

## Synthesis of CZA Catalysts and Selectivity Studies for CO<sub>2</sub> to Methanol Reaction

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### ABSTRACT

Methanol synthesis from CO<sub>2</sub> hydrogenation on supported Cu catalysts is of considerable importance in the chemical and energy industries. Although extensive experimental and theoretical efforts have been carried out in the past decades, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have been prepared by a co-precipitation method. The co-precipitation was operated continuously under exact control of pH, temperature, concentration and ageing time. The precipitation was performed with sodium, ammonium and potassium carbonate as well as sodium hydroxide. The effect of the post condition, on the structure, surface properties of the catalysts and their precursors, as well as the catalytic activities for methanol synthesis from CO<sub>2</sub> hydrogenation has been studied. The results showed that the washing with ethanol or drying directly derived a large specific surface area, highly dispersion ultrafine Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts, which exhibited a higher catalytic activity and optimum methanol selectivity for methanol synthesis from CO<sub>2</sub> hydrogenation. The catalysts were characterized by N<sub>2</sub> adsorption-desorption, X-ray diffraction, field emission scanning electron microscope, temperature programmed decomposition, and temperature programmed reduction.

Keywords: X-ray diffraction, pH, adsorption, desorption, catalyst activity.

### 1. INTRODUCTION

CO<sub>2</sub> the major man-made greenhouse gas, to more useful compounds is currently under consideration among the possible approaches for mitigating its emission to the atmosphere. The concentration of carbon dioxide in the atmosphere has consequently risen from 280 ppm before the industrial revolution to 397 ppm in 2012, which is further predicted to be 570 ppm by the end of the century. Reducing CO<sub>2</sub> emission is an extensive and long term task. In principle, there are three strategies with this regard reduction of the amount of CO<sub>2</sub> produced, storage of CO<sub>2</sub>, and usage of CO<sub>2</sub>.

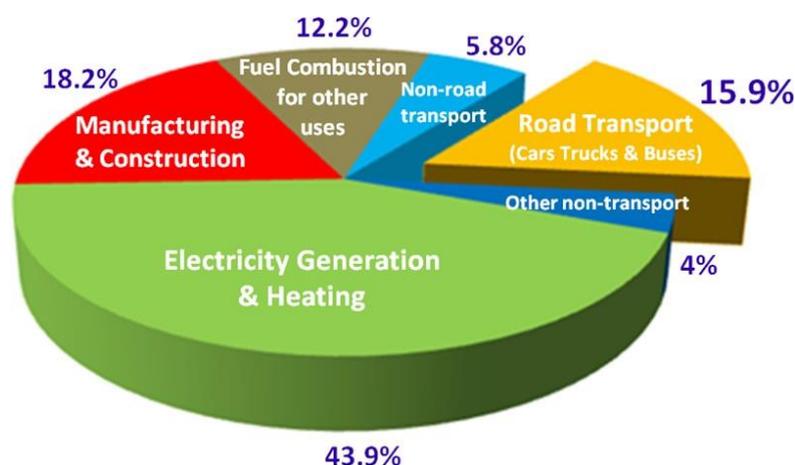


Figure 1.1: CO<sub>2</sub> Emissions from various sources

The first strategy requires energy efficient improvements and switching from fossil fuels towards less carbon intensive energy sources such as hydrogen and renewable energy. Storage of CO<sub>2</sub> involving the development of new technologies for capture of CO<sub>2</sub>, is a relatively well established process.[6] As an economical, safe, and renewable carbon source, CO<sub>2</sub> turns out to be attractive C<sub>1</sub> building block for making organic chemicals, materials,

carbohydrates (e.g., foods). The utilization of  $\text{CO}_2$  as a feed-stock for producing chemicals not only contribute to alleviating global climate changes caused by the increasing  $\text{CO}_2$  emission, but also provides a grand challenge in exploring new concept and opportunities for catalytic and industrial development. However,  $\text{CO}_2$  is not used extensively as a source of carbon in current laboratory and industrial practices. Indeed, the use of  $\text{CO}_2$  as chemical feed-stock is limited to a few industrial processes synthesis of urea and its derivatives, salicylic acid, and carbonates. This is primarily due to the thermodynamics stability of  $\text{CO}_2$  and thus high energy substances or electro reductive processes are typically required to transform  $\text{CO}_2$  into other chemicals.

Hydrogen is high energy material and can be used for  $\text{CO}_2$  transformation as the reagent. The main products of  $\text{CO}_2$  hydrogenation can fall into two categories fuels and chemicals. Indeed, the needs for fuels are ever increasing with growing energy consumption. However, the resources of fossil fuels are being diminished and fuel prices have undergone strong fluctuation in recent years therefore it would be highly desirable to develop alternative fuels from non-fossil fuel sources and processes. The product of  $\text{CO}_2$  recall potential issues associated with hydrogen such as production, storage and transportation. Hydrogen sources for chemical recycling of  $\text{CO}_2$  could be generated either by using still-existing significant sources of fossil fuels (mainly natural gas) from splitting water. The conversion of  $\text{CO}_2$  that would otherwise get into the atmosphere into useful, e.g. methanol, is an attractive way to protect the global environment since  $\text{CO}_2$  is an important greenhouse gas and methanol itself is a useful raw chemical and solvent. For  $\text{CO}_2$  hydrogenation, the thermodynamics analysis that when the reaction temperature is increased,  $\text{CO}_2$  conversion is slightly decreased and methanol selectivity is decreased, so that the yield of methanol is decreased [7]. An industrial  $\text{CO}_2$  hydrogenation process should be operated at a relative low reaction low reaction temperature. However, a conventional  $\text{Cu/Zn/Al}_2\text{O}_3$  catalyst that is active for methanol production from synthesis gas is not as active and selective for methanol synthesis from a  $\text{H}_2/\text{CO}_2$  mixture at temperatures below  $250^\circ\text{C}$  [8], even though it is now accepted that methanol synthesis from synthesis gas actually proceeds through  $\text{CO}_2$  hydrogenation.

