Hydrogen Production via Thermocatalytic Decomposition of Methane Using Carbon-Based Materials

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SUPPLEMENTARY INFORMATION

S1. Catalyst Preparation and Characterization Techniques

S1.1 Catalyst Preparation

S1.1.1 Commercial Catalysts

Among six catalysts, ZSM-5 and AC were bought from Alfa Aesar. ZSM-5 (Zeolite Scony Mobil-5) had SiO_2/Al_2O_3 ratio 23:1, (stock no. 45879, Lot # T16B032). Molecular weight of activated carbon (AC) is 12.01 and melting point is 3550 ^oC (stock no. 242241-250G, Lot# MKBW724BV).

S1.1.2 Ru-doped Catalysts

Ru was doped on ZSM-5 and AC by wet impregnation method. Ruthenium (III) nitrosyl nitrate solution ($Ru(NO)NO_3$) was used as Ru precursor solution. This Ru-solution was bought from Alfa Aesar and had 1.5 w/v % Ru (stock no. 12530, Lot# S17B028). The solution had density 1.07 kg/m^3 and molecular weight 317.09. Since chloride ions are hard to eliminate entirely in pre-treatment process, nitrate solution was chosen over chloride solution.

The required amount of Ru precursor solution was manually mixed with ZSM-5 and AC following the incipient wet impregnation method in several steps. Initially, the total amount of precursor

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solution required for the wet impregnation process was calculated based on the concentration of the precursor solution and the desired doping percentage. Then, the precursor solution was slowly added to the support material until the mixture became sticky. This quantity of solution indicated the amount of solution could be added in one single steps. The total amount of required precursor solution was divided by the amount of precursor solution that made support sticky gave the number of mixing steps. In between every step, the mixture of ruthenium precursor solution and support material (ZSM-5 or AC) was dried for 12 h in the presence of air in a Thermolyene furnace. After drying step, the Ru-ZSM-5 catalyst was calcined at 500 ^{o}C for 5 h in the presence of air in a Thermolyene furnace. In the case of Ru-AC, the catalyst was calcined in a fixed bed reactor at 500 ^{o}C for 5 h in the presence of nitrogen to get the inert environment. Figure S1 and Figure S2 represent Ru-ZSM-5 and Ru-AC catalysts appearance after every preparation steps, respectively.

Figure S1: Ru-ZSM-5 catalyst after different steps

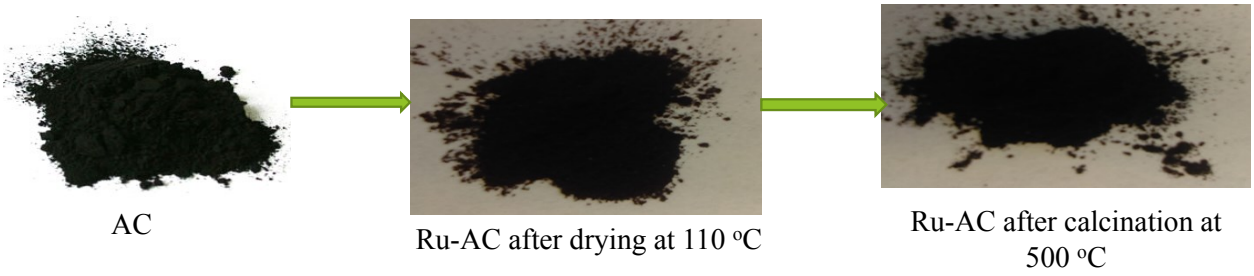

Figure S2: Ru-AC catalyst after different preparation steps

S1.1.3 Biochar Catalysts

Douglas fir biomass (0.8 mm crumbles from chips) was used in this study. Biomass was obtained from ForestConcepts, LLC. (Auburn, Washington). Biomass sample was stored in cold room at 4 ^{o}C until used in this study. Fast pyrolysis process was used to produce biochar. Two different treatments (heat treatment and activation) were done to obtain HB and AB. Figure S3 represents biomass used in this study.

