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(54) Title: HIGHLY ACTIVE, NOVEL, AND REUSABLE CATALYSIS SYSTEM FOR CO2 HYDROGENATION INTO METHANOL

(57) Abstract: The present invention relates to a heterogeneous catalyst for both batch and continuous mode of reaction which can directly convert process gaseous CO2 from flue gas to methanol in continuous mode of operation. The present invention also relates to a process of preparing the heterogeneous catalyst.

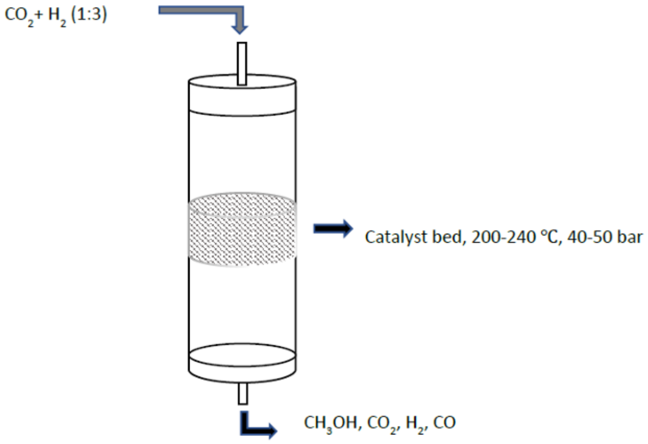

Figure 1

FORM 2

THE PATENTS ACT 1970
(39 OF 1970)
&
The Patent Rules, 2003

Complete Specification

(See Section 10 and Rule 13)

1. TITLE OF THE INVENTION

HIGHLY ACTIVE, NOVEL, AND REUSABLE CATALYSIS SYSTEM FOR CO_2 HYDROGENATION INTO METHANOL

2. APPLICANT(S)

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3. PREAMBLE TO THE DESCRIPTION

COMPLETE

The following specification particularly describes the invention and the manner in which it is to be performed

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FIELD OF THE INVENTION

[0001] The present invention relates to a heterogeneous catalyst for both batch and continuous mode of reaction. The present invention also relates to a process which can directly convert process gaseous CO_2 from flue gas to methanol in continuous mode of operation.

BACKGROUND OF THE INVENTION

[0002] The Global warming occurs due to the steady upsurge in the overall temperature of the atmosphere of the Earth which causes melting the ice glaciers rapidly. Main cause of Global warming is the accumulation if carbon dioxide (CO_2) and other air pollutants which prevents the escape of radiation into space and heat as trapped cause the planet to get hotter. Carbon dioxide is one of the major heat-trapping pollutants, called greenhouse gas.

[0003] Global leaders set a goal of Net-Zero emissions by 2050 to curb the global warming to 1.5 °C from preindustrial level. The net zero accumulation of CO_2 must be achieved if one ton emitted CO_2 must met by one ton CO_2 removal from the atmosphere. The presence of CO_2 in the atmosphere absorbs and insulates heat, creating an invisible vail that keeps sun's energy from escaping into outer space, resulting increasing temperature of earth's surface.

[0004] To tackle the issue of global warming a dual approach method should be adopted. Firstly, a low-carbon development path should be explored and adopted in order to achieve lower carbon emitting process, consumption and management. Secondly, post-production carbon should be captured at the source and sequentially stored or converted into valuable chemical form.

[0005] Among variety of ways of CO_2 utilizations, one of the most promising candidates is the conversion of CO_2 to Methanol. The worldwide production of methanol was around 88.43 Mt in 2017, which is primarily from synthesis gas ($CO+H_2$). Methanol itself can be used as a fuel or as C1 feed stock for a variety of chemical synthesis. It is also an attractive liquid hydrogen carrier (12.6 wt% of H_2). Methanol is among the top five commodity chemicals and the global annual production capacity of it reached approximately 157 million tons in 2020. Captured CO_2 utilization for methanol production is a very promising way to reduce carbon footprint significantly.

Additionally, it is an important raw material to produce other important fuels, solvents and base chemical products, such as light olefins, BTX aromatics, methyl amines, chloromethane, dimethyl carbonate, methyl tertbutyl ether (MTBE) and others.