## 2. LITERATURE REVIEW

As a major greenhouse gas, carbon dioxide with increased concentration in the atmosphere is being considered responsible for the global warming and climate changes. Therefore, the reduction of  $\text{CO}_2$  concentration becomes the global focus. Being a renewable and environmentally friendly source of carbon, conversions of  $\text{CO}_2$  to fuels and chemicals offer opportunities to mitigate the increasing  $\text{CO}_2$  build up. Hydrogenation of  $\text{CO}_2$  is a feasible and powerful process with this regard. However, one need to recall the nature of  $\text{CO}_2$  chemically stable and thermodynamically unfavourable. To eliminate the limitations on the conversion and selectivity, various technical directions and specific research approaches on rational design of catalysts, reactor optimization, and exploration of reaction mechanisms have been presented.

Both homogeneous and heterogeneous catalysts play crucial roles in the hydrogenation of  $\text{CO}_2$ . Homogeneous catalysts are efficient for the formation of formic acid and formates. The reactions can be accelerated by the

addition of solvents such as water, supercritical CO<sub>2</sub>, and ionic liquids. However, the need for expensive catalyst, high operating pressure, and the tedious work up procedures involved for catalyst separation and recycling make these processes unattractive for commercial applications. Heterogeneous catalysts are, of course, more practical for industrial applications compared to homogeneous catalysts. The catalyst with larger surface area, ultra-fine particle, and higher metal dispersion can usually possess higher activity and selectivity, and longer life in the hydrogenation of CO<sub>2</sub>. However, these heterogeneous catalysts frequently suffer from low yield and poor selectivity due to fast kinetics of the CH bond formation.

Furthermore, preparation methods have considerable influences on the nature of the catalysts (such as BET surface area, particle size, metal dispersion, etc.), leading to the disparities of the catalytic performance. Therefore, in order to make CO<sub>2</sub> hydrogenation economically feasible, significant improvements in new catalytic systems with rational design and molecular simulations would be necessary. In heterogeneous reaction, the prevalent consensus is that the active site is provided by the synergy between the primary catalyst and the support or the promoter. Nevertheless, the nature of the active sites and interactions among active components, support, and promoter as well as reaction mechanisms are still elusive, even for the synthesis of formic acid, the first step of the hydrogenation. For both homogeneous and heterogeneous catalyst, the primary focus of the mechanisms for CO<sub>2</sub> hydrogenation is on how and where CO<sub>2</sub> is activated and interacts with hydrogen and/or hydroxyl species under different reaction conditions. Surface science approaches coupled with molecular simulations would bridge the gap between the macroscopic characteristics (e.g., kinetics) of practical catalysts and molecular understanding of the reaction.

### **2.1 HETEROGENEOUS CATALYST**

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen). [9] The total surface area of solid has an important effect on the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles. Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Supports prevent or reduce agglomeration and sintering of the small catalyst particles, exposing more surface area, thus catalysts have a higher specific activity (per gram) on a support. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly alumina, zeolites or various kinds of activated carbon.

### **2.2 HOMOGENEOUS CATALYSTS**

Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles invoked in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with

the substrates. One example of homogeneous catalysis involves the influence of  $H^+$  on the esterification of carboxylic acids, such as the formation of methyl acetate from acetic acid and methanol.[10] For inorganic chemists, homogeneous catalysis is often synonymous with organometallic catalysts.

### 1) Comparison of homogeneous catalyst and heterogeneous catalyst

Majority of the industrial catalyst are solids. In contrast, the proportion of non-solid catalysts (liquid and gases) are very small, based on many criteria and properties, such as mass, value and size of industrial plants. Solid catalysts often contain two or several solid components in various composition providing specific porosity and surface area that must be carefully controlled to provide high activity, good selectivity and stability in time during the catalytic reaction.

Table 2.1: Comparison of homogeneous catalyst and heterogeneous catalyst

Property	Homogeneous catalyst	Heterogeneous catalyst
Catalyst recovery	Difficult and sometimes impossible	Easy
Thermal stability	Poor	Good
selectivity	Excellent single active site	Good-multiple active sites
Cost of production	Expansive	Potentially cheap

### 2.3 THE EFFECT OF CALCINATION TEMPERATURE ON PROPERTIES AND ACTIVITY OF $Cu/ZnO/Al_2O_3$ CATALYSTS

Data available in the literature show that catalytic properties of such systems significantly depend on the structure of a precursor and its preparation method. The precursor is a mixture of complex hydroxy carbonates of copper-zinc aluminum with a hydrotalcite type structure. Other crystallographic structures can also be present. At special conditions of precursor materials thermal decomposition (calcination) high-dispersion components systems can be obtained. For this reason calcination of precursor is an important step in a process of catalyst activation.

