cation to aluminium molar ratio for a full and stoichiometric exchange is equal to 0.33 according to the following reaction,

$$Fe^{+3} + 3[H^+ \cdot AlO_2^-] \rightleftharpoons 3H^+ + Fe^{+3} \cdot 3AlO_2^-$$

The Fe/Al molar ratio calculated (using ICP-OES data) for the higher iron content exchanged ZSM5 was 3.66. However, its H/Al molar ratio was equal to 0.43 which suggests that not all Fe³⁺ cations are truly exchanged and are present as ions or precipitated species. It is worthwhile to mention that dissolution of framework aluminium due to the conditions of the ion exchange have significant influence in the calculated molar ratios.

	Fe content	Langmuir Surface area	Micropore	Mesopore
Catalyst	(wt %)	(m^2/g)	volume	volume
H-ZSM5	0	473.7	0.14	0.04
ZSM5/Fe non-aqueous IE	0.9	487.9	0.13	0.06
ZSM5/Fe SSE	5.4	435.8	0.12	0.05
ZSM5/Fe alkaline IE	13.4	432.7	0.09	0.17

Table 1: Composition and textural properties of fresh catalysts

In general, depositing iron on H-ZSM5 reduces its surface area. However, correlating this with iron loading is not straightforward, as exceeding the exchange capacity of the zeolite has little influence on the surface area of the resultant material and is comparable with the surface area

of the catalyst prepared by solid state exchange (Table 1). As evident by the high nitrogen adsorption at low *P/Po* values, ion exchange is the only method of iron deposition that does not decrease the microporosity of the starting H-ZSM5 (**Error! Reference source not found.**). This was attributable to both low iron content (0.9 wt %) in the prepared catalyst and the nature of the preparation method, where iron deposits preferentially on ion-exchangeable sites of the support (equal in number to the aluminium atoms present in the framework) [35]. For the other catalysts, iron incorporation was thought to cause substantial blocking in micropores, while for the alkaline ion exchanged catalyst, desilication is invoked to explain the reduction in microporosity, as observed previously by other authors [31].



. Nitrogen adsorption isotherms for fresh catalysts at -196 °C

The iron alkaline ion exchange procedure not only affected the micropores but induces mesoporosity (in the range of pores sizes between 50 and 200 Å) into the zeolite, as disclosed in Figure 1. Framework silicon extraction due to the alkaline conditions imposed during exchange is a known strategy for generating mesoporosity [36].



Figure 1. BJH adsorption pore distribution for fresh catalysts

Figure 3 discloses scanning electron micrographs of the starting material and the synthesised iron catalysts. Images were collected using a secondary electron detector which explains the absence of brighter areas corresponding to iron. However, the presence of iron under SEM was confirmed by Energy Dispersive Spectroscopy (EDS) (Figure 3) which was conducted following secondary electron imaging for each sample. EDS results were consistent with the catalyst iron content as determined by ICP. While the morphology of ZSM5-supported iron catalysts prepared by solid state exchange and non-aqueous ion exchange resemble that of H-ZSM5, the alkaline treatment procedure resulted in additional catalyst alterations such as deagglomeration and a "sponge-like" morphology as reported by Possato et al. for desilicated zeolites [31]. This type morphology is generally associated with silicon dissolution in the parent material.



Figure 2. a. SEM-EDS of H-ZSM5 catalyst. b. SEM-EDS of 1 wt % Fe catalyst prepared by a non-aqueous ion exchange. c. SEM-EDS of 5 % Fe-ZSM5 catalyst prepared by solid state exchange. d. SEM-EDS of 13 % Fe-ZSM5 catalyst prepared by alkaline ion exchange

Fresh catalysts as prepared were analysed by x-ray diffraction (Figure 3). Even though phase changes were not observed where iron was present, the data suggests a reduction of the crystallinity of H-ZSM5 due to iron deposition through the different exchange methods, which is in agreement with previous research [31, 37]. The intensity of the reflections are inversely proportional to the iron concentration of the material, as evident in Figure 3, whereas the intensity of the background is directly proportional to the iron content, predominately at high angles (Figure 4). A significant reduction in the intensity of the reflections associated to H-ZSM5 was observed on samples with high iron loading, which is not only attributed to a higher iron content but also to the severity of the conditions used during alkaline impregnations, as reported by other authors [31].