Figure S3: Douglas fir biomass

Biochar Production Process

Douglas fir biomass was dried at 50^{o}C for 24 h to get moisture content less than 10 %. A bubbling fluidized bed reactor was used for fast pyrolysis. Figure S4 represents fluidized bed reactor set-up for fast pyrolysis. Briefly, the reactor set-up has a biomass hopper connected with a twin screw auger and an injection screw, a bubbling fluidized bed reactor which is connected with a high temperature filter (HTF) (filter temperature is maintained at 350^{o}C), two series condenser which is cooled by a circulating condenser (cooling agent is a mixture of ethylene glycol and water which is maintained below 3^{o}C), an electrostatic precipitator (ESP) (20 kV is supplied in top attached rod), bio-oil collector, and a NOVA gas analyzer (Note: All the units are connected in series, respectively). The fluidized bed reactor consists of main reactor and freeboard. The main reactor

has 2 in (50 mm) diameter and 22.75 in (580 mm) height, and freeboard has 4 in (100 mm) diameter and 8 in (200 mm) height.

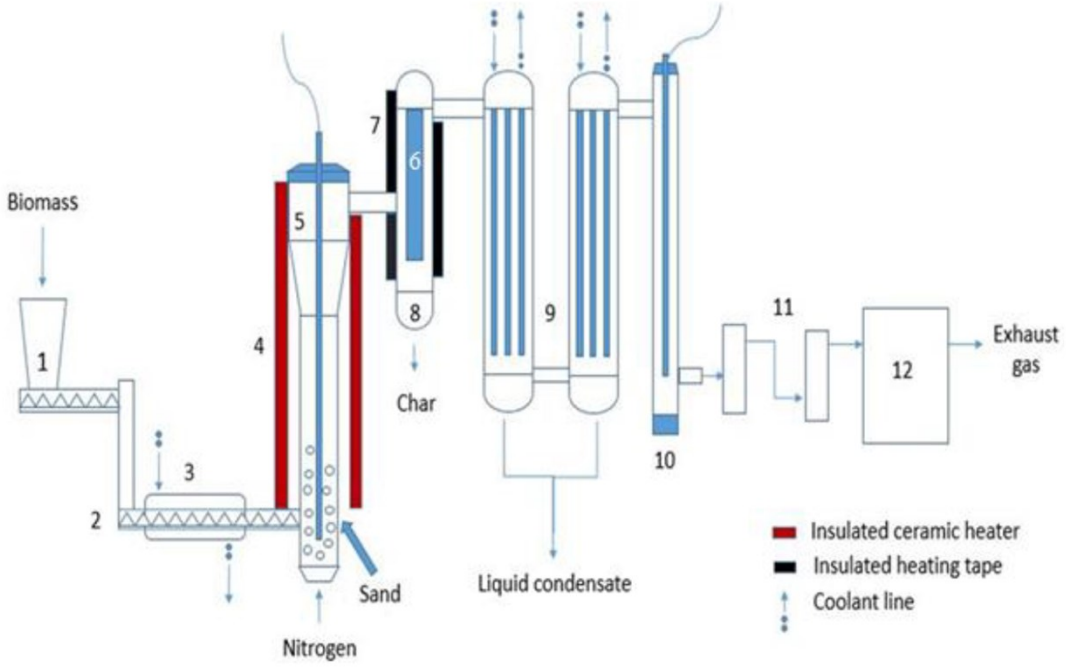

Figure S4: Fast pyrolysis reactor system. 1) Hopper, 2) Screw auger, 3) Heat exchanger, 4) Heater, 5) Fluidized bed reactor, 6) High temperature filter, 7) High temperature filter heater, 8) Char Collector, 9) Condenser, 10) ESP, 11) Gas absorber, 12) NOVA gas analyzer