[0006] CO_2 present in the atmosphere directly captured by amine and converted *in-situ* by homogeneous metal complexes to produce methanol as a promising technology. However, the most common issues related to homogeneous catalysis are product recovery and catalyst recycling, which are the main bottle neck for scaleup studies. Another approach is to convert CO_2 to methanol in a fixed bed reactor in gaseous state in the presence of heterogenous catalyst at moderate temperature and high pressure. Among all existing reaction routes developed in the last four decades, the most evolved heterogeneous catalysis technology is still suffering from many challenges due to elevated temperatures, activity, stability, recyclability, and selectivity.

[0007] Industrially, Cu/ZnO-based catalysts are the most popular catalysts to synthesize CH_3OH from CO_2 hydrogenation under high temperatures and pressures. However, for Cu/ZnO-based catalysts, methanol selectivity and yield are often affected by the by-products such as carbon monoxide (CO) which is the result of the reverse water-gas shift (RWGS) reaction. For Cu/ZnO catalysts, deactivation was proposed to follow the oxidation of Cu^0 to Cu^{2+} and the agglomeration of ZnO species.

[0008] Therefore, there is a need to develop a novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

OBJECTIVE OF THE INVENTION

[0009] Main objective of the present disclosure is to provide a heterogeneous catalyst for both batch and continuous mode of reaction.

[0010] An objective of the present disclosure is to provide a process which can directly convert process gaseous CO_2 from flue gas to methanol in continuous mode of operation.

[0011] Another objective of the present disclosure is to provide a novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

[0012] Still another objective of the present disclosure is to provide a process for synthesis of novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

SUMMARY OF THE INVENTION

[0013] Main aspect of the present disclosure provides a heterogeneous catalyst for both batch and continuous mode of reaction.

[0014] An aspect of the present disclosure provides a process which can directly convert process gaseous CO_2 from flue gas to methanol in continuous mode of operation.

[0015] Another aspect of the present disclosure provides a novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

[0016] Still aspect of the present disclosure provides a process for synthesis of novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Fig 1: Represents schematic diagram of gas phase reaction of Example 1.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Main embodiment of the present disclosure provides a heterogeneous catalyst for both batch and continuous mode of reaction.

[0019] An embodiment of the present disclosure provides a process which can directly convert process gaseous CO_2 from flue gas to methanol in continuous mode of operation.

[0020] Another embodiment of the present disclosure provides a novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

[0021] Still another embodiment of the present disclosure provides a process for synthesis of novel heterogeneous catalyst which can be equally active, selective and stable for liquid phase batch reaction and gas phase continuous reaction.

[0022] Still another embodiment of the present disclosure provides a heterogeneous catalyst comprising metals and support preparation.

[0023] Still another embodiment of the present disclosure provides a heterogeneous catalyst comprising at least two metals and support preparation.

[0024] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein support preparation is made up of a material selected from Silica, carbon, γ-alumina etc.

[0025] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein support preparation is Mesoporous.

[0026] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein support preparation is Mesoporous silica (Si) support preparation or Meso Cellular foam (MCF) preparation.

[0027] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein metal is selected from but not limited to a group comprising of Sn, Ce, In, Cu, Zr, Zn, Na, K, Ca, Fe, Co, Ni, Ga, Al, Ru, Rh, Pd, Pt, Au.

[0028] Still another embodiment of the present disclosure provides a heterogeneous catalyst, which is represented by the Formula M-In-Cu-Zr /Si.

[0029] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein M is selected from Sn or Ce.

[0030] Still another embodiment of the present disclosure provides a heterogeneous catalyst, which is represented by the Formula Sn-In-Cu-Zr /Si or Sn-In-Cu-Zr /MCF.

[0031] Still another embodiment of the present disclosure provides a heterogeneous catalyst, which is represented by the Formula Ce-In-Cu-Zr /Si or Ce-In-Cu-Zr /MCF.

[0032] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of M is 0.5-2.0 in the supported catalyst.

[0033] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of M is 0.5-1.5 in the supported catalyst.

[0034] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of In is 0.5-2.5 in the supported catalyst.

[0035] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of In is 0.5-1.5 in the supported catalyst.

[0036] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of Cu is 1-30 in the supported catalyst.

[0037] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of Cu is 6-20 in the supported catalyst.