Figure 3. XRD patterns at low angles of fresh H-ZSM5 and ZSM5/Fe patterns prepared by different methods.



Figure 4. XRD patterns at high angles of fresh H-ZSM5 and ZSM5/Fe catalysts prepared by different methods.

3.2 Catalytic performance of iron-ZSM5 catalysts

Catalytic measurements using H-ZSM5 as reference material resulted in selectivities of allyl alcohol of approximately 1 %, as evident in Figure 5 which is in general agreement with other reports of zeolite-catalysed glycerol conversion [4, 31, 38, 39]. The performance of the synthesised Fe-ZSM5 catalysts was assessed on the basis of allyl alcohol production, disclosing a relationship between iron loading and the activity of the catalyst towards allyl alcohol (Table 1 and Figure 5). The highest yield of allyl alcohol and the lowest average selectivity to acrolein (Table 2) were obtained over the catalyst with the highest iron content (synthesised by alkaline ion exchange) following six hours of time-on-stream catalytic measurements. Even though experiments were conducted under conditions where complete conversion of glycerol was achieved, conclusions can be drawn in terms of net selectivity of allyl alcohol over the catalysts studied. While catalysts with an iron content ≤ 5 wt % afforded a low but virtually constant allyl alcohol selectivity as function of time on stream, over the 13 wt % iron zeolite, allyl alcohol is only detected in significant quantities following 4 hours of time on stream. This may suggest that mass transfer limitations, changes in iron speciation with time on stream, poisoning of acid sites due to coke deposition or/and that the reaction follows a different pathway when iron is present in such high concentration.



Figure 5. Allyl alcohol selectivity as a function of time on stream over ZSM5/Fe catalysts. $GHSV = 1240 h^{-1}$, Reactant: 35 wt % glycerol.

The decreased rate of formation of acrolein using the ZSM5/Fe 13 wt % catalyst could be explained by a combination of two factors; one is the severity of the treatment conditions used for iron deposition. This was reported by Possato et al. for their desilicated zeolites and was attributed to changes in the density of Lewis and Brønsted sites [31]. A second explanation is also related to acid-base properties, as a decrease in acid site density was found to occur due to iron deposition on the zeolite where the amount of iron exceeded the theoretical exchange capacity of the material (Figure S1 ESI). Moreover, using the same catalyst, an increase in the rate of formation of both acetic and propanoic acid was observed (Table 2). Even though H-ZSM5 is a stable catalyst for glycerol conversion, iron deposition (where iron was present in concentrations ≤ 5 wt %) reduces catalytic activity, as observed by a drop in glycerol conversion after 6 hours of time on stream. However with the catalyst of higher iron content, glycerol conversion remained constant at the end of the test (Table 2).

Table 2. Average product distribution over ZSM5/Fe catalysts and support during 6 hours of time on stream. GHSV = 1240 h^{-1} , Temperature = 340 °C, Reactant: 35 wt % glycerol.

		ZSM5/Fe 0.5 %	ZSM5/Fe 5	ZSM5/Fe 13 %
	H-ZSM5	(non-aqueous IE)	% (SSE)	(alkaline IE)
Conversion (%)	98.9	96.8	84.8	99.9
Molar carbon				
selectivity (%)				
Allyl alcohol	0.7	1.4	2.7	2.7
Acrolein	13.1	11.9	8.2	7.0
Acrolein (gas phase)	28.9	22.9	20.1	11.2
Acetaldehyde	4.6	5.2	4.3	6.4
Acetaldehyde (gas phase)	9.0	4.2	3.7	4.0
Hydroxyacetone	7.3	8.6	10.2	8.0
Acetic acid	0.7	0.6	1.1	2.1
Propanoic acid	0.3	0.4	0.7	3.1
Carbon dioxide	0.8	0.3	0.7	1.7
Carbon monoxide	0.2	0.4	0.4	1.0
Others	28.9ª	38.9ª	42.6 ^b	47.0 ^b
Coke	5.5	5.2	5.2	5.8

