

Copper based catalysts in the selective dehydration of polyols

by

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DEDICATION

To my father, Marshall Fidelis Bejile

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ABSTRACT

The goal of current work is to design, develop and understand a catalytic system for the dehydration of 1,2,6 hexanetriol, optimising the selective removal of the secondary hydroxyl group. The nature of biorenewable resources, in particular the existence of multiple functional groups poses a huge challenge for their catalytic upgrading to useful commodity chemicals. We have successfully demonstrated copper modified silica alumina as well as copper modified silica catalysts as viable catalysts for this reaction. In order to understand the catalytic conversion of biorenewable feedstocks, 1,2,6 hexanetriol has been selected as the platform molecule and the catalytic routes to known commodity chemicals over copper based catalysts have been investigated. A collection of these catalytic rules can in future be used in the development of a catalytic toolbox which will provide some insights into the general catalytic conversion of biorenewables. The ultimate goal is to develop a comprehensive catalytic toolbox that will facilitate the logical design of catalytic systems from given starting biorenewable platforms to desired commodity end product.

Despite the fair amount of research that has been done on the catalytic dehydration of diols and mono-ols not much work has been done on dehydration of triols. There is therefore a lack of kinetic, mechanistic and active site identification work in the catalytic dehydration of higher order polyols reported in literature. This work investigates the role of the metal functionality in copper based composites for the dehydration of 1,2,6 hexanetriol. We found that the copper catalysts that were active in flows of H₂ were virtually inactive in flows of inert gas, a discovery that led us to the proposal of 3 hypotheses based on the experimental data. We propose that the copper metal

surface facilitates the dissociative adsorption of H₂ followed on by some events (extensively discussed in chapters 3 and 4), which ultimately result in the production of protonic active sites which participate in the catalytic reaction. A second hypothesis was proposed concurrently with the first one, stating that the H₂ played the role of keeping the copper metal in its reduced state, as Cu⁰ and we proposed that Cu⁰ was the active site for the reactions proceeding. Correlations between catalyst specific activity and Cu⁰ surface concentrations revealed a strong dependency between the two variables suggestive of the fact that Cu⁰ was indeed the active site for the reactions proceeding. Lastly, we propose that H₂ is preventing the catalysts from coking, by working together with the copper metal to remove product from the catalyst surface, thus preventing product polymerization which leads to coke formation.

We established that copper metals supported on high acid strength materials had the propensity to drive ring closing reactions, thereby increasing selectivity toward pyranic and cyclohexyl products under those conditions. On the other hand, copper catalysts supported on moderate to low acid strength materials yielded higher selectivities toward linear products such as 1,6 hexanediol and its precursors. Higher H₂ partial pressures produced increases in catalytic activity and these conditions steered selectivities towards 1,6 hexanediol and its precursors. Strong synergic effects between Cu⁰, acid support and choice of carrier gas were exhibited by all catalysts; therefore experimental work is mostly focused on decoupling the effects of the variables so as to determine the individual roles played by each component in the system.

Finally, we proposed some reaction mechanisms for the formation of ring products obtained in this study.

CHAPTER 1: INTRODUCTION

1.1 Introduction

In order to alleviate the depletion of petroleum based feedstocks as well as to avert the impending crisis of global warming, focus is being turned to alternative sources, such as biorenewable feedstocks. Fossil carbon depletion is primarily attributed to the increased demand on fuel and commodity chemical production. The production of commodity chemicals do not utilize nearly as much fossil feedstocks as with the production of fuels, however, an alternative source for commodity chemicals would provide immense relief on fossil feedstocks demand and avert the impending depletion. Although this work is focused on the conversion of biorenewable feedstocks to higher value commodity chemicals, it is reasonable to assume that as we delve deeper into the chemistry of converting biorenewables to commodity chemicals; we may make interesting discoveries that could prove to be beneficial to the fuel industry as well.

Biorenewable feedstock is categorized in three groups, namely starch, oils and lignocellulose and the platform investigated in this work is starch based. The conversion of biorenewable feedstocks poses a huge challenge associated with catalytic upgrading unlike the relative ease with which petroleum based feedstocks are catalytically upgraded. This is attributed to the fundamental differences in the nature of the two feedstocks. Petrochemical industry feedstocks possess much less functionality and as such their catalytic upgrading requires mostly the addition of functionality in order to acquire useful chemicals. On the contrary, biorenewables are inundated with multiple functionalities which require removal prior to catalytic upgrading. At the present moment, commodity chemicals are being largely produced by the petrochemical industry; including

chemicals such as benzene, toluene, xylene, ethylene etc. all of which are essential molecules and are the building blocks to most important commodity chemicals used in today's world. However, in light of the impending fossil feedstock depletion, biorenewable feedstocks are a sustainable alternative to achieving these commodity chemicals, therefore there is a need to resolve the challenges associated with the catalytic upgrading of these feedstocks as well the raw material handling challenges. As previously mentioned, the multifunctionality and high oxygen content innate in biorenewable feedstocks will require selective removal prior to further upgrading to achieve commodity chemicals akin to those produced by the petroleum industry. This requires the development of a new catalytic paradigm that is able to tackle the selective removal of functionality as opposed to adding functionality, so as to build onto already established systems used in the catalytic upgrading of petrochemicals. The development and fine tuning of these technologies will allow for the accessibility to a vast number of commodity chemicals from biorenewable feedstocks, most of which are currently only accessible through processes involving petroleum feedstocks.

1.2 General background of the catalytic conversion of polyols

Polyols are the class of biorenewables selected for this work. These are sugar alcohols consisting of a carbon backbone possessing multiple hydroxyl groups, unlike petroleum based feedstocks which mostly consist of carbon and hydrogen. The removal of excess oxygen from biorenewables has been the subject of most research work surrounding the upgrading of biorenewables to date.

Some pioneering work in conversion of biorenewables has been done by Dumesic et al who studied the transformation of sugar alcohols such as sorbitol and glycols over bifunctional catalysts to

hydrogen and alkanes [1-6]. This work is mostly focused on the conversion of sugar alcohols to hydrogen which can be used for fuel cells, as well as alkanes, in novel processes for synthesis of commodity chemicals from biorenewables. A considerable amount of work was done on sorbitol, and the main pathway of its transformation was said to proceed via a series of dehydration-hydrogenation steps over bifunctional catalysts possessing metal and acid functionality, in a process called aqueous phase dehydration/hydrogenation, (APD/H) [7]. Kirilin et al has also investigated sorbitol transformation over Pt/Al₂O₃ and they observe over 260 compounds involved in APD/H transformation of sorbitol, making biorenewable platforms versatile resulting in the production of a wide range of commodity chemicals [8].

1.3 Catalytic reactions employed in biorenewable upgrading

Polyol transformations can generally be categorized into two classes namely C-O and C-C bond cleavage reactions. The knowledge of bond cleavage mechanisms of sugar alcohols is important because it gives us a good background of understanding product selectivity drivers. C-C bond cleavages usually occur on terminal carbons on aldehyde or carboxylic acid groups via decarbonylation or decarboxylation reactions [9, 10], or via retro-aldol reactions if the cleavage occurs in the middle of the carbon chain by dehydrogenation and/or hydrogenation reactions [11]. C-O bond cleavages occur via dehydration-hydrogenation reactions on the alcohol possessing carbons [12]. These reactions occur in succession or simultaneously, resulting in complex mixtures of products, intermediates and reactants [13]. Hydrogenolysis of the C-O bond can also be employed to selectively remove excess oxygen from biorenewable feedstocks. C-O bond hydrogenolysis occurs in the presence of hydrogen and yields a water molecule. Unlike the dehydration reaction which results in unsaturated bonds hydrogenolysis yields saturated

molecules, because hydrogen is added during C-O bond cleavage. Catalytic hydrodeoxygenation is also a viable reaction for the upgrading of sugar alcohols. Peng et al has investigated the catalytic hydrodeoxygenation of C₃ alcohols such as 2-propanal and 1,3 propanediol in the aqueous phase. They show that the number of hydroxyl groups in a molecule is important in determining reaction pathways. They find that the presence of water in aqueous phase reactions suppresses the dehydration of monoalcohols as water molecules shield the Lewis acid sites; while dehydration is the dominating reaction for diols as the presence of more OH groups weakens the C-O bond [14]. Based on the understanding of these principles a rational approach to controlling selectivity drivers of biorenewable platforms can be developed.

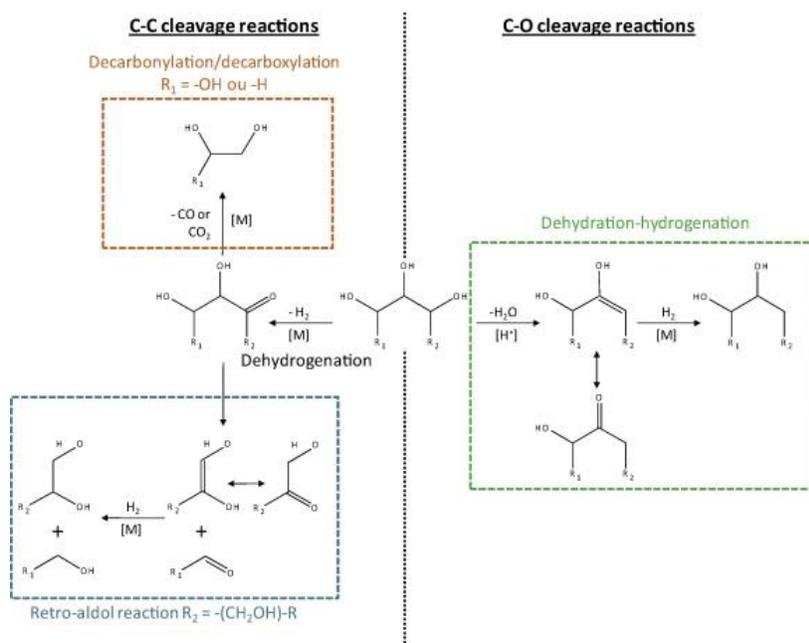


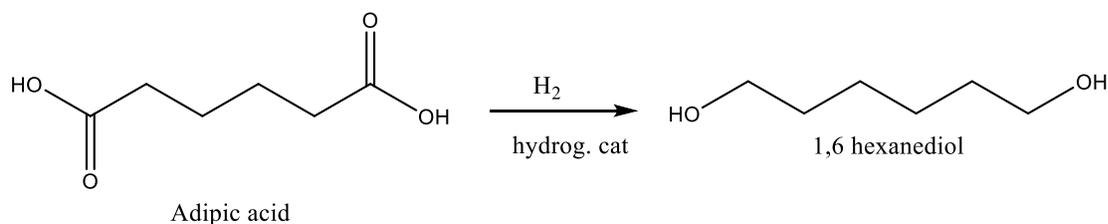
Fig 1: Reactions for polyol transformation over bifunctional catalysts ^[13]

1.4 Catalyst considerations

It has been established that bifunctional catalysts are efficient for biorenewable conversions, and these catalysts usually contain a hydrogenating metallic phase such as Pt, Pd, Ru, Cu, Ni, as well as a dehydrating acidic phase such as $\text{SiO}_2\text{-Al}_2\text{O}_3$, Al_2O_3 , $\text{ZrO}_2\text{-PO}_x$. Dehydration is a reaction which largely proceeds over acid catalyst resulting in the liberation of a water molecule resulting in unsaturated alkenes. However, a few sources have reported dehydration over basic catalysts with Yong Kim et al presenting a novel type of dehydration of diols to epoxides over Cs/SiO₂ for a reaction termed dehydrative epoxidation [15]. Dehydration holds a lot of potential in the upgrading of biorenewables because of its capacity to reduce the amount of largely abundant oxygen in these feedstocks. Chedda et al present the production of furfural and HMF from fructose achieving the removal of half the oxygen in fructose via dehydration reaction; proving that the selective removal of excess oxygen from biorenewable feedstocks is highly achievable via dehydration reactions [16-18].

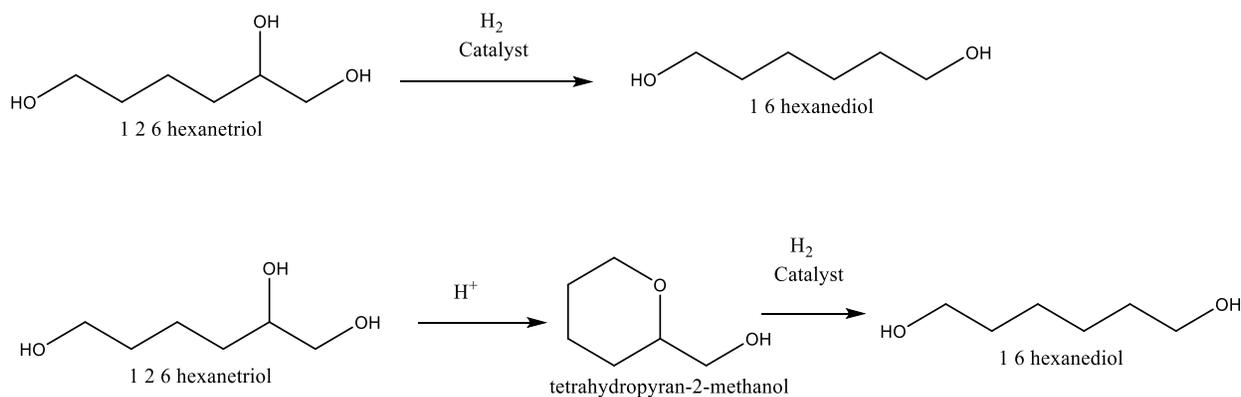
The development of heterogeneous catalysts that are stable in the liquid phase will make dehydration an even more important reaction in biorenewable processing, as it would give opportunity for the catalytic conversion of higher order polyols. Vilcoq et al investigate sorbitol transformation over heterogeneous bifunctional catalysts and among other reactions they explore C-O bond cleavage via a dehydration reaction. They report the elimination of water from sorbitol leading to the production of a myriad unsaturated compounds, i.e alkenes, ketones and heterocycles, which subsequently undergo hydrogenation in the presence of hydrogen over the metallic active site [13].

Current work explores viable catalytic systems for the dehydration of 1,2,6 hexanetriol to 1,6 hexanediol. 1,6 hexanediol is a useful commodity chemical with various uses in industry including the production of polyester, polyurethane and resins [19]. Literature previously reports 1,6 hexanediol as attainable through various routes such as the one reported by Van de Vyver et al who achieved 1,6 hexanediol via the hydrogenation of adipic acid over Ru-Pt-Sn composites supported on carbon [20].



Scheme 1: Production of 1,6 hexanediol from adipic acid [20]

Chedda et al also documents that 1,6 hexanediol is accessible through the hydrogenation and oxidation processes of aromatic benzene albeit reporting it to be a difficult process [4]. Buntara et al have also investigated the conversion of 1,2,6 hexanetriol to 1,6 hexanediol via hydrodeoxygenation reactions over various metal based catalysts [21]. They test both monometallic and bimetallic catalysts, and find that Rh-ReO_x supported on SiO₂ gave the best selectivities to 1,6 hexanediol. The reaction is performed inside an autoclave at pressures ranging from 10 to 80 bar at 260°C. The group reports 1,6 hexanediol as achievable in one or two steps with tetrahydropyran 2 methanol as the intermediate molecule. Higher 1,6 hexanediol selectivities are observed for the two step alternative, (see Scheme two shown below).



Scheme 2: One step approach shown above, (73% selectivity to 1,6 hexanediol, 100% conversion), two step approach shown below, (96% selectivity to 1,6 HD, 26% conversion). Buntara et al ^[21]

1.5 On the selective dehydration of polyols

Since the goal is to selectively remove excess oxygen from biorenewable feedstocks, selective dehydration can be employed as a way to selectively remove hydroxyl groups from polyols usually in the presence of bronsted acid catalysts. Owing to the multiple hydroxyl groups on a polyol, dehydration usually results in a number of different products depending on which hydroxyl group/s are eliminated. It is important to note that biorenewable feedstocks can either have multiple functionality, (such as aldehyde, ketone or ester groups), or have the same functional groups recurring over again, like in sorbitol. Thus, catalysts that target a particular functionality in order to achieve required selectivity to desired products are vital.

Significant amount of studies have been done on dehydration of biorenewable using substrates such as glycerol and other diols. Reactions have mostly been performed over acid catalysts and the general dehydration rules of these molecules are reported in literature [22] [23]. Previous work on selective dehydration of hydroxylated molecules is mostly focused on the optimization of the

reaction to selectively remove particular hydroxyl groups from diols and mono-ols to produce the desired target products. However, the dehydration of higher order polyols, such as triols, (three hydroxyls), tetraols, (four hydroxyls) and even more polyhydroxylated molecules such as glucose has yet to be fully explored. In order to bridge the gap between the catalytic upgrading of lower order polyols and higher order polyols, we need to sufficiently understand the catalytic rules governing the dehydration of lower order polyols. A collection of these rules will be used to develop a catalytic toolbox chemical engineers can use to logically and rationally design catalytic systems for the upgrading of biorenewables.

Acid catalysts have been found to be effective for the removal of functional groups from carbon, since the carbocations formed over acid catalyst tend to be stable. A variety of acid catalysts have been investigated for various dehydration reactions in literature. Sato et al. reports several acid catalysts for the dehydration of diols finding that CeO_2 exhibits high activity for the selective dehydration of 1,3 diols [24, 25] and 1,4 butanediols to unsaturated alcohols [25]. They also investigate the dehydration of diols over solid acid catalysts such as silica alumina, ZrO_2 and TiO_2 , and based on their findings they make the important observation that catalytic activity of the acid catalysts is strongly dependent on their acidic properties [26].

1.6 Carbocation protocol

Acid catalyzed dehydration has been found to follow a certain protocol that favors the preferential abstraction of the functional groups on the tertiary carbon before the abstraction of functional groups on the secondary carbon and primary carbon respectively [27, 28]. This protocol is dependent on the stability of the resultant carbocations. Carbons possessing the most bonds to

other carbons form the most stable carbocations, so that tertiary carbocations are the most stable and the primary carbocation the least stable. The energy levels required to form the secondary and primary carbocations are 52 and 134 kJ/mol higher than the energy levels required for the formation of the tertiary carbocation respectively [29]. It is important to understand this protocol as the carbocation intermediate dictates product selectivity and catalytic activity. The dehydration of glycerol to hydroxyacetone relies on the carbocation stability principle, since the secondary OH is preferentially abstracted over the primary OH. Another example is the dehydration of 1,2 propanediol to propanal where the secondary OH group is also preferentially abstracted over acid catalysts. These observations have led to the general consensus that protonic acids readily dehydrate the secondary OH group of lower order polyols as governed by Markonikoff's rule [30]. Reactions of triols over acid catalysts also proceed via the formation of a secondary carbocation according to the same principle, leading to formation of enols which tautomerise to ketones [31]. Other acid catalysts also reported in literature for dehydration of polyols include heteropoly acids, (HPA's). The dehydration of higher diol homologues, (such as 1,4 butanediol and 1,5 pentanediol) was done over HPA's, and they were found to undergo dehydration with high selectivity to cyclic ethers [32].

1.7 Other dehydration rules

A few catalytic rules of dehydration have been compiled from analyzing the work on the dehydration of polyols previously reported in literature. Sato et al has reported the dehydration of diols to mono-ols in a gas phase flow reactor over metal oxide catalysts at temperatures within 325-425°C [26] [33] [34]. This group observes that use of different catalysts results in different products being formed, with classic acid catalysts, (such as alumina, silica alumina and zirconia)

yielding high selectivity towards ring products while catalysts such as ceria and ytterbia gave higher selectivities to linear unsaturated alcohols [35] [36]. This begins to provide insight that catalyst choices influence product selectivities, since the same starting molecules yield different products under different catalytic conditions. We see that product selectivity is influenced by catalyst acidity. The work of Sato et al also gives us the insight into the hydroxyl group location effects on product selectivity. Sato et al who reported extensively on the dehydration of butanediols, found that neighbouring hydroxyl groups on the diols yielded higher selectivity towards ketones or aldehydes, while terminal hydroxyl groups tend to give higher selectivities to ring products.