It seems that  $Cu/ZnO/Al_2O_3$  catalysts obtained from hydrotalcite like precursors possess the best catalytic properties such as high and constant activity [5]. There is an extensive literature study on this type of systems such as Cu-Ni-Al, Cu-Mg-Al, Cu-Zn-Cr [4]. Numerous works on preparation and properties of Cu-Zn-Al precursors are mainly focused on the structure, kinetic studies and physicochemical properties [5]. There are few works about mechanisms of processes running during the thermal decomposition of these systems. The paper by Frost [9] presents the results of calcinations in the range 30-500 °C limited to precursors of stoichiometric composition of hydrotalcite, different content of copper and zinc ( $0 \leq x \leq 6$ ). The results indicate a multi course of this process, which consists of the stages of evolution of adsorbed water, dehydroxylation and decomposition of carbonate groups. The study of thermal and spectroscopic methods shows that during the calcination process changes in the relative positions of hydroxyl and carbonate groups in the crystallographic structure occur. The following paper presents the study of thermal decomposition conditions of the model precursor (up to 973 K), whose composition is in the range for typical copper catalysts applied in water gas shift and methanol synthesis processes. An effect of

calcination temperature on the properties of catalysts has been studied for several values of this parameter corresponding to several characteristic bands. Industrial utilizations of  $\text{CO}_2$  as solvent and reactant amount to only 0.5 wt percent of the total anthropogenic  $\text{CO}_2$  emissions every year. In principle, chemical utilizations of  $\text{CO}_2$  do not necessarily help mitigate the greenhouse effect considering energy input and carbon circulation. However, if  $\text{CO}_2$  could be chemically transformed to fuels, it would be helpful to circulate carbon to alleviate the greenhouse effect. Particularly, production of fuels that can be easily stored and transported is preferable. Commercially, methanol is produced from synthesis gas, mainly containing  $\text{CO}$  and  $\text{H}_2$  along with a small amount of  $\text{CO}_2$  as the additive. Therefore, the utilization of  $\text{CO}_2$  enriched synthesis gas mixtures for  $\text{CO}_2$  hydrogenation would be a potential process to chemical industries. The future research should certainly emphasize on the rational design of highly active catalyst and integral process to satisfy the economic development and sustainable utilization of carbon sources.

#### **2.4 THE EFFECT OF REACTION TEMPERATURE**

$\text{CO}_2$  hydrogenation takes place at temperatures from 483 to 543 K. The relationship between reaction temperature and  $\text{CO}_2$  conversion or methanol yield is shown in Figure. Reaction temperature was higher, the reaction rate increased, and more  $\text{CO}_2$  was converted into methanol when the system is far from thermodynamic equilibrium. At 523 K,  $\text{CO}_2$  conversion can reach 0.258. However, the  $\text{CO}_2$  conversion was decreased to 0.251 when the temperature was 543 K because of thermodynamic equilibrium. With the increase of temperature, the  $\text{CO}_2$  conversion reached to thermodynamic gradually. It was noticed that only a fraction of  $\text{CO}_2$  was converted to methanol, while the rest was converted to  $\text{CO}$ . Methanol yield increased from 11.4 at 483 K to 17.9 at 523 K, which is 36% higher than the yield at 483 K. However, although methanol synthesis is an exothermic process and the temperature increasing further is not favourable, We can also see that methanol synthesis was more sensitive than the reverse water shift reaction with respect to the reaction temperature. The fibrous catalyst has its highest methanol yield at 523 K at a space velocity of 6000 ml and a pressure of 5 MPa.

#### **2.5 THE EFFECT OF THE PRESSURE**

From the thermodynamics, a high pressure is beneficial for methanol production from  $\text{CO}_2$ . On the fibrous  $\text{Cu/Zn/Al/Zr}$  catalyst, the relationship between the pressure and  $\text{CO}_2$  conversion and methanol yield is shown in Fig. 3. At 2.0 MPa,  $\text{CO}_2$  conversion was just 0.190. When the pressure was increased to 5.0 MPa is shown in Fig.,  $\text{CO}_2$  conversion was increased to 0.258. When the pressure increased, the difference between the experimental results and thermodynamic equilibrium was also increased. Furthermore, the yield of methanol also showed similar trends: methanol yield was 0.061 and 0.179 at pressures of 2.0 and 5.0 MPa, re-respectively. It was also observed that the methanol yield increased faster than the  $\text{CO}_2$  conversion which meant that methanol synthesis was more sensitive than the reverse water shift reaction with respect to the re-action pressure. This is in agreement with many other reports. A high pressure was also effective for the  $\text{Cu/Zn/Al/Zr}$  catalyst in our case. Meanwhile, the flow rate through the reactor was also increased. Too high a reaction pressure has a much higher requirement for the material of the facility and also poses a safety.

