

Composite Catalytic System for the Conversion of Carbon Dioxide to Useful Compound

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Abstract- This experimental work done on the production of valuable product from Carbon dioxide by composite catalytic conversion system of carbon dioxide to Alcoholic and acidic compounds. Different mixtures of catalysts utilized to check and enhanced the reactivity of the system as well as increased the production of Valuable product from Carbon dioxide: Fischer-Tropsch synthesis, hydrogenation, water-gas-shift and methanol synthesis. These results showed that composite catalytic system played important role for the syntheses of valuable products from Carbon Dioxide. We have concluded that if methanol synthesis sites were present adjacent to the carbon –carbon chain growth sites, the formation rate of C₂ oxygenates would be increases. Production of methanol increased by increasing temperature and using of catalyst PdZnAl in composite catalytic system. Composite catalyst (PdZnAl) was stable at high temperature 390 °C. It was showed that conversion efficiency was high at high temperature. The results showed that the process can be emphasize by operating at high temperature using Pd-based methanol synthesis catalyst. Organic Byproduct of the steam reforming was demonstrated that a means to facilitate additional hydrogen. Primary process design for the Composite Catalytic System for The Conversion of Carbon Dioxide to Valuable Compound, simulation, and economic analysis of the proposed were carried out. It is observed from analyses data Cost of the Carbon dioxide and hydrogen increase the production cost of the Methanol

Keywords- CO₂ utilization; syngas. higher alcohols; Fischer-Tropsch

Highlights:

- Effects of temperature on CO₂ Conversion
- Effects of temperature on mixed catalysts activity
- Effect of PdZnAl catalyst on Oxygenate Production on high temperature
- Effects of the composite catalyst method on CO₂ conversion
- Effects of CO on conversion of CO₂ in feed stream
- Primary Process Design

Pictorial Abstract

I. INTRODUCTION

Capturing, utilization and storage system, as well as reduction of carbon dioxide become a important issue in the world by the conversion of carbon dioxide in to valuable product. carbon dioxide emission in the atmosphere is a major cause of global warming [1]. government of United State America introduce a law on the emission of carbon dioxide in the air. a large number of pilot scale plants installed on carbon dioxide capture and isolation are in process (CCI). In CCI, carbon dioxide is first separated from exhaust gas mixture by either physical solvents process or chemical solvents process, then compressed carbon dioxide

and shifted to a nearby process site where carbon dioxide is injected into underground geological formations [2].

CCI provide us a root for the management of waste Carbon dioxide in the atmosphere without any raw material cost as well as give approach in which CO₂ is treated with composite catalysts. By the investments on the development and capturing of Carbon dioxide in CCI, huge amount of revenue can get on by the small investment and high quality as well as high purity carbon dioxide will be available. Large number of experimental work done on the utilization of Caron dioxide as well as the Carbon dioxide conversion into other valuable products [3-4].

Previous experimental work and study revealed that there is only 5%–10% of total carbon dioxide emitted from different sources utilized in fuel generation and chemical manufacturing which can be increased by the implementation of advanced process [5].

Carbon dioxide can be used in the methanation reaction in low temperature condition for the production of natural gas for fuels of industries. Different catalysts used for this methanation process like Ni, Ru, Pd, Rh [6-9]