Silica sand (7062-06, Macron Fine Chemicals) was used as bed material in a fluidized bed reactor. 1000 g silica sand was placed in the reactor. The reactor was heated to 500 ^{o}C with a 20 ^{o}C/min heating rate. At the same time, chiller was started and was set at 3 ^{o}C. 12 LPM air was passed through the reactor system to fluidize bed material and to ensure the uniform heating. 500 g Douglas fir biomass was placed into the biomass hopper. After that, the hopper was sealed. When the bed material and middle part of the reactor reached at 500 ^{o}C, the air was turned off, and 12 LPM nitrogen was passed through the whole reactor system to get the inert environment for fast pyrolysis. The inert atmosphere was ensured by NOVA gas analyzer. When oxygen concentration

was low down to ≤ 0.1 %, biomass was feed into the main reactor through auger feeder (feed rate 1.5 g/min). O_2, H_2, CH_4, CO and CO_2 contents of product gases were monitored continuously to ensure inert environment and successful pyrolysis. The clear drop tube between hopper and feeder was monitored continuously to ensure all the biomass was fed into the reactor. When all the biomass was fed into the reactor, the feeder was turned off. However, the heater was kept on for about 10 min to ensure complete pyrolysis of biomass. After 10 min, the heater was turned off, but nitrogen was passed through the system for an additional 30 min to exhaust all the pyrolysis gases. After 30 min, the whole system was shut down. Char from HTF was collected when the reactor system cooled down to the room temperature. The collected biochars were stored in a cold room at 4 ^{o}C until use. Figure S5 represents biochar produced from the fast pyrolysis process.

Figure S5: Biochar

Heat-treated Biochar Catalyst

A fixed bed reactor was used to perform the heat-treatment of biochar. Figure S6 represents the experimental set-up for carrying out the heat-treatment process. Fixed bed reactor has a diameter of 1 in (25 mm) and length about 11 in (279.4 mm). The reactor is connected to a nitrogen cylinder by the bottom feed line. The product line is connected to a condenser which is cooled down by ice. The outlet from the condenser is passed through a water trap and finally exhausted to vent.

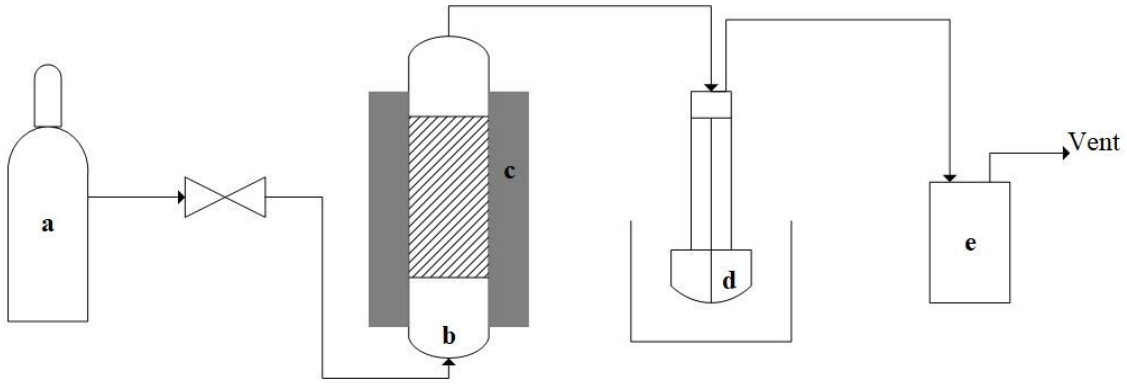

Figure S6: Biochar heat-treatment set-up: a) nitrogen cylinder, b) fixed bed reactor, c) furnace, d) condenser, e) water trap

For this process, about 25 g biochar was placed in the fixed bed reactor, and then a small quartz wool and 316 stainless steel mesh were placed on the bottom of the reactor. Nitrogen at 0.3 LPM was passed through the reactor system continuously to get the inert environment for heat-treatment. Bubbling in water trap ensured nitrogen gas flow through the reactor system. The reactor was heated to 800 ^{o}C with a 5 ^{o}C/min heating rate. The heat-treatment was done for 2 h once the temperature reached 800 °C. After two hours, the furnace was turned off. Nitrogen flow was reduced to 0.1 LPM and kept on until the reactor cooled down to room temperature. Heat-treated biochar (Figure S7) was ball milled with a Retsch ball miller (model PM 100) at 400 rpm for 2 h to get uniform particle size and also increase the surface area.