## 2.6 THE EFFECT OF THE SPACE VELOCITY

The space velocity, which is a parameter that reflects the reactor efficiency, was also tested with a  $H_2/CO_2$  ratio of 3 and a pressure of 5.0 MPa. Space velocities from 1000 to 10000 ml were used to test the catalytic behaviour. At the space velocity of 1000 ml,  $CO_2$  conversion was about 0.262. When it was increased to 10000 ml the  $CO_2$  conversion was decreased to 0.232. But it was noticed that the  $CO_2$  conversion decrease was 11.4, while the methanol yield was decreased 31.0 from a space velocity of 1000 ml to 10000 ml. With a higher space velocity, more reactant was introduced into the reactor and the residence time was shorter, and  $CO_2$  conversion decreased.

Table 2.2: The effect of Reaction Temperature

S.No	Reactor Type	Temperature $^{\circ}C$	Surface Area	Reaction time (hr)	WHSV	Catalyst	Selectivity %	Conversion%
1	Fixed Bed Reactor	240	110.8	4	6000	Cu/Zn/Al <sub>2</sub> O <sub>3</sub>	60	21
2	Fixed Bed Reactor	230	16.62	24	4000	Cu/Zn/Al/Zr	55	23.9
3	Fixed Bed Reactor	299.85	122.4	3	3600	Cu/ZrO <sub>2</sub>	72.4	6.21

Table 2.3: The Effect of Calcination Temperature

S.No	Reactor Type	Calcination Temperature $^{\circ}C$	Surface Area	Reaction time (hr)	WHSV	Catalyst	Selectivity %	Conversion%
1	Fixed Bed Reactor	350	110.8	4	6000	Cu/Zn/Al <sub>2</sub> O <sub>3</sub>	60	21
2	Fixed Bed Reactor	400	16.62	24	4000	Cu/Zn/Al/Zr	55	23.9
3	Fixed Bed Reactor	380	122.4	3	3600	Cu/ZrO <sub>2</sub>	72.4	6.21

Table 2.4: The effect of Pressure

S.No	Reactor Type	Pressure (MPa)	Surface Area	Reaction time (hr)	WHSV	Catalyst	Selectivity %	Conversion%
1	Fixed Bed Reactor	5	110.8	4	6000	Cu/Zn/Al <sub>2</sub> O <sub>3</sub>	60	21
2	Fixed Bed Reactor	5	16.62	24	4000	Cu/Zn/Al/Zr	55	23.9
3	Fixed Bed Reactor	0.10	122.4	3	3600	Cu/ZrO <sub>2</sub>	72.4	6.21

### 3. METHOD

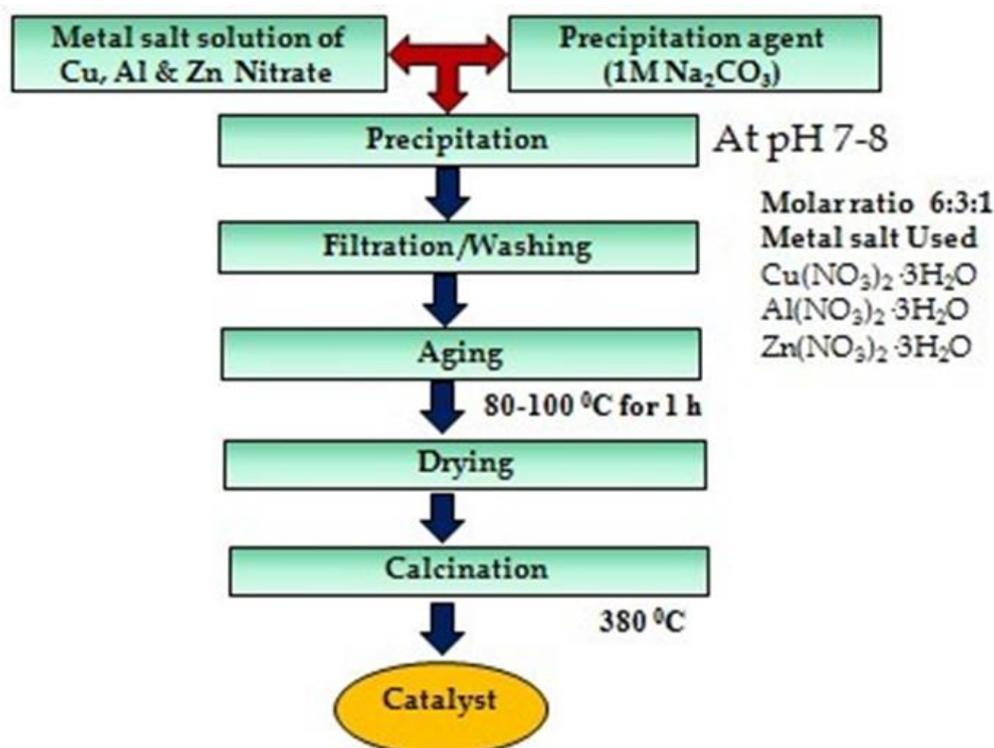
#### Preparation method

The catalysts we have prepared by using co-precipitation method by mole ratio of 6:3:1. The precursor were  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$ . Initially the appropriate weight of metal nitrate precursors taken in round bottom flask under continuous stirring, then we prepared one molar solution of  $Na_2CO_3$  as a precipitating agent. The amount of water was calculated on the basis of the weight of the support. For proper dissolution of metal salt magnetic stirrer is used at  $70^\circ C$  with help of water bath controlled with thermometer for 3hr. After complete dissolution of metal salt, we start adding drop wise precipitating agent  $Na_2CO_3$  with constant stirring and continuously check the pH of the solution, precipitating agent is added till the pH of solution reached at 7 to 8. At this pH bluish white precipitate is appearing. The solution mixture was allowed to stirrer for next 3 hr at  $80^\circ C$ . After the reaction the mass was filtered and washed five times with deionised water and dried overnight at  $120^\circ C$  to remove moisture and calcined at  $380^\circ C$  for 6 hr in the muffle furnace.