In some condition conversion of carbon dioxide to valuable products is not feasible due to some harmful greenhouse gases generation. Dilution of Carbon dioxide and the separation is highly expensive from small source of Carbon dioxide. Furthermore, oil and chemical manufacturing investor did not take interest and not add any value to their business. There are no driving forces to attract investors of oil companies for the investment on CO₂ disposal. Governmental technical expertise and incentives are required to attract them in participation. In late 1990s, carbon dioxide to ethyl alcohol conversion process developed [10-13]. As calorific value/ heating value of greenhouse gases is zero, efforts on conversion of CO₂ to chemicals will be facing an uphill battle thermodynamically. However, economic value can be obtained if low cost hydrogen containing compounds (H₂, CH₄, etc.) can be utilized to react with carbon dioxide. There were different techniques for the conversion of Carbon dioxide into valuable products was, -“Reduced graphene oxide-CuO nanocomposites for photocatalytic conversion of CO₂ into methanol under visible light irradiation” (Rashi et al, 2015), ‘electrochemical method for the conversion of CO₂’ [14-18] This research work does not mean to debate only on the validation of carbon dioxide conversion into hydrogen containing compound, also for the conversion of carbon dioxide into inorganic compounds. It provides us information for the utilization of carbon dioxide to achieve the environmental benefits as well as revenue generation techniques by the utilization of these techniques. We report composite catalytic reaction performance outcomes from experimental work for the synthesis of valuable compound from CO₂ using a composite catalytic conversion system. Mixtures of different properties of catalysts comprising of, water-gas-shift, hydrogenation functionalities and Fischer-Tropsch, methanol synthesis were employed. Various catalyst mixtures and process parameters were examined. Aim of the overall experimental work to optimize process parameters and catalyst conversion system for the maximum oxygenates such as alcohol and acids. By products of these catalytic conversion system separated and reformed in a separate reactor, as demonstration for a means to facilitate extra hydrogen for carbon dioxide Hydro-treater. A basic process design was designed for a comprehensive CO₂ conversion process. Process economics aspects and sensitivity features on the basis of CO₂ prices and hydrogen were discussed.

II. EXPERIMENT

2.1 Preparation of composite catalyst

Different types of chemical reagents are used for the preparation of catalyst composite. Analytical grade Chemical reagents purchased from local market of SIGMA ALDRICH brand and used as received are Fe(NO₃)₃, Cu(NO₃)₂, Al(NO₃)₃ and KNO₃. There were five composites of catalysts prepared for the conversion of Carbon dioxide to valuable products.

- Composite A, represent as FeCuAlK; is called Fe- Based Fischer- Tropsch catalyst and prepared composite by co-precipitation techniques. The atomic ration of this composite was controlled such a ratio, 1.0 : 0.03 : 2.0 : 0.7. during the preparation of this composite catalyst, all these chemicals of given ration dissolved in deionized water and precipitation was started by the addition of 28% ammonium hydroxide solution till the solution PH was maintained at 8.0. precipitate was filtered and dried overnight at 120°C and calcined at 360 °C for one hour.
- Composite B, represent as CuZnAlK is known as low temperature methanol synthesis catalyst. The atomic ration of this composite was controlled such a ratio, Cu: Zn:Al: K was controlled at about 1.0:1.0: 1.0: 0.1. it was prepared same like as Composite A
- Composite C, represent as PdZnAl, is known as a high temperature methanol synthesis catalyst having partial hydrogenation functionality. Composite PdZnAl catalyst was prepared by incipient wetness impregnation of an Al₂O₃ with a Pd nitrate solution (21.21 wt% Pd in nitric acid) as a supporting agent into which a Zinc nitrate precursor (Sigma Aldrich) was added, [11,12]. The catalysts were dried at 120 °C like Composite A catalyst for 8 h and calcined at 360 °C for 3 hours. The resulting Pd concentration was 9 wt% and Pd: Zn molar ratio was 0.38.
- Composite D, represented as FeCuAlZnK, was prepared by 1:1 weight ratio of already prepared, as described above, Composite A and Composite B. Composite A was physically mixed with an equal weight of Composite B. The two powdered catalysts were ground together with a pestle and mortar then pelletized, crushed and sieved to 50–110 mesh prior to activity testing. The resulting atomic ratio of Fe: Cu: Al: Zn: K was approximately 1.0:0.9:2.9:0.9:0.8.
- Composite E, represented as 1% Pd/Al₂O₃, was prepared by incipient wetness technique. Palladium nitrate was impregnated on γ -Al₂O₃ first, and then dried at 120 °C overnight and calcined at 360 °C for 3 hours. This catalyst was utilized for its hydrogenation ability.