Figure S7: Heat-treated biochar (HB)

Activated Biochar (AB) Catalyst

KOH was used to activate the biochar. Reagent grade KOH was bought from VWR and used in this study. Biochar from fast pyrolysis was dried at 105 ^{o}C for 12 h. The required amount of KOH pellets (3 g KOH for 1 g biomass) were mixed with water (3 mL water for 1 g KOH) in a glass biker. For better mixing, the solution was stirred with a magnetic stirrer for 30 min. Dried biochar was added into KOH solution on a weight basis. The mixture was stirred with a magnetic stirrer for 2 h to ensure uniform mixing. Then, the solution was dried at 105 ^{o}C for 12 h in a corrosion resistant crucible. The mixture was not dried completely because complete drying causes the KOH to stay at the top of dried mixture. The dried mixture was crushed by hand crusher (pestle and mortar) for homogeneity. The crushed mixture was placed in a fixed bed reactor which was used for heat-treatment (Figure S6). 0.3 LPM nitrogen was passed through the reactor system for 30 min to get the inert environment for heat-treatment. Then the reactor was heated initially to 400 ^{o}C with a 5 ^{o}C/min heating rate. Once the reactor reached at 400 ^{o}C, nitrogen flow was reduced to 0.05 LPM. The reactor was kept at 400 ^{o}C for 1 h. After heat-treatment at 400 ^{o}C, the mixture was heated to 800 ^{o}C and kept that temperature for 2 h. Finally, the furnace was turned off, and 0.1

LPM nitrogen was passed through the reactor system until it cooled down to room temperature. Heat treated mixture was washed continuously with 0.1 M HCl and DI water until pH was closer to 7.0. Neutralized activated biochar was dried at 105 ^{o}C for 12 h. Finally, dried activated biochar was ball milled with a Retsch ball miller (model PM 100) (400 rpm for 2 h) to get higher surface area. Biochar activation process train is represented in Figure S8.

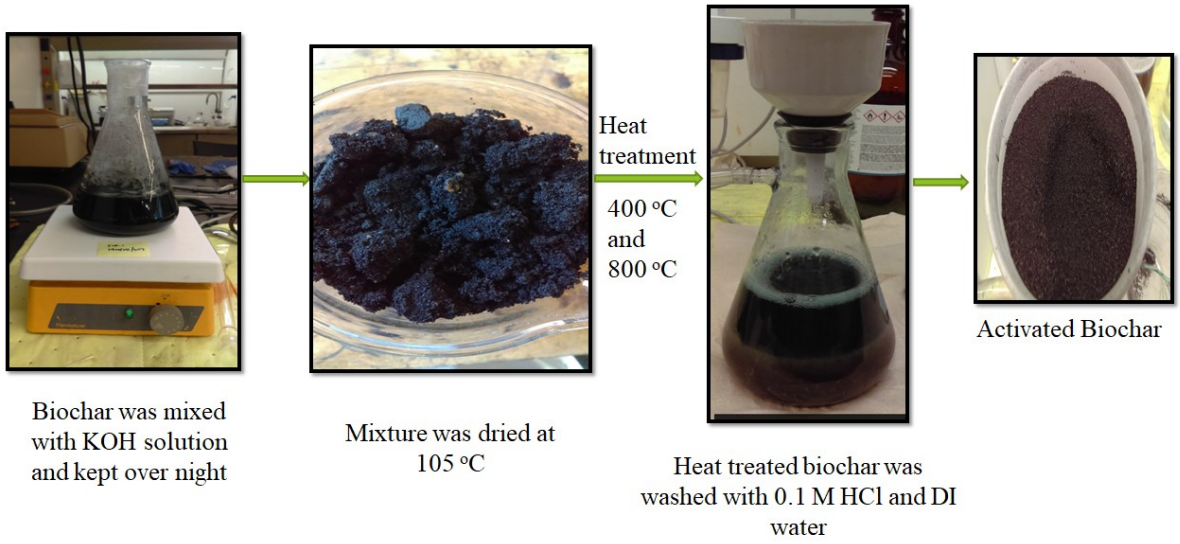

Figure S8: Biochar activation procedure

S1.2 Catalyst Characterizations

Following analysis were performed to characterize the catalysts.