#### Catalyst Preparation

**Unsupported Catalyst** are typically usually very active catalyst that do not require high surface area e.g., Iron catalyst for ammonia production are usually used for high temperature applications e.g., refractory aluminates for catalytic combustion intrinsically have a large surface area e.g., gamma alumina catalyst for isomerization clay catalyst for hydrogenation.

**Supported Catalyst** requires a high surface area support to disperse the primary catalyst, the support may also act as a co-catalyst or secondary catalyst for the reaction.



**Catalyst can be prepared by variety of ways to suit a chemical process. Usually, the methods used for catalyst preparation are:**

- a. Co-precipitation
- b. Solgel
- c. Co-impregnation
- d. Incipient wetness
- e. Deposition-precipitation
- f. Urea-nitrate combustion
- g. Glycine-nitrate combustion

### ***Co-precipitation method***

Co-precipitation method is the most common method used in preparing mixed oxide- based solid catalyst. It is a controlled chemical equilibrium shifting process involving incorporation of trace elements into a mineral structure during solid formation and re- crystallisation of minerals. This process will reduce the mobility and toxicity of the trace elements in the mineral. Co-precipitation can be conducted with many specific steps involving preparation of the specific solution, drying and calcination. Further validation of solid catalyst properties and characteristics are via characteristics analysis

### ***Advantages of Co-precipitation method***

The co-precipitation technology is preferred over other catalyst development technologies because

1. The particle size and composition are easy to control
2. There are various possibilities to modify the particle surface state and overall homogeneity
3. It gives high output and recovery
4. All these factors lead to low production cost

### **Chemical used for preparation of Catalyst**

Name	Chemical formula	Molecular weight
Cu nitrate tri hydrate	$Cu(NO_3)_2 \cdot 3H_2O$	241.6
Zinc nitrate hexa hydrate	$Zn(NO_3)_2 \cdot 6H_2O$	297.49
Aluminium nitrate nano hydrate	$Al(NO_3)_3 \cdot 9H_2O$	375.15
Sodium carbonate anhydrous AR	$Na_2CO_3$	105.19
Water for HPLC and Spectroscopy	$H_2O$	18.015

**4. RESULTS AND DISCUSSION**

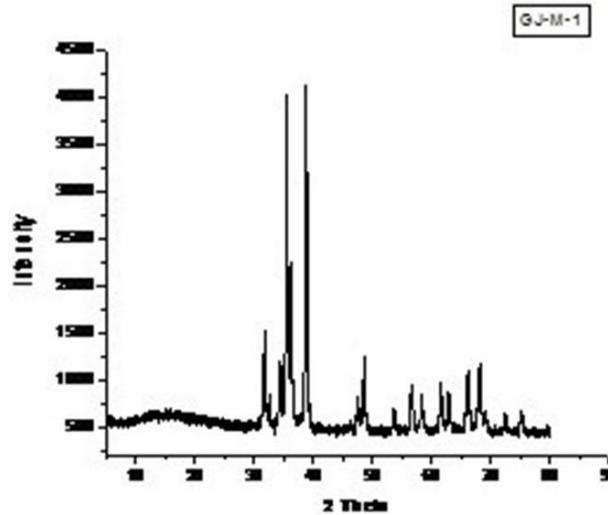


Table 4.1: XRD image of CZA catalyst Sample 1

Molar Ratio	Ppt.Agent	pH	Temperature	Calcination Temperature
6:3:1	$Na_2CO_3$	7	80	380

$CuO^0$	$ZnO^0$
32.6	31.8
35.6	34.5
38.8	36.3
48.5	
58,61.5	

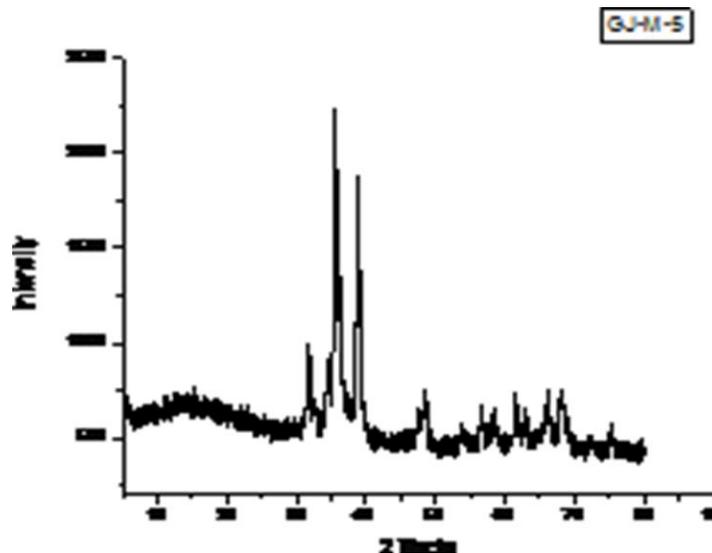


Table 4.2: XRD Data of CZA catalyst Sample 2

Molar Ratio	Ppt.Agent	pH	Temperature	Calcination Temperature
6:3:1	$Na_2CO_3$	7	75	350