1.2. Test for Composite Catalyst Activity

High Pressure fixed-bed reactor system was used for this experiment work. Process parameter of this experiment: 270–420°C, 90atm, 40000–75000h⁻¹ gas hourly space velocity (GHSV). Feed stream gas having percentage of: CO₂ =28%, H₂ =69%, Ar=3% (Ar was used as internal standard for GC analysis). Prior to reaction, catalyst (50–110 mesh particle size) was reduced at 470 °C in 15% hydrogen for 10hours, reactor temperature and pressure was controlled by the feed flow rate. Two condensers installed in series and controlled its temperature at -1°C for the reactor outlet condensation. GC-MS installed for the analysis of reactor vapors condensate GC and HPLC, respectively. The un condensed gaseous products were analyzed by online GC.

III. RESULTS AND DISCUSSION

3.1 Effect of temperature on reaction for oxygenates generation.

The effect of the temperature on the generation of oxygenate was observed by the application of composite catalyst such as mixture of composite Catalysts A, B and E. These composite catalyst were Fischer-Tropsch, low temperature methanol synthesis, and Pd-based hydrogenation catalysts, respectively. Every composite catalysts pelletized, crushed and screened into 50–110 mesh size before mixing. Composites of these catalysts transferred in the and reduced in 15% hydrogen before CO₂/H₂ feedstock was introduced. Reaction is operated in the temperature range of 260–280°C which is different from this reaction parameter and this composite catalyst systems used in this study were operated at higher temperature and high gas hourly space velocity. As shown in Figure 1, at 320 °C, GHSV=55000h⁻¹, CO₂ conversion of about 25% was obtained. Methane and ethanol selectivity's were 8.5% and 3.3%, respectively. By the increasing of reaction temperature to 390 °C, CO₂ conversion was increased to 40.7%, methane and ethanol selectivity's increased to 12.8% and 8.9%, respectively. The influence of temperature on space-time yield (STY) is shown in Figure 2. The Space Time Yield of ethanol content

3.2 Stability of Copper containing Composite Catalyst

Composite catalyst system having mixture of Composite A, Composite B and composite E further describe in detail. Remember, these are Fischer Tropsch, low temperature methanol synthesis, and Pd-based hydrogenation catalysts, respectively. composite A, composite B and composite E were again physically mixed together with a weight ratio of 1:1:1. During 108 hours testing, a step change of reaction temperature was decided in the range of 290 °C to 380 °C. As shown in Figure 3, on increasing reaction temperature from 290 to 350 °C, CO₂ conversion increased from 31% to 45%. STY(oxy), examined as total STY of methanol, ethanol and acetic acid, reached maximum level of 488g·L⁻¹ Cat·h⁻¹. As the reaction in forward condition and temperature was further increased to 380 °C, conversion of

increased from about 65 to 333 g·L⁻¹ Cat·h⁻¹. The STY of acetic acid was also increase twice time. A little bit content of methanol STY was also observed. In general, at higher temperature the kinetics assist in the formation of these oxygenates.

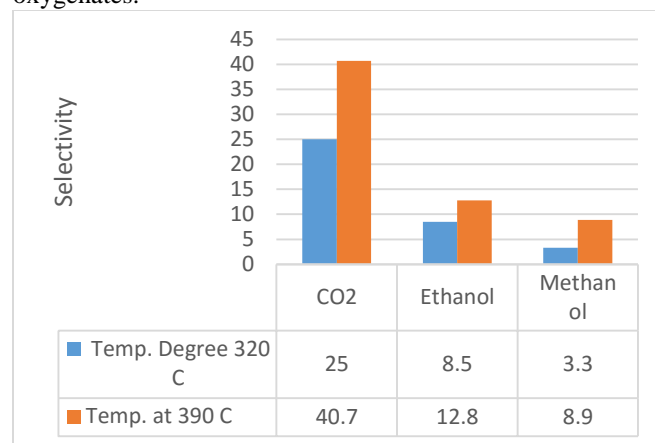


Figure 1 Effect of temperature on CO₂ Conversion and Selectivity (mixed Catalysts A, B, and E with ratio 1:1:1 , P=8.0 MPa, GHSV=55000h⁻¹)