^a: Others include 1,3-dioxan-5-ol and propanal 3-methoxy

^b: Others include 2,3 butanedione, glyceraldehyde, acetone and acetoin

3.3 Post reaction studies

Catalyst surface areas were significantly affected by the reaction, as evident in Figure 6 in comparison with Figure 1. A reduction in surface area in the range of 92 - 94 % occurred with

low iron content catalysts, whereas the same parameter decreased by approximately 82 % over the ZSM5 supported 13 wt % iron catalyst (Figure 6). Nevertheless, changes in surface area were found to be reversible with catalyst regeneration (in air flow at 550 °C for five hours with a heating rate of 1 °C·min⁻¹) as observed for H-ZSM5 catalysts (Figure S2 ESI).



Figure 6. Nitrogen adsorption isotherms for used catalysts at -196 °C.

Post reaction analyses were also conducted using X-ray powder diffraction analysis, where a change in the diffraction pattern was notable (Figure 7). Diffraction patterns of the catalysts studied revealed that reflection doublets at $2\theta = 23.08^{\circ}$, 23.15° ; 26.49, 26.84; 35.77, 35.95 and 37.14, 37.51 were altered following the reaction, and appear as singlet reflections at $2\theta = 23.09$, 26.69, 35.86 and 37.45 respectively. In order to confirm that the structural change was due to carbon deposition, experiments were conducted for up to six hours with water as feed and nitrogen as carrier gas at 340 °C and atmospheric pressure. The XRD pattern of these samples resembles those of fresh catalysts (Figure S3 ESI). Phase identification of the resultant patterns showed an association between peak position and intensity of fresh catalysts to orthorhombic crystals, while patterns of used catalysts corresponded to tetragonal crystal systems (not

shown). This observation is consistent with the work of Alvarez et al. in which cell parameter calculations confirm the presence of carbonaceous deposits within the zeolite channels [40]. The phase change was proven to be reversible with reactivation in air at 550 °C for five hours (Figure 7).



Figure 7. XRD patterns of used H-ZSM5 and ZSM5/Fe catalysts prepared by different methods.

In order to determine whether the alkaline ion exchange procedure influenced the nature of the iron species deposited on ZSM5, a 70 wt % ZSM5/Fe catalyst was prepared using 2.5 g of H-ZSM5 in an iron nitrate aqueous solution of 0.4 M ammonium hydroxide. X-ray diffraction patterns of the resultant materials exhibited additional reflections (other than the associated to MFI), disclosing the presence of the iron oxide phase hematite (Figure 8). This is in agreement with previous reports in which iron hydroxides precipitates were observed to form hematite following calcination [41].



Figure 8. XRD patterns of H-ZSM5, $Fe_2O_3^a$ and 80 wt % Fe-Z-SM5 catalysts. ^a Prepared by calcining $Fe(NO_3)_3$ in air flow at 400 °C for 4 hours.

3.4 Alkali metal deposition

The ZSM5 supported 13 % iron oxide catalyst was modified by the deposition of rubidium nitrate, as basicity has been suggested to favour the formation of allyl alcohol when reacting glycerol over iron catalysts [5, 7]. Despite the vast utilization of Cs exchanged zeolites, a Rb salt was selected to conduct the ZSM5-supported iron catalysts modification based on previous investigations with alumina-supported iron catalysts [5]. In this study, it was found that even though γ -alumina/Fe/Cs resulted in the most stable catalyst, γ -alumina/Fe/Rb was highly selective to allyl alcohol production from glycerol. Likewise, lower selectivity towards acrolein was obtained over the latter catalyst in comparison to γ -alumina/Fe/Cs. At this stage the reason for this catalytic behaviour is still unclear. In preliminary tests over H-ZSM5 catalysts, deactivation was not an important issue following 360 min of catalytic measurement (Table 2) which influenced in the selection of the Rb modified zeolite as opposed as the Cs treated material.