In the catalytic conversion of higher order polyols such as sorbitol and xylitol, dehydration can be employed to selectively remove excess oxygen and intermediates subsequently hydrogenated to produce fuel products. The dehydration of sorbitol to isorsobide involves a double dehydration by means of elimination of two hydroxyl groups effecting the production of two water molecules and the double ring structure of isorsobide [37] [38].

1.8 Lewis and bronsted acidity

Acid catalysts can be classified into two main classes; Bronsted and Lewis acid catalysis. The Bronsted acid mechanism is hinged on the H^+ proton donation and acceptance. Bronsted acid catalyzed dehydration involves the protonation of a polyol resulting in the removal of a water group during reaction. The Lewis acid mechanism is hinged on the donation and acceptance of an electron pair. Lewis acid catalyzed dehydration occurs over heterogenous catalyst and it is thought that the hydroxyl groups on the polyol interact with metal ions on the catalyst surface resulting in

dehydration. This mechanism though not very well understood is thought to be dependent on the ease of formation of the alkoxide intermediates which become the primary driver of the reaction.

1.9 Generation of acid sites in $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts

In SiO_2 , each Si atom is surrounded tetrahedrally by O atoms and neighboring Si atoms thus maintaining charge neutrality. However, as Si is isomorphously substituted by Al a charge imbalance arises. Therefore, to compensate the charge imbalance a cation such as H^+ has to be located near the AlO_4 tetrahedral, to create a charge “neutrality” and this yields a bronsted acid site [29]. If a water molecule is removed from the tetrahedral by dehydroxylation a lewis acid site is formed instead, see Fig 2 below.

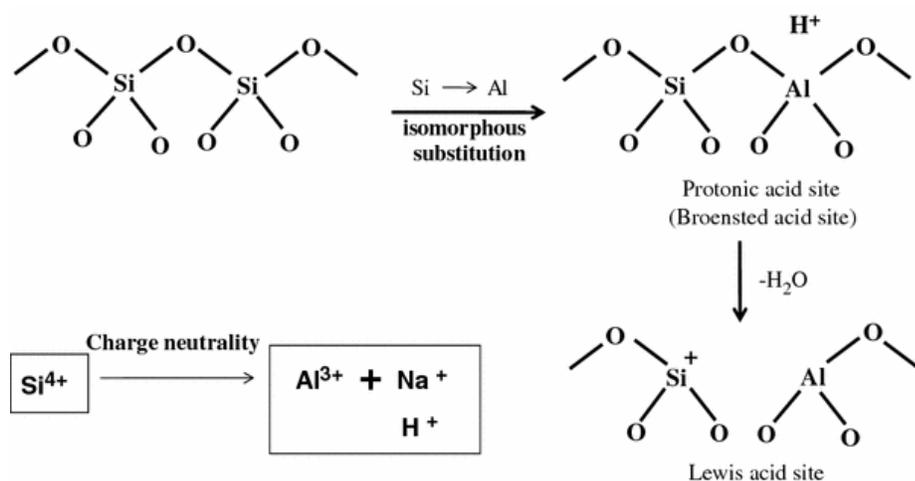


Fig 2: The generation of acid sites in silica alumina [29]

1.10 Acid site generation on metal acid bifunctional catalysts

As discussed in the preceding sections, various sources in literature have reported metal based acid catalysts as effective for biorenewables upgrading processes such as for hydrogenolysis and dehydration reactions. [39, 40]. Acid catalysts have been modified by metals such as Pt, Ni, Ru, Pd, and Cu yielding good results for dehydration reactions among others. Bimetallic catalysts have also been reported as efficient for several biorenewable upgrading reactions. However, the reaction mechanisms and catalyst active sites are not yet well established or extensively documented in literature.

The concept of metal modification of solid acid catalysts was presented by Hattori et al who proposed a general model for the formation of protonic acid sites in the presence of H₂ [29]. They propose that in the presence of a noble metal, hydrogen molecules are dissociatively adsorbed producing hydrogen atoms which subsequently spillover to the support. The hydrogen atom then migrates to lewis sites inherent in the acid support, loses an electron to form a proton, which therefore enhances the bronsted acidity of the catalyst.

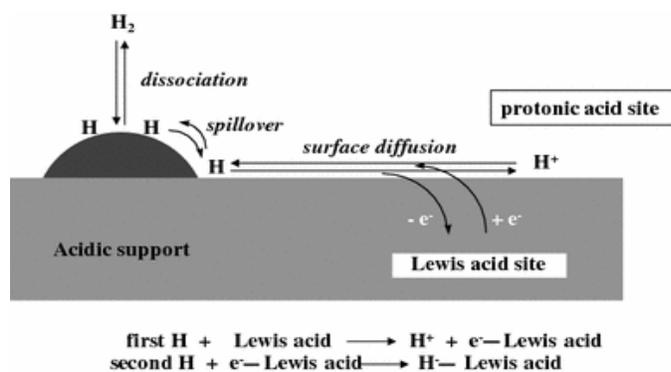
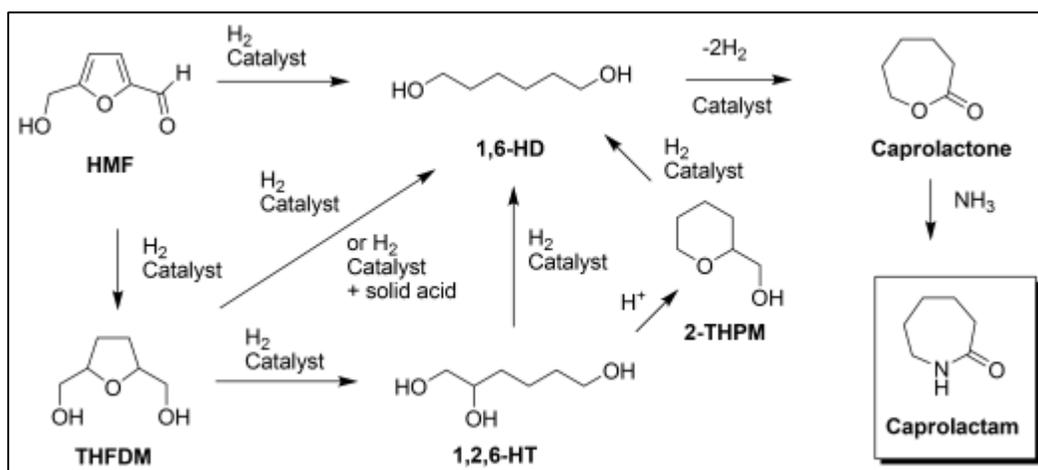


Fig 3: Solid acid catalyst modified by metals [29]

1.11 Metal based catalysts for biorenewable conversion

Buntara et al reports the production of diols, such as 1,6 and 1,5 hexanediol from 1,2,6 hexanetriol over metal based catalysts [41]. Their work involves the investigation of the catalytic conversion of 5-hydroxymethyl furfural, HMF to caprolactam. This is not a single step process therefore HMF is first converted to 1,6 hexanediol, and 1,6 hexanediol caprolactone, then ultimately caprolactam from caprolactone. The involving the production of 1,6 hexanediol is the one of particular interest to us, see the proposed reaction in Scheme 3 below.



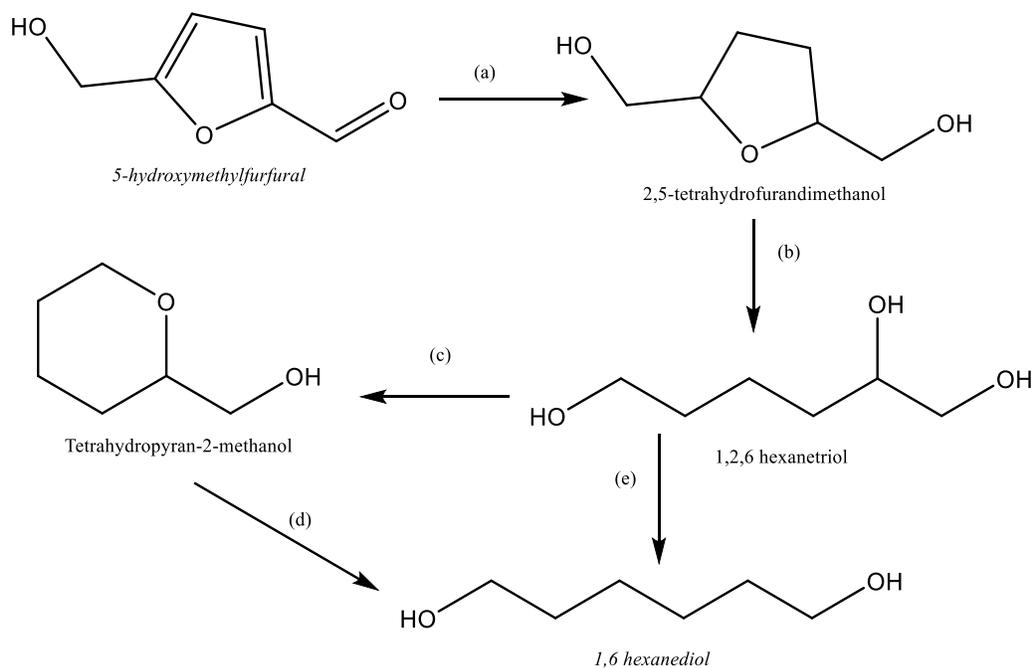
Scheme 3: Synthetic routes for the conversion of HMF into caprolactam ^[41]

Since the production of caprolactam was dependent on the successful production of 1,6 hexanediol from HMF the group tried to directly hydrogenate HMF to 1,6 hexanediol over copper chromite and Pd/C catalysts. However, this route yielded many products, (especially C5 compounds a result of decarbonylation of the aldehyde group), thus resulting in very low selectivities to 1,6 hexanediol (<4%), so this option was not ideal. An alternative route was attempted next, were they tried to

hydrogenate HMF to THF dimethanol, over metal catalysts, followed by the subsequent hydrogenolytic ring opening of THFDM to 1,6 HD over CuCr catalyst. They report that this route was easier to achieve as opposed to the direct hydrogenation option, but unfortunately very low selectivities to 1,6 HD were recorded making this option unsuitable for scale up operations. In an attempt to increase selectivity to 1,6 hexanediol they employ a reaction similar to the one first developed by Tomishige et al, who report the hydrogenolytic ring opening of tetrahydrofuran-2-methanol over a Rh-Re/SiO₂ catalyst to yield 1,5-pentanediol at >94% selectivity [42]. Under these same conditions THFDM, (obtained from the hydrogenation of HMF in the previous step), was ring opened to produce 1,2,6 hexanetriol. This was followed on by the selective hydrogenolysis of secondary alcohol over metal based catalysts to obtain 73% selectivity to 1,6 hexanediol, see Scheme 2. To attempt to increase selectivity towards 1,6 hexanediol, untethered bronsted acid catalysts were added to the bimetallic catalytic system with the intention to dehydrate of 1,2,6 hexanetriol at the 2 position alcohol. However, instead of the expected production of 1,6 hexanediol, the catalytic conditions favored a ring closing reaction and large quantities of tetrahydropyran 2 methanol, THP-2M were produced instead. They proceed by hydrogenolytically ring opening THP-2M over Rh-Re/SiO₂ and they successfully achieve this with 100% selectivity to 1,6 hexanediol at lower conversions, see Scheme 4. A dehydration rule we can gather from this study is the propensity for 1,2,6 hexanetriol to ring close over bronsted acid catalysts.

The development of heterogenous catalysts is paramount to making strides in the conversion of biorenewables, because they afford us to achieve cleaner separations and present the opportunity of catalyst reusability.

As we can see from the work presented above, the development of a selective, one pot multifunctional catalyst with multiple sites that are all active under the same reaction conditions would be very beneficial to biorenewable processing [43].



Scheme 4: Route from HMF to 1,6 hexanediol. (a) metal catalyst, H_2 , (b) Rh-Re/ SiO_2 , H_2 , H_2O , (c) Bronsted acid added to Rh-Re/ SiO_2 , H_2 , H_2O system, (d) Rh-Re/ SiO_2 , H_2 , H_2O , (e) hydrogenation over metal catalysts including CuCr, Rh-Re/ SiO_2 , (yielding a mixture of 1,6 and 1,5 hexanediol)

1.12 Copper based catalysts for biorenewable conversion

Current work is focused on the investigation of the dehydration of 1,2,6 hexanetriol over copper based catalysts in a flow of hydrogen. Copper catalysts have attracted wide interest in the field of heterogenous catalysis because of their affordability and efficiency as compared to other metal

catalysts [44]. Sitthisa et al. has reported Cu/SiO₂ for the hydrogenation/hydrodeoxygenation of furfural at 290°C. They determine that dihydrogen dissociates to atomic hydrogen which are subsequently adsorbed onto the copper surface facilitating the hydrogenation / hydrodeoxygenation reactions. They also record the robustness of the catalyst throughout the reaction, as well as very minimal deactivation with time on stream [45]. Zhang et al. investigates the hydrogenolysis of diethyl maleate over a Cu-Zn-Al-O catalyst composite [46], and they postulate the existence of two active sites; Cu⁰ and Cu⁺ which they deem responsible for the formation of the different hydrogenolysis products. They suggest that the acid support either alters the population of the two sites in the Cu catalyst, reporting synergistic effects between the metal and the acid. They also propose that the support also does directly participate in the reaction. Wang et al. postulates that the metallic components occupy support acid sites thus muting overall catalyst acidity [47]. Deutsch et al extensively reports copper based catalysts in the hydrogenolysis of the C-O bond in biorenewable derived compounds and investigates the active sites of Cu/Cr composites [48]. The relationship of Cu⁺/ Cu⁰ catalyst surface concentrations and overall catalytic activity was examined. Quantification of Cu⁰ active sites was determined using N₂O titration using the stoichiometry of 2Cu⁰:1N₂O and irreversible CO adsorption isotherms were used to quantify the Cu⁺ active sites. Based on experimental data the group offers two hypotheses explaining catalytic activity. They propose that the catalyst only had one active site, Cu⁰, over which molecular H₂ was activated, while the reactant was simultaneously adsorbed onto the catalyst surface via its hydroxyl. The second hypothesis offered was based on a 2 site mechanism similar to a proposal initially made by Rao et al [49, 50]. The two site mechanism proposes the simultaneous existence of both Cu⁰ and Cu⁺ active sites, whereby both sites play different roles. Cu⁰ is hypothesized to activate molecular hydrogen, while Cu⁺ is responsible for adsorption of the

carbonyl group, which is the hydroxyl group in this case. To validate these hypotheses, the group examines the relation between catalyst specific activity and surface concentrations of the Cu^0/Cu^+ active sites. A strong correlation was established between Cu^0 site density and specific activity, while only a positive but weak correlation was observed for Cu^+ . They conclude that the first scenario of existence of Cu^0 active sites was more likely than a two site mechanism. The group goes further to point out that Cu^0 was present in surface concentrations approximately 10-30 times those of Cu^+ so that comparisons between the two components could not be easily made; based on this fact they were unable to completely rule out the possibility of a two site mechanism. In a subsequent paper Deutsch et al presents the hydrogenolysis of 5-methylfurfural to dimethyl furan over Cu/Cr, Cu/Fe and Cu/Mn composites to investigate the relationship between Cu^0 surface concentrations and C-O bond hydrogenolysis [51]. No direct correlation between Cu^0 and catalytic activity was observed for any of the composites, leaving a high possibility of a two site mechanism to explain the observed activity.

An analogous study to the work reported herein was recently carried out by Sun et al, and it focused on the vapour phase dehydration of 1,2, propanediol to propanal over several solid acid catalysts, such as silica alumina and metal modified alumina catalysts [52]. Propanal - a structural isomer of acetone, otherwise obtainable by hydroformylation, a process combining synthesis gas and ethylene over metals; it has industrial applications in alkyl resin production. The biorenewable approach provides a sustainable alternative because 1,2 propanediol is obtainable via the dehydration/hydrogenation of glycerol over copper or silver metals. The group expects that the secondary OH group in 1,2 propanediol will be preferentially abstracted over acid catalysts, (according to the carbocation formation protocol), similar in nature to the dehydration of glycerol

to acrolein. It is interesting to note that glycerol is dehydrated to acrolein over acid catalysts and to hydroxyacetone over copper based catalysts, implying that the dehydration mechanism was altered by presence of the metal functionality. Acid catalyst tested in their work were significantly stabilised by addition of the metal functionality, a phenomena also reported by other groups. The vapor phase dehydration of tetrahydrofurfural alcohol to 3,4 dihydropyran was reportedly slowed down significantly by severe acid catalyst deactivation showing that acid catalysts were prone to coking in this reaction [53]. Sun et al records a loss of acid catalyst activity in N₂, but record a marked improvement when the acid catalyst is modified by Cu addition under H₂ flows. Cu catalysts reported in this work were reduced in H₂ prior to reaction, and it was hypothesized that metallic Cu and the flowing hydrogen acted together as a product remover thereby preventing the formation of coke.

TPD analyses showed that the addition of metals significantly reduced catalyst medium and strong acid sites, while increasing weak sites; implying that metal functionality reduced catalyst acidity see Fig 4. In a prior study silicotungstic acid and zeolites possessing strong acid sites were severely deactivated during the dehydration of PDO to propanal, implying that strong acid catalysts were unstable for these reactions. This observation is consistent with the fact that metals stabilized acid catalysts perhaps by lowering catalyst acidity [30].

Silica alumina in the dehydration of PDO was found to produce the best selectivities to propanal before they deactivated with time on stream. Thereafter the catalyst was modified by Cu, Co and Ag addition and this significantly stabilized the catalysts. Of the 3 metals selected, Ag at a loading of 3wt% produced the highest selectivity to propanal at 300°C and 90ml/min H₂ flowrate.

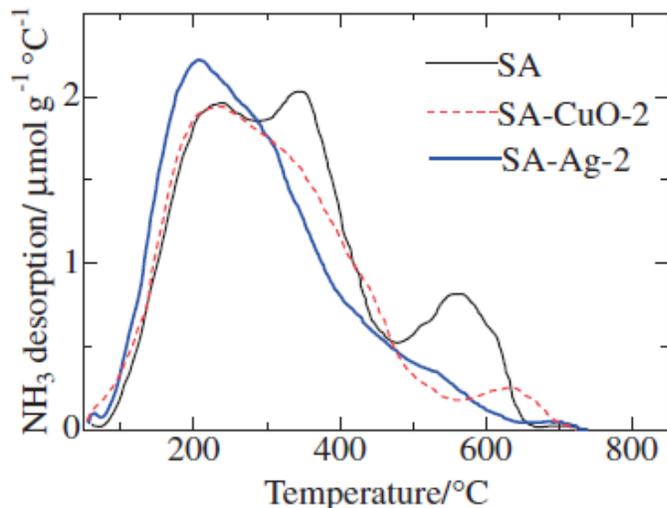


Figure 4: NH_3 TPD of silica alumina before and after metal loading [52]

In other work, 3,4 dihydropyran was produced via the catalytic dehydration of tetrahydrofurfural alcohol, over transition metal modified acid catalysts. Prior work has shown that alumina is active for this reaction particularly in the initial stages of reaction, before the acid catalyst is deactivated [53] [54]. Alumina was subsequently modified by addition of Rh, Pt and Pd, but the resultant composites were found to still deactivate in H_2 . Cu was then added and it was determined that copper metal significantly stabilized the alumina catalyst and improved selectivity to 3,4 dihydropyran in a flow of hydrogen. However, the same copper based alumina catalyst was seen to deteriorate in a N_2 flow. The group suggests that CuO is reduced to metallic Cu prior to reaction so that the presence of hydrogen plays the role of keeping the metal in its reduced state. Copper was found to have synergistic effects with hydrogen that inhibited coke formation thereby stabilizing the catalyst.

1.13 Effect of carrier gas choice on catalytic activity and catalyst longevity

The effect of hydrogen carrier gas on activity of acid catalysts has been studied by many researchers. In most of the cases reported, the presence of hydrogen is seen to suppress acid catalyst activity, and sources propose that this is a result of hydrogen atoms and hydride ions shielding the Lewis acid sites [55-58]. However, Baba et al reports that the activity of Ag ion exchanged Y zeolites were largely enhanced by the presence of hydrogen, while activity of the plain unmodified zeolite seemed to be unchanged by the presence of hydrogen [59]. Hydrogen's promoting effects on acid catalyzed reactions over AgY zeolite is attributed to the release of a proton after Ag^+ reacts with hydrogen to form Ag^0 . The proton thereafter acts as the active site for acid catalyzed reactions. The effects of the hydrogen were found to be reversible; when hydrogen was removed catalytic activity plummeted, but when it is re-introduced catalytic activity was gradually restored.