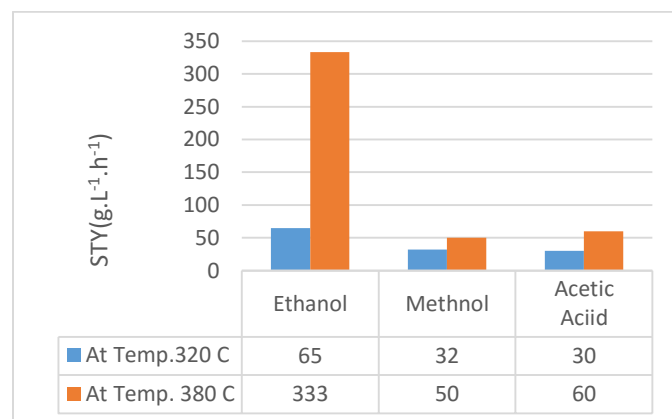


Figure 2 Effect of temperature on STY (mixed Catalysts A, B, and E with ratio 1:1:1 , P=8.0 MPa, GHSV=55000h⁻¹)

CO₂ raised and so as the selectivity to methane. However, a sharp decline in STY(oxy) was observed. At 108 h time-on-stream, STY(oxy) dropped to 22 g·L⁻¹ Cat·h⁻¹. It is come to know from the figure-3 and parameter activation of catalyst decrease due to the surface of catalyst covered with the sintering of copper component in composite, shutting down methanation reaction. Previous researcher evaluated that Cu/ZnO/Al₂O₃ readily deactivated at similar temperature such as 375°C. this is well known idea that copper metal particles during methanol synthesis catalyst sinter at temperatures in excess of 280 °C [twigg et al,1989]. So for the synthesis of oxygenate synthesis by the conversion of Carbon best to change copper-based composite catalysts with thermally more stable methanol catalyst

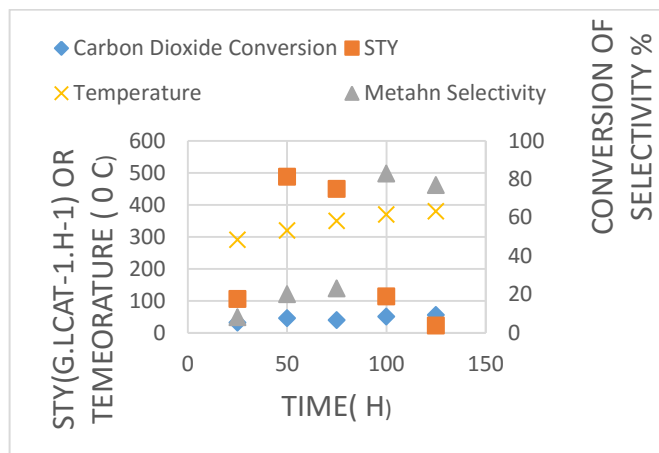


Fig. 3

3.3. Impact of PdZnAl catalyst on oxygenate production at high temperature

In previous research data we come to know that PdZnAl composite catalyst was active catalyst for methanol synthesis [13] and for steam reformation of methanol [19-21]. This PdZn can be utilized at high temperature (e.g. 375 °C) in steam environment without metal sintering. It is evaluated that PdZnAl as a viable methanol catalyst can be used as a combination of composite Catalyst A (Fischer-Tropsch) and composite Catalyst C (PdZnAl). Composite Catalyst C has both methanol synthesis activity and partial hydrogenation activity; therefore, hydrogenation composite Catalyst E is not useful. We can observe from Figure 4, increasing temperature enhance in an increase in CO₂ conversion. Methane selectivity and ethanol selectivity having same behavior. The impact of temperature on STYs of three major oxygenates are represented in Figure 5. Ethanol selectivity increased from 85 to 340 g·L⁻¹·Cat·h⁻¹. The increase in STY of methanol and acetic acid was not as dramatic as ethanol.