1. Moisture analysis
2. Elemental analysis
3. BET analysis
4. XRD analysis
5. TPR analysis
6. Chemisorption analysis

7. SEM and EDS
8. TGA analysis

S1.2.1 Moisture Analysis

Moisture analysis of biomass was performed before fast pyrolysis process to check the moisture content. Mettler Toledo moisture analyzer (Model: MJ33) was used in this analysis. About 0.7 g sample was taken in an aluminum pan and placed in the moisture analyzer. The temperature inside the machine was increased to 105 ^{o}C to calculate weight loss of samples. Moisture content (MC) of the samples in percent was obtained directly from the machine based on the mass loss. Machine follows equation 1 to calculate moisture content.

$$MC(\%) = \frac{W_a - W_d}{W_a} \times 100 \quad \text{.....(1)}$$

where, W_a= Weight of samples before drying

W_d = Weight of samples after drying

S1.2.2 Elemental Analysis

Elemental analysis was performed to evaluate the carbon (C), nitrogen (N), hydrogen (H) and sulfur (S) content on biomass, biochar and biochar catalysts (AB and heat-treated biochar). Oxygen (O) content in the catalyst samples were then estimated by difference ([O %] = 100-sum ([C %] + [H %] + [N %] + [S %]). Ultimate analysis was performed using Elementar Vario Micro Cube CHNS analyzer.

S1.2.3 XRD (Powder X-ray Diffraction) Analysis

XRD was performed to evaluate the surface species of catalysts and structure of catalysts (amorphous or crystalline). This analysis helped to find the type of Ru phase present in the Ru-doped catalyst (Ru-ZSM-5 and Ru-AC) after the calcination step. It also gave an idea about how

the surface species and structure changes with different types of pre-treatment for biochar catalysts (AB and HB). XRD patterns for different catalysts were obtained by XRD analyzer (Bruker D2 Phaser Advance Diffractometer with LynxEye detector). Powder catalyst samples were placed in a sample holder with a very fine straight top surface. Then, sample holder was placed inside the machine. Patterns were achieved from 10^{o} to 80^{o} angle with an incremental step of 0.05^{o} and scanning time every 1 s.

S1.2.4 TPR (Temperature Programmed Reduction) Analysis

After calcination, metals in catalyst are present in their oxides form. To get active metal phase on catalysts, the *in-situ* reduction was performed before every experiments. Reduction temperature was varied from the catalyst to catalyst. TPR analysis uses hydrogen to determine the reduction temperature of catalysts. In case of carbon catalysts, different impurities (from ash content) are present on catalysts surface, and the reduction is required to obtain better performance. TPR analysis was done with TPR analyzer (Quantachrome, ASIQC0YV200-4). 0.17 g Ru-ZSM-5 catalyst sample was placed in a quartz tube. Then quartz tube was placed on the machine for analysis. For Ru-AC, 0.08 g catalyst sample was used and for biochar catalysts, (AB and HB) 0.05 g catalyst sample was used. The sample was first heated to 100 ^{o}C with 50 ml/min N_2 flow for 1 h. Then, the sample was cooled down to room temperature. After that, temperature was increased to 800 ^{o}C with a heating rate 5 ^{o}C/min. At that time, carrier gas was changed to (5% H_2 in N_2) with a flow rate of 50 ml/min. H_2 consumption pattern was recorded by a computer.

S1.2.5 Chemisorption Analysis

ZSM-5 and activated carbon were doped with 3% Ru. Chemisorption analysis was done on Ru-doped catalysts to determine the percentage of metal dispersed on the catalyst surface and active metal surface area. Chemisorption analysis was done on Quantachrome, ASIQC0YV200-4. All

the catalyst samples were dried at 105 ^{o}C for 12 h before analysis. Around 0.17 g of Ru-ZSM-5 and 0.12 g of Ru-AC samples were used for chemisorption analysis. The sample of catalysts was placed on a quartz tube for analysis. The sample was first heated to 105 ^{o}C with a heating rate 20 ^{o}C/min in the presence of helium. This temperature was maintained for 30 min. Then purging gas was changed to hydrogen and sample was heated to 400 ^{o}C with a heating rate 20 ^{o}C/min. The hydrogen gas flowed for 120 min, and the system was evacuated for 120 min.