Other sources who have also investigated hydrogen effects are Shishido et al who seek to determine if the bronsted acid activity of platinum modified zirconium oxide was enhanced by hydrogen carrier gas. They record increased conversions coupled by very little catalyst deactivation in a flow of hydrogen with time on stream [60]. However, they find that activity was quickly diminished when carrier gas was changed to inert helium; and activity was gradually restored when carrier gas is switched back to hydrogen. Similar to the findings of Sun et al [52] they find that coking was minimized in the presence of hydrogen, while carbonaceous residues increased in the absence of hydrogen. The effect of hydrogen promoting catalytic activity was rationalized by the formation of protonic acid sites from the hydrogen molecules. Hattori et al have studied the interaction of molecular hydrogen with platinum and sulfate ion modified zirconium oxide catalysts for the isomerization of hydrocarbons [61]. They report the isomerization of butane and propane at 250°C and find that the presence of hydrogen markedly improves butane

isomerization; while the isomerization of pentane only occurred in a flow of hydrogen. The group proposes that molecular hydrogen is dissociated on the platinum surface yielding hydrogen atoms, and these are spilled over to a Lewis acid site where they are converted to an electron and a proton, H^+ which acts as the active site for acid catalyzed reactions. Infrared spectroscopy studies of pyridine adsorption showed that when the catalyst was heated to temperatures between 150 and 350°C in the presence of hydrogen, the amount of protonic acid sites formed coincided well with the amount of support Lewis acid sites lost, suggesting that molecular hydrogen was responsible for acid sites production. In a typical acid catalyzed reaction e.g. the ring opening of cyclopropane, the presence of hydrogen increased catalytic activity only by a small percentage, and hydrogenation products scarcely occurred; implying that hydrogen carrier gas was not participating in hydrogenation activity supporting the theory of acid site production.

1.14 Reaction mechanisms for gas phase dehydration over heterogeneous catalysts

Pines and co-workers investigate the dehydration of aliphatic and cyclic alcohols over alumina catalysts. They show that secondary isomerization reactions that usually accompany dehydration can be suppressed by the use of bases, such as ammonia [62]. The dehydration chemistry of stereoisomers is explored using menthol and neomenthol as probe molecules and it was observed that neomenthol dehydrated 3 times faster than menthol. They conclude that the elimination of water is easily achievable from adjacent diaxial, (trans) hydrogen and hydroxyl groups. The dehydration mechanism by which the alcohol attaches itself to alumina surface is shown in Fig 5 and this is followed by trans elimination of a the water molecule as shown.

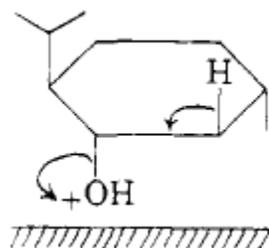
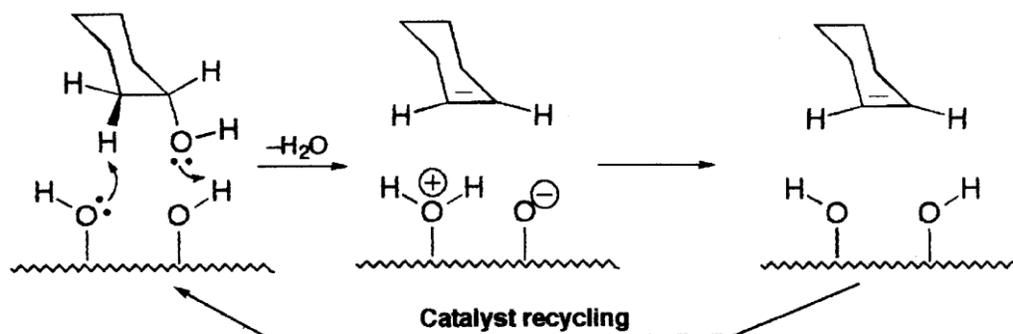


Fig 5: *Trans* elimination in the dehydration of neomenthol^[62]

Gas phase dehydration of alcohol reactants over acid catalysts takes place by either one or both of two mechanisms [62]. The first scenario is a concerted dehydration mechanism whereby the catalyst provides both the acid site to facilitate reaction with the hydroxyl group and a basic site to abstract the proton in a similar mechanism liquid phase E2 elimination. The second scenario is a non-concerted dehydration mechanism, similar to the E1 elimination whereby the catalyst provides an acid site used for the abstraction of the hydroxyl group resulting in a carbocation formation, followed by double the loss of a water molecule resulting in the production of alkenes [63].



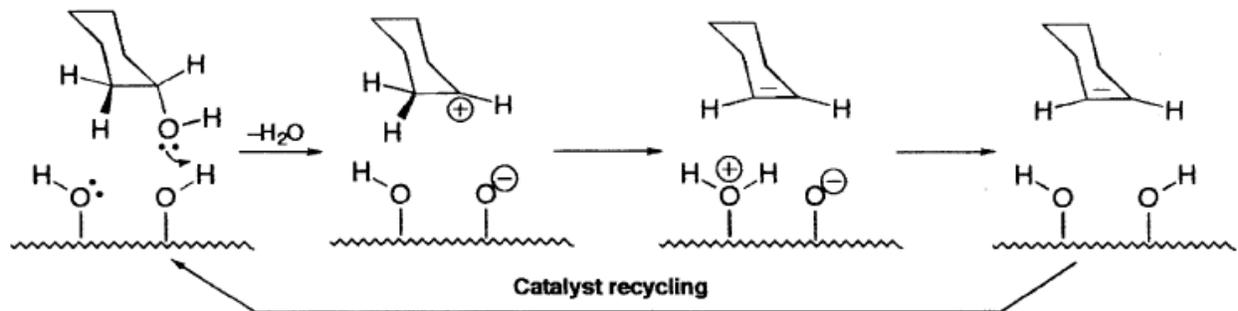


Fig 6: Concerted dehydration mechanism shown above and non-concerted dehydration below ^[63]

Johnstone et al have used deuterium labeling to investigate the dehydration of cyclohexanol to cyclohexene over zirconium phosphate. They determine that the reaction proceeds not by a concerted process but via the carbocation formation mechanism [64]. As we know the most stable carbocation is formed by the tertiary alcohol, but the group highlights that the tertiary alcohol experiences trouble in binding onto the catalyst surface unlike the secondary alcohol. This effect is attributed to steric hindrances resulting from the crowding brought about by the methyl group which causes slower adsorption and ultimately slower dehydration rates.

1.15 Approach to current work

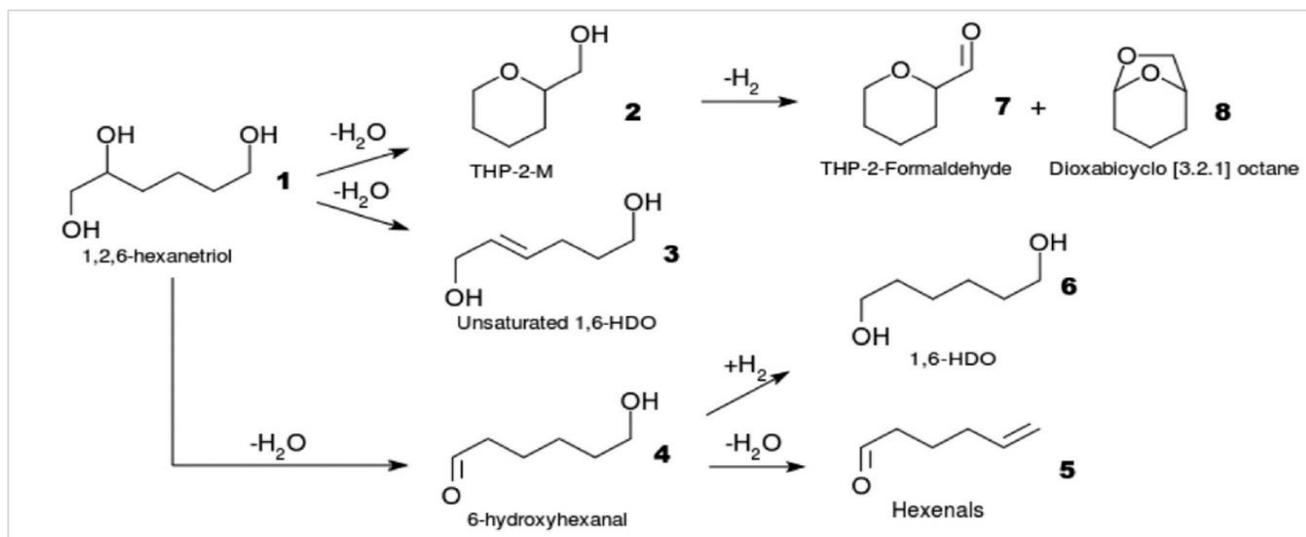
Current work is focused on developing a catalytic system that can selectively remove the secondary hydroxyl group in 1,2,6 hexanetriol and maximize selectivity to linear products. 1,2,6 hexanetriol - a molecule derivable from biorenewable sources is comprised of a 6 carbon chain consisting of 3 hydroxyl groups at the 1,2 and 6 carbon locations. 1,2,6 hexanetriol is the ideal model compound for investigating selectivity drivers because it offers an added level of complexity to the molecules previously reported in literature. The desired end product is 1,6

hexanediol, has been previously reported as obtainable via selective hydrogenolysis of tetrahydropyran - 2 - methanol over metal alloys [41] [65]. 1,2,6 hexanetriol has to undergo selective abstraction of the secondary hydroxyl group via an acid catalysed dehydration reaction to achieve the desired product. The ground work done on the dehydration of this molecule was performed over solid acid catalysts prior to acid catalyst modification by metal addition. Upon metal addition we observed higher selectivities towards 1,6 hexanediol and its precursors. Linear products were found to decrease with increasing catalyst acid strength while it was determined that ring products could not be ring opened over acid catalyst [66]. The approach taken in this work to is to maximize selectivity to 1,6 hexanediol by developing a bifunctional catalyst with acidic and hydrogen activation capabilities that can convert 1,2,6 hexanetriol to 1,6 hexanediol in a single step. In reality however, the dehydration of 1,2,6 hexanetriol yields many other by-products such as pyranic products among others; therefore we must develop a catalyst that can maximize selectivity towards 1,6 hexanediol and its precursors.

Nolan et al proposed a reaction pathway for the dehydration of 1,2,6 hexanetriol over acid catalysts which can be used as a guideline in current work, see Scheme 5 below [66]. The reaction pathway was proposed based on the observation that THP-2M did not ring open; while 1,6 hexanediol did not ring close over plain acid catalysts. Therefore, both processes required the presence of metal functionality.

The dehydration of 1,2,6 hexanediol to 1,6 hexanediol and its precursors over copper modified silica alumina and silica catalysts at a Cu loading of 0.5wt% is presented in the following chapters.

We discuss product selectivity drivers, catalyst activity/stability, catalyst characteristics and determine the active sites involved in this reaction.



Scheme 5: Reaction pathway for the dehydration of 1,2,6 hexanetriol over acid catalysts ^[66]

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CHAPTER 2: RESEARCH OBJECTIVES, METHODOLOGY AND BROADER IMPACTS

The goal of this work over and above explaining the Cu metal effect on the selective dehydration of 1,2,6 hexanetriol, is to better understand catalytic dehydration of multifunctional substrates within the context of polyols. It has been established that acid supported copper metals are capable of selectively abstracting the secondary hydroxyl group in 1,2,6 hexanetriol to yield 1,6 hexanediol as well as minimizing ring closing reactions that yield pyranic products. 1,2,6 hexanetriol has been selected as an ideal model compound for this investigation because it possesses a third hydroxyl group, which offers an added dimension of complexity as compared to the molecules previously reported in literature namely diols and monols. Although 1,2,6 hexanetriol has an added complexity dimension it still allows for the simplicity of performing reactions in the gas phase, since reactions require to be done in the liquid phase as we move to 4 hydroxyl groups and up.

There were many variables in our system that worked together to alter the Cu composites' catalytic activity on the dehydration of 1,2,6 hexanetriol. The variables of this system are; choice of catalyst, choice of carrier gas, support acidity, hydrogen partial pressure and reactant partial pressure. The determination of the effects of individual variables on the catalytic activity was complicated because the variables had synergistic effects that convoluted the catalytic activity altering it upward or downward. Therefore, it was necessary to decouple the effect of the variables prior to making any conclusions about the observed catalytic activity. Selectivity studies are used as the basis for comparison of catalytic activity for the variables investigated in this work.

Changing the variables mentioned above was seen to have definite effects on the catalytic activity for the dehydration of 1,2,6 hexanetriol. Previous work by Nolan et al on the dehydration of 1,2,6 hexanetriol over plain acid catalysts determined that the reactants tend to go through a ring closing reaction in the presence of an acid catalyst leading to high selectivity toward pyranic products in a typical bronsted acid catalyzed reaction [1]. It was seen that the ring closing reactions were all the more pronounced at higher catalyst acidities so that selectivity towards pyranic products varied proportionately with catalyst acid strength; higher catalyst acidities increased selectivity to pyrans and vice versa. Not only was high selectivity to pyrans undesirable, (since the target molecule is a linear product) but plain acid catalysts were seen to succumb to copious amounts of coking which led to catalyst deactivation. In subsequent work still to be published by Nolan et al, the issue acid catalyst deactivation was addressed by modifying the catalyst by the addition of metal functionality using metals such as Ni, Ru, Pd, Pt and Cu. It was determined that Cu produced the highest selectivity towards the desired linear product and that this favorable result was accompanied by minimal catalyst deactivation. The positive results obtained after Cu addition led to many questions arising about the synergies between the Cu and acid support catalyst components that were causing the positive catalytic behavior. Answering these questions forms the main motivation for this work. We focus on establishing a deeper understanding of the behavior the Cu based acid catalysts for the dehydration of 1,2,6 hexanetriol.

In this work a copper metal was supported on various supports, mainly silica alumina; were the silica to alumina ratios were tuned to obtain catalysts of varying acidity. Among the copper catalyst slate tested was a unique copper metal catalyst supported on silica which was obtained from collaborates at the University of New Mexico and was used as is. Pure acid catalysts prior to metal

addition were also tested to provide a control experiment for comparison purposes with the experimental results obtained from the metal modified acid catalysts. Our study reveals that the addition of copper metals to acid catalysts has the effect of lowering overall catalyst acid strength as determined by TPD data profiles obtained before and after Cu metal addition. This result is consistent with reports made by other sources in literature such as Sun et al who report the loss of strong acid sites in silica alumina catalysts after Ag was added [2]. Based on acid catalyst reaction testing data obtained by Nolan et al [1], we expect that since metal addition has the effect of lowering the catalyst acidity, the lower acidic conditions will suppress ring closing reactions and increase selectivity towards linear products. According to our reaction testing data these expectations were upheld as lower acidity catalysts obtained after metal addition yielded higher selectivity to linear products. As previously mentioned, copper metal catalysts were supported on material of varying acid strengths; and it was seen that as the support acidity increased the selectivity towards pyranic products also increased consistent with our initial expectations. The selectivity data also reveals that the addition of metal functionality to acid catalysts was significantly stabilizing the catalyst; because the activity of the catalysts was not significantly altered with catalyst time on stream. These observations were later validated by thermogravimetric analysis, TGA data which showed that the catalysts were significantly stabilized by metal addition. Current work shows that acid catalysts experienced large amounts of weight losses as seen in TGA data symbolic of heavy catalyst coking, while metal modified acid catalysts did not experience nearly as much weight loss. Therefore, not only was the Cu metal increasing selectivity to linear products, but it was also significantly stabilized the catalyst by suppressing coking processes.

In order to elucidate the key observations made in this work the selectivity data was analyzed and two branches of hypotheses were proposed to explain the catalytic activity. Both branches were comprised of cascading events occurring in series leading up to the main event that formed the hypothesis. The first hypothesis states that copper metal surface facilitates the dissociative adsorption of molecular hydrogen leading to a series of events (explained in chapter 4), that end up with the production of a unique active sites that supplements or otherwise substitutes the support active site taking over catalytic activity. The second hypothesis projected that the hydrogen carrier gas was playing the role of keeping the copper metal in its reduced state Cu^0 ; and that the reduced metal sites were acting as the active site for the reactions proceeding. The analysis of the experimental data as well as the hypotheses testing experimental data served to validate the two branches of hypotheses, see chapter 3. An in depth discussion of the two hypotheses as well as some proposed reaction mechanisms based on selectivity data are presented in chapter 4. Both hypotheses were seemingly upheld and with the current experimental information we found them to be both equally likely. It still remains to be determined whether one hypothesis was more likely over the other, or if both processes proposed by the hypotheses were proceeding simultaneously. Therefore, we will present the two hypotheses concurrently. Future experiments to further distinguish between the two hypotheses are suggested in the final of this work.

The information gleaned from this study can ultimately be used for the creation of a catalytic toolbox that is applicable to the general upgrading of polyols in particular the selective dehydration of polyols. Investigations of noble metals supported on acid catalysts are still being developed and the fundamental principles regarding reaction mechanisms and pathways are not well established. To date, most polyol dehydration work has been done over acid catalysts, so this work provides a

new relatively unexplored approach of using metal acid bifunctional catalysts. Copper based acid catalysts have been established as viable catalysts for the dehydration of 1,2,6 hexanetriol, therefore it is important to study and understand their catalytic behavior; a vital resource for the further development of these dehydration catalytic systems.

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CHAPTER 3: INVESTIGATING EFFECTS OF METAL FUNCTIONALITY, SUPPORT ACIDITY, CARRIER GAS AND VARIABLE SYNERGY EFFECTS ON THE DEHYDRATION OF 1,2,6 HEXANETRIOL

3.1 Introduction

Acid catalyzed dehydration has been widely researched and extensively reported by many sources in literature. Well established is the carbocation protocol mechanism which occurs during non-concerted dehydration. This protocol allows for preferential abstraction of the tertiary alcohol, followed by the secondary alcohol and lastly the primary alcohol. This is driven by the energy levels of the secondary and primary carbocations which are 52 and 134 kJ/mol higher than the tertiary carbocation respectively [1].

The selective dehydration of biorenewable derived platforms is a relatively new field not widely documented in literature. However, strides have been taken to understand these systems and to shed light on the reaction mechanisms. As discussed in the preceding chapter, Sato et al have done extensive work on the dehydration of butanediols, propanediols and glycerol [2-9]. The information gleaned from these studies shows that 1,4 and 1,5 butanediols have the propensity to readily dehydrate to form cyclic ring products over solid acid catalysts. In this work, the desired product is 1,6 hexanediol therefore a successful catalyst should have the capacity to suppress ring closing reactions, while increasing selectivity to linear di-oxygenates which can easily be hydrogenated to diols including 1,6 hexanediol.

As seen in preceding chapters, 1,6 hexanediol has been acquired from 1,2,6 hexanetriol over bimetallic catalysts possessing oxophilic and hydrogenating capabilities, with the acidic nature of the oxophilic metal catalysing the hydrogenolysis of the C-O bond [10]. Dumesic et al presents C-O bond hydrogenolysis of polyols and cyclic ethers over Rh/Re based catalysts. They also find that metal acid bifunctional catalysts are effective for selective hydrogenolysis of the C-O by acid catalyzed ring opening and dehydration reactions [10]. Buntara et al presents the hydrogenolytic ring opening of tetrahydrofuran-dimethanol, THFDM over Rh/Re bimetallic catalysts supported on SiO₂ to produce 1,2,6 hexanetriol [11]. Their goal is to selectively remove the secondary hydroxyl alcohol on 1,2,6 hexanetriol to achieve 1,6 hexanediol over Rh/Re/SiO₂ composites, however they only realize low selectivities over that catalyst. In order to maximize selectivity to 1,6 hexanediol they modify the Rh/Re-SiO₂ composites with untethered Brønsted acids with the hopes of maximizing the selective removal of the 2-position alcohol on 1,2,6 hexanetriol. Instead, after addition of the Brønsted acids they surprisingly end up with high yields of tetrahydropyran-2-methanol, THP-2M with no trace of 1,6 hexanediol. This implies that 1,2,6 hexanetriol has the propensity to ring close over Brønsted acid catalysts. Nolan et al thereafter reports the inability of pyrans ring opening over acid catalysts during selective dehydration of polyols over heterogeneous Brønsted acids [12]. This phenomena has also been previously reported by Buntara et al, who assert that Brønsted acids promote ring closing reactions, and that resultant ring structures do not subsequently ring open over plain acid catalysts [11].