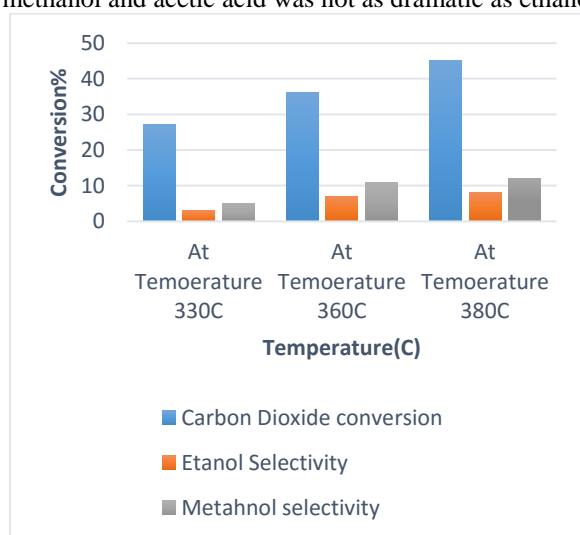


Figure 4 Effect of temperature on the conversion of CO₂ and product selectivity, physically mixed composite catalyst with the ratio 2:1, P=8.0 MPa, GHSV=55000 h⁻¹.

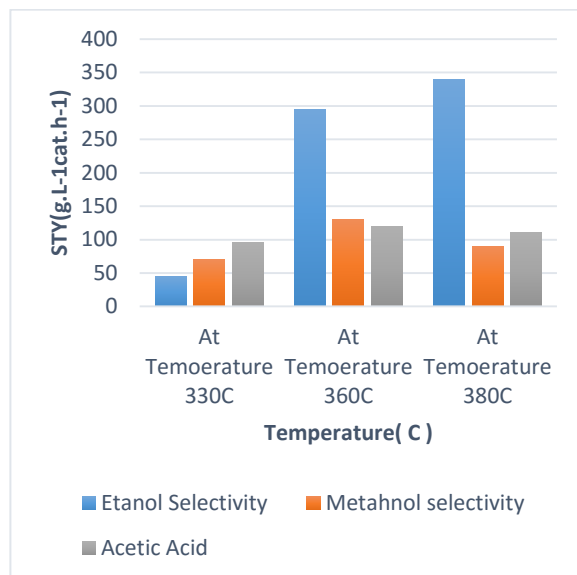


Figure 5 Effect of temperature on STY Physically mixed composite catalyst with the ratio 2:1, P=8.0 MPa, GHSV=55000 h⁻¹.

3.4. Effect of the catalyst combination method

Composite catalyst effect on the catalyst performance positively [22]. There was evaluated by combining of composite Catalysts A and C in a 2:1 weight ratio and in two different ways. Comparative performance results are shown in Figure 6. In “ground catalyst” mode, the two powder catalysts were ground, pelletized, crushed and screened into 50–110 mesh size. In “packed catalyst” every composite catalyst was individually pelletized,

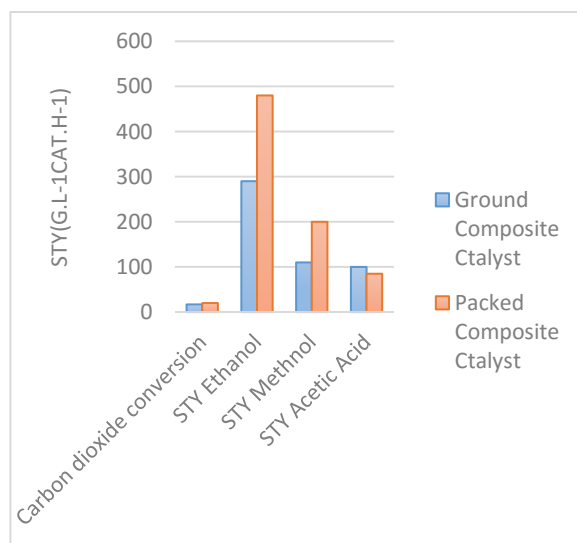


Figure 6 Effect of composite catalyst on the conversion of CO₂ and STY ground catalyst, Packed catalyst of Composite Catalyst A and Composite catalyst C, Physically mixed composite catalyst with the ratio 2:1, P=8.0 MPa, GHSV=55000 h⁻¹.