As disclosed in Figure 9, the yield of allyl alcohol effectively doubled as result of the catalyst treatment with rubidium. Simultaneously, a decrease in the yield of acrolein was observed with the presence of the rubidium modifier.



Figure 9. a. Allyl alcohol and b. Acrolein yield as a function of time on stream over Rb modified Fe-ZSM5 catalysts. GHSV = 1240 h^{-1} , Temperature: 340 °C, Reactant: 35 wt % glycerol.

Complete glycerol conversion was observed following 6 hours of time on stream. An apparent reduction in coke formation was attributed to rubidium deposition. Over the 13 wt % iron oxide on ZSM5 catalyst, the carbon content of the post reaction catalyst decreased from 11 wt %

(unmodified sample) to 10 wt % due to the alkaline metal modification. Changes in product distribution are also thought to be a consequence of the reduction of acid sites, which promote the formation of acrolein. If the concentration of acrolein is reduced, then the rate of side reactions, such as the reaction between acrolein and glycerol or polymerisation of acrolein [4] that lead to coke formation, are also reduced.

To study acid site density, ammonia was absorbed on both unmodified and modified iron ZSM5 catalysts, and the course of its desorption (TPD trace) is disclosed in Figure 10. Even though the intensity of weak acid sites (150 - 300 °C) [42] remained unchanged following the alkaline treatment of the iron catalyst, a significant reduction in the concentration of medium strength acid sites (characterised by desorption of NH₃ from the catalyst between 300 and 500 °C) [42] was observed in the presence of rubidium.



Figure 10. Ammonia temperature program desorption profiles for ZSM5/Fe and ZSM5/Fe/Rb catalysts, m/z = 16.

In spite of the significant influence of the rubidium modification on the rate of formation of acrolein and allyl alcohol, little effect was observed on hydroxyacetone yields, particularly

following 240 minutes of catalytic measurements (Figure 11). Previous studies on glycerol conversion over unmodified and sodium-exchanged niobium oxide catalysts allowed correlating acrolein yields with the concentration of Brønsted sites as well as hydroxyacetone yields with the concentration of Lewis sites. The presence of alkali metals reduced Brønsted acidity and therefore the rate of formation of acrolein, while the concentration of Lewis sites remained constant so did hydroxyacetone yields [43]. Current ammonia TPD results confirmed reduced acidity upon alkali addition. The study of Foo et al., other precedent literature [31, 44-47] and current product distribution suggest that the rubidium modification of ZSM5-supported iron catalysts mainly affects the concentration of Brønsted sites.



Figure 11. Hydroxyacetone yield as a function of time on stream over Rb modified Fe-ZSM5 catalysts. $GHSV = 1240 h^{-1}$, Temperature: 340 °C, Reactant: 35 wt % glycerol.

Zeolite supported iron catalysts undergoing post synthesis modification resulted in stable materials that supress acrolein formation and simultaneously enhance selectivity towards allyl alcohol. For benchmarking purposes, Table 3 discloses glycerol conversion and selectivity values obtained over different zeolites when converting glycerol operating under various conditions. In studies conducted by other authors, molar carbon selectivity towards allyl

alcohol does not exceed 2 % [4, 31, 38, 39]. Despite differences in catalysts and operating conditions, hydroxyacetone selectivity values reported previously are in agreement with the current results which also suggest that the iron exchange has considerably influence on Brønsted sites as opposed to Lewis sites.