Gathering of all the key points presented above we see that it would be beneficial to develop a catalyst that can convert 1,2,6 hexanediol to α, ω diols in a single step - without having to go through a ring closing reaction which require subsequent ring opening. On the dehydration of 1,2,6

hexanetriol over bronsted acids, Nolan et al record low yields to 1,6 hexanediol over bronsted acids, while they observe high yields to THP-2M, similar to the findings reported by Buntara et al. Therefore, to maximize selectivity toward desired linear dioxegenates which can subsequently be hydrogenated to α,ω diols we require the design of catalysts that promote the protonation of the secondary alcohol while suppressing ring closing reactions.

Current work is focused on bronsted acid catalysts modified by Cu metal addition to mimic the catalytic system observed in the bimetallic systems that possess both oxophilic and hydrogenating properties. Such a catalytic system is expected to maximise selectivity to 1,6 hexanediol and its precursors by facilitating the direct dehydration of 1,2,6 hexanediol linear dioxegenates followed by hydrogenation to 1,6 hexanediol.

3.2 Experimental design and methodology

3.21 Biorenewable platform molecule

The platform molecule used in this work is 1,2,6 hexanetriol acquired from Sigma Aldrich. This work reports the dehydration of the pure triol, as well as 10wt% triol diluted in water.

3.22 Catalysts tested

For this study a slate of copper modified acid catalysts were prepared at varying acid strengths. Cu loading was kept at 0,5wt % for all catalysts while support acidity was tuned by the varying silica to alumina ratios. Catalysts are named according to their support acidity, for example CuSiAl10; implied a copper modified silica alumina catalyst with a silica to alumina ratio of 10:1, with copper

loading at 0.5wt%. The complete slate of catalysts tested in this work included CuSiAl10, CuSiAl4, CuSiAl2, CuSiAl1, CuSiO₂ as well as plain acid catalysts SiAl10, SiAl4, SiAl2 and SiAl1.

3.3 Catalyst sample preparation

Different ratios of silica alumina support materials were prepared by the precipitation method following guidelines of a method prescribed by Nolan et al with slight modifications [12]. Sodium metasilicate and aluminium sulphate hexadecahydrate were massed to specific quantities for the required silica to alumina ratios, dry mixed in a stirred round bottom flask and thereafter dissolved in 500ml of water. For instance to acquire a silica alumina ratio of 10:1 5g of sodium metasilicate and 1.29g aluminium sulphate hexadecahydrate were used to prepare a support of silica to alumina ratio 10:1. Once the precursors were dissolved, a 10wt% hydrochloric acid stock solution was added until the mixture began to precipitate at a pH of around 8.5. Drops of acid were thereafter carefully added until pH 7 was reached. The precipitate was then filtered and washed 3 times in deionised water. The resultant filter cake was dried at 110°C overnight, crushed and calcined at 500°C for 4 hours. Copper was supported on the silica alumina catalyst by the incipient wetness method. A prescribed amount of copper (II) nitrate trihydrate was dissolved in a 0.1M solution of ammonium nitrate and added to the silica alumina catalyst according to its pore size. The resultant catalyst was dried at 120°C for two hours and re-calcined at 500°C for 4 hours. The metal acid bifunctional catalysts were named, CuSiAl10, 4, 2 or 1 which represented copper on silica alumina and the numbers referred to the different silica alumina ratios. A second type of catalyst was obtained from collaborates at the University of New Mexico, who prepared CuSiO₂ catalyst using an alcohol reduction method - Cu loading was kept at 0.5wt% as with the SiAl based catalysts.

All catalysts were pelletised by pressing in a Carver benchtop pellet press at 40 000psi. The pellets were broken up and sieved through two meshes of 250 and 350 μ m and resultant particles sizes were used for reaction testing. The catalyst pellets were mixed with 1mm glass beads, and loaded into the reactor. Cu modified based catalysts were reduced in-situ in a flow of H₂ gas at 300°C for a minimum of 4 hours before the reaction was started. The reduction temperature was chosen based on the findings by Deutsh et al who report that reducing copper based catalysts at 240°C resulted in low copper surface area, at 300°C copper surface area was doubled, while copper was sintered at temperatures beyond 300°C [13]. The reduction step concludes the catalyst synthesis and preparation processes.

3.4 Catalyst characterization

Fresh catalysts were characterized by ammonia temperature programmed desorption - (NH₃-TPD) to quantify acid sites; N₂O chemisorption - to determine catalyst surface properties, i.e Cu⁰ surface concentrations and Cu dispersion; BET method - to determine total surface areas of the synthesized copper composites. Spent catalysts were characterized by thermo gravimetric analysis, (TGA), for carbon deposition quantification.

3.4.1 Ammonia TPD, (NH₃-TPD)

A typical NH₃-TPD experiment was performed in a Micrometrics AutoChem 2920. Samples of between 50mg and 60mg were reduced in 10% H₂ diluted in Ar for three hours at 300°C. The temperature was thereafter cooled to 240°C and held for 30 minutes, after which it was further cooled to ambient to allow for H₂ desorption. Samples were subsequently heated from ambient to

700°C, at a ramp rate of 10°C/min in a flow of helium gas to eliminate chemisorbed water. The system was thereafter cooled to 50°C in a flow of 9.9969% NH₃ in helium for 30 minutes. The gas flow was then changed to helium to allow for all the excess ammonia to be purged out from the container. The samples were then heated to 700°C at a ramp rate of 10°C/min in a helium flow. The amount of NH₃ desorbed over the temperature range was recorded and data peaks obtained. These were integrated to ascertain the number of acid sites for all peak areas.

3.42 N₂O chemisorption

The N₂O chemisorption experiment was carried out in a Micrometrics Autochem II Chemisorption Analyser. Irreversible N₂O adsorption isotherms were used to quantify the amount of surface Cu⁰ according to a method presented by Evans et al using some of the specifications provided by Bansode et al [14] [15]. Helium was flowed over the sample and held for 30 minutes and followed by a gas change to 10% H₂ in argon flowed at 30cm³/min. The temperature was ramped to 300°C at the rate of 10°C/min and held for 4 hours to reduce the catalyst, so as to mimic reaction conditions where catalysts are reduced 4 hours insitu prior to reaction. The gas flow was subsequently changed to helium and the temperature cooled to 90°C and held for 30 minutes. The system waited for the baseline to be stable and then started dosing 97% N₂O while simultaneously recording the signal. The pre-reduced copper was oxidized upon dissociative chemisorption of N₂O on its surface according to $2Cu^0 + N_2O \rightarrow Cu_2O + N_2$. A total adsorption isotherm was collected and the system evacuated for 30 minutes, after which the measurement was repeated to determine the reversible isotherms. The difference between the total and reversible isotherms gave the irreversible isotherms which was a quantification of the chemisorbed N₂O. This value is then used to determine a actual measurement of the exposed Cu⁰ active surface area.

3.43 N₂-physisorption, BET method

The N₂ physisorption BET method was used to determine total surface areas of the bifunctional catalysts and was performed by a Micrometrics ASAP 2020 machine. Catalyst masses of approximately 100mg were brought to a 10 μ mHg vacuum and heated to 423K for 6 hours. A known amount of N₂ was dosed and an N₂ adsorption isotherm was recorded. The amount of physisorbed N₂ was measured and used to determine the catalyst surface areas.

3.44 Thermogravimetric analysis, TGA

Spent catalysts that were recovered from the reaction were allowed to dry overnight prior to coking in a Perkin Elmer Simultaneous Thermal Analyser (STA 6000) equipment. The analysis was carried out using about 5mg of sample which was oxidised in a 20ml/min air flow causing the formation of passivated oxide layers on the catalysts. The temperature was ramped from 50°C to 910°C at a rate of 10°C/min resulting in weight loss. The weight loss observed in the catalyst was assumed to be due to the oxidation of coke.

3.5 Catalyst reaction testing

The materials used in this step are 1,2,6 hexanetriol, sodium metasilicate, aluminum sulphate hexadecahydrate, copper (II) nitrate trihydrate, ammonium nitrate, all of which were purchased from Sigma Adrich; H₂ and N₂ both purchased from Airgas. 0.1g of catalyst, with particle sizes between 250 and 350 μ m, were diluted in 1mm glass beads, packed into the reactor and reduced insitu in a flow of hydrogen gas for 4 hours at 300°C as explained in preceding sections. The reaction was performed in a packed bed stainless steel flow reactor, 12mm in diameter and 15cm

in length at 300°C. The reactor top and bottom temperatures were monitored and regulated by 2 thermocouples, so that the temperature was kept at 300°C±2°C. An aqueous solution of 10wt% 1,2,6 hexanetriol, (or neat 1,2,6 hexanetriol depending on the reaction test) was pumped by a syringe pump at a feed rate of 5ml/hr - 41mmol/hr and fed into a stainless steel preheater equipped with a thermocouple which regulated the temperature keeping it at 300°C±2°C. The reactant was heated to vapor, mixed with a carrier gas and the resultant mixture co-fed into the packed bed reactor. The reaction was performed in a carrier gas of either N₂ or H₂ at 100ml/min flowrate. For experiments involving the investigation of the effects of H₂ partial pressure N₂ gas was used as the make-up gas so as to hold reactant partial pressure constant for all runs. The cumulative flowrate was maintained at 150ml/min for all partial pressure experiments; for instance the initial run was done at 150ml/min H₂, the next 120ml/min H₂ with 30ml/min N₂ as makeup gas. After the reaction was completed the resultant product vapors flowed into a condenser unit; where condensation occurred. Liquid products were subsequently collected in sample vials while effluent carrier gas exited the system via an exit pipe attached to the system. A total of 5 samples were collected for most catalyst runs, while 20 samples were collected for catalyst deactivation experiments.

Liquid products were analyzed in an Agilent 7890 gas chromatogram equipped with both mass spectrometer and flame ionization detector. Products obtained from runs involving 10% 1,2,6 hexanetriol were analysed as is, while pure triol samples were prepared by diluting 1g of product in deionized water to make a 10wt% solution due to high viscosity of the samples. 10µL of methanol was used as internal standard.

3.6 Results

3.7 Catalyst properties

1. Acid site properties

Acid site distributions peaks obtained from TPD data are illustrated in Fig 1. The first peaks on the far left represented the very weak acid sites, followed by weak sites, medium sites and strong acid sites on the far right. As expected, a close inspection of the data collected revealed that the total number of acid sites varied proportionately with catalyst acidity based on the silica to alumina ratios. This implies that the catalysts possessing the highest alumina to silica ratios possessed the strongest acid sites. For the catalyst slate tested in this work CuSiAl1 contained the strongest acid site peak with maximum temperatures of $>690^{\circ}\text{C}$ being noted. CuSiAl2 was next in line, with two peaks comprising a broad strong acid peak and a smaller weak acid peak. CuSiAl4 contained a weak acid site peak and a broad peak of medium strength acid sites while CuSiAl 10 had the broadest peak of weak sites and no medium or strong acid site peaks. TPD data profiles for CuSiO₂, (not shown in Fig 1), revealed small a concentration of very weak sites at about 100°C . Based on this information we could rank the catalysts according to their acidity as follows; CuSiAl1 $>$ CuSiAl2 $>$ CuSiAl4 $>$ CuSiAl10 $>$ CuSiO₂; were CuSiAl1 was the most acidic and CuSiO₂ was the least acidic.

TPD analysis was also used to determine how metal functionality addition to an acid catalyst affected the acid site distribution. To achieve this, analyses were done before and after metal addition to allow for comparison between the two. The comparison of the data reveals that addition of metal functionality significantly reduced the acid sites population originally possessed by the support material. SiAl4 and CuSiAl4 were used for this comparison. We can therefore conclude

that addition of metal functionality has the effect of muting all the strong acid sites initially possessed by the support as shown in Fig 1 below. See the acid site distribution of SiAl4 and compare with CuSiAl4. We see that the strong acid sites of SiAl4 found at 700°C were eliminated after metal addition. This phenomenon is well documented in literature and it was consistent throughout all the copper based catalysts tested.

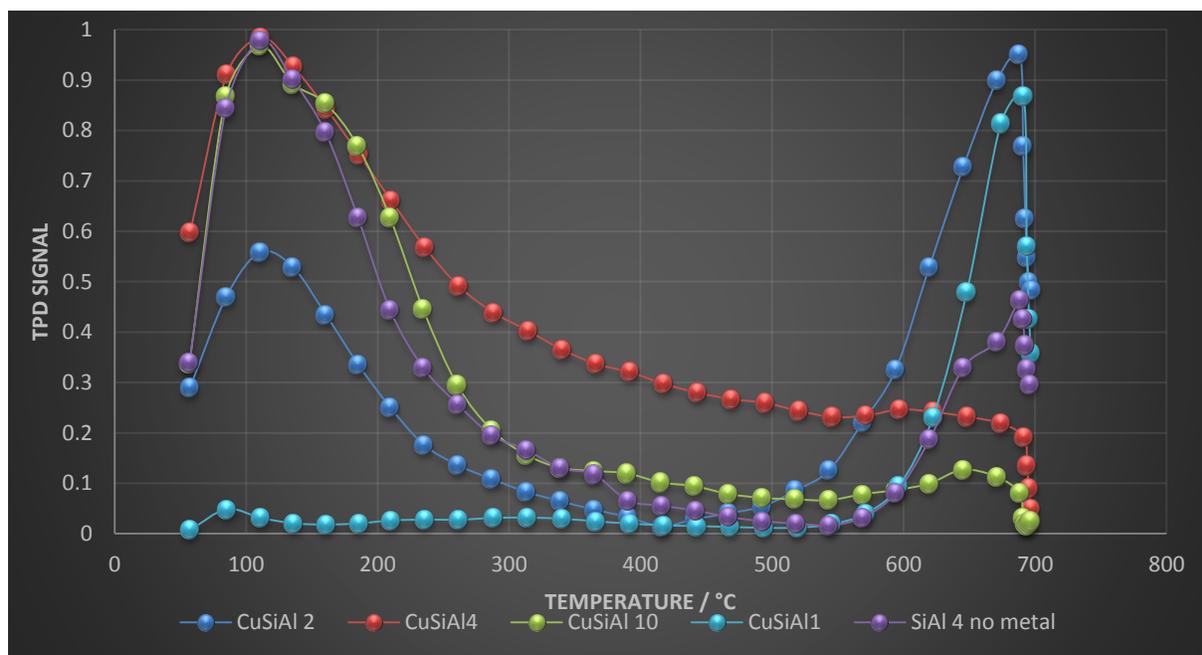


Fig 1: TPD profiles of fresh catalysts

2. Surface properties

a) N₂O chemisorption

The N₂O chemisorption data obtained revealed key information about the catalytic surface properties. Importantly Cu⁰ surface concentrations were quantified as shown in Table 1. We were able to deduce that metal catalysts supported on stronger acid material exhibit higher copper metal dispersions, for instance CuSiAl 1 had dispersions of over 3 times higher than those of CuSiO₂

(no-acid support) catalyst, see Table 1 for a summary of the surface properties. This probably explains why higher catalytic activity was noted for copper metal catalysts supported on the higher acid supports. According to Huang et al. the copper particles synthesized in this work were considerably large for catalysts synthesized by the incipient wetness impregnation method, and this occurrence could explain the relatively low to medium dispersions noted throughout the slate of copper catalysts tested [16]. As expected the smallest particle sizes were associated with largest the copper dispersions while the formation of larger particles, was attributed to particle sintering which led to reduced copper dispersions.

b) BET surface area

Surface area properties were investigated using the BET method and the surface areas obtained ranged from 5 to 445m²/g as shown in Table 1. No notable correlations between catalyst surface area and silica-alumina ratios of the supports were noted. The CuSiO₂ catalyst prepared by alcohol reduction had the largest surface areas when compared to copper catalysts prepared by the incipient wetness method and this difference in surface area was attributed to the different synthesis methods employed. SiAl₄ was tested before and after metal addition, and data obtained demonstrated that metal addition reduced the surface area of the acid catalyst quite significantly.

1. Coking studies

Catalyst coking was investigated by the thermogravimetric analyser, and the observed weight losses were assumed to be associated with the incineration of coked carbonaceous material leaving the surface of the catalyst. The weight losses for the tested spent catalysts ranged from 11% to 26% as shown in Fig 2. All catalysts experienced the most weight loss between 300°C and 500°C.

Table 1: Summary of characterization and reaction data for 4 catalysts

Catalyst	Cu ⁰ loading %, Si:Al ratio ^(a)	Cu ⁰ surface area m ² /g catalyst ^(b)	Cu ⁰ dispersion % ^(c)	Cu ⁰ particle size Nm ^(d)	Total BET surface area/ m ² /g ^(e)	Specific activity (μ mol/m ² /min) ^(f)
Cu/SiO ₂	0.5, 1	0.45	14	7.4	445	7.36
Cu/SiAl 10	0.5, 10:1	0.74	23	4.5	95	67.59
Cu/SiAl 4	0.5, 4:1	0.39	12	8.5	5	1332
Cu/SiAl 2	0.5, 2:1	0.56	18	5.9	96	36.16
Cu/SiAl 1	0.5, 1	1.32	41	2.5	21	423.03
SiAl 4 (no metal)	--, 4	-	-	-	20	-

^a Percentage of copper loading per catalyst and silica to alumina ratio

^b Cu⁰ from N₂O chemisorption data

^c Dispersion percentages from chemisorption data

^d Cu⁰ particle sizes from chemisorption data

^e Total surface area determined by N₂ BET method

^f Specific activity = $\frac{\text{initial reaction rate determined by rate of consumption of 1,2,6 hexanetriol}}{\text{total BET surface area}}$

Metal acid catalysts that had been reaction tested in N₂ experienced slightly more weight loss when compared to the exact same catalysts tested in H₂. For example, CuSiAl10 catalysts tested in a flow of N₂ experienced a 16mass% weight loss, while the same catalyst in a H₂ flow only experienced a 12mass% loss. We initially thought that catalysts experienced more coking in N₂ than in H₂ flows, in order to explain the low catalytic activity observed in N₂ flows. However, this theory was disregarded after a look at the TGA data showed that the weight losses experienced by catalysts in

both N_2 and H_2 were very comparable so that catalyst coking could not be held responsible for the low catalytic activity in N_2 . This means that other factors affecting catalytic activity were at play; especially since the individual components of the system had synergistic effects which altered catalytic effect.

Unmodified acid catalysts experienced much higher weight losses especially in a flow of H_2 making them the catalysts most susceptible to coking catalyst. $CuSiAl_2$ experienced the least weight loss and $SiAl_{10}$ in H_2 experienced the most weight loss. When we included carbon losses as evidenced by TGA data we managed to close carbon mass balances to the upwards of 95% and the other 5% assumed to be lost through leakages etc.