crushed and screened into 50–110 mesh size, then packed in series (Catalyst C followed by Catalyst A). Similar conversion of carbon dioxide observed in ground as well as packed in series.. but the packed composite catalyst series showed high conversion of CO₂ to methanol whereas ground composite catalyst mode represent higher selectivity towards ethanol as well as acetic acid. This indicates that methanol is the precursor for C₂ oxygenates. In packed catalyst mode, because methanol catalyst and F-T catalyst are more spatially segregated, methanol produced on Catalyst C has to re-adsorb on the surface of composite Catalyst A in order to form C₂ oxygenates. In ground catalyst mode, C–C chain growth sites are in closer proximity to methanol synthesis sites, enabling further conversion of methanol to C₂ oxygenates.

3.5. Effect of CO addition in feed

In our experiment work CO₂/H₂/permeate was operated in once through mode, but in practically, for the economical process, recycling of unconverted feed is necessary factor for the 100% conversion. So for this function CO it was also added in feed for H₂/CO ratio control.

3.6 Process design and preliminary economic analysis

In our preliminary process design, steam reformer installed in the recycle loop for the conversion of by product/undesired hydrocarbons (HCs) and oxygenates to H₂ and CO₂. The fresh feedstock CO₂/H₂ was fed to Hydrotreater reactor, where CO₂ is converted over multifunctional mixed composite catalyst conversion system. The product from the Hydrotreater reactor was separated into gas and liquids by the G-L Separator. Overhead product of G-L Separator was sent to a membrane reactor (specifically designed, a pervaporation unit having Molecular sieves), where permeate H₂/CO₂ was recovered, compressed and then recycled back to Hydrotreater reactor. The Bottom products G-L separator was fed to three distillation columns to recover acetic acid, methanol and ethanol respectively. The non-permeate from Membrane reactor and undesired oxygenates from distillation columns were fed to a reformer which are converted to CO₂, CO and H₂. Following the reformer, a WGS reactor was installed to further convert CO to CO₂ and H₂. A condenser at the outlet of the water-gas-shift (WGS) reactor was used to remove water, and the gaseous product was fed to pressure-swing adsorption (PSA) unit where H₂ was recovered. The recovered H₂ was combined with unconverted CO₂/H₂, compressed and recycled to the front of the Hydrotreater reactor.

One of the important equipment in the process is the steam reformer because it converts unwanted byproducts to Hydrogen and carbon dioxide. Future improvement of the Hydrotreater selectivity to desired end products (methanol, ethanol and acetic acid) would greatly improve the overall economics.

IV. CONCLUSIONS

Three composite catalyst systems comprising of Fischer Tropsch, methanol synthesis, water-gas-shift and hydrogenation functionalities were employed for the direct conversion of carbon dioxide into valuable products such as methanol, ethanol and acetic acid. Various composite catalyst combinations and process parameter were explored for the achievement of maximum selectivity for methanol, ethanol and acetic acid. If we want to increased pace time yield(STY) to obtained required valuable product, it is only possible if we were able to achieved higher temperatures (i.e. >330 °C). PdZn based methanol synthesis catalyst system is useful for smooth and stable operation at higher temperatures. Byproduct oxygenates were steam reformed, offering supplemental hydrogen feed for CO₂ Hydrotreater. Preliminary design for a complete CO₂ conversion process was developed. Process can be improving, if we will be able to find the cheap source of hydrogen feedstock, and/or government incentives are required for this current process to be economically and attractive.

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