Table 3. Product distr	bution obtained of	over zeolites for	glycerol conversion

Catalyst	H-ZSM5 ^b	HZSM5 ^c	HZSM5 ^c	SAPO-11	HZSM5 ^c /Fe/Rb
Conversion (%)	57.0	36.3	74.0	88.0	99.9
Allyl alcohol Selectivity (mol %)	2.0	0.9	1.1	1.5	11.9
Acrolein selectivity (mol %)	67.0	45.8	22.0	62.0	3.8
Hydroxyacetone selectivity (mol %)	12.0	11.0	4.0	10.0	9.0
Temperature	320	315	300	280	340
GHSV ^a	1438 h ⁻¹	1392 h ⁻¹	1177 h ⁻¹	43 h ⁻¹	110 h ⁻¹
Reference	[39]	[37]	[31]	[4]	This work

^a: GHSV calculated respect to glycerol

^b: SiO₂/Al₂O₃ = 30

^c: $SiO_2/Al_2O_3 = 23$

Iron speciation has been observed by Groen et al. for iron-containing zeolites undergoing desilication through post synthesis alkaline treatment [48]. Figure 12.a shows the XPS survey spectrum of the ZSM5/Fe 1% catalyst as prepared, in which iron was not detected. For the ZSM5/Fe 13% and ZSM5/Fe/Rb catalysts, Fe^{3+} was found to be present as evident by the Fe2p_{3/2} peak at 711.5 eV, the Fe2p_{3/2} satellite peak at 719.3 eV, the Fe2p_{1/2} peak at 725.0 eV and the Fe2p_{1/2} satellite peak at 733.7 eV. In the ZSM5/Fe 5% catalyst, the presence of Fe²⁺

and Fe³⁺ was confirmed by the Fe2p_{3/2} peak at 711.0 eV, the Fe2p_{1/2} peak at 724.4 eV and the absence of satellite peaks as disclosed in Figure 12.b. [49-51]. The peak at 533.1 eV, present in all cases, has been attributed as reported elsewhere [52, 53] to ZSM5 lattice oxygen. The shoulder at lower binding energy values (530.6 eV) observable for high iron content catalysts suggests the presence of extra framework iron oxide species which is in line with previous works [52, 53].



Figure 12 a. XPS survey spectrum of ZSM5/Fe 1% catalyst. b. High resolution O1s spectra of ZSM5 supported iron catalysts. c. High resolution Fe2p spectra of ZSM5 supported iron catalysts.

UV-vis spectroscopy allowed distinguishing between different Fe^{3+} species present in the studied catalysts. As evident on Figure 13.a, the Rb modification results in an increase in isolated tetrahedrally coordinated Fe^{3+} species (associated with the oxygen to iron charge transfer band at 240 nm) as well as of Fe^{3+} species coordinated with high number of oxygen ligands (band at 290 nm) at the expense of oligomeric iron clusters (bands between 300 nm and 400 nm) and iron particles (bands above 400 nm) [48, 54]. In agreement with the work of Yue et al. with iron modified ZSM5 catalysts, the absence of reflections corresponding to iron oxides was thought to be due to the size of such particles which do not exceed 4 nm [52]. Based on product distribution these isolated Fe^{3+} species were thought to enhance the rate of formation of allyl alcohol from glycerol.



Figure 13 a. UV-vis spectra of ZSM5/Fe and ZSM5/Fe/Rb fresh catalysts. b. UV-vis spectra of ZSM5/Fe used catalyst.

Following catalytic measurements over ZSM5/Fe 13%, the used catalyst was analysed by XPS. XPS spectrum suggests iron ions in divalent oxidation state, as evident by the Fe2p_{3/2} peak at 711.0 eV, the Fe2p_{1/2} peak at 724.4 eV and the absence of satellite peaks (Figure 12.b). Likewise, the UV-vis spectrum of the used catalyst is comparable to that of Fe₃O₄ [55] (Figure 13.b) and therefore is in agreement with the current XPS results. This is evidence of changes in iron speciation with time on stream.