[0038] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of Zr is 1.5-8 in the supported catalyst.

[0039] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of Zr is 2.5-6 in the supported catalyst.

[0040] Still another embodiment of the present disclosure provides a heterogeneous catalyst, wherein the ratio of Si is 70-90 in the supported catalyst.

[0041] Still another embodiment of the present disclosure provides a process for synthesis of heterogeneous catalyst, comprising the following steps:

A) Preparation of mesoporous silica (Si) support (MCF); and

B) Catalyst composition.

[0042] Still another embodiment of the present disclosure provides a process, comprising the following steps:

A. Dissolving measured quantity of Pluronic (P123) in aqueous HCL solution, followed by stirring the mixture for 0.5 to 5 hours at room temperature;
B. Adding predetermined amount of TMB (fixed ratio of TMB/ polymer) into mixture and stirring the mixture vigorously for 15 to 80 min at 30 to 70 °C;
C. Adding calculated amount of TEOS (a fixed proportion of polumer/TEOS) to the mixture and stirring for another 12-36 hours at 30-70 °C; followed by transferring the resulting solution to an autoclave and aged at 90-140 °C for 36-90 hours;
D. Adding 40-50 mg of NH_4F as the mineralizing agent into mixture in order to increase the pore size of MCF;
E. Filtering the white precipitate and washing repeatedly with DI water, followed by air dried in oven at 100-120 °C for 8-16 hours;
F. The dried material was calcined in muffle furnace at 550-700 °C for 2-8 hours to obtain the mesoporous silica (MCF) support;
G. Loading active metal on the mesoporous silica support (MCF support was 10-30 wt%) via Incipient wetness impregnation method;
H. Dissolving the desired amount of $Cu(NO_3)_2, 3H_2O$, $Zr(NO_3)_2,6H_2O$, $In(NO_3)_3, xH_2O$, $Ce(NO_3)_3,6H_2O$ / $SnCl_2, 2H_2O$, in deionized water to produce an aqueous solution (0.5M), followed by stirring the solution for 60 to 120 min for getting a homogenized solution;
I. Adding the metal mixture solution in drop wise manner into a beaker containing 1g support under continuous stirring for 12-36 hours;

[0043] Still another embodiment of the present disclosure provides a process, wherein prior to metal loading in step G), already synthesized MCF was pre-heated at 500-600°C for 2-6 hours to remove impurities and to prepare the support surface to be active for adsorbing the precursor solution.

[0044] Still another embodiment of the present disclosure provides a process, wherein during the addition of precursor solution in step I), the pH was maintained at 7 using $NaCO_3$ solution (0.5 M). Then the slurry was filtered and washed with hot deionized water. The resulting paste was air dried for 12-36 hours at 100-140 °C followed by calcination in the muffle furnace at 350-450 °C for 4-6 hours.

[0045] Still another embodiment of the present disclosure provides the process of evaluation of the catalyst for testing its activity and methanol selectivity in a fixed-bed downflow continuous flow gas phase reactor.

[0046] Still another embodiment of the present disclosure provides the process of evaluation of the catalyst, comprising following steps:

A. Loading the catalyst inside the stainless-steel tubular reactor after sieving through a 20-70μ mesh;
B. Packing the catalyst in the middle of the reactor and sandwiching between glass wool and quartz beads with the following sequences, glass wool-quartz beads- glass wool-catalyst-glass wool -quartz beads-glass wool; and
C. Introducing the reaction gas mixture of (CO_2: H_2 with 1:3 molar ratio) into the tubular reactor;
D. Separating and analysing the gas samples for CO_2 conversion and respective product selectivity were measured by calculating the mass balance of the average of three independent samples taken.

[0047] Still another embodiment of the present disclosure provides the process, wherein prior to starting the actual experiment, the catalyst was reduced under H_2 flow of 15-45 ml/min and the reactor temperature was hiked to 200-400 °C at a heating rate of 2-6 °C/min and 1-3 MPa of pressure and the same conditions were maintained for 5-15 h. After that, the reactor temperature was reduced to the desired reaction temperature under H_2 flow.

[0048] Still another embodiment of the present disclosure provides the process, wherein the feed gas of step C) was pre-heated to 150-200 °C by utilizing a preheater.