CuO <sup>0</sup>	ZnO <sup>0</sup>
32.6	31.8
35.6	34.5
38.8	36.3
48.5	
58,61.5	

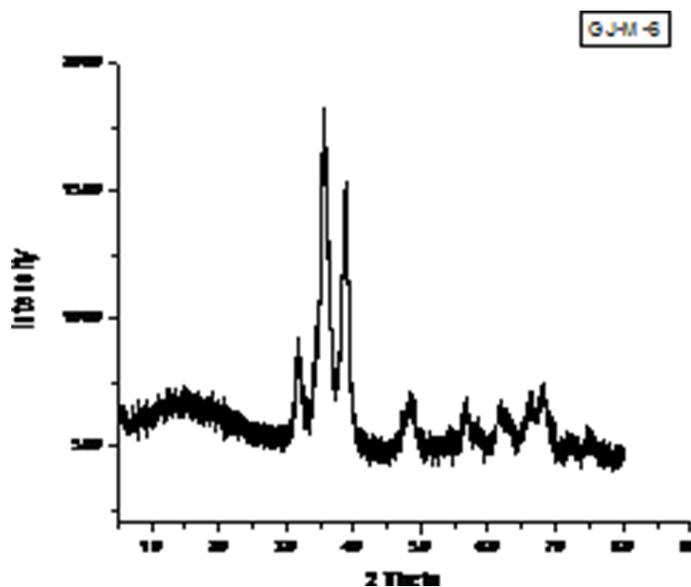


Table 4.3: XRD Data of CZA catalyst Sample

Molar Ratio	Ppt.Agent	pH	Temperature	Calcination Temperature
6:3:1	$Na_2CO_3$	7	80	380

CuO <sup>0</sup>	ZnO <sup>0</sup>
32.6	31.8
35.6,71.2	34.5
38.8,66	36.3
48.5	
58,61.5	