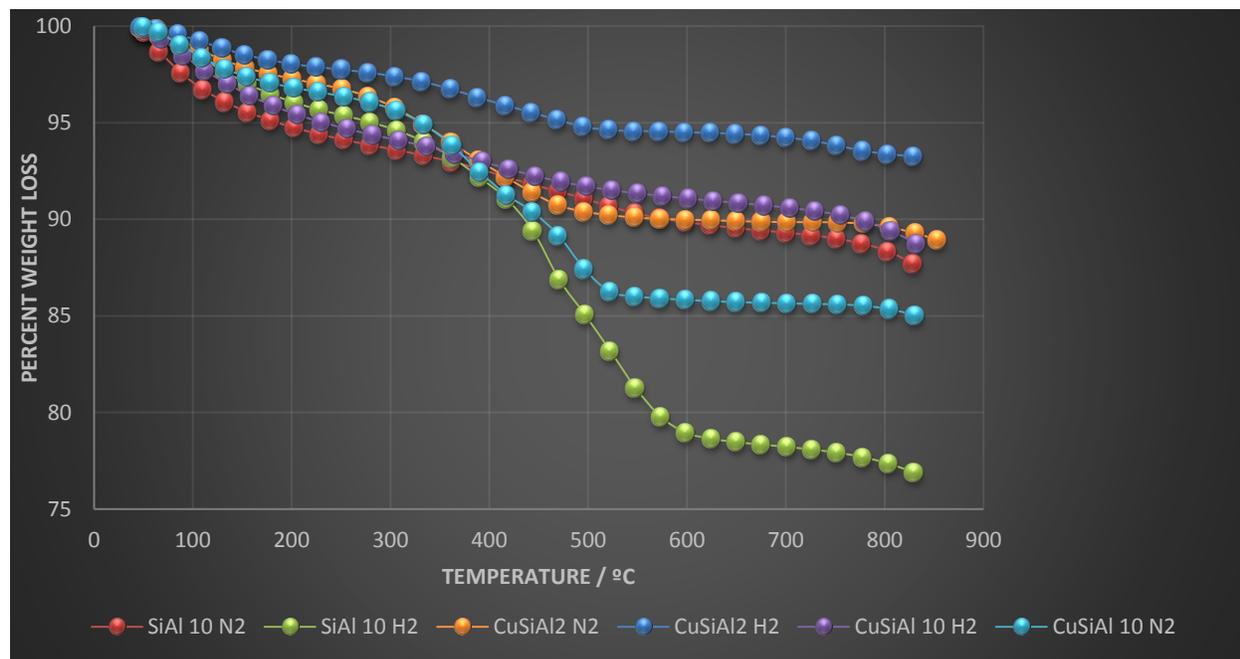


Fig 2: TGA curves of spent catalysts

3.8 Support acidity effect

To determine the effect of support acidity five catalysts, namely $CuSiAl_{10,4,2,1}$ and $SiAl_{10}$ were tested under reaction conditions in flows of both N_2 and H_2 and the results are shown in 2a,b and Fig 2a,b. As demonstrated the results revealed that increased support acid strengths led to higher

conversions and higher selectivity towards pyranic and cyclohexyl ring products. The data also showed that lower support acidities resulted in higher selectivities to linear products which includes 1,6 hexanediol and its precursors, (compare CuSiAl10 and CuSiAl1 in Fig 2a). To reinforce this data an unmodified acid catalyst prior to metal addition was tested under the same conditions; however the acid catalysts experienced rapid deactivation due to coking so that completely sound conclusions about catalytic activity could not be made. Nevertheless, the results obtained could still be used to provide some insights about the fundamental differences in catalytic behavior of metal acid and plain acid catalysts. We recorded similar selectivity trends of higher selectivities towards linear products over both SiAl10 and CuSiAl10. However, we observed that in SiAl10 condensation products accounted for a large percentage of the linear products implying that acid catalysts catalyzed condensation reactions while the metal functionality suppressed them.

To further test the support acidity effect, a copper based catalyst, CuSiO₂ – basically a copper catalyst supported on a no acid support material was tested under the same reaction conditions. Results obtained over this catalyst show much higher selectivities towards 1,6 hexanediol and precursors. Low selectivities towards pyranic products were recorded as shown in Figs 3a and 3b. We observed a fundamental difference between the product slates obtained over CuSiO₂ and Cu-SiAl catalysts. Tetrahydropyran-2-methanol, THP-2M, which was the most prominent product over Cu-SiAl catalysts was not seen in the product slate for reactions over CuSiO₂, while much higher selectivities towards linear products were attained. This difference in product selectivity points to the occurrence of different chemistry over the two catalysts, implying that the synergy between the metal functionality and the support was altering the catalytic activity of the catalysts. Based on these key findings, we can conclude that the higher the acidity of the bifunctional catalysts the more ring closing reactions were favoured, giving higher selectivity to ring products.

Lower catalyst acidities increased selectivity to linear products including our target product of 1,6 hexanediol and its precursors.

All experiments were repeated in a flow of N_2 , to investigate the synergies between carrier gas and the catalyst. The two key observations that were made, were the extremely low conversions obtained over all copper based catalysts in N_2 flows, and the differences in product selectivity distribution for both carrier gases. However, the difference in selectivity could be overlooked because of the very low conversions attained in N_2 flow, such that meaningful conclusions about the catalytic activity in N_2 could not be drawn.

Table 2a: Results for dehydration of 10wt% 1,2,6 hexanetriol @ 300°C, 1 bar H_2 100ml/min

Catalyst	Conversion	All Linear	All Pyran	Cyclohexyls	Condensation
CuSiAl10	9.87	76.05	12.05	5.15	2.89
CuSiAl4	9.65	68.83	16.05	7.94	6.62
CuSiAl2	17.95	39.20	50.21	9.27	4.26
CuSiAl1	17.96	34.32	54.33	9.37	0.13
SiAl10	1.68	62.68	17.62	8.25	11.64

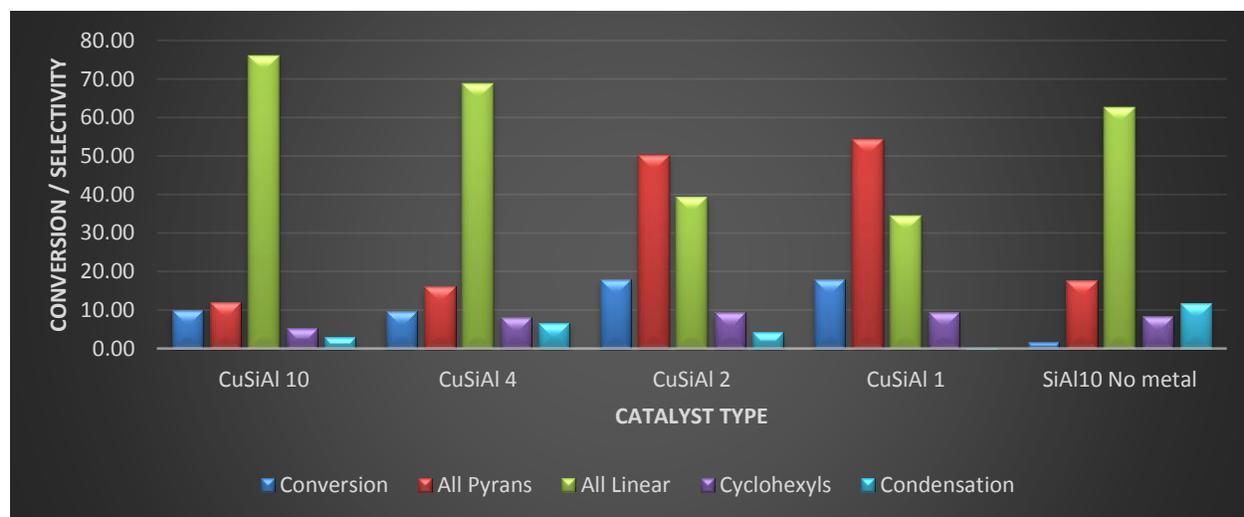


Fig 2a: Results for dehydration of 10wt% 1,2,6 hexanetriol @ 300°C, 1 bar H_2 100ml/min

Table 2b: Results for dehydration of 10wt% 1,2,6 hexanetriol @ 300°C, 1 bar N₂ gas 100ml/min

Catalyst	Conversion	All Linear	All Pyran	Cyclohexyls	Condensation
CuSiAl10	1.98	61.06	24.91	5.85	0.00
CuSiAl4	1.93	39.34	39.36	5.53	0.70
CuSiAl2	8.20	17.54	54.80	6.99	4.80
SiAl10	0.99	39.96	39.96	13.53	12.42

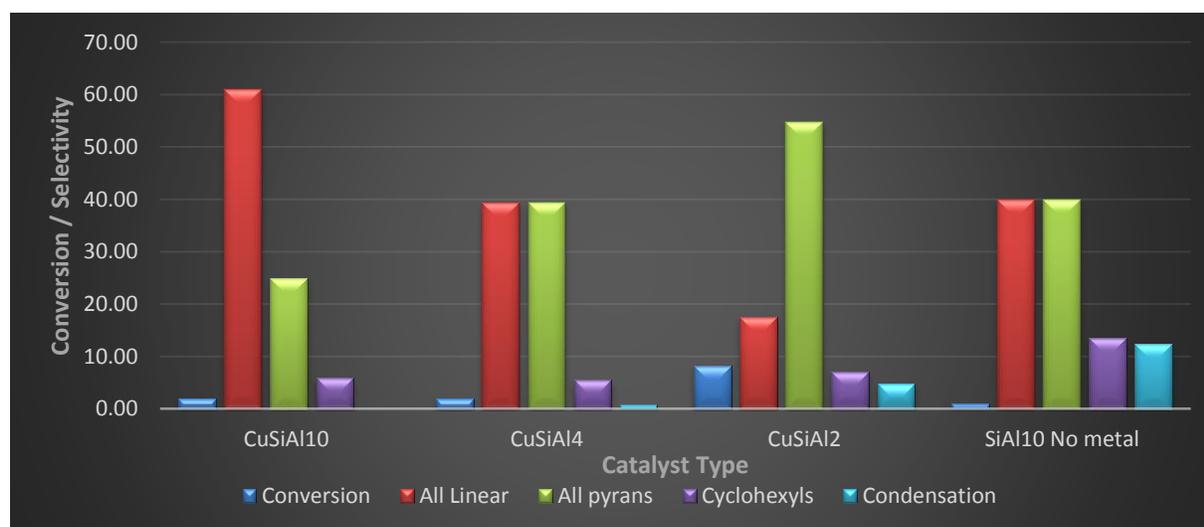


Fig 2b: Results for dehydration of 10wt% 1,2,6 hexanetriol @ 300°C, 1 bar N₂ gas 100ml/min

3.9 Metal Effect

The effect of modifying acid catalyst by metal addition was first seen in the TPD data. We observed a significant reduction of the strong acid sites after addition of copper metal functionality implying that the metal somehow muted the support acid sites. To test the catalytic activity implications of metal addition and to isolate the metal functionality effect, we tested a copper metal supported on a no-acid support material, so as to eliminate any synergies between the metal and acid functionalities. CuSiO₂ was obtained from collaborators at University of New Mexico and tested in the dehydration of 1,2,6 hexanetriol in both N₂ and H₂. As highlighted in the previous section,

the product slate and selectivity over CuSiO_2 was quite different from that obtained over CuSiAl catalysts signifying the occurrence of different chemistry over both catalysts. Very low catalytic activity in flows of N_2 were recorded over CuSiO_2 catalysts, a similar to what was observed over Cu-SiAl catalysts see Figs 3a and 3b. Since both catalysts only had copper metal functionality in common, the observed phenomena suggested that it was the metal functionality (and not the support), that was interacting with the carrier gas to yield positive or negative results. This data provided great insights into the synergies between carrier gas and copper metal catalysts, since CuSiO_2 possessed virtually no acidity.

3.10 Metal effect and metal-acid synergy

To further investigate the synergies between the metal and support and to further determine the isolated metal effect on the dehydration of 10wt% 1,2,6 hexanetriol a different set of experiments was performed over a new batches of catalyst. SiAl_2 was prepared and split into two; half was used as is, and the other half modified by copper metal addition using the incipient wetness method. The two catalysts, CuSiAl_2 and SiAl_2 were subjected to the exact same reaction conditions and the results obtained were compared so as to demonstrate the effect of the metal functionality. The results of the CuSiAl_2 catalyst could demonstrate the synergy between the metal and acid functionality when compared with the results over the plain acid catalyst. There were some differences noted in product selectivity over both catalysts pointing to apparent differences in the chemistry brought about by the added metal functionality.

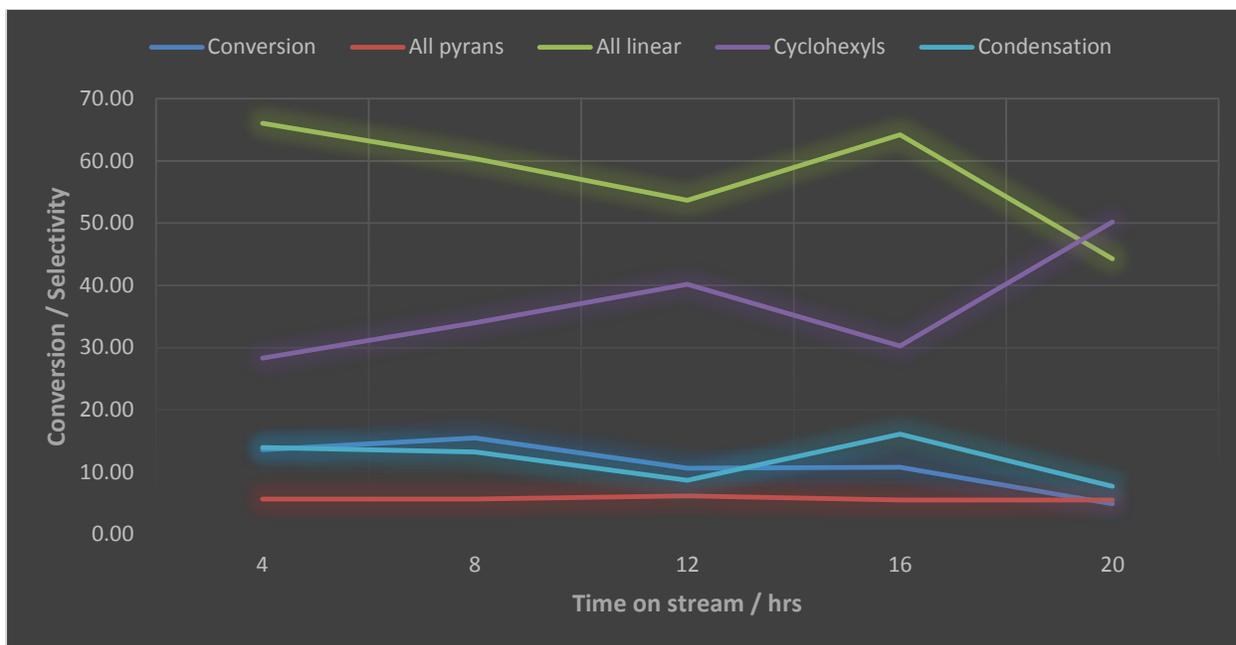


Fig 3a) Dehydration of 10wt% triol over CuSiO_2 in H_2 @ 1 bar, 100ml/min, 300°C

3.11 Carrier gas effect

To offset investigations on the synergies between the carrier gas and the catalyst all reaction testing experiments were performed in both H_2 and N_2 flows. Metal modified acid catalysts revealed consistent trends across the board regardless of the support material used. Much higher catalytic activity was recorded for all copper based catalysts in H_2 flow, yet the same catalysts were virtually inactive in N_2 flow. It was initially thought that the copper based catalysts were being severely deactivated by accumulation of carbonaceous material in flows of N_2 , but this theory was discarded upon inspection of the TGA data.

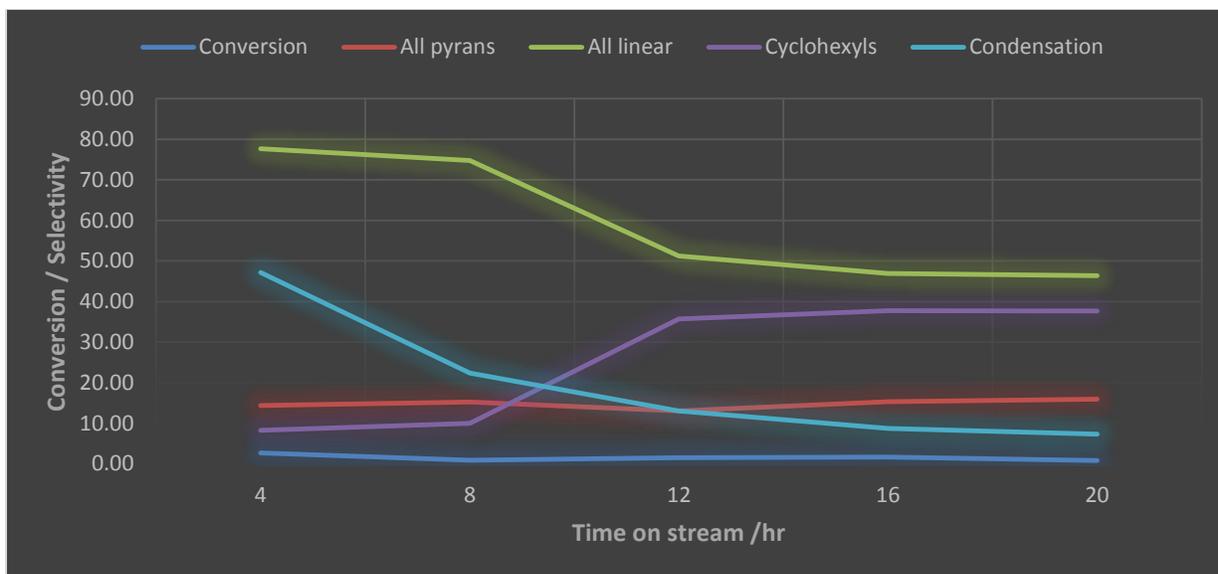


Fig 3b) Dehydration of 10wt% triol over **CuSiO₂** in H₂ @ 1 bar, 100ml/min, 300°C

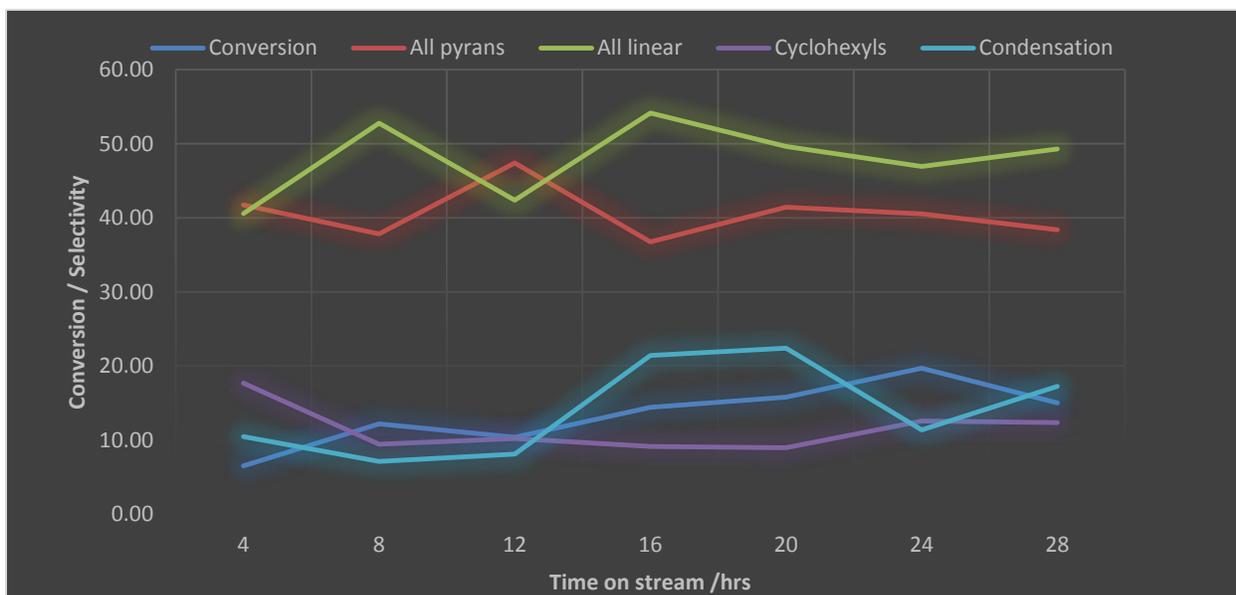


Fig 4b: Dehydration of 10wt% triol over **CuSiAl₂** @ 300°C, 1 bar H₂

Thermogravimetric incineration of spent catalysts to test for coked material revealed that catalysts tested in N₂ did not to experience massive weight losses as was expected.

Moreover, the weight losses experienced by catalysts in N₂ were found to be very comparable to the weight losses recorded in H₂.