3.5 Kinetic diameter calculations

Studies conducted by Gu et al. [56], over several zeolites with differing channel configurations and diameters, suggest that, optimal catalysts for glycerol conversion to acrolein were those with channel dimensions slightly larger than the molecular diameter of glycerol (5.0 Å), as for instance H-ZSM5 (straight channels with dimensions of 5.1 Å \times 5.5 Å). Their observation was based on the existence of straight channels in H-ZSM5, which facilitate enhanced rates of diffusion when compared to more complex pore architectures. Moreover, H-ZSM5 steric hindrance (found to play a more important role than acidity) limits coke formation. The same kinetic (4 Å) diameter has been reported for other alcohols and their corresponding aldehydes such as ethanol and acetaldehyde [57, 58]. However, to the best of our knowledge, the kinetic diameters for allyl alcohol and acrolein have not been reported in the literature. Kinetic diameters for biomass feedstocks and their possible products were calculated by Jae et al. [2] using equations by Bird et al. [59]. Adopting a similar procedure, we have estimated the diameters for the desired product and primary by-product of the reaction of glycerol over zeolites. As found previously [2], there are variations between the estimation based on critical volume, critical temperature-pressure and molecular weight respectively (

Table 4). However regardless the method employed in the calculations, similar estimates of the molecular dimensions of acrolein and allyl alcohol products were determined.

	Allyl alcohol	Acrolein	Units and references
$K_{d1} = 0.841 V_c^{\frac{1}{3}}$	5.9	5.7	Critical volume in cm ³ ·mol ⁻¹
$K_{d2} = 2.44 \left(\frac{T_c}{P_c}\right)^{\frac{1}{3}}$	5.2	5.2	Critical temperature in K Critical Pressure in atm
$K_{d3} = 1.234 M_w^{\frac{1}{3}}$	4.8	4.7	-

Table 4. Acrolein and allyl alcohol kinetic diameters calculated according to Jae et al. [2].

Acrolein and allyl alcohol appear to have similar transport characteristics controlling their rate of diffusion in zeolite channels, given by minor differences in their kinetic diameters. However, channel structure and dimensions influence coke formation [56]. Increased mesoporosity was observed with the zeolite with the highest iron content, which correlates with an increased rate of coke formation and reduced rate of acrolein formation. This is in agreement with the work of other authors [56] in which selectivity to acrolein decreased over catalysts of larger diameters pore channels. This behaviour was attributed to secondary reactions (some leading to coke production) and reduced interaction of the central OH in the glycerol molecule with the bridging OH on the catalyst compared to smaller channel diameter zeolites. For instance, over materials such as ferrierite, coke production increased and the rate of formation of acrolein decreased compared to results obtained over H-ZSM5 at the same reaction conditions [38]. Moreover materials such as MCM-41 are well known to catalyse the formation of polyglycerols [3, 60]. The production of allyl alcohol over this catalyst does not depend strongly on transport limitations, but seems to be mainly governed by acidity (as evident in Figure S1 in the ESI by ammonia temperature desorption on H-ZSM5 and H-ZSM5/Fe catalysts) and/or redox site density.

A series of experiments were conducted to study the effect of transport limitations on the reaction, initially by reducing the catalyst weight by 90 % in order to operate under low conversion conditions.

A preliminary test was used as base line in the detection of internal and external mass transfer limitations. This test involved using 500 mg of ZSM5/Fe 13 % catalyst, feeding a 35 wt % glycerol solution at a flow rate of 0.75 mL min⁻¹, with nitrogen as gas carrier at a flow rate of 180 mL min⁻¹ for a GHSV of 19250 h⁻¹. In a separate experiment, 500 mg of ZSM5/Fe 13 % catalyst was sized between 600 μ m to 1 mm, while the remainder operating conditions remained unchanged. With a larger particle size, conversion is expected to drop if the reaction is limited by internal diffusion [61]. Following 360 min of catalytic measurements at these conditions, glycerol conversion was approximately 25.0 % as shown in

Table 5, which is comparable to tests where catalysts with smaller particle size were used, suggesting no internal diffusion limitations.

Moreover, a follow up series of experiments involved increasing the catalyst mass up to 1 g, where the flow rates of glycerol solution and gas carrier were adjusted such that the GHSV was maintained constant. Under these conditions, an increase in conversion is expected if the reaction is limited by external diffusion [61]. As shown in

Table 5, glycerol conversion levels roughly double over 1 g of catalyst with respect to tests in which 500 mg of catalyst was used, suggesting the reaction was under external diffusion control conditions.