S1.2.6 Surface Area, Pore Volume and Average Pore Diameter Analysis

The surface area of catalysts plays a vital role in the reaction rate. The higher surface area gives more place to accommodate methane molecules and gives stability to resist against deactivation for a longer period. Surface area and average pore size were calculated from BET (Brunauer Emmett Teller) analysis. Brunauer Emmett Teller method calculates surface area, pore volume and pore diameter from nitrogen adsorption-desorption isotherm. For pore size distribution, two different methods were used. DFT (Density Functional Theory) method works well with materials those have a microporous structure, and BJH (Barrett Joyner Halenda) works well when mesopores and macropores are present. DFT method does not give any results if macropores are present in the material. Since Ru-ZSM-5 and ZSM-5 have a mesoporous structure with macropores, the BJH method was used for pore size distribution analysis. Similarly, Ru-AC, AC, and AB have a microporous structure with mesopores and the DFT method was used for pore size distribution analysis. About 50 mg of Ru-ZSM-5 and ZSM-5 samples were taken into a quartz tube for degassing. Degassing profile for Ru-ZSM-5 and ZSM-5 samples are given in Table S1. About 20-15 mg of carbon catalysts (Ru-AC, AC, AB, HB) were taken for the analysis. Degassing profile for carbon catalysts is given in Table S2.

Table S1: Degassing profile for ZSM-5 and Ru-ZSM-5 catalysts

Temperature (°C)	Heating Rate (°C/min)	Soaking Time (min)
80	2	30
120	2	30
250	2	600

Table S2: Degassing profile for carbon catalysts (Ru-AC, AC, AB, HB)

Temperature (°C)	Heating Rate (°C/min)	Soaking Time (min)
80	2	30
120	2	30
300	2	720
300	2	720

After degassing, the sample was weighed again and placed in adsorption chamber with liquid nitrogen and nitrogen gas was passed through the sample cell to get Langmuir adsorption isotherm.

S1.2.7 SEM (Scanning Electron Microscope) and EDS (Energy Dispersive X-ray Spectroscopy)

SEM was used to get the microscopic image of different catalysts. Zeiss, EVO 50, UK SEM analyzer was used in this experiment. Before taking SEM images, the samples were coated with gold (Au) to make samples conductive. Backscatter mode was used for Ru-ZSM-5 catalyst to distinguish between Ru and ZSM-5 phase. In case of Ru-AC, secondary electron mode was used.

Carbon is a small molecule, and EDS detector could not capture backscatter electrons of carbon. EDS was used to determine the composition of catalysts. After reaction, spent catalysts were analyzed by SEM to identify the nature of the carbon produced in reaction. Spent catalysts were coated with gold (Au) and placed in SEM vacuum chamber for capturing image.

S1.2.8 TGA (Thermogravimetric Analysis)

TGA was performed to determine ash content on biomass, biochar, activated biochar, heat-treated biochar. 10-15 mg sample was placed on an aluminum pan. Then, the sample was placed in a weighing pan for analysis. The temperature profile for analysis is represented in Table S3. At first, the sample was heated up to 105^{o}C at a heating rate of 10^{o}C/min and maintained at that temperature for 30 min. After that, the sample was heated up to 575^{o}C with a heating rate 10^{o}C/min and kept that temperature for 120 min. Air of 20 ml/min was flown through the sample during the analysis.

Table S3: Temperature profile for TGA analysis

Step	Hold Temperature (^{o}C)	Heating Rate (^{o}C/min)	Time(min)
First	105	10	30
Second	575	10	120

S3. Methane Conversion and Hydrogen Yield

Methane conversion for different catalysts at 800 ^{o}C and 0.1 WHSV is presented in Figure S9. Additionally, the influence of feeding rate at 0.4 WHSV suggested good methane conversion and hydrogen production on AB and Ru-AC. (see Figure S10).