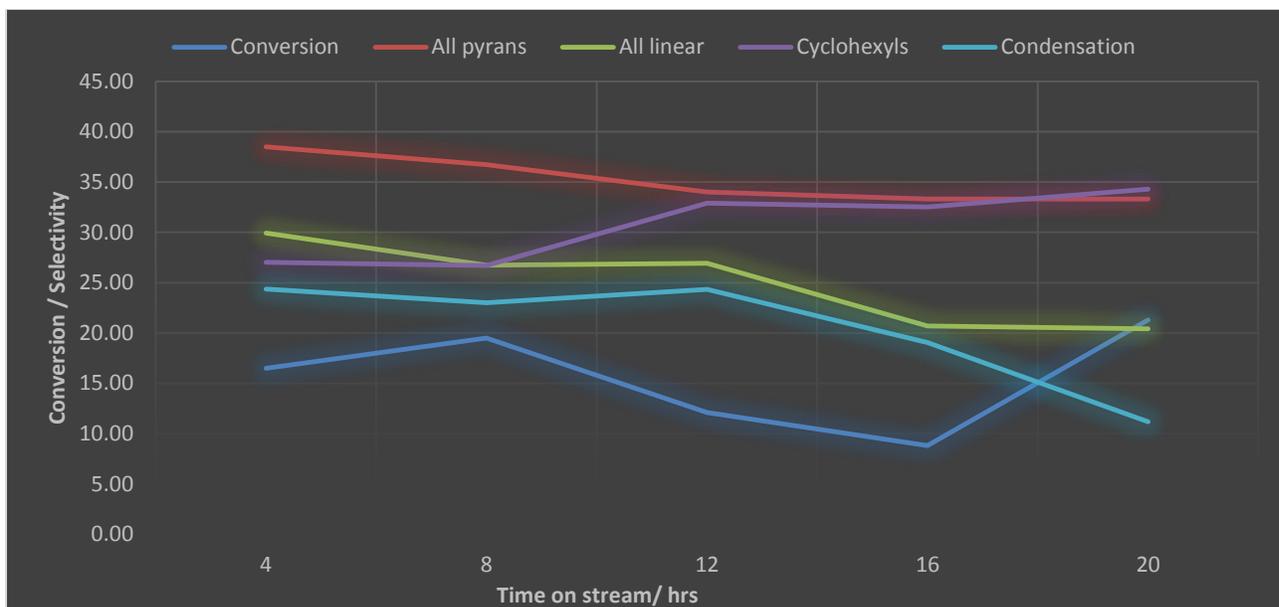


Fig 4b: Dehydration of 10wt% triol over *SiAl2* @ 300°C, 1 bar H_2

At this point we catalyst deactivation due to coking was eliminated as the explanation of catalyst inactivity in flows of N_2 . It was clear however that the carrier gas was playing an important role that largely influenced the catalytic activity. In conclusion, we found that H_2 had positive effects on the catalytic activity of the copper based catalysts while N_2 produced negative effects see Figs 5a,b below. This observation was consistent throughout all copper based catalysts tested in this work.

3.12 Catalyst Stability

In order to investigate the stability and robustness of the bifunctional catalysts over extended times of reactant exposure, two copper based catalysts were selected, and subjected to 80 hours of time

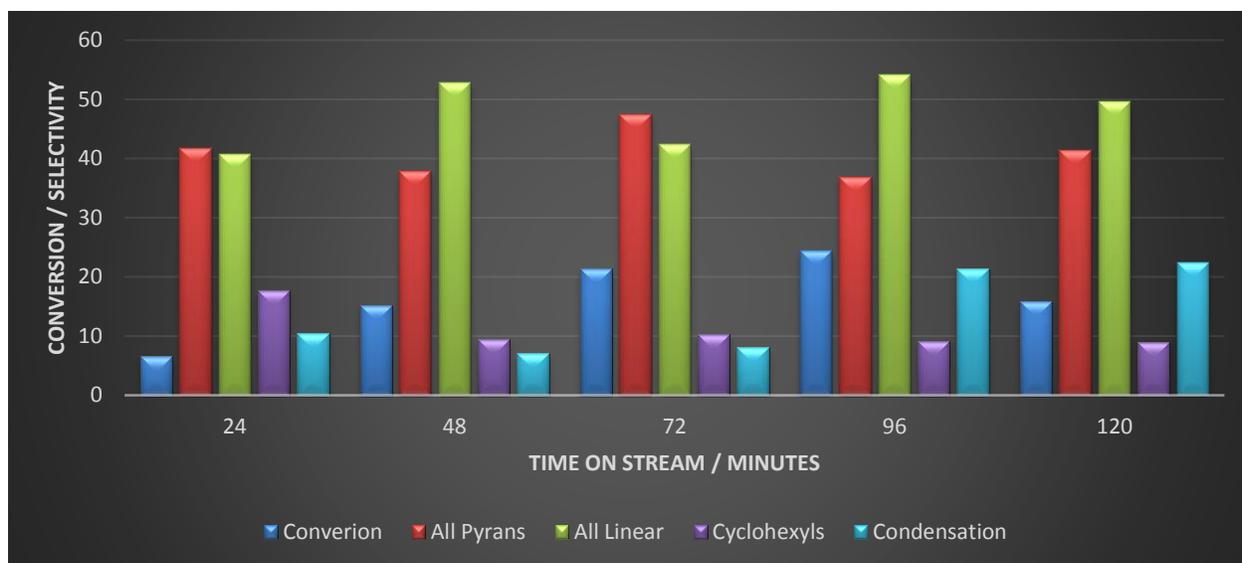


Fig 5a) Dehydration of 10wt% triol over **CuSiAl2** in H_2 @ 1 bar, 100ml/min, 300°C

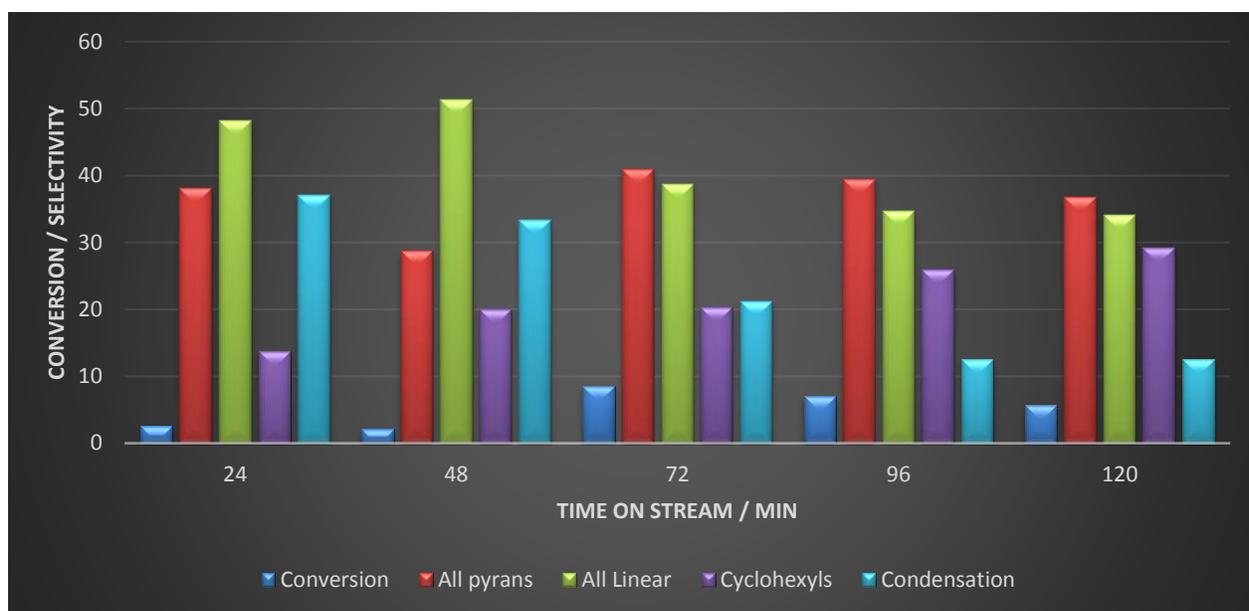


Fig 5a) Dehydration of 10wt% triol over **CuSiAl2** in N_2 @ 1 bar, 100ml/min, 300°C

on stream. The conversion and selectivity data collected revealed very little loss of catalytic activity during the time period indicating that the synthesized catalysts were highly stable in nature. However, TGA data recorded small weight losses of spent copper catalysts signifying catalyst coking, but the reaction testing data made it clear that those quantities of coke were not enough to

significantly lower the catalytic activity. Another explanation we suggested was that the main active site of the bifunctional catalysts were not as adversely affected by coking as were the plain acid catalysts. Nolan et al reports excessive catalyst deactivation in plain acid catalysts, and the TGA data collected in current work corroborates these findings see Fig 1, (where SiAl10 experienced the most weight loss - indicative of coke build up on the catalysts surface). Gathering all this information together we conclude that the metal functionality played the role of significantly stabilizing acid catalysts that would be otherwise prone to severe deactivation. It is also reasonable to assume that the metal works together with the hydrogen to remove product from the catalyst surface thereby inhibiting product polymerization which leads to catalyst coking. Therefore the metal functionality had positive synergic effects with H₂ carrier gas that significantly reduced catalyst coking thus stabilizing the catalyst.

3.13 H₂ partial pressure effect

We have established that activity of the bifunctional catalysts was positively influenced by the presence of H₂ gas, as discussed in preceding subsections. In order to better understand the synergy between the catalysts and hydrogen it was interesting to determine the effect of varying H₂ partial pressure on the catalytic activity. CuSiAl2 was chosen for this experiment because it has demonstrated high conversions and consistent selectivity trends.

Total carrier gas flowrates was kept at 150ml/min for all experiments. For lower H₂ flowrates N₂ was added to maintain the gas flowrate and keep the reactant partial pressures constant throughout. We observe that at H₂ flowrates above 100ml/min conversion steadily increased as did selectivity towards linear products.

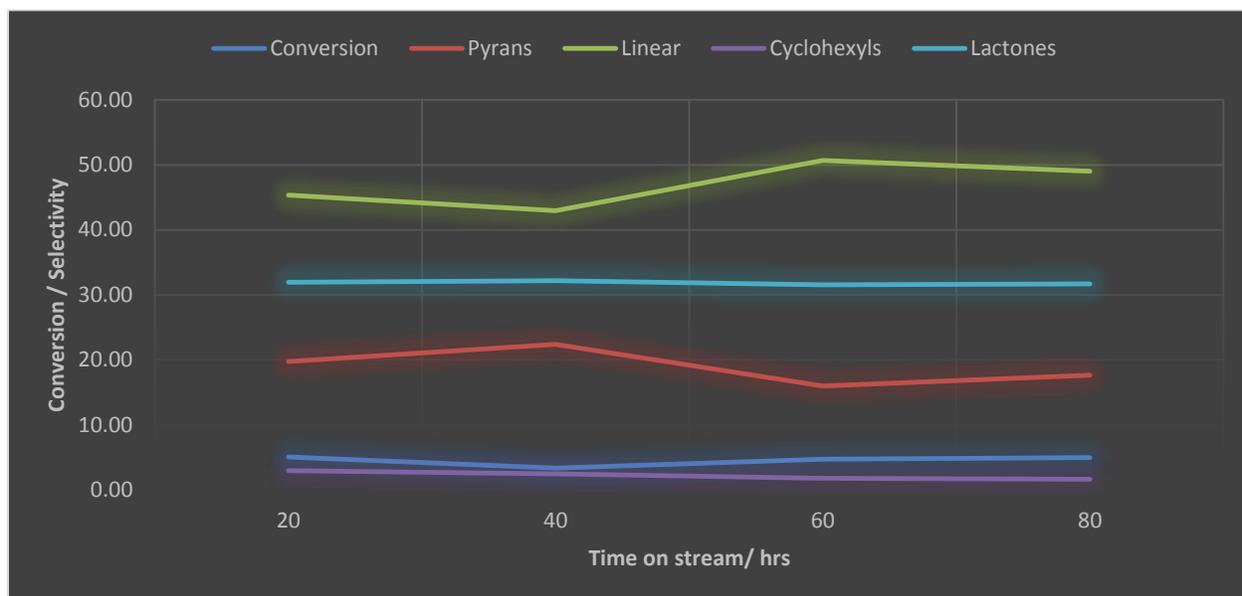


Fig 6a: Deactivation of CuSiAl10 over 80hrs in H₂ @ 1 bar, 100ml/min, 300°C

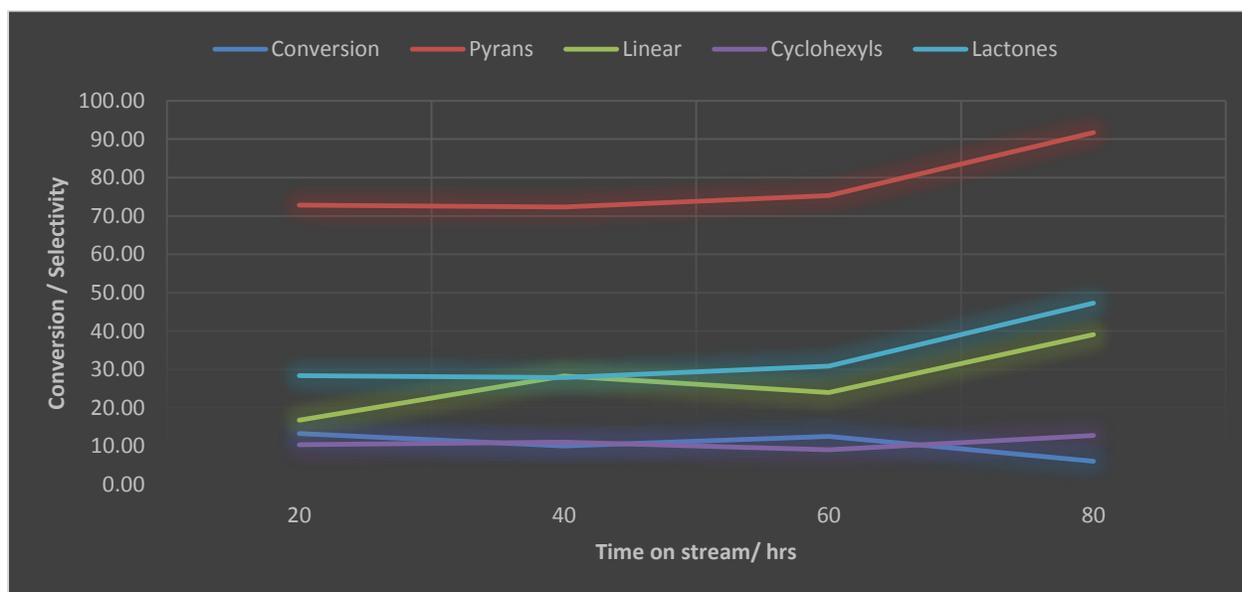


Fig 6b: Deactivation of CuSiAl2 over 80hrs in H₂ @ 1 bar, 100ml/min, 300°C

This was indicative of increased catalytic activity and we attribute this to the population of active sites being increased by dissociative adsorption of H₂ according to our first hypothesis as will be seen in the next chapter. The other explanation could be that the copper catalyst active sites were

more activated at higher H₂ partial pressures. Higher H₂ partial pressures did not seem to favor ring closing reactions, so that higher selectivities towards linear products were obtained, see Figs 7a and 7b. In conclusion, the experimental data obtained from variation of H₂ partial pressure experiments reveals that higher H₂ partial pressures yield higher selectivities to linear products including 1,6 hexanediol and precursors.

Fig 7b shows a breakdown of the selectivity trends obtained at 150ml/min.

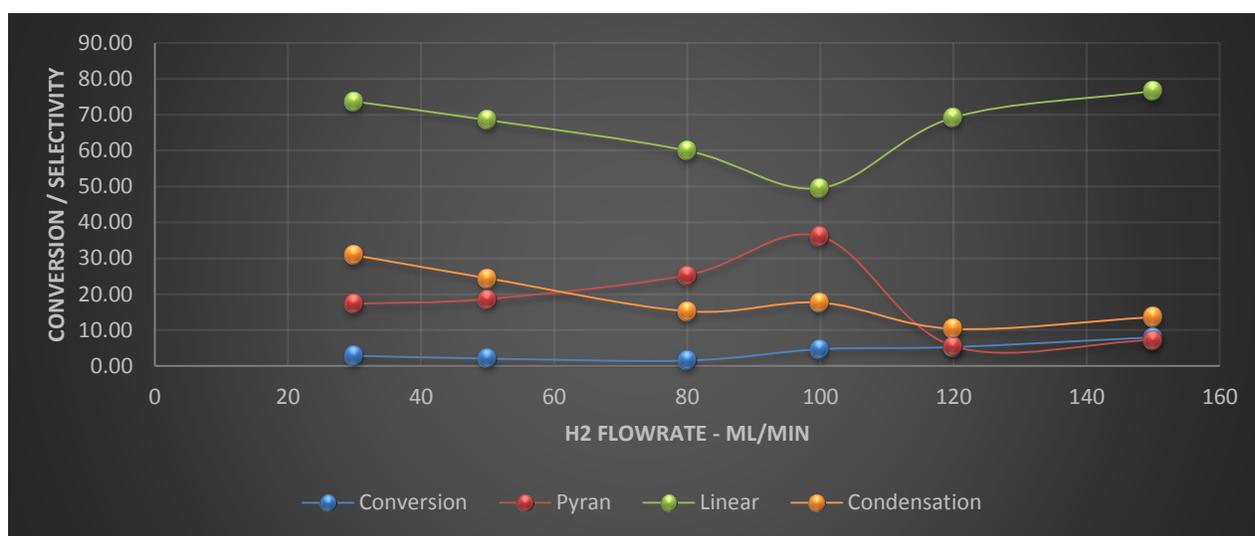


Fig7a: Dehydration at varying H₂ partial pressure-CuSiAl₂ @300°C

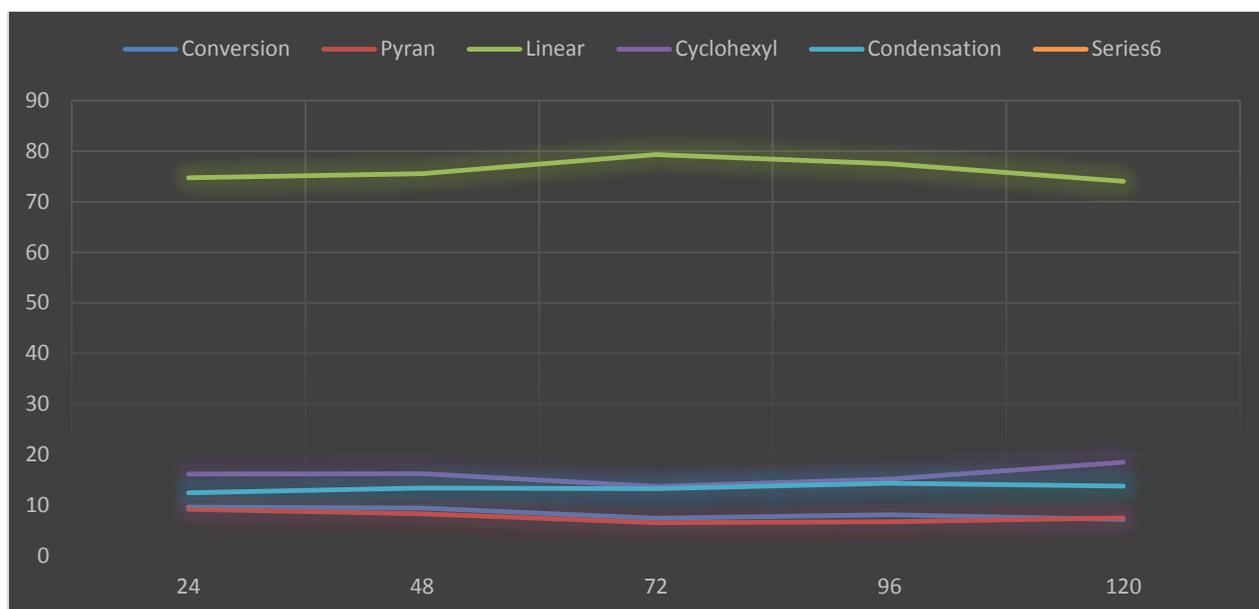


Fig7b: Dehydration at 100ml/min H_2 and 50ml/min N_2 - $CuSiAl_2$ @300°C

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CHAPTER 4: HYPOTHESES, DISCUSSION AND REACTION MECHANISM PROPOSALS

4.1 Hypotheses and discussion

The data obtained from reaction testing and NH₃-TPD, N₂-BET, N₂O chemisorption as well as TGA characterization techniques was used to elucidate the catalytic activity of the copper catalysts. An important piece of information was obtained from our initial reaction testing experiments which revealed that *all* copper based catalysts were virtually inactive in flows of inert gas. We initially assumed that the reason for this was catalyst deactivating due to the buildup of coke. However, subsequent TGA data later showed that the observed inactivity was not a result of catalysts deactivating due to coking therefore that theory was thrown out. It was paramount to find an explanation for the observed phenomenon as this would help us further understand the catalytic system. The variables had synergistic effects therefore we needed to decouple the system variables so as to isolate and identify the catalyst component/s that were responsible for the observed inactivity. Several reaction tests were performed in order to deconvolute the system synergies and determine the individual variable effects on catalytic activity. With this information at hand we had the opportunity of getting insight into the behavior of our synthesized catalysts. Based on the experimental results gathered, we were able to ascertain that copper metal functionality was the catalytic component responsible for low catalytic activities observed in N₂. Using this information we concluded that the main active component in the bifunctional catalysts for the dehydration of 1,2,6 hexanetriol was derived from the metal functionality.