	Conversion (%)			
-	500 mg (250 μm - 600	500 mg (600 μm -	1 g (250 μm - 600	
Time (min)	μm)	1 mm)	μm)	
60	26.6	26.2	50.6	
120	28.0	24.1	51.4	
180	23.8	27.5	50.5	
240	26.0	25.8	54.8	
300	25.7	26.1	54.0	
360	25.8	25.0	54.0	

Table 5. Glycerol conversion as a function of time on stream over ZSM5/Fe 13 %. GHSV = 19250 h^{-1} , Temperature: 340 °C, Reactant: 35 wt % glycerol.

In the light of these results, additional experiments were conducted in order to determine whether the induction period for allyl alcohol production observed in Figure 5 was exclusively a consequence of external mass transfer limitations or if it was also influenced by intrinsic kinetics. These tests were designed to operate in a differential reactor mode which often simplify kinetic investigations and where transport and heat limitations are negligible [62]. As shown in Table 6, similarities were found in glycerol conversion values when 50 mg and 100 mg of ZSM5/Fe 13 % catalyst are used. Interestingly, Table 7, an induction period for allyl alcohol selectivity is observed. These suggest that the formation of ally alcohol at certain time on stream is not only a result of external transfer limitations (

Table 5), but also a consequence of intrinsic kinetics (Table 7).

Table 6. Glycerol conversion as a function of time on stream over ZSM5/Fe 13 %. GHSV = 192500 h^{-1} , Temperature: 340 °C, Reactant: 35 wt % glycerol.

	Conversion (%)			
Time (min)	50 mg (250 μm - 600 μm)	100 mg (250 μm - 600 μm)		
60	5.5	5.1		
120	5.7	5.0		
180	2.6	3.1		
240	1.8	2.1		
300	1.7	1.4		

Table 7. Allyl alcohol selectivity as a function of time on stream over ZSM5/Fe 13 %. GHSV = 192500 h^{-1} , Temperature: 340 °C, Reactant: 35 wt % glycerol.

	Selectivity (%)			
Time (min)	50 mg (250 μm - 600 μm)	100 mg (250 μm - 600 μm)		
60	24.3	23.5		
120	14.4	22.8		
180	41.8	29.6		
240	61.1	50.1		

300	61.8	60.1

Based on these results and on product distribution over different catalysts as function of time on stream, the induction period required for the production of allyl alcohol it is not exclusively attributed to transfer mass limitations, but also two events might have an effect: the reduction to Fe²⁺ and the poisoning of acid sites on the catalysts by means of coke deposition. Evidence for the former is the shorter induction period for allyl alcohol formation when ZSM5/Fe 5% catalysts prepared by SSE catalyse the reaction. Fe²⁺ was identified to be present in this catalyst by XPS (Figure 12.b). Evidence for the latter are ammonia TPD of used ZSM5/Fe 13 wt %, which suggests a substantial reduction of both weak and medium acid sites (Figure S4 ESI) and the shorter induction time required for allyl alcohol production when glycerol conversion is conducted over ZSM5/Fe/Rb 13% catalysts, in which the concentration of acid sites was found to be reduced by the presence of the alkali metal.

3.6 Insights into the reaction mechanism for allyl alcohol formation

When reacting glycerol using alumina as catalyst support instead of H-ZSM5 and operating at similar conditions, a reduction on the rate of formation of hydroxyacetone coincided with an increase in allyl alcohol yields. The alkali metal modification of alumina supported catalysts increased the production of carbon monoxide and hydrogen from glycerol which were thought to act as sacrificial reductants resulting in the formation of allyl alcohol and carbon dioxide at the expense of hydroxyacetone [5]. Even though in the current experiments (using zeolites as support), the use of a rubidium-modified catalyst increased the yield of carbon monoxide (from 0.9 % to 1.5 %) and carbon dioxide (from 1.7 % to 2.3 %), selectivity towards hydroxyacetone remained virtually constant suggesting a different mechanism.