[0049] Still another embodiment of the present disclosure provides the process, wherein methanol synthesis was carried out at a variety of temperatures (such as 150 – 300 °C) with GHSV in the range of 1000-10000 mL $gcat^{-1}$ h^{-1} and the reaction pressure was varied from 3 to 6 MPa by a back pressure regulator.

[0050] Still another embodiment of the present disclosure provides the process, wherein all the gas samples (H_2, CO_2, CO, CH_4) were analyzed by a thermos Scientific GC Trace 1110 fitted with a TCD detector and MeOH present in the gas samples were analyzed by a Thermo Scientific ISQLT 1300 fitted with FID detector.

[0051] Still another embodiment of the present disclosure provides the process, wherein for both the analysis, the gas samples were separated by a Porapak Q packed column. The CO_2 conversion and respective product selectivity were measured by calculating the mass balance of the average of three independent samples taken, and the errors were within ±2%.

EXPERIMENTAL SECTION:

SYNTHESIS OF CATALYST:

[0052] A) Preparation of Mesoporous silica (Si) support (MCF):

[0053] Mesoporous silica (Si) support is also known as Mesocellular Foam (MCF). Pure MCF support preparation was commenced by dissolving measured quantity of Pluronic (P123) in 180 mL of 1.6 M aqueous HCL solution and the mixture was stirred for 2 hours at room temperature in a round bottom flask (RBF). Then, predetermined amount of TMB (fixed ratio of TMB/ polymer) was added into mixture and again the mixture was vigorously stirred (30 rpm) continuously for 60 min at 40°C. After that, calculated amount of TEOS (a fixed proportion of polumer/TEOS) was added to the mixture in RBF and continued stirring for another 24 hours at 40 °C. Then, the resulting solution was transferred to an autoclave and aged at 110-120 °C for 48-72 hours. In order to increase the pore size of MCF 40-50 mg of NH_4F added as the mineralizing agent into mixture. Then, the white precipitate was filtered and repeatedly washed with DI water and air dried in oven at 120 °C for 12 hours. Finally, the dried material was calcined in muffle furnace at 550 °C for 6 hours.

[0054] B) Synthesis of metal composition Sn-In-Cu-Zr /Si or Ce-In-Cu-Zr /Si:

[0055] The ratio of M:In:Cu:Zr:Si in the supported catalyst are (0.5-1.5 : 0.5-1.5 : 6-20 : 2.5-6:70-90). Active metal loading on the Mesoporous Silica (MCF support was 20-30 wt%). Incipient wetness impregnation method was used to load the active metals on the MCF support. Prior to metal loading, already synthesized MCF was pre-heated at 550 °C for 4 hours to remove impurities and to prepare the support surface to be active for adsorbing the precursor solution. Firstly desired amount of Cu $(NO_3)_2$, $3H_2O$, Zr $(NO_3)_2$,$6H_2O$, $In(NO_3)_3$, xH_2O , Ce $(NO_3)_3$,$6H_2O$ / $SnCl_2$, $2H_2O$ was dissolved in deionized water to produce an aqueous solution (0.5M) and then the solution was stirred for 90 min for getting a homogenized solution. Then the metal mixture solution was added in drop wise manner into a beaker under containing 1g support under continuous stirring for 24 h. During the addition of precursor solution, the pH was maintained at 7 using $NaCO_3$ solution (0.5 M). Then the slurry was filtered and washed with hot deionized water. The resulting paste was air dried for 24 hours at 120 °C followed by calcination in the muffle furnace at 350 °C for 4 hours.