To elucidate the catalytic system we have come up with two main hypotheses that propose two processes we assume are occurring either individually or concurrently.

The first hypothesis is comprised of a number of events occurring in series presented below.

The initial proposal made was based on the observation that copper metal addition led to the attenuation of support acid sites as evidenced by the TPD data. In light of this observation, we propose that copper metal sites block the support acid sites causing the reduction of the catalysts overall acid site population. We assume that the acid blocking is either partial, as in the case of higher acid strength supports, (were support acid sites were more abundant) or complete, as in the case of lower acid strength supports, (were acid sites were fewer). Acid site blocking was either complete or partial because all catalysts had the same Cu loadings of 0.5wt%. In simpler terms, there were only so many Cu sites available to block the support acid sites; so that in supports possessing more acid sites, the copper sites were only capable of blocking a fraction of the total sites; while in lower acid strength supports the available copper sites were enough to block all the support acid sites, leading to the observed catalyst acidity gradient.

Contrary to the suggestion made by our proposal, copper catalysts supported on lower acid supports were found to be active; going against our expectations as the proposal suggests that all support acid sites in the low acid catalysts were blocked. This observation prompted us to postulate the existence of a different active site that was introduced via the metal functionality. The formation of this new active site over the copper metal forms the premise of the first hypothesis.

The hypothesis states that the copper metal facilitates the introduction of a new active site which takes over some or all of the catalytic activity after all or almost all the support acid sites have been blocked by the copper sites. The mechanism by which the new active sites are formed requires the

presence of H₂ carrier gas which explains why little or no catalytic activity has been recorded in flows of N₂. We propose the dissociative adsorption of H₂ onto the copper surface enabling the production of two hydrogen atoms. The hydrogen atoms then spill over to the acid support where they come into contact with Lewis acid sites. We propose the existence of a few Lewis acid sites on the support, and that these sites act as electron acceptors of two electrons donated by H atoms, resulting in the formation of H⁺ protons. We hypothesize that these newly generated unique protonic acid sites are responsible for the catalytic activity observed in the Cu composites, especially for the low acid strength catalysts where all support acid sites were supposedly blocked according to our initial proposal.

To test the acid site blocking hypothesis, we re-visit the selectivity data obtained from reaction testing over metal-acid catalysts of varying acidity. High selectivity toward ring products were recorded over copper catalysts supported on higher support acidities, while low acid supports yielded higher selectivity toward linear products. Previously, Nolan et al investigated dehydration of 1,2,6 hexanetriol over plain acid catalyst and showed that catalysts of higher acidities gave higher selectivity to ring products, while ring products did not subsequently ring open over plain acid catalysts [1]. In another study Buntara et al finds that the modification of Rh/Re catalysts by untethered Brønsted acids yielded 100% selectivity to THP-2M instead of the expected 1,6 hexanediol expected over Rh/Re catalyst [2]. The observations from current work as well as the findings of Nolan and Buntara et al were fitted to the acid site blocking hypothesis, and we found that the hypothesis could explain the product selectivities obtained over CuSiAl catalysts of varying acidity. As prior explained according to our hypothesis, higher acidity supports only lost a fraction of their acid sites to copper blocking while the same amount of copper metal was capable

of blocking all the acid sites in lower acidity supports. Therefore, catalysts of higher acidity had remnant bronsted acid sites that were still available to drive ring closing reactions yielding higher selectivity to pyrans particularly THP-2M consistent with the findings by Buntara et al. Thus, in the lower acid catalysts were most of or all support bronsted acid sites were blocked by the copper sites ring closing reactions were at a minimum resulting in higher selectivities to linear products. On the other hand, in higher acid catalysts were only a fraction of the bronsted acid sites was blocked by the copper sites, there were remnant acid sites which drove ring closing reactions, yielding high selectivities to pyrans. These observations validated the acid site blocking hypothesis.

The proposal of the production of more protonic acid sites over copper metal was however seemingly in contradiction with the TPD data - which recorded a *decrease* of acid sites upon copper addition instead of an *increase* as suggested by our hypothesis. We therefore propose that the “protonic” active sites generated over the copper surface are different in nature from the support acid sites, so that the TPD only recorded the support bronsted acid sites. This proposal would therefore explain the observed dip in acid site population after copper metal was added to acid catalyst. Proposing a different kind of active site implies that the chemistry taking place over plain acid catalyst and over metal acid bifunctional catalyst is different. This would explain the different selectivities recorded over both catalysts - with metal and sans metal functionality; since low selectivities to linear products were recorded over acid catalysts yet high selectivities towards linear products were obtained over the exact same acid catalyst after metal modification.

To test the first hypothesis all reactions were performed in H_2 and an inert gas. The carrier gas was switched from H_2 to N_2 over both plain acid catalysts and copper based acid catalysts. We find that N_2 did not have detrimental effects to the catalytic activity of plain acid catalysts, as also previously reported by Nolan et al, but on the other hand very minimal to non-existent catalytic activity over the Cu based composites was obtained. Figs 1a and 1b below demonstrate the differences in catalytic activity of copper catalysts in N_2 and H_2 by showing the product quantification peaks as determined by the GC-FID.

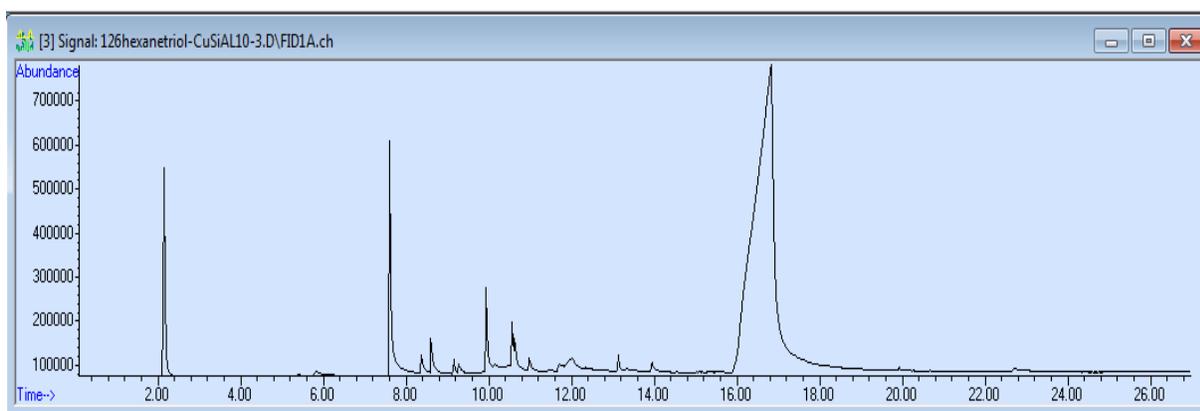


Fig 1a: GC-FID peaks for dehydration of 10wt% triol over CuSiAl10 in H_2 gas – sample 31

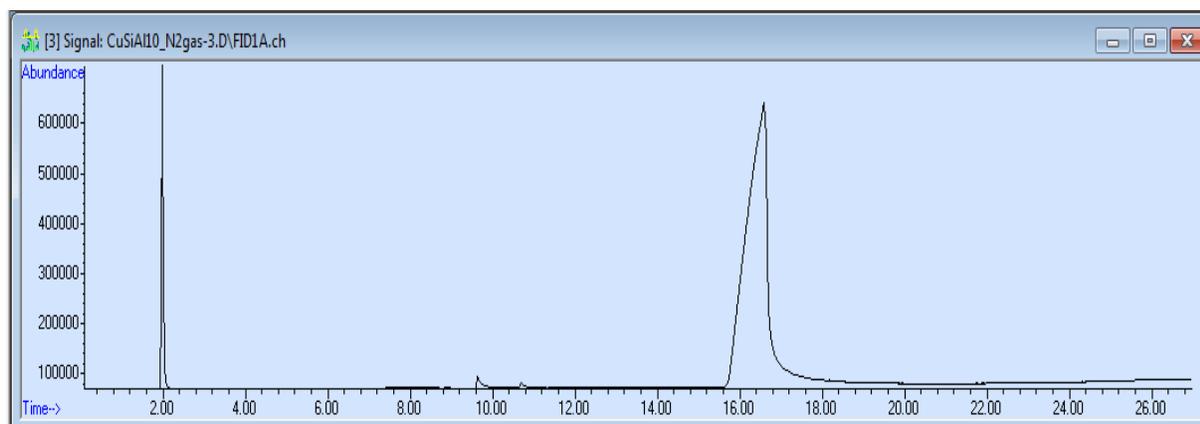


Fig 1b: GC-FID peaks for dehydration of 10wt% triol over CuSiAl10 in N_2 gas – sample 3

The observation that copper catalysts were inactive in N₂ and active in H₂ suggests that copper metal was interacting with the H₂ in a way that increased catalytic activity; so our first hypothesis was validated.

The second hypothesis proposed was based on the experimental data obtained from catalyst characterization and reaction testing. As we did for the first hypothesis, we initially propose that the addition of copper metal to an acid support attenuates support acid sites as a result of acid site blocking by the copper sites. This proposal is made in order to explain the observed loss of catalyst acidity after the addition of copper metal as shown by TPD data. The premise of the second hypothesis lies on the observation that copper based composites were active only in H₂ and virtually inactive flows of inert gas flow. Nolan et al, reports moderate to high catalytic activity of acid catalysts in inert gas, therefore it became apparent that the metal and H₂ carrier gas had a synergistic effect that somehow edified catalytic activity. Based on these observations, a second hypothesis was concurrently made alongside the first, stating that H₂ carrier gas plays the role of keeping the Cu metal in its reduced state; Cu⁰. We hypothesize that Cu⁰ takes over as the active site of the reaction after some or all of the bronsted acid sites were been rendered unavailable by copper site blocking.

Literature has not established the active copper species involved in the dehydration of polyols, therefore, the exploration and identification of the copper active site presents an opportunity to understand and account for the behavior of the synthesized catalysts. This is a useful tool which can be applied to the further development, modification and upgrading of the current catalytic system to optimize dehydration results.

To test the second hypothesis we had to prove that copper in its reduced state, Cu⁰ was the species responsible for the observed catalytic activity. This would prove that H₂ was keeping the metal in

its reduced state so that Cu^0 was the reaction active site. In order to achieve this goal we quantified Cu^0 surface sites using N_2O chemisorption and correlated that quantity to catalyst specific activity. This was possible because although copper loading was constant for all catalysts the Cu^0 concentrations varied from catalyst to catalyst. This fact enabled us to explore correlations between Cu^0 concentration and catalyst activity and the data obtained suggest that Cu^0 was primarily responsible for the catalytic activity.

The specific catalytic activity displayed in Table 1 in chapter 3 is calculated by dividing the initial reaction rates by the BET surface area. Initial reaction rates were used because of the relatively low conversions attained over all catalysts. We calculated initial reaction rates by subtracting the final reactant concentration from the initial concentration and dividing the result by the residence time. Residence times were calculated using the formula shown in equation 1;

$$\tau = \frac{C_{AO}V}{F_{AO}} = \frac{\left(\frac{\text{moles of } A \text{ entering}}{\text{volume of feed}}\right) (\text{volume of reactor})}{\left(\frac{\text{moles of } A \text{ entering}}{\text{time}}\right)}$$

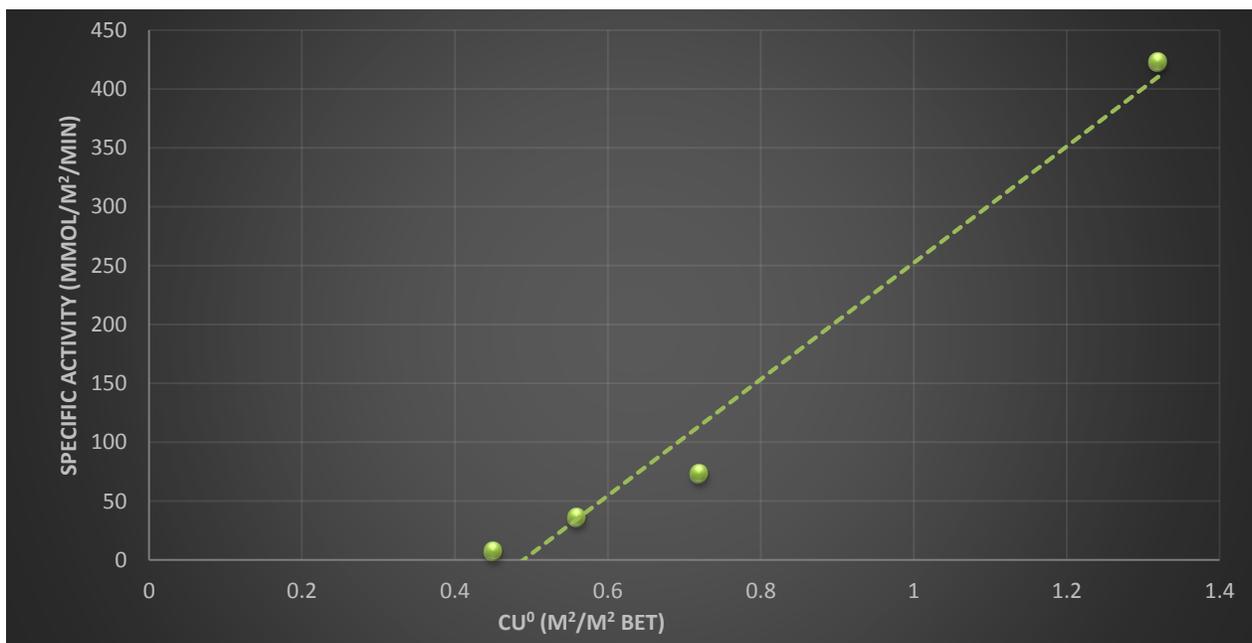
Equation 1: Formula for residence time calculation

Residence times were different for both the pure triol and 10wt% case as shown in Table 1, because the reactant partial pressures were different, so the appropriate values were used in the calculations.

Table 1: Residence time calculation

<i>Conditions</i>	<i>Triol wt %</i>	<i>Overall system pressure</i>	<i>Reactant Flowrates</i>	<i>Reactant Partial Pressures</i>	<i>Residence Time</i>
<i>Pure Triol</i>	<i>100wt%</i>	<i>1.2808atm</i>	<i>5ml/hr</i>	<i>0.2808atm</i>	<i>11.655sec</i>
<i>Dilute triol</i>	<i>10wt%</i>	<i>1.1918atm</i>	<i>5ml/hr</i>	<i>Reactant pp: 0.02827atm H₂O pp: 0.189atm</i>	<i>2.91sec</i>

The obtained values of specific activity were then plotted against Cu^0 surface concentrations as determined by N_2O chemisorption, see Fig 2 below. We observed a positive correlation between Cu^0 site density and catalyst specific activity, suggesting that Cu^0 was the active site for the reactions proceeding. The data was fitted to a line of best fit, which demonstrated a strong correlation.

Fig 2: Correlation between Cu^0 site density and catalyst specific activity, including a trend line

Previous work by Nolan et al reports severe deactivation of acid catalysts during the dehydration of 1,2,6 hexanetriol. In current work, the acid catalysts tested showed a similar trend of catalyst deactivation within the first hour of reaction testing. Spent acid catalysts were thereafter analyzed by thermogravimetric analysis, TGA and the results obtained were consistent with heavy catalyst coking, which was the most likely reason for the observed loss of acid catalyst activity in the initial stages of reaction. The same experiments were replicated over copper acid bifunctional catalysts and reaction testing data did not show much loss of catalytic activity even after 80 hour periods of time on stream see Fig 6 in chapter 3. Spent bifunctional catalysts were also analyzed by TGA and very little catalyst weight losses were observed, implying that copper based catalysts were not susceptible to deactivation by coking as the plain acid catalyst were. A closer look at the reaction testing data and TGA data reveals that the copper metal functionality played the role of stabilizing the acid catalyst so that very little catalyst deactivation due to coking occurred since after metal addition acid catalysts did not succumb to nearly as much coking as plain acid catalysts. We also assumed that in the copper modified acid catalysts, excessive coking did not occur since most of the acid sites that were prone to coking were not available after being blocked by the copper sites. This angle also corroborated the proposal made of copper metal blocking acid sites on the support, rendering them unavailable for coke build up.

A third and last hypothesis was proposed based on this phenonema. The hypothesis is similar to one proposed by Sun et al suggesting that the metal functionality played the role of removing product from the surface of the catalyst preventing product polymerization that leads to coking [3]. This would explain why catalyst TGA weight losses for metal based acid catalysts were not nearly as high as they were in plain acid catalysts.

Since we have established the role of H₂ in the system we were interested in finding out how the catalytic activity would vary with varying H₂ partial pressures. Prior to obtaining experimental data we expected that increasing the H₂ partial pressure would result in increased catalytic activities since our first hypothesis suggests that the increase of H₂ molecules could facilitate the production of more unique active sites. Experimental results reveal that our expectations were upheld, because higher H₂ partial pressures did in fact lead to an increase in catalytic activity, see Fig 7 in chapter 3. This strengthens our first hypothesis which proposes the generation of protonic acid sites over copper metal facilitated by H₂ molecules; so that higher H₂ partial pressures led to the production of more unique active sites, thereby increasing catalytic activity. We expect that at some point the continual increase of H₂ partial pressure will cease to increase catalytic activity; because there are only so many Cu sites available to facilitate the dissociative adsorption of H₂ which leads to the production of the unique active site. Therefore catalytic activity is expected to plateau after a point. Future work can focus on determining the optimum H₂ partial pressures at which point the catalytic activity reaches a maximum.

It was interesting to note that increasing the H₂ partial pressures did not lead to any more hydrogenation products. The products obtained at lower H₂ partial pressure were the same as those obtained at higher H₂ partial pressures suggesting that the H₂ was not taking part in hydrogenation reactions but was rather altering the catalyst.

4.2 Product slate

Below is a list of products as identified by the GC-MS.