Iron oxide has been reported to catalyse hydrogen transfer reactions in the presence of glycerol [20], as well as oxidation reactions of glycerol dehydration products [63]. Moreover, iron has been found to chelate with a diol resulting in the formation of 1,3-propanediol from glycerol [64]. Previous studies proposed 1,3-propanediol as a possible intermediate in the synthesis of allyl alcohol from glycerol [65]. Additionally, γ -Fe₂O₃ has been reported to catalyse deoxygenation reactions via disproportionation [66].

In a recent review of the available literature in polyols transformations, the van Krevelen diagram was used to point out three pathways for allyl alcohol formation from glycerol. A first possibility is the single dehydration of the glycerol molecule to hydroxyacetone and its subsequent deoxygenation. However, in this reaction, acrolein is typically produced in high selectivities. The second route is glycerol deoxygenation resulting in the formation of 1,2-propanediol which is then dehydrated to allyl alcohol. The deoxydehydration (DODH) reaction, generally catalysed by rhenium complexes, arises in an attempt to overcome the difficulties in controlling selectivity in the other reaction pathways [67].

In the current experiments, when H-ZSM5 catalysed the conversion of glycerol, high selectivity towards 1,3-dioxan-5-ol was observed. This latter compound is most likely to be generated by the condensation of a glycerol molecule with a formaldehyde molecule [68, 69]. For the aldehyde to be present in the system in significant quantities to produce 1,3-dioxan-5-ol, the 1,3-dehydration of glycerol must occur [70]. Likewise acrolein was produced in high yields over this catalyst. However, when zeolite supported iron materials catalyse the same reaction, the rate of formation of 1,3-dioxan-5-ol was reduced and selectivity towards compounds such as acetic acid, propanoic acid, acetone, glyceraldehyde, 1,3-propanediol and 1,3-dioxolane-4-methanol,2-ethyl (product of condensation of 1,3-propanediol and acrolein [65]) increased, which suggests redox processes. This coincided with an enhancement in the rate of formation of allyl alcohol. Based on product distribution, a two-step reaction mechanism

was thought to be involved in the formation of allyl alcohol from glycerol over iron exchanged zeolites. Firstly, the glycerol molecule undergoes single 1,2-dehydration for which acid sites on the zeolite are required. Excessive 1,2-dehydration results in the formation of acrolein while 1,3-dehydration allows 1,3-dioxan-5-ol to be formed. The second step is a deoxygenation process where iron provides redox sites for the reaction to take place. Evidence of this are the decreased rates of formation of acrolein and 1,3-dioxan-5-ol in the presence of iron and the formation of the oxygenates mentioned above. For the formation of these compounds, reactions that involve the removal of oxygen atoms from glycerol dehydration products are likely to occur. Such reactions were thought to result in the formation of allyl alcohol.

In summary the role and function of iron in the formation of allyl alcohol is to provide redox sites for deoxygenation and hydrogen transfer reactions to occur. Rubidium, instead, poisons acid sites in the catalyst which prevents excessively dehydration to take place. Even though dehydration is necessary for the formation of allyl alcohol, the double glycerol dehydration leads to the formation of acrolein as opposed to allyl alcohol.

4. Conclusions

Using an alkaline solution instead of methanolic to conduct ion exchange in HZSM-5 resulted in the synthesis of a 13 wt % iron zeolite, which performed better for allyl alcohol production compared to catalysts synthesised by other methods. The severity of the preparation procedure promoted partial dissolution of both framework silicon and aluminium, affecting the micropore volume and engendered the zeolite with mesoporosity. Post synthesis modification by rubidium deposition resulted in additional enhancement in the yield of allyl alcohol and decreased the yield of acrolein. Reduction in the rate and extent of coke formation were attributable to the rubidium deposition, which is speculated to be due to a decrease in the concentration of medium acid sites, which was confirmed by ammonia TPD. Kinetic diameter calculations showed that

the production of allyl alcohol over the assessed catalysts does not depend strongly on pore size distribution, but seems to be mainly governed by acidity and/or redox site density.

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