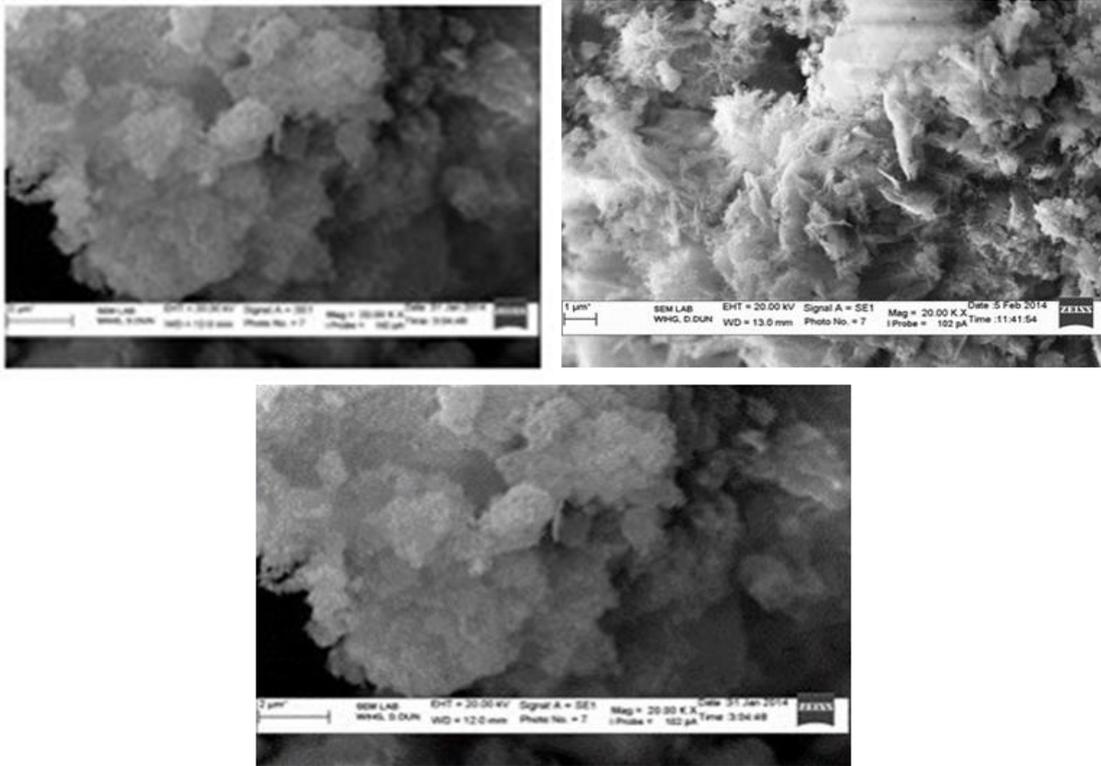
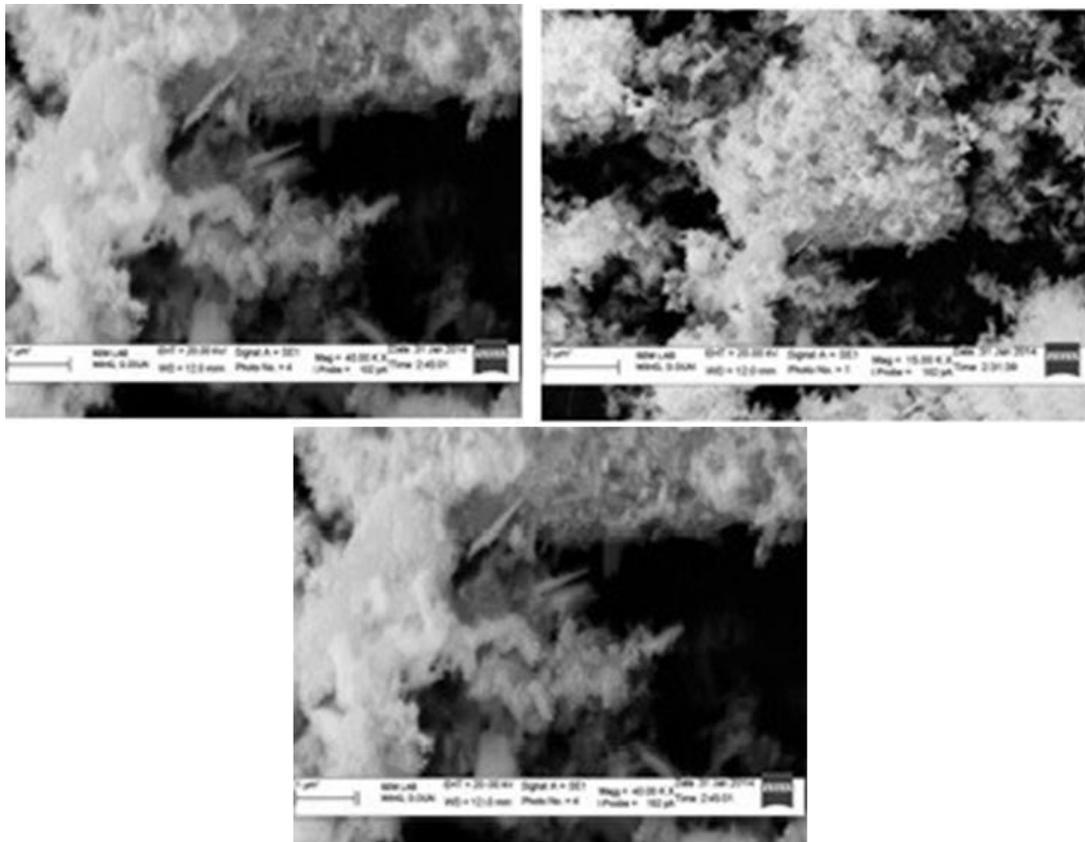