Table 2: Observed product slate for dehydration of 1,2,6 hexanediol over copper based catalysts

<i>Linear Products</i>	<i>Ring Products</i>
<i>1,6 hexanediol</i>	<i>Tetrahydropyran-2-methanol, THP -2M</i>
<i>Hexenals</i>	<i>Cyclohexanediol</i>
<i>Epoxy-alcohol</i>	<i>Cyclohexanone</i>
<i>5-hexen-1-ol</i>	<i>Cyclopentanediol</i>
<i>Unsaturated 1,6 hexanediol</i>	<i>Caprolactone</i>
<i>6-hydroxy-hexenal</i>	<i>Tetrahydropyran-aldehyde</i>
<i>Unsaturated 1,6 hexanediol</i>	<i>Dioxabicyclo (3.2.1) octane</i>
<i>Condensation products</i>	<i>Valerolactone</i>

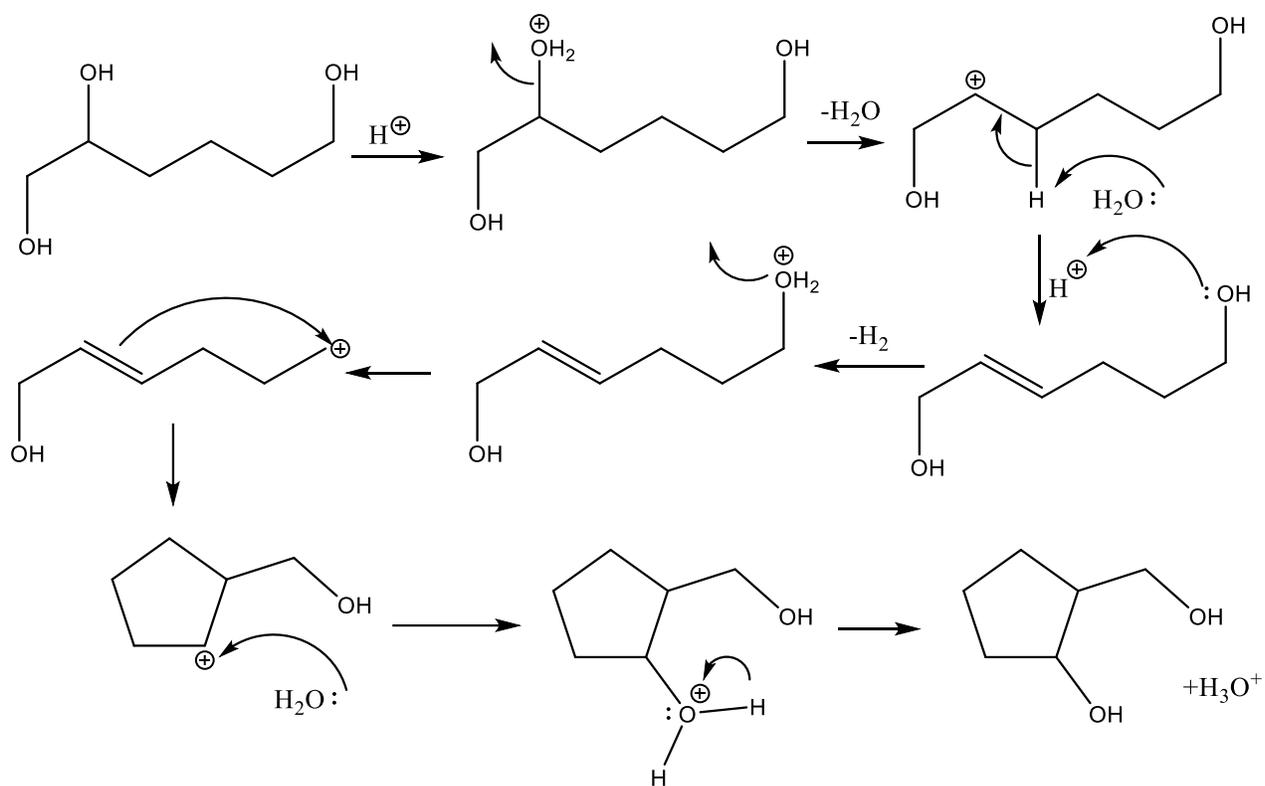
4.3 Proposed reaction mechanisms for ring product formation

We propose reaction pathways for the formation of ring products obtained from the dehydration of 1,2,6 hexanetriol over copper metal catalysts supported on silica alumina. The pathways are based on the information gathered from experimental data like that the increase in catalyst acidity led to increased selectivity to ring products. We revisit our acid site blocking hypothesis, which states that higher support acidity catalysts have remnant bronsted acid sites after some of the acid sites were blocked by the copper sites, and these bronsted acid sites drive ring closing reactions as previously reported by Buntara et al and Nolan et al.

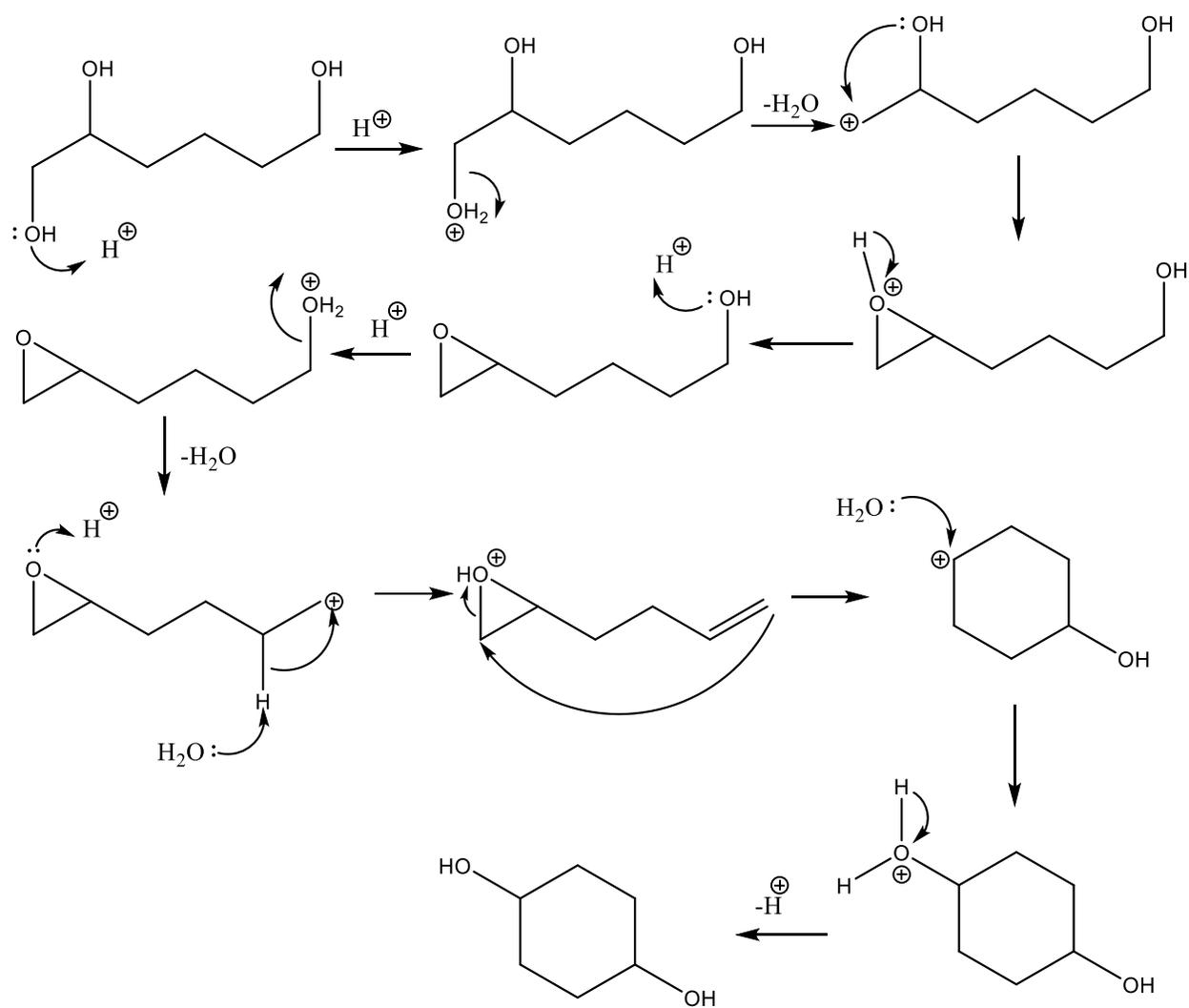
The mechanisms are hinged on the principle of carbocation stability. Acid catalyzed dehydration follows the protocol of preferential abstraction of the hydroxyl group on the tertiary carbon, followed functional groups on the secondary carbon and lastly the primary carbon [4, 5]. The

protocol is dependent on the stability of the carbocations formed; the tertiary carbocation being the most stable and the primary carbocation the least stable. Therefore we hypothesize that an increased amount of bronsted acid sites enables the unlikely event of a primary hydroxyl group abstraction leading to formation of the relatively unstable primary carbocation. We propose that the synergy between the remnant bronsted acid sites and the copper metal functionality facilitates a reduction in the activation energy required for the production of a primary carbocation. Thus when both primary hydroxyl groups are abstracted the ring can close at the 1 and 6 or the 1 and 5 carbon locations resulting in the formation of ring products. On the other hand, in copper catalysts supported on lower acid strength supports, all the bronsted acid sites are blocked according to our hypothesis, therefore the activation energy barrier for the abstraction of the primary hydroxyl groups is not overcome leading to higher selectivity to linear products. Therefore, lower acid strength catalysts facilitated the preferential abstraction of the secondary OH according to the carbocation formation protocol, giving rise to high selectivity towards linear products such as 1,6 hexanediol.

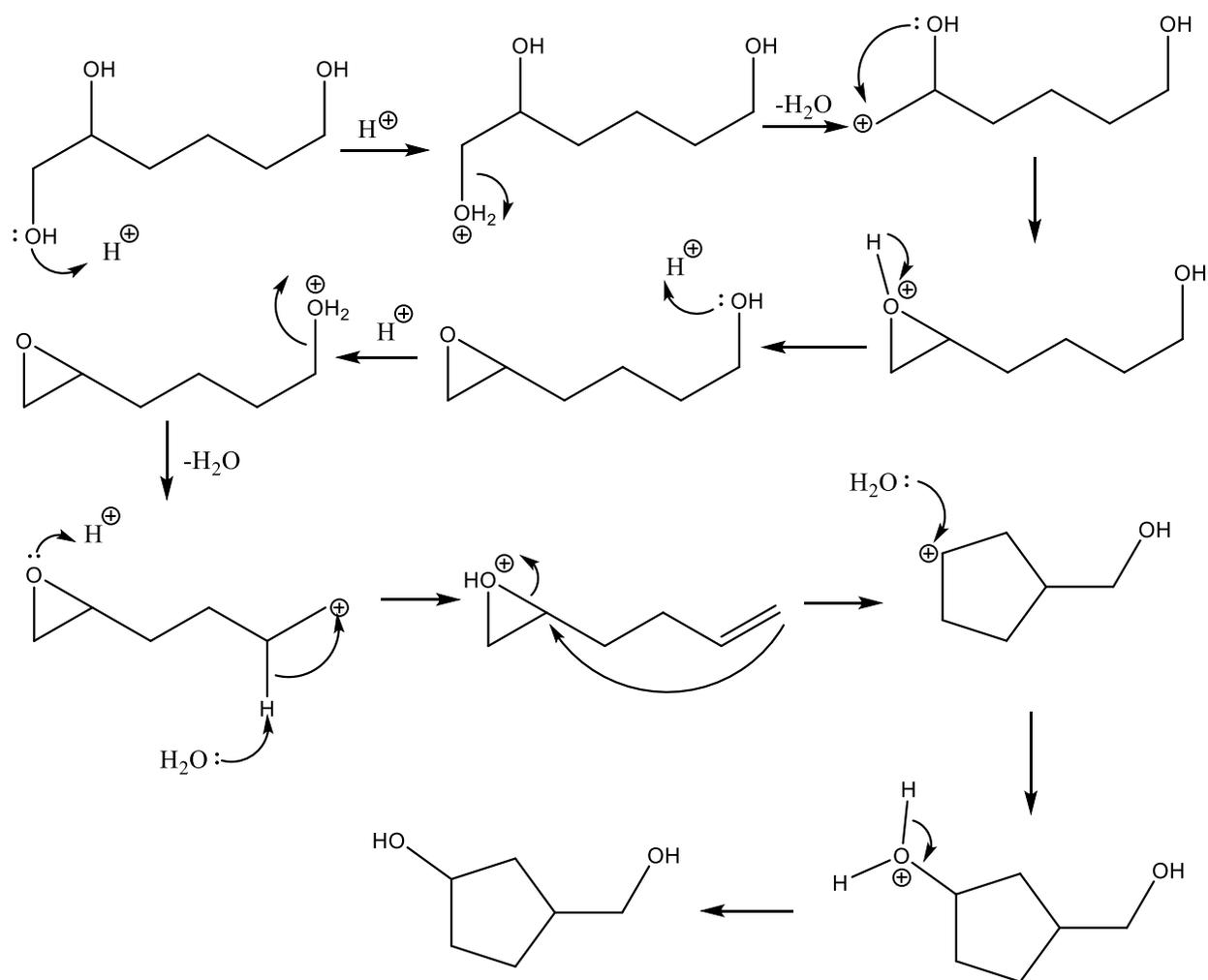
Below we show the reaction mechanism schemes for the dehydration of 1,2,6 hexanetriol to cyclohexanone and cyclohexanediol as well as two alternate pathways for the production of cyclopentanediol.



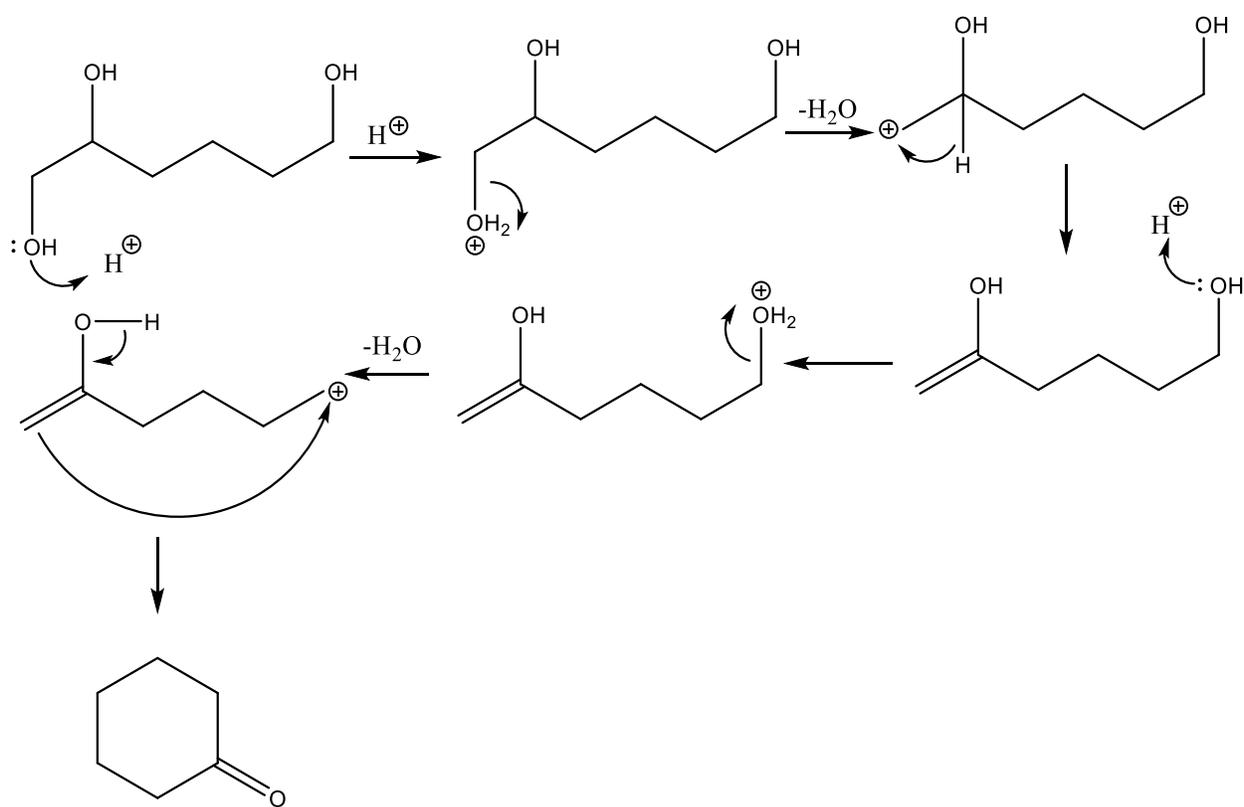
Scheme 1: Proposed reaction mechanism for the formation of cyclopentanediol from 1,2,6 hexanediol



Scheme 2: Proposed mechanism for the formation of cyclohexanediol via epoxy - alcohol



Scheme 3: Proposed mechanism for the formation of cyclopentenediol via epoxy-alcohol



Scheme 4: Proposed mechanism for the formation of cyclohexanone from 1,2,6 hexanediol

4.4 Conclusion

Copper based catalysts were synthesized, characterized and extensively tested for catalytic activity in the dehydration of 1,2,6 hexanetriol. NH_3 -TPD was used to determine the acid distribution of the catalysts and we found that addition of metal functionality to acid catalysts attenuated strong acid sites possessed by the acid catalysts. We proposed that copper metal had the effect of blocking the support acid sites rendering them unavailable for reaction. TGA data showed that the inactivity of copper based catalysts in N_2 was not due to catalyst deactivation by coking, implying that the carrier gas and metal functionality had a synergy which affected catalytic behavior. Based on numerous reaction tests performed over metal acid catalysts in the presence of H_2 we hypothesized that the copper metal surface facilitated the dissociative adsorption of H_2 resulting in the production of unique protonic acid sites which took over catalytic activity after the support acid sites had been blocked by the copper metal.

A second hypothesis was proposed concurrently with the first, based on the observation that copper based catalysts were only active in flows of H_2 and inactive in flows of inert gas. We propose that H_2 plays the role of keeping the copper metal in its reduced state as Cu^0 , so that Cu^0 provides the active site for the reactions proceeding. N_2O chemisorption was used to determine the surface properties of the copper based catalysts and the results obtained were used to determine the dependency between catalytic activity and Cu^0 active sites. Catalyst specific activities were correlated to Cu^0 surface concentration, and we determined that catalytic activity was very dependent on the Cu^0 surface sites, suggesting that Cu^0 was primarily responsible for catalytic activity of the catalyst.

Further studies will be necessary to determine which hypothesis is more likely, or if the two hypothesis occur simultaneously. We found that increasing H₂ partial pressure did not give rise to any hydrogenation products, suggestive of the fact that H₂ was not taking part in hydrogenation activities. Reaction mechanisms were proposed based on the experimental data.

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CHAPTER 5: FUTURE WORK

The work on the dehydration of 1,2,6 hexanetriol over copper based acid catalysts revealed the intricacies of the system as well as the synergies exhibited by the variables in the system. Therefore, more work to decouple the synergies of this system needs to be done. This work is more of a foundation upon which future work build on to further understand the reaction system.

The brunt of the future work lies on the distinction between the two hypotheses in order to ascertain which is more likely over the other, or if they indeed occur concurrently. Further experimental work can be done in order to fully differentiate between these two possibilities.

This work only pursues the existence of Cu^0 active sites on the catalyst surface; as determined and quantified by N_2O chemisorption; but we do not investigate the possibility of the existence of other copper active sites in other oxidation states. X-ray Photoelectron Spectroscopy, XPS and Auger Electron Spectroscopy, AES can be employed to determine the species found on this catalyst. There was a great possibility that copper was present on the catalyst in the first oxidation state of Cu^+ given. We deemed it was highly unlikely that higher oxidations could be present owing to the H_2 carrier gas flow condition which was bound to keep the metal oxide in its lowest oxidation state. Carbon monoxide, CO chemisorption can be employed to obtain irreversible CO isotherms that will be used to quantify the Cu^+ active sites. Thereafter, if the presence of other oxidation states is established, the same process of correlating catalyst specific activity to Cu^+ surface concentrations (or other species) can be done to determine which species affected the catalytic activity. With this information, the second hypotheses can be tuned to accommodate the new

information, and the existence of multiple active sites can be explored if at all. At that point further experiments to distinguish between the first and second hypotheses can be performed.

The first hypothesis proposes the generation of unique “protonic” active sites over the copper surface, which takes over catalytic activity after the support acid sites were blocked. However, the nature of this unique active site is unknown; therefore further characterization experiments can be done to elucidate its nature.

We hypothesize that remnant support bronsted acid sites and copper metal functionality have a synergic relationship that perhaps provides an alternative route with a lower activation energy allowing for the preferential abstraction of primary hydroxyl group which lead to the ring closing reactions. The aspect of activation energy lowering over copper metal based acid catalysts is a subject that can be explored further in future work.

Also, it was determined in the experiments involving the variation of H_2 partial pressures that as H_2 partial pressure was increased catalytic activity increased as did the selectivity to the desired linear products. However, since there are only so many copper sites available to facilitate the dissociative adsorption of H_2 which lead to production of the unique protonic sites, we anticipate that at some point the catalytic activity will plateau. Therefore, future work can carry this work forward and determine the optimum H_2 partial pressure, beyond which catalytic activity will not change.

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