THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Pentaerythritol Synthesis via a Solid Catalyst Route

for process related CO_2 reductions

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CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2024

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Cover:

Schematic diagram illustrating a comparison of pentaerythritol synthesis process between homogeneous and heterogeneous catalysis route.

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Abstract

Pentaerythritol (penta) is a platform chemical that has been produced from formaldehyde and acetaldehyde industrially through a homogeneous catalysis route. The commercial penta synthesis process has issues with the intensive separation involved due to by-product formation, which makes the process energy intensive and emits process related CO_2. In comparison, a solid catalysis route can be a better alternative to avoid rigorous post synthesis separation and to make penta formation process more selective with reduced CO_2 emissions.

In this work, alkaline solid catalysts Na/MO_x (MO_x=TiO_2, SnO_2, and γ-Al_2O_3) were tested for penta formation instead of the liquid alkaline NaOH solution. The catalysts were prepared by a conventional impregnation method. All the products obtained after the catalyst activity test were analyzed by GCMS analysis. The Na alkali metal amount was quantified with ICP analysis for both fresh and spent catalysts to check the stability of the catalyst. Moreover, the textural, and physiochemical properties of the catalyst were investigated through BET, XRD, and CO_2 TPD.

All the prepared catalysts stated above were active for penta synthesis along with other by-product formation, mainly consisting of penta-derivatives and diol compounds. Moreover, Na/SnO_2 showed the highest activity among all the tested catalysts with 39% selectivity for penta at 59% conversion of formaldehyde. However, it was found that 26 wt.% of the Na metal also leached out of the catalyst during the synthesis reaction. To conclude, we have shown that it is possible to synthesize penta via a heterogeneous catalysis route using Na/SnO_2 as a catalyst. Due to leaching and selectivity issues, further catalyst development is needed.

Keywords: Pentaerythritol, Solid alkaline catalyst, formaldehyde, acetaldehyde, aldol condensation, Cannizzaro reactions.

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Aqsa Noreen

List of Abbreviations

Penta	Pentaerythritol
Dipenta	Dipentaerythritol
Tripenta	Tripentaerythritol
FA	Formaldehyde
AA	Acetaldehyde
Diol	1,4-butenediol
PMF	Linear monoformal of penta
CPF	Cyclic monoformal of penta
BET	Brunauer-Emmett-Teller
IS	Internal Standard
BJH	Barrett-Joyner-Halenda
GC	Gas Chromatography
GHG	Greenhouse gas
ICP-SFMS	Inductively Coupled Plasma Sector Field Mass Spectrometry
XRD	X-Ray Diffraction
TPD	Temperature Programmed Desorption
MS	Mass Spectrometry
IR	Infra-Red
TMSI	1-Trimethylsilylimidazole
BSTFA	*N,O*-Bis(trimethylsilyl)trifluoroacetamide

Contents

1. Introduction

1.1 Introduction

The reduction of CO_2 emissions (GHG) is vital to slow the rate of global warming and mitigate its effect on our health and environment.[1] Among various contributors to GHG, industrial CO_2 emissions are also contributing to global warming. For example, according to a report, in Sweden the manufacturing and construction areas combined with the industrial sector produced 10 million tons of CO_2 in 2020.[2] Therefore, it is an important step to improve the chemical manufacturing industrial processes towards the development of a sustainable and green society. In Sweden, Perstorp is a leading manufacturing industry that produces and supplies platform chemicals, including pentaerythritol (penta) and dipentaerythritol (dipenta). Today, penta is produced from acetaldehyde and formaldehyde in the presence of an alkaline media such as NaOH.[3] The industrial process of penta production involves this conventional homogeneous catalysis route in which many side products form and so an intensive separation process is needed to obtain 86-90% monopenta (technical grade).[4] Multiple separation steps such as flash evaporation, crystallization, filtration, and decolorization involve the usage of large amounts of water solvent which results in an energy intensive process and so the CO_2 emissions become high.[5, 6] Another issue of the industrial homogeneous process for penta formation is that an excess of added formaldehyde forms sodium formate (NaCOOH) during the synthesis reaction of penta, which is an undesired product and consequently causes a loss of both the alkaline catalyst and formaldehyde. The removal of sodium formate requires an increase in temperature, which leads to the formation of

other by-products during the separation steps. During penta synthesis, MeOH is also produced in a side reaction, which is later combusted and thus contributes to CO_2 emissions. The formaldehyde production process emits a lot of CO_2 from related processes, which is a secondary source of CO_2 emissions in the penta synthesis.

Solid basic catalysis in comparison is an attractive alternative to produce penta with less by-product formation and easy separation steps, that resultantly can reduce the process cost and CO_2 emissions.[7]

1.2 Aim and Scope of the thesis

The overall goal of the project is to investigate means to produce penta in a more efficient way with the effectual use of feedstocks and less solvent usage, leading to reduced by-product formation. The aim is to substitute the alkaline media (e.g. NaOH) in the penta synthesis reaction by a solid alkaline heterogeneous catalyst. Several solid catalysts have been synthesized and tested for the penta formation reaction, where their activity and stability were also evaluated. With optimized active sites on a solid catalyst, a selective formation of penta with high yield and involving fewer separation steps should be achieved.

1.3 Main Challenges

There are several challenges in the project such as:

i. A lack of any literature on penta formation by solid alkaline catalysis routes

Over the past few decades, limited research efforts have been made to improve the penta synthesis process. Only a few studies have been performed recently concerning improvements in penta formation, however through the

homogeneous catalysis route. Instead, there is a lot of literature available for applications of penta. To the best of my knowledge, there is presently no literature openly available concerning the synthesis of penta via a solid alkaline catalyst. Nevertheless, researchers are trying to produce penta from other sources such as via an enzymatic catalysis route, producing bio-based penta from 3-hydroxypropanal.

ii. Isolation of the penta in the reaction mixture

It is challenging to isolate the produced penta in the reaction mixture after finishing the reaction, as penta in the reaction mixture can readily produce its derivatives and can convert to its derivative compounds. It is highly desirable to separate out penta from the reaction mixture to retain selectivity and yield of penta. Therefore, the optimum reaction conditions and post reaction separation steps are highly important to isolate penta.

iii. Other side reactions during penta synthesis

As stated earlier, penta forms from formaldehyde and acetaldehyde in the presence of an alkaline media. In this reactive mixture, a lot of other by-products form due to the self and cross condensation reactions of both the aldehydes. Except for the condensation reactions, formaldehyde undergoes a Cannizzaro reaction forming methanol and formates, which resultantly causes a reduction in penta yield. Apart from these reactions, penta also reacts with formaldehyde to produce other penta-derivatives that makes the process less selective.

1.4 Outline of the thesis

Chapter 2 introduces the background of penta, its applications, chemical reactions, and conventional synthesis process. It also includes literature on

the processes of penta formation and different strategies that have been reported to improve the yield of penta. Except this, the section describes the potential for solid alkaline catalysts that can be investigated for their activity for penta synthesis.

Chapter 3 describes the details of the experimental techniques used during the research work.

Chapter 4 describes the key findings and critical explanation of the results.

Chapter 5 presents the concluding remarks and outlook.

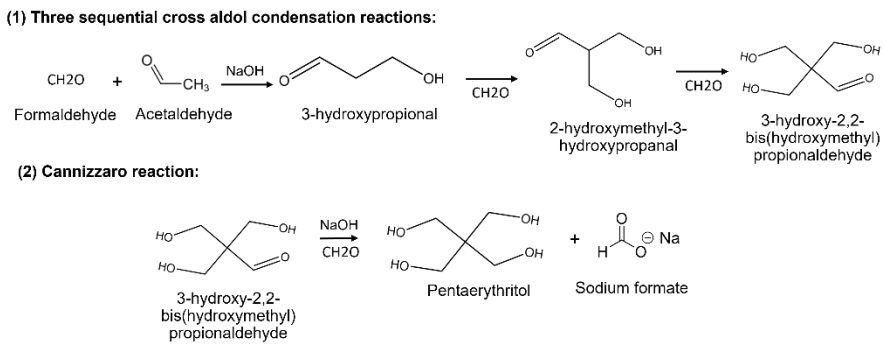
2. Background

2.1 Pentaerythritol (Penta)

Pentaerythritol (penta) is a common substrate polyalcohol with the chemical formula $C_5H_8(OH)_4$. It is a white crystalline odorless solid that has a melting point of 260 °C and boiling point of 276 °C. It is a tetraol compound, which makes it a versatile compound as its four hydrogens attached to each of its -OH groups can be substituted for any other ions of interest.[8] Due to this multifaceted property, penta gained popularity and a product from penta later became patented by an explosive manufacturer in 1894 as pentaerythritol tetranitrate $C_5H_8(NO_3)_4$, which was extensively used as an explosive in world war I and II.[9] Penta is now used to obtain fundamental resins to produce plastics, paints, explosives, cosmetics, oil additives, as a catalyst, medicines, and various other commercial products.[10-17] Due to its various applications, penta has a huge market and demand worldwide. Specifically, the increasing demand for penta in paints and coatings applications, along with a rising usage of penta in the automotive industry, is estimated to drive the market for penta. The penta market size is expected to reach 686 kilotons in 2024 and is estimated to grow to 889 kilotons by 2029 at a compound annual growth rate (CAGR) of more than 5% during the forecast period (2024-2029).[18]

Penta is generally synthesized in a homogeneous catalyst system, where formaldehyde and acetaldehyde undergo three sequential cross condensation reactions followed by the Cannizzaro reaction in the presence of a liquid alkaline solution (Scheme 1).[6] In detail, formaldehyde and acetaldehyde react with each other in the presence of NaOH to form 3-hydroxypropional through a cross-aldol condensation reaction (step 1 in Scheme 1), which

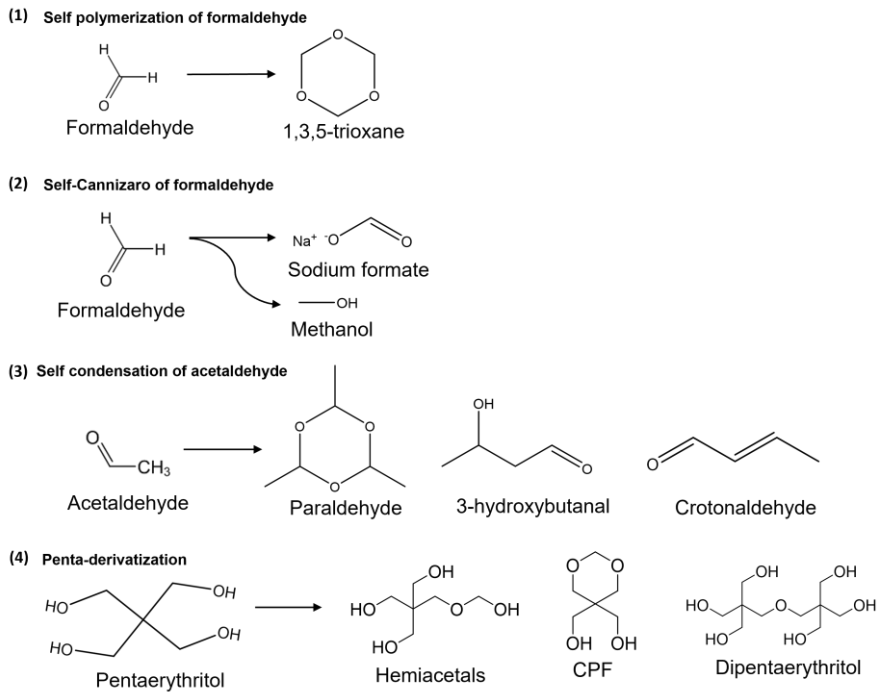
further reacts with formaldehyde to form 2-hydroxymethyl-3-hydroxypropanal and sequentially converts to 3-hydroxy-2,2-bis(hydroxymethyl)propionaldehyde. This final condensation product 3-hydroxy-2,2-bis(hydroxymethyl)propionaldehyde (pentaerythrose) finally undergoes a Cannizzaro reaction in the presence of formaldehyde and NaOH to give penta as shown in Scheme 1.[19]



Scheme 1. Penta formation reaction.[6, 19]

However, a controlled amount of formaldehyde, acetaldehyde and alkali media is required at optimum reaction conditions to drive the reaction in the desired direction. During the penta synthesis reaction, many other side reactions can occur, which resultantly reduces the selectivity for penta. As shown in Scheme 2, there could be four different types of side reactions occurring, such as (1) a polymerization reaction of formaldehyde to form trioxane or long chain formaldehyde, (2) a Cannizzaro reaction of formaldehyde which can produce methanol and sodium formate, and (3) acetaldehyde self-condensation reactions. A few examples of formed compounds can be seen in Scheme 2. It is difficult to avoid the formation of sodium formate in the alkaline liquid solution, as this is a product of the cannizzaro reaction when pentaerythrose converts to penta.[6] Besides these side reactions, penta also can react with formaldehyde in the reaction mixture

to form different derivatives, [5] such as linear hemiacetals of penta, cyclic monoformals of penta (CPF), and dipentaerythritol (dipenta), as shown in Scheme 2. This is why it is highly desirable to avoid the long contact of produced penta with the reaction mixture and to isolate it so that the penta selectivity will not be compromised. From a reaction engineering perspective, it is possible then that residence time or space velocity of a reactor could be used to control the by-product formation from penta-derivatization.



Scheme 2. Side reactions that can occur during penta synthesis.

2.2 Industrial processes for penta synthesis

Industrially, penta is produced when formaldehyde in surplus amounts is added with acetaldehyde in a strong alkaline aqueous medium that acts as a

catalyst under controlled conditions. In the reaction mixture, except for the desired penta reaction as shown in Scheme 1, the alkaline catalyst reacts with formaldehyde in a Cannizzaro reaction to give rise to undesired sodium formate salt and methanol. Other hydroxylated by-products are also formed in considerable amounts, for example dipentaerythritol (dipenta), and hemiformals (as shown in Scheme 2). After the reaction finishes, the reaction mixture undergoes an acid neutralization step to neutralize any remaining alkaline hydroxides.[6] Following this, the penta together with other hydroxylated by-products are dried to evaporate water from the reaction mixture. The ultimate pure penta is obtained after multiple steps of crystallization, filtration and decolorization.[6, 20] However, during these separation steps, some amount of penta is inevitably lost which resultantly reduces the overall penta yield.[6, 20] Furthermore, the additional separation steps lead to more water losses. Thus, industrial processes producing penta face two primary challenges: Firstly, the formation of the undesired formate salts which necessitates the use of excess formaldehyde and the additional acid neutralization and formates separation steps. Secondly, ensuring high overall yields and a good product grade of penta through the conventional homogeneous synthesis route. Typically, a molar ratio of formaldehyde to acetaldehyde of 5:1, with an optimum amount of water resulting in a formaldehyde concentration of 12-20% at 80-85 ^{o}C for 1-2 h of reaction time, are the reported favorable reaction conditions for penta synthesis [6]. The alkali with 8-10% excess of the theoretically required amount is usually used to complete the penta reaction.[6] Formic acid or sulphuric acid are commonly used for the neutralization step and after this the formates are separated out by filtration at elevated temperature.[6] Later the mother liquor is cooled down to 5-10 ^{o}C for 1 day to obtain the penta in crystalline form and it is separated out through centrifugation.[6] After the separation steps, 77% of the total penta

is recovered in the first-crop crystallization according to Peters et. al.[6] Bengtsson et. al. in a patent reported that 99.9 wt.% mono-penta purity could be achieved where the conventional synthesis process with controlled reactant ratios and improved separation steps were used. [4] Another patent stated the importance of the sequence of reactant addition in terms of managing the reaction time and temperature to obtain a high purity of penta.[3] A continuous addition of buffered formaldehyde during the penta synthesis reaction to increase the penta yield and control by-product formation was also investigated. Moreover, the influence of varying temperature during the synthesis has been investigated. Raising the temperature gradually in stages within the ranges 22-28 ºC, 32-38 ºC, and 42-48 ºC for different periods of time has been reported to be favorable to obtain 98% purity of penta.[21] Furthermore, instead of using the liquid NaOH solution, an ion exchange resin anionite was used to synthesize penta and later the resins were regenerated to use again in the process.[22] Maury et. al. in 1957 patented an interesting method to improve the yield of penta by reconverting penta formals into penta. In order to achieve this, an extra step was introduced wherein penta formals in aqueous media are subjected to heating at temperatures ranging from 150-300 ºC in the presence of a cracking catalyst such as silica or metal oxides.[23] More recently, in 2002, a patent reported the synthesis of polyols with three to four -OH groups from condensation of formaldehyde and acetaldehyde followed by a hydrogenation reaction. Thus, instead of the Cannizzaro reaction, a catalytic hydrogenation reaction was carried out at high temperature to transform the pentaerythrose intermediate into penta. It was reported that a weak basic anion exchange resin at 50-100 ºC was used for the first step of aldol condensation to produce the pentaerythrose intermediate. Later, a solid hydrogenation catalyst such as Ni or Pd/C was used to convert the intermediate into the ultimate product penta

at 60-90 °C in the presence of water. [24] However, various obstacles remain unresolved so far, such as the large amount of liquid waste due to homogeneous catalysis, excess use of formaldehyde, and product isolation (neutralization step) during the penta synthesis in industrial processes.

2.3 Potential solid alkaline catalysts for aldol and cannizzaro reactions

Lately, solid base materials, such as heterogeneous catalysts, have been considered as a potential substitute to resolve the above problems associated with the application of liquid alkali catalysts. Solid base catalysts play a key role, as their application in many base catalyzed industrial procedures suggests options to assist separation, avoid reactor corrosion, and other waste handling problems.[25] There are many previous studies that have focused on using solid base catalysts such as metal hydroxides, zeolites, and hydrotalcites, that have been examined for aldol condensation and Cannizzaro reactions individually for different chemical syntheses.[26, 27] There are also a few studies published on Cannizzaro reactions for other chemical systems. For example, Marczewski et al. examined the Cannizzaro reaction in which benzaldehyde was transformed to benzyl alcohol in the presence of ion exchange resins.[28] Mojtahedi et al. also studied Cannizzaro reactions of aromatic aldehydes in a solvent free environment by using solid LiBr and Et_3N catalysts and observed high yields.[29] Researchers have also reported the use of solid catalysts for aldol condensation reactions for various chemical systems. For example, Melita et. al. used protonated titanium nanotubes as solid catalysts for aldol condensation between benzaldehyde and cyclohexanone.[26] Weihan et. al. used hydrotalcite as a solid catalyst for aldol condensation of isobutyraldehyde and formaldehyde to produce hydroxypivaldehyde. It was also concluded in this study that weak Brønsted-

Lowry basic sites serve as active centers to catalyze the aldol condensation reaction.[27] From the investigation of the literature of solid catalyzed systems, it is possible that the solid basic catalyst can also have the capability to initiate both aldol condensation and Cannizzaro reactions to synthesize penta.

3. Experimental Protocol

3.1 Catalyst preparation

The catalysts containing alkali metal Na on metal oxide supports, such as SnO_2 (tin(IV) oxide, ≤100nm avg. part. size, Sigma-Aldrich), TiO_2 (titanium(IV), anatase, nanopowder, <25nm particle size, 99.7%, Sigma-Aldrich), and ɤ-Al_2O_3 as aluminium oxide (gamma-phase, 99+%, Alfa Aesar), were prepared by a wetness impregnation method [30]. In this method, the alkali salt was first dissolved in a small amount of water and then the solution was impregnated on the support at room temperature. A nominal 50 wt.% loading of Na was used and for this sodium nitrate (ACS reagent, ≥99.0%, Sigma-Aldrich) was used as the precursor. The samples were then ultrasonicated for an additional 30 min. Later, after subsequent drying at 80 ^oC for 3 h, calcination was carried out at 450 ^oC for 4 h at the heating rate of 5 ^oC/min from room temperature. This procedure yielded the final catalyst.

3.2 Feedstock

Acetaldehyde (anhydrous, ≥99.5%, GC, Sigma-Aldrich), and different formaldehyde solutions (37% formaldehyde and 10-15%MeOH in water, from Sigma-Aldrich or 'formalin' 36.4-37.0% formaldehyde in water, ≤1%MeOH, from Perstorp AB) were used as the sources of the aldehydes to perform the penta synthesis experiments. The formaldehyde solution with low methanol content ('formalin' 36.4-37.0% in water, ≤1%MeOH) was stored in an oven at 50 ^oC and in dark bottles to avoid formaldehyde oxidation and polymer formation. Its concentration was confirmed with Karl Fischer method and GCMS analysis after each four weeks prior to its use to ensure a consistent formaldehyde feed composition.

3.3 Procedure for penta synthesis

All the experiments for catalyst activity tests were performed in a batch reactor consisting of a round bottom glass flask of 100 mL capacity connected with a water-cooled reflux condenser. Blank reactions with only formaldehyde and acetaldehyde were performed prior to testing of catalysts. Blank reactions were performed to measure losses of both the aldehydes at 70 ^{o}C in the experimental setup and to evaluate the reactivity of the formaldehyde and acetaldehyde without catalyst at the specific reaction conditions. For the blank reactions, the experiment was performed for 2 h and samples were taken after each 30 min period. All the prepared catalysts such as Na/TiO_2, Na/SnO_2, and Na/γ-Al_2O_3 were then tested under the reaction conditions with an initial formaldehyde to acetaldehyde molar ratio of 5:1, and a catalyst amount of 0.2 g. The complete reaction process involved heating from room temperature to 70 ^{o}C in 10-15 min, followed by a 15 min isothermal reaction period at 70 ^{o}C. Constant stirring was used for all the experiments at 200 rpm. Both the reactants and catalyst were added in the flask, the cooled reflux condenser was connected and stirring started before heating from room temperature to the reaction temperature at an average rate of 5 ^{o}C/min. After achieving the desired reaction temperature, the 15 min isothermal reaction period at 70 °C was started.

After completing the reaction, the reaction mixture was cooled down to room temperature by terminating the heating and immediately placing the reaction flask in an ice bath for 15-20 minutes. Then the catalyst was separated out from the liquid through vacuum filtration by using a filter of porosity 5. The residue (solid catalyst and solid product) that was obtained after vacuum filtration was dried at 90 ^{o}C for 2 h in an oven and saved for later, performing ICP analysis to evaluate the stability of catalyst and to perform silylation and

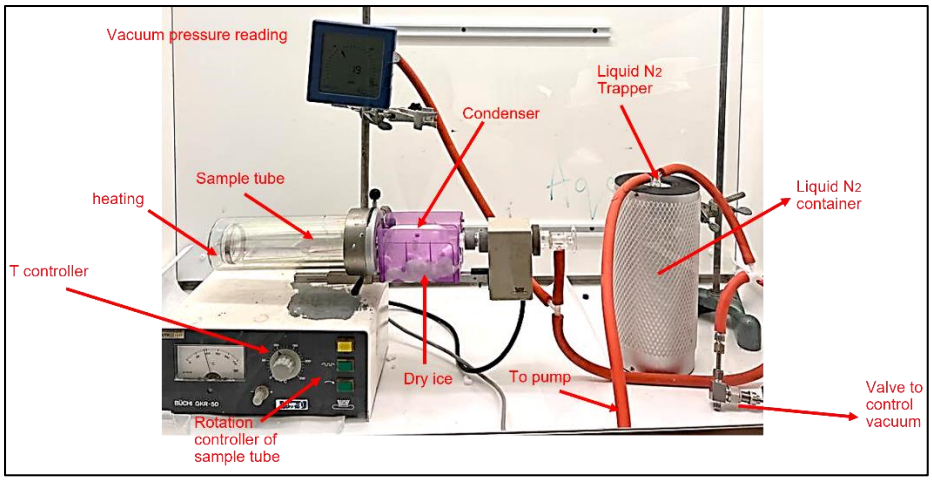
GCMS analysis to examine the solid product composition and quantities. The filtrate recovered after the filtration step was passed through other separation steps to isolate and quantify penta from reaction mixture. These steps are explained in detail below in section 3.4.

3.4 Penta separation and isolation from reaction mixture

3.4.1 Filtrate drying to obtain solid penta

As discussed earlier, penta in the presence of a formaldehyde solution can produce its derivatives and resultantly the purity can be compromised. So, it is very important to isolate and separate out the penta from the reaction product mixture to avoid the formation of penta-derivatives and to improve the yield of penta, as illustrated by the detailed separation steps shown in Scheme 3. For this purpose, penta present in the filtrate, obtained as described in Section 3.3, was isolated and separated out from the reaction product mixture.

From the collected liquid filtrate product, a small amount of it was sampled into a GC vial, to do GC-MS analysis to measure the unreacted formaldehyde, acetaldehyde, and other low molecular weight products. For the analysis, 1,3,5-trioxane (≥99%, Sigma-Aldrich as IS) at 10000 ppm concentration was used as an internal standard. The remaining liquid filtrate underwent vacuum evaporation in a glass tube furnace (Buchi GKR50 setup). This setup was attached to a condenser tube covered with ice that was further connected to a liquid N_2 (LN2) trap to condense all the possible filtrate. The vacuum evaporation took 20-25 min at 20-40 mbar pressure and 100 ^oC temperature. The vacuum evaporation setup is illustrated in Setup 1.



Setup 1. Vacuum Evaporation setup (Buchi GKR50 setup).

The condensate liquid after completing the evaporation was then weighed and analyzed in the GC-MS with 10000 ppm of 1,3,5-trioxane (IS) to quantify the products that remained in the condensate. The solid product obtained after drying was weighed to close the mass balance.

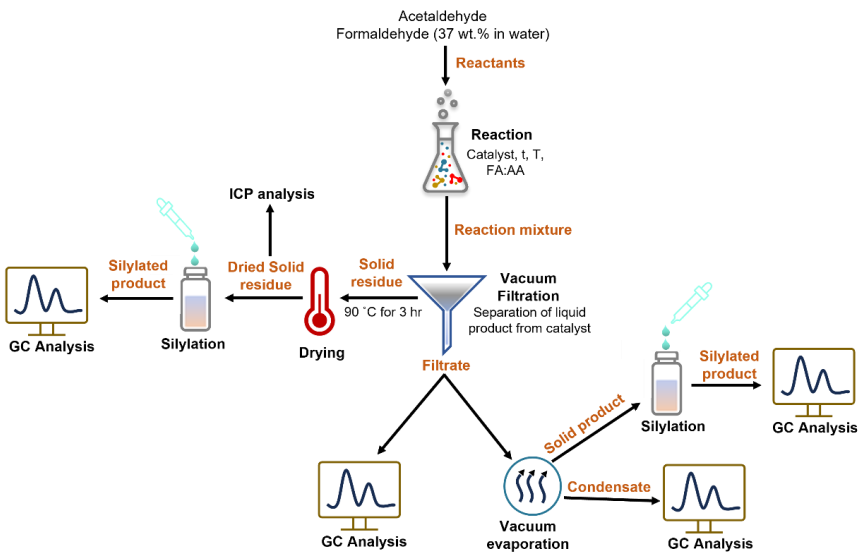
3.4.2 Silylation of solid penta

25 mg of the dried homogenized solids from vacuum evaporation were pretreated prior to GCMS analysis by using a silylation method to quantify penta, penta-derivatives and other products as shown in Scheme 3.

For silylation, 25 mg of the solid was added together with 0.3 mL of trimethylsilylimidazole (TMSI, >98%, Sigma-Aldrich) and 0.6 mL of pyridine (99%, Sigma-Aldrich) and heated for 0.5 h at 120 ºC until completely dissolved. A 0.1 mL aliquot of the resulting solution was added to a vial with 0.1 mL *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, ≥98.5%, Sigma-Aldrich), 0.7 mL pyridine and 0.1 mL of 1000 ppm n-eicosane (C20, ≥99%, Sigma-Aldrich as IS). This mixture was then heated

for 0.25 h at 120 ºC. In most cases the silylation of -OH is a fast reaction occurring at moderate temperatures and prevents further pentaerythritol dimerization. This method also gives an excellent selectivity for the silylation of primary -OH groups of the polyols such as penta and penta-derivatives. The resulting silylated derivative compounds were analyzed by GC-MS.

As penta and its derivatives are not completely soluble in water at room conditions, they can remain in the solid residue along with the catalyst following the filtration. To completely quantify the penta and other penta-derivative products accurately, a small amount of the dried homogenized residual solids was also silylated as described above before performing the GCMS analysis.



Scheme 3. Process steps for collecting and characterizing products in each step of product analysis.

3.5 Product analysis

3.5.1 Gas Chromatography-Mass Spectrometry analysis (GC-MS)

Gas Chromatography-mass Spectrometry (GC-MS) analysis was performed for identification and quantification. All the compounds obtained in the filtrate, the condensate, and silylated products obtained from both the residual solids and the solid products after vacuum evaporation (Scheme 3) were analyzed and measured. A GC-MS method was developed to quantify the obtained filtrate after vacuum filtration and the condensate after vacuum drying. The samples were injected into a GC-MS system consisting of an Agilent 7890B GC coupled with a mass spectrometer in the Electron Impact (EI) mode with the electron energy set at 70 eV and the mass range at m/z 20 – 200. A moderately polar VF1701ms column (30m × 0.25mm × 0.25μm) in the GC was used. The carrier gas (He) flow was set at 0.8 NmL/min. The temperature of the injector port and MS interface were set at 280 °C. The oven temperature program was set initially at 27 °C and held for 3 min, then heated up to 150 °C at a 2.5 °C/min heating rate.

For silylated samples, the same GC-MS system was used but with different method settings. The electron energy was set again at 70 eV, but a mass range of m/z 45 – 700 was instead selected. The temperature of the injector port and MS interface were set at 280 °C with a carrier gas flow rate of 2 NmL/min used. The oven temperature program was set initially at 100 °C and held for 1 min, then heated up to 280 °C at the heating rate of 12 °C/min. The data from both the runs was processed through the Mass-Hunter Qualitative Analysis Software. Calibration was performed for each product in both methods with the respective pretreatment methods. For example, for silylated samples the calibration curve was made for silylated pentaerythritol

(>99%, Sigma-Aldrich), dipentaerythritol (>99%, Sigma-Aldrich), and tripentaerythritol (technical grade, Sigma-Aldrich) by regressing the relative amount injected to the GC to the relative resulting area compared to the internal standard. Calibration curves of products were well correlated (R^2 > 0.988) within the range of 2000 – 10000 ppm (wt/wt). For filtrate and condensate products, the calibration curves were obtained for formaldehyde, acetaldehyde, and 1,4-butenediol (later named as diol) by using the earlier explained method where 1,3,5-trioxane was used as internal standard. Calibration curves of these components were well correlated (R^2 > 0.988) within the range 2000 – 10000 ppm (wt/wt). The formaldehyde and acetaldehyde conversion, product yield, selectivities and carbon recovery were calculated according to equations 1−4, respectively:

$$\text{Formaldehyde Conversion (mol\%)} = \frac{\text{mole of formaldehyde converted}}{\text{mole of initial formaldehyde}} \times 100 \qquad \text{(Eq. 1)}$$

$$\text{Acetaldehyde Conversion (mol\%)} = \frac{\text{mole of acetaldehyde converted}}{\text{mole of initial acetaldehyde}} \times 100 \qquad \text{(Eq. 2)}$$

$$\text{Product Yield (mol\%)} = \frac{\text{n x (mole of product)}}{\text{mole of equivalent formaldehyde fed}} \times 100 \qquad \text{(Eq. 3)}$$

$$\text{Selectivity (wt.\%)} = \frac{\text{Yield (mol \%)}}{\text{Conversion of formaldehyde (mol\%)}} \times 100 \qquad \text{(Eq. 4)}$$

$$\text{Carbon recovery (wt.\%)} = \frac{\sum(\text{moles of carbon out})}{\sum(\text{moles of initial carbon in})} \times 100 \qquad \text{(Eq. 5)}$$

n is the stoichiometric moles of formaldehyde that are required to produce one mole of the product. Product selectivity and yield were calculated based on the conversion of formaldehyde, as non-negligible losses in acetaldehyde occurred during the blank test reactions. The losses in the case of formaldehyde were recorded to be 2 wt. % and for acetaldehyde it was nearly 12 wt. % in the blank test reactions. Consequently, the acetaldehyde conversion could not be correctly measured and would likely always be

overestimated. It is important to state here that the moles of all the individual products and reactants detected in each of the routes in Scheme 3 were added up to calculate the final yield, selectivity, and conversion.

3.6 Catalyst Characterization

3.6.1 Inductively Coupled Plasma Sector Field Mass Spectroscopy (ICP-SFMS) analysis

To quantify the amount of metals such as Sn, Ti, Al in the fresh catalyst and alkali metal Na in spent catalysts, Inductively Coupled Plasma Sector Field Mass Spectroscopy (ICP-SFMS) analysis was performed by ALS Scandinavia AB, Sweden. Furthermore, it was presumed that the leached alkali metals reacted with the formaldehyde to form formates in the presence of formaldehyde during the Cannizzaro reaction. The selectivity for alkali formates was then calculated based on the Na metal amount that had leached out during the experiment and quantified by ICP later.

3.6.2 X-Ray Diffraction (XRD) analysis

X-ray diffraction (XRD) patterns of the prepared samples were obtained with a Bruker D8 Advance Powder diffractometer using Ni-filtered Cu K_α radiation ($\lambda = 0.15418$ nm). The X-ray tube was operated at 40 kV and 40 mA. The intensity data were collected over a 2θ range of 20°–80° at the scan speed of 1°/min and with a step size of 0.02°.

3.6.3 Brunauer-Emmett-Teller (BET) analysis

The textural properties of all the supports and prepared catalysts were calculated from nitrogen adsorption measurements performed at the temperature of 77.4 K using a TriStar 3000 analyzer. Prior to measurements, the samples were outgassed for 3 h at 120°C under a constant flow of nitrogen

gas. The surface areas, micropore and mesopore size distributions of all the supports and prepared catalysts were calculated by using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) theories.

3.6.4 Temperature Programmed Desorption (TPD) of CO_2

The CO_2-TPD measurements for all supports and prepared catalysts were performed on a multifunction chemisorption analyzer with a quartz reactor. The obtained signals were analyzed by using a digital scanning calorimeter (Sensys DSC, Setaram) coupled with a mass spectrometer (HPR-20 QUI, Hiden). About 30-40 mg of catalyst was pretreated with a flow of Ar (30 NmL/min) at 350 °C for 2 h. After the pretreatment step, the sample was cooled down to room temperature in flowing Ar and then exposed to a stream of CO_2/Ar gas (50% CO_2 by volume, 30 NmL/min) for 0.5 h followed by purging with pure Ar flow for 1 h. Then the TPD analysis was done by ramping from room temperature to 600 °C at a heating rate of 10 °C/min in a flow of Ar (30 NmL/min). The effluent gas was analyzed by examining the mass number of m/z=44 as a function of temperature. Basicity was calculated based on the total amount of CO_2 released during the thermal programmed desorption that considers the number of desorbed CO_2 molecules as equal to the basic adsorption sites present on the catalyst surface. Moreover, the desorption of CO_2 at different temperatures distinguished the strength of the basic sites.

4. Results and Discussion

4.1 Catalyst Characterization

4.1.1 N_2 physisorption

The results of the textural properties of all the supports and prepared catalysts are shown in Figure 1 and Table 1. The surface area and pore volume reduced in all the impregnated catalysts as compared to the supports as shown in Table 1. ɤ-Al_2O_3 possesses higher surface area as compared to the other supports. The impregnation of Na on ɤ-Al_2O_3 (Figure 1b) led to a decrease in the surface area and specific pore volume. On the other hand, the pore width increased in the case of Na over ɤ-Al_2O_3. The results reported in the table and pore size distribution curves showed that the impregnation of Na over ɤ-Al_2O_3 likely blocked the small pores, resulting in that the remaining pores were larger as shown in Table 1 and Figure 1. It has been seen that impregnated Na reacts with ɤ-Al_2O_3 forming $Al(OH)_3$ species, changes the pore structure.[31] For all the three supports, the pore widths increased due to the addition of Na metal. The effect was pronounced for the case of TiO_2 and simultaneously the surface area and pore volume reduced considerably due to the loading of Na over TiO_2 and blocking of small pores.

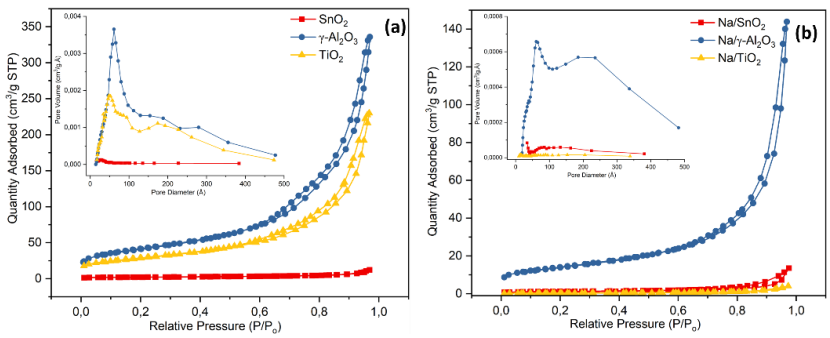


Figure 1. N_2 physisorption isotherms and pore diameter distribution for **(a)** supports, and **(b)** Na based catalysts.

Table 1. BET data of all fresh catalysts.

Catalyst	$S_{BET}(m^2/g)^a$	$V(cm^3/g)^b$	Pore width (nm)
SnO_2	35.2	0.061	8.7
ɤ-Al_2O_3	149.6	0.515	11.4
TiO_2	103.8	0.357	10.9
Na/SnO_2	4.4	0.018	13.8
Na/ɤ-Al_2O_3	49.9	0.217	15.0
Na/TiO_2	1.5	0.005	10.5

[a]S_{BET} (total surface area) calculated using the BET equation.
[b]V(total pore volume) calculated by single-point method at P/P_0=0.95.

4.1.2 X-Ray Diffraction (XRD)

Figure 2 showed the XRD patterns of supports and all the prepared catalysts. In the prepared catalyst samples, the peaks for the supports such as SnO_2, and TiO_2 can still be clearly observed. Moreover, the Na peaks at nearly 30° can also be clearly seen in all the samples. However, interestingly, the Na peak intensity is quite small in the case of the alumina support compared to the other two catalysts. This could be due to Na becoming fused in the alumina pores instead of only staying on the surface.

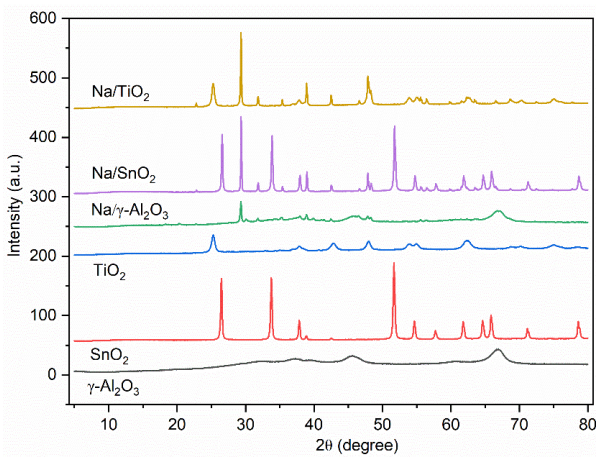


Figure 2. XRD analysis of all the supports and catalysts.

4.1.3 CO_2 Temperature Programmed Desorption (CO_2 - TPD)

The basicity of the catalyst is a key factor in the catalytic performance for both aldol condensation and cannizzaro reactions. The CO_2-TPD curves for all supports and prepared catalysts are shown in Figure 3. The distribution of the basic sites as weak, intermediate, strong, and very strong on the samples can be depicted through the CO_2 desorption peaks in the temperature ranges of 20-150, 150-300, 300-450 and above 450 ^oC respectively. In figure 3a, ɤ-Al_2O_3 is the only support among all the tested supports that has weak basic sites corresponding to 58.8 μmol/g of CO_2 adsorption (Table 2). Na on the supports enhanced the abundance of basic sites specifically with the medium basic strengths as shown in Figure 3b. Basic sites strengths were different in all the supported catalysts. The TPD curve for Na/ɤ-Al_2O_3 indicates that it has medium and dominantly strong basic sites and a total basicity calculated as 163.2 μmol/g CO_2. The TPD curve for Na/TiO_2 also exhibited a strong basic site peak with relatively low intensity corresponding to 112.4 μmol/g of CO_2 adsorption. Na/SnO_2, on the other hand, exhibits a small peak corresponding to only strong acid sites as shown in Figure 3. The higher basicity in the case of Na/ɤ-Al_2O_3 might be linked to the high surface area of ɤ-Al_2O_3 allowing a high dispersion of the alkali metal and thus increasing the basic sites of the catalyst. The differences in basicity of the catalysts and their respective distinctive adsorption of CO_2 considerably affect their catalytic performance for penta synthesis which is explained in Section 4.4.

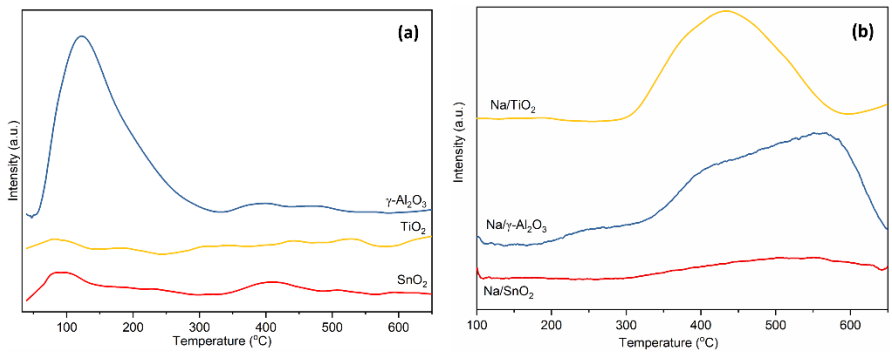


Figure 3. CO_2 TPD curves of **(a)** supports, and **(b)** Na based catalysts.

Table 2. Basic strengths as CO_2 adsorption values (μmol/g) for prepared catalysts and supports.

Catalyst	μmol/g,cat
ɤ-Al_2O_3	58.8
TiO_2	undetected
SnO_2	undetected
Na/ɤ-Al_2O_3	163.2
Na/SnO_2	67.3
Na/TiO_2	112.4

4.2 Blank test reactions

Prior to the catalyst activity test, the blank reactions of formaldehyde and acetaldehyde were performed for heating and isothermal reaction at 70 ºC with a formaldehyde to acetaldehyde molar ratio of 5:1. The reaction mixture products were sampled after each 30 min period during 2 h at isothermal operation. In the GCMS analysis, no other compounds were detected than the reactants other than traces of acetaldehyde self-condensation products as shown in Figure 4. The by-products 2-butenal and paraformaldehyde detected remain constant in % GCMS area ratio throughout the sampling for 2 h (Figure 4).

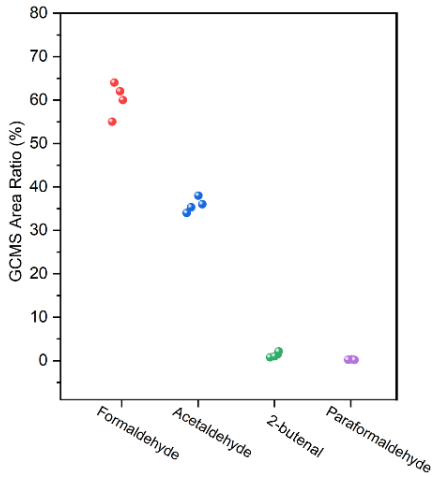


Figure 4. Blank (i.e. without catalyst) reaction products (GCMS area %) at 0, 0.5 ,1.5, and 2 h time during isothermal reaction conditions of formaldehyde to acetaldehyde ratio 1:5 (molar), and 70 °C isothermal temperature.

4.3 Effect of formaldehyde feed composition

Commercially available formaldehyde is a 37 wt. % solution in water with 10-15 wt.% methanol also usually presents in the solution as a stabilizer to avoid the polymerization of the formaldehyde. A reaction experiment was performed with formaldehyde solution that contained 10-15 wt.% MeOH and acetaldehyde (ratio 5:1) in the presence of the Na/TiO_2 catalyst. The same reaction conditions were used as in blank tests. The product distribution after finishing the reaction can be seen in Figure 5. A broad spectrum of by-products was formed along with the penta peak (retention time 68.9 min.). This might be due to the active enolate formation that can form in abundance in the presence of MeOH which promotes many condensation reactions.

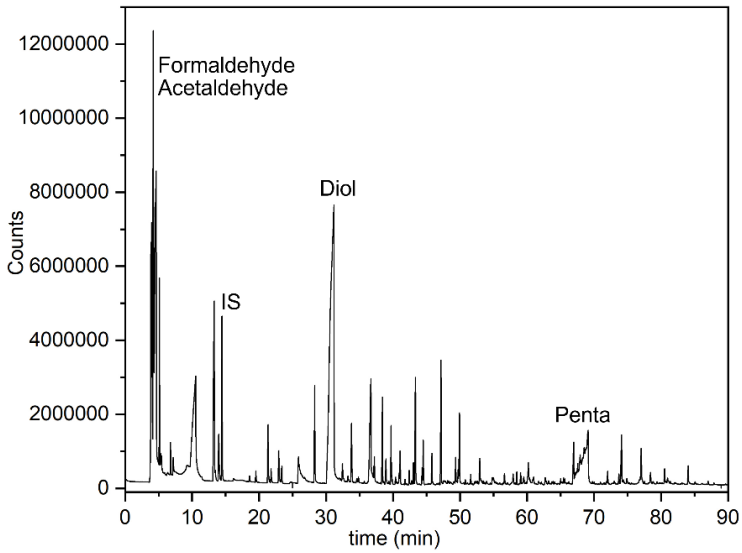


Figure 5. GCMS product spectra for reaction mixture when formaldehyde solution with 10-15 wt. %MeOH was used as the feed. Reaction conditions: formaldehyde to acetaldehyde ratio 5:1, at 70 ^{o}C, reaction time of 45 min including ramping and cooling period.

While in the case of all other experiments where formaldehyde solution containing less than 1 wt.% of MeOH was used, few cross-condensation reaction products were detected as shown in the GCMS spectra in Figure 6. A low concentration of MeOH in the feed also suppresses the self-condensation reactions of both formaldehyde and acetaldehyde as no self-condensation product of acetaldehyde i.e.: 2-butenal and paraformaldehyde were detected which were present in case of the blank reaction tests (Figure 4).

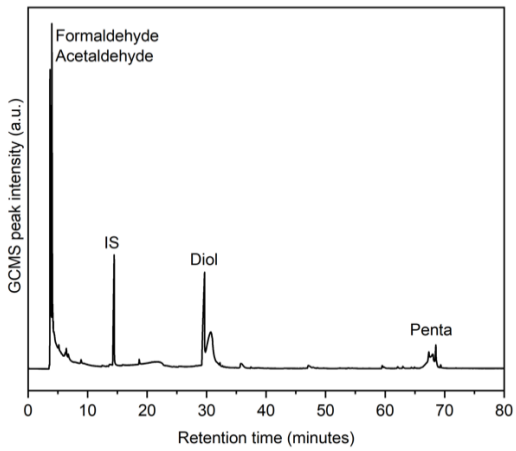


Figure 6. Complete GCMS spectra of product distribution of reaction mixture when formaldehyde solution containing <1%MeOH was used as the feed with acetaldehyde. Reaction conditions: formaldehyde to acetaldehyde ratio 5:1, at 70 ºC, reaction time of 45 min including ramping and cooling period.

4.4 Catalyst activity test

All the prepared catalysts were tested under the same reaction conditions as in the blank experiment (formaldehyde: acetaldehyde = 5:1 molar ratio, 70 °C temperature, 15 min isothermal reaction period, and continuous stirring at 200 rpm) and with the formaldehyde solution containing <1 wt.% MeOH as reactant. Na alkali metals on different supports exhibited different behavior. The Na/TiO_2 catalyst showed a low conversion of 11% of formaldehyde and mostly produced penta derivatives with 85% selectivity as shown in Figure 7a and Table 3. However, the pentaerythrose intermediate (as shown in Scheme 1) was not detected in the GCMS analysis which is common in the literature dealing with the homogeneous catalyst systems for penta formation, because the further reaction of the 3-hydroxy-2,2-bis(hydroxymethyl)propionaldehyde intermediate to penta occurs at a rapid

rate. The low conversion with Na/TiO_2 might be due to the high leaching rate of Na in this case, as the catalyst loses active sites because of high leaching which resultantly decreases the aldol condensation reaction between formaldehyde and acetaldehyde. On the other hand, $Na/\gamma\text{-}Al_2O_3$ displayed a higher conversion of formaldehyde of 29% and the product distribution was selective for diol synthesis with 37% and formed penta with only 24% selectivity. The high basic strength in the case of $Na/\gamma\text{-}Al_2O_3$, likely due to better dispersion of sodium on the high surface area $\gamma\text{-}Al_2O_3$, might lead to the synthesis of diol products. However, Na/SnO_2 showed the highest activity among all the prepared catalysts with 59% formaldehyde conversion with 39% and 40% selectivity for penta and penta-derivatives respectively (Figure 7a and Table 3). It was observed that the Na/SnO_2 catalyst with the lowest basic site density (Table 2) and medium pore volume (0.018 cm^3/g in Table 1) among all the catalysts appeared to be best for the synthesis of penta with better selectivity and good conversion of formaldehyde. To conclude, it is not only the dispersion of sodium and surface area of the support that is important, but there are also interactions with the support, possibly in the edges between sodium particles and support that are different between the samples.

Na alkali metal leaching for all spent catalysts was also checked and for this purpose the weight percent content of Na was measured for all the spent catalysts through ICP analysis. The leached Na metals could possibly be an indirect indication and measure of the occurrence of the Cannizzaro reaction. As discussed already in Scheme 1, during the Cannizzaro reaction, formiates easily react with sodium to form sodium formates, so it is assumed that sodium formates are present in equal amount as the Na metal leached. However, the state of the leached sodium, and whether it is entirely sodium

formates is not directly known. The formate selectivity reported in Table 1, for simplicity, was calculated based on the Na metal ions that leached during the reaction and the calculated values are shown in Table 3.

The obtained results from ICP were reported as alkali metal leaching which is shown in Figure 7b. Generally, the different sodium-based catalysts leached between 19-37 wt. % of their alkali metal content.

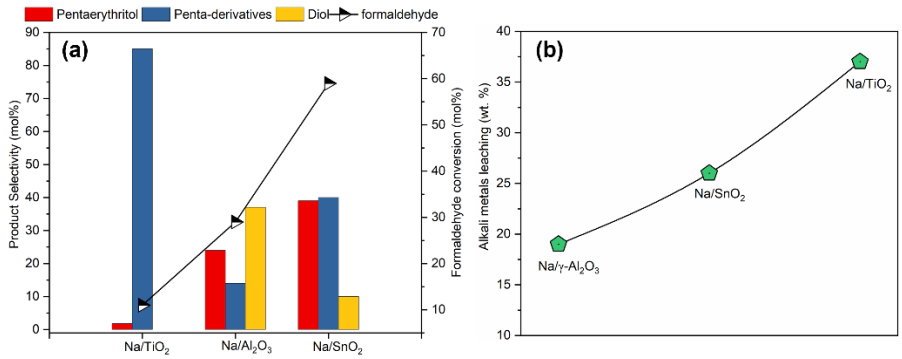


Figure 7. (a) Catalysts activity tests, and **(b)** Na leaching (wt.%) of all the spent catalysts during penta synthesis at reaction conditions of formaldehyde to acetaldehyde ratio 5:1 (molar), 15 min isothermal reaction time at 70 °C and catalyst amount of 0.2 g.

Table 3. Na-based catalysts activity tests for penta synthesis at reaction conditions of formaldehyde to acetaldehyde ratio 5:1 (molar), 15 min isothermal reaction time at 70 °C and catalyst amount of 0.2 g.

Catalyst	FA conv. (mol %)	Product distribution (selectivity in mol %)				Carbon Balance (%)
		Penta	Penta-derivatives	Diol	Formate	
Na/ɤ-Al_2O_3	29	24	14	37	26	92
Na/TiO_2	11	2	85	0	13	89
Na/SnO_2	59	39	40	10	11	98

As discussed earlier in Section 2.1, penta-derivatives that are reported in Table 3 are mainly CPF and dipenta which mechanistically are produced

from penta as shown in Scheme 2. To understand the route for the formation of penta, either in the form of mono-penta or penta derivatives, the molar ratios of formaldehyde consumed to produce formates to formaldehyde consumed for producing penta and penta-derivatives are calculated and compared with the theoretical value in the case of homogeneous catalytic route as shown in Figure 8. Theoretically, if the reaction is solely occurring due to homogeneous catalysis, then the ratio of formaldehyde consumed to produce formates to that for penta is 4:1 (0.25), as shown in Scheme 1 (Section 2.1). However, for the solid catalysts from a comparison of the formaldehyde consumption ratio, it can be deduced that in case of the Na/ɤ-Al_2O_3 catalyst, penta and its derivatives might be entirely produced through the Cannizzaro reaction, consuming formaldehyde due to the Na-alkali metal leaching as the formaldehyde consumption ratio is higher than the homogeneous catalyst value (Figure 8). The reason could be that the formate formation in the case of these catalysts could be due to the loosely bounded Na alkali on the support of the solid catalyst dissolving into the aqueous media and acting as a homogeneous catalyst. However, more interestingly, in the case of the Na/TiO_2 and Na/SnO_2 catalysts, the formaldehyde consumption ratio is 0.14 and 0.15 respectively, which is lower than the theoretical value for homogeneous catalysis (Figure 8). This clearly indicates that the penta is not only formed due to the leached Na in case of Na/TiO_2 and Na/SnO_2, but also from the heterogeneous basic active sites of the catalysts.

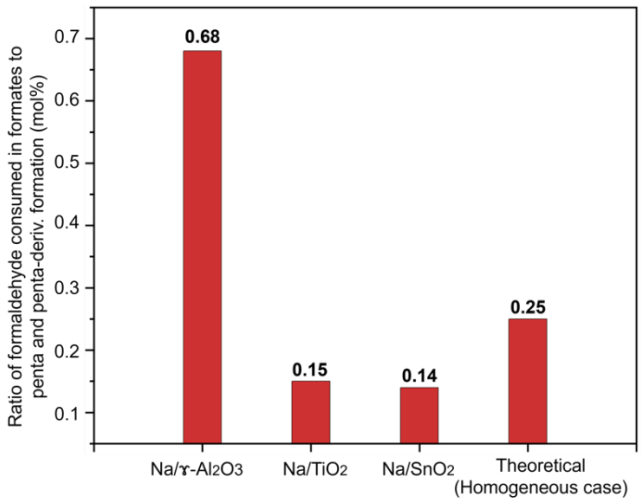


Figure 8. (a) Molar ratio comparison of formaldehyde consumed to produce formates to that for penta in case of solid catalysts Na/ɤ-Al_2O_3, Na/TiO_2, Na/SnO_2 and in case of the homogeneous catalytic route.

5. Conclusion and outlook

This thesis includes studies on pentaerythritol synthesis by using a solid alkaline catalyst and the conclusions are based on the catalyst activity tests that were performed for the synthesis of penta.

Blank reactions were performed to check the reactivity of the aldehyde reactants before testing the prepared catalysts. It was observed that a small amount of self-condensation products formed under certain reaction conditions. It has been investigated that the formaldehyde feed with <1% MeOH is better than 10-15% MeOH. A higher content of MeOH in formaldehyde causes more side reactions and hence decreases the selectivity and yield of penta. From the catalyst activity tests, it has been observed that the catalyst with lowest basic site density was sufficient to form penta with less by-product formation. Na/SnO_2 shows the highest activity among Na-based catalysts with 59% formaldehyde conversion with 39% and 40% selectivity for penta and penta-derivatives respectively. Generally, the sodium-based catalysts leached between 19-37% of their Na contents in all the prepared catalysts which might be through the Cannizzaro reaction of sodium formate. However, more interestingly, in case of the Na/TiO_2 and Na/SnO_2 catalysts, the amount of penta and its derivatives produced was so much higher than the Na formate possibly formed, that the Cannizzaro and condensation reactions must also occur on heterogeneous active sites of the catalysts to synthesize penta. Hence, conclusively, the solid catalysts can be potentially applied as promising replacements of homogeneous liquid alkaline solutions to produce pentaerythritol.

It would be interesting to further analyze the leached Na structure with IR or Raman spectroscopy in the future, to ascertain if Na leached is present in the reaction mixture in form of sodium formates. Moreover, it would also be of interest to examine the spent catalyst surface with the IR spectroscopy technique to see if formates form on the surface of the solid catalysts.

The findings from this study encourage us to design even better catalysts in terms of stability and bifunctionality to probe both the aldol condensation and Cannizzaro reaction on solid catalysts to improve the formaldehyde conversion and penta selectivity.

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