Figure 4.3: SEM image of CZA catalyst sample 1



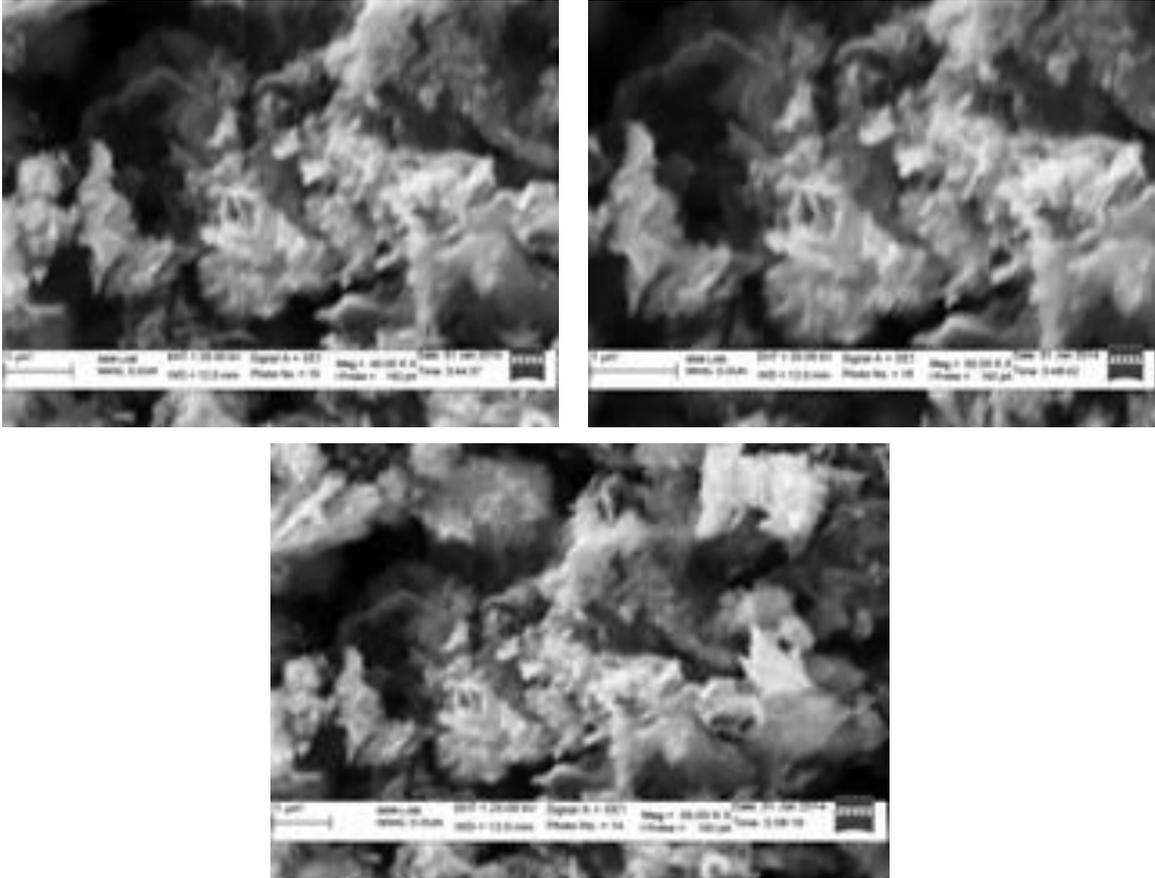


Figure 4.5: SEM image of CZA catalyst sample 3

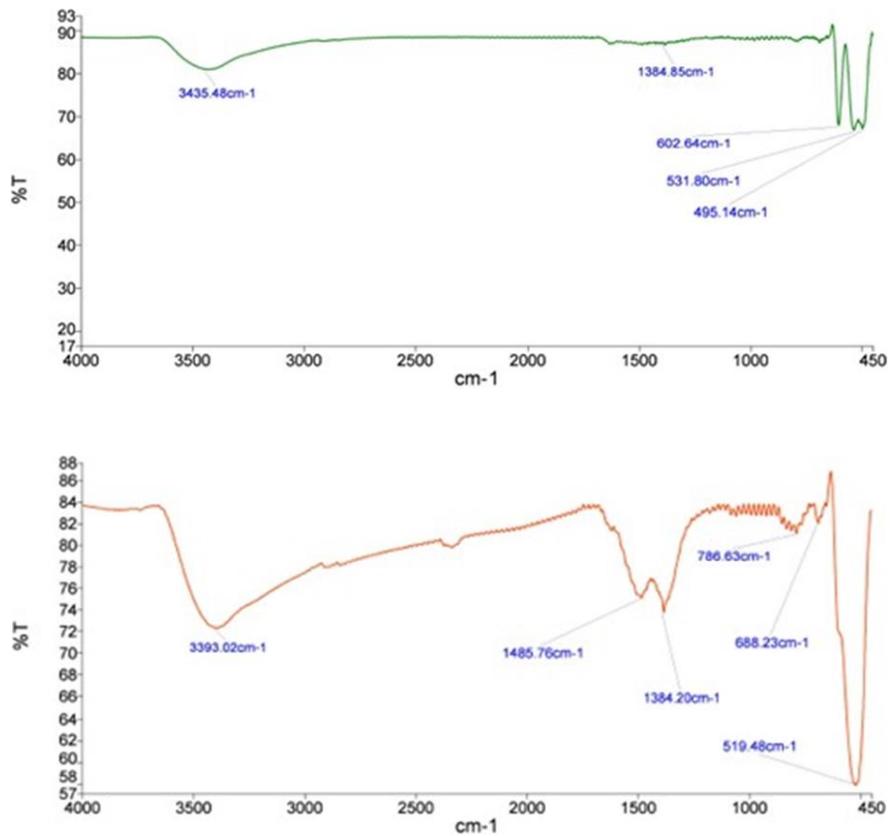


Figure 4.7: FTIR image of CZA catalyst sample

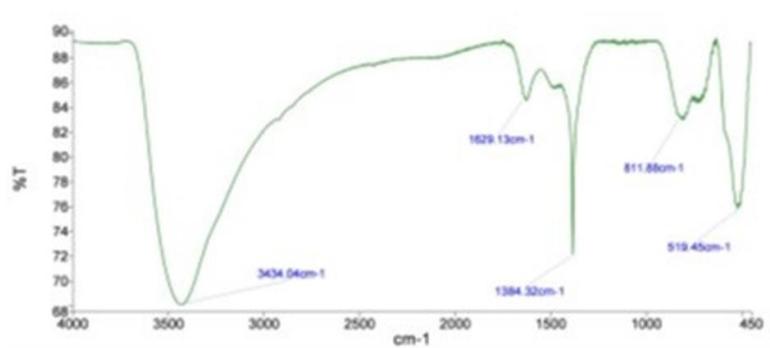


Figure 4.8: FTIR image of CZA catalyst sample 3

## 5. CONCLUSION

To improve the catalyst for CO<sub>2</sub> hydrogenation, we modified the ageing during the preparation by adding CO<sub>2</sub> in to mother solution. CO<sub>2</sub> from dissolved CO<sub>2</sub> promoted the conversion of hydroxy nitrate to hydroxy carbonate. The hydroxy nitrate in the precursor that did not have CO<sub>2</sub> decomposed before it could be converted to hydroxy carbonate. Ageing modified catalyst had a higher surface area, large pore volume, smaller particle size and higher catalytic activity.

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