[0056] Gas Phase Reaction

[0057] The catalyst was evaluated for testing its activity and methanol selectivity in a 300 ml fixed-bed downflow continuous flow reactor. A total 5 g catalyst was loaded inside the stainless-steel tubular reactor and before loading, the catalyst was sieved through a 40-50 mesh. The catalyst was packed in the middle of the reactor and sandwiched between glass wool and quartz beads with the following sequences, glass wool-quartz beads- glass wool-catalyst-glass wool -quartz beads-glass wool. Prior to starting the actual experiment, the catalyst was reduced under H_2 flow of 30 ml/min and the reactor temperature was hiked to 300 °C at a heating rate of 4 °C/min and 2 MPa of pressure and the same conditions were maintained for 10 h. After that, the reactor temperature was reduced to the desired reaction temperature under H_2 flow, and then the reaction gas mixture of (CO_2: H_2 with 1:3 molar ratio) was introduced into the tubular reactor as shown in Figure 1. The feed gas was pre-heated to 150 °C by utilizing a preheater. Methanol synthesis was carried out at a variety of temperatures (200 – 230 °C) with GHSV in the range of 1000-10000 mL $gcat^{-1}$ h^{-1} and the reaction pressure was varied from 1 to 4 MPa by a back pressure regulator. All the gas samples (H_2, CO_2, CO, CH_4) were analyzed by a thermos Scientific GC Trace 1110 fitted with a TCD detector and MeOH present in the gas samples were analyzed by a Thermo Scientific ISQLT 1300 fitted with FID detector. For both the analysis, the gas samples were separated by a Porapak Q packed column. The CO_2 conversion and respective product selectivity were measured by calculating the mass balance of the average of three independent samples taken, and the errors were within ±2%. Results were provided in below Table 1.

Reaction Mechanism:

[0058] On methanol synthesis catalyst, the exothermic CO_2 hydrogenation to CH_3OH (Eq. 1) is accompanied by the formation of untargeted CO *via* the endothermic reverse water–gas shift reaction (Eq. 2). The so-formed CO can subsequently also undergo hydrogenation to yield CH_3OH (Eq. 3). $HCOOCH_3$ may as well be synthesized by esterification of HCOO–intermediates in presence of CH_3OH.

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \qquad \Delta H^0 298K = -40.9 \text{ kJ mol}^{-1} \qquad \text{(Eq. 1)}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \qquad \Delta H^0 298K = 49.8 \text{ kJ mol}^{-1} \qquad \text{(Eq. 2)}$$

$$CO + 2H_2 \leftrightarrow CH_3OH + H_2O, \qquad \Delta H^0 298K = -90.7 \text{ kJ mol}^{-1} \qquad \text{(Eq. 3)}$$

Catalyst	H_2/CO_2 mol ratio	T_R (°C)	P_R (MPa)	GHSV [mL $g^{-1}h^{-1}$]	Conversion [%]	MeOH Selectivity [%]
Sn-In-Cu-Zr/MCF Composition (mol%) Cu=6-20 Zr= 2.5-6 Sn= 0.5-1.5 In= 1-2.5 Si= 70-90	3/1	200-250	3-5	2000-6000	25-36	95-98
Ce-In-Cu-Zr/MCF Composition (mol%) Cu=6-20 Zr= 2.5-6 Ce= 1-2.5 In= 0.5-1.5 Si= 70-90	3/1	200-250	3-5	2000-6000	23-34	96-99

WE CLAIM:

1. A heterogeneous catalyst comprising metals and support preparation, wherein support preparation is made up of a material selected from Silica, carbon, γ-alumina etc.

Dated this 12th day of November 2024

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ABSTRACT

HIGHLY ACTIVE, NOVEL, AND REUSABLE CATALYSIS SYSTEM FOR CO_2 HYDROGENATION INTO METHANOL

The present invention relates to a heterogeneous catalyst for both batch and continuous mode of reaction which can directly convert process gaseous CO_2 from flue gas to methanol in continuous mode of operation. The present invention also relates to a process of preparing the heterogeneous catalyst.

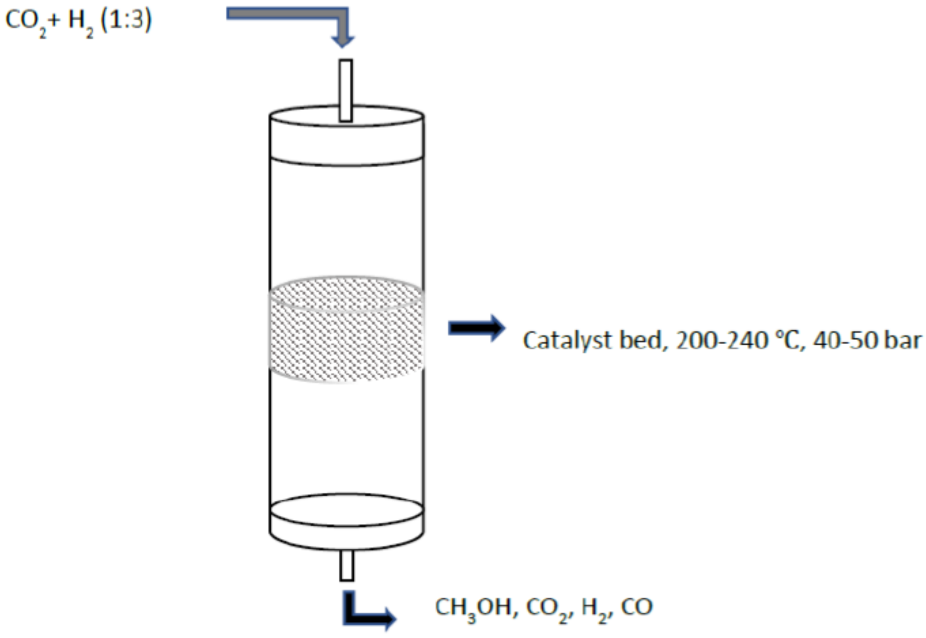

Figure 1

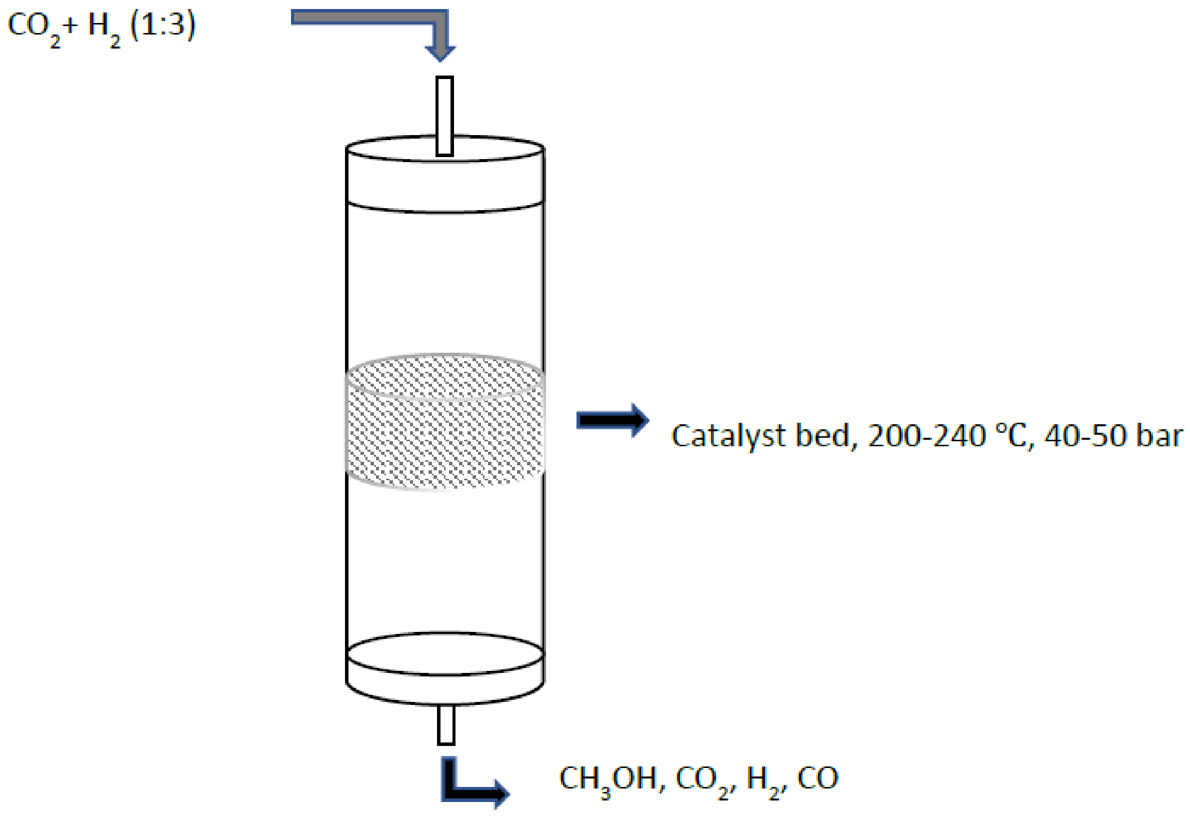

Figure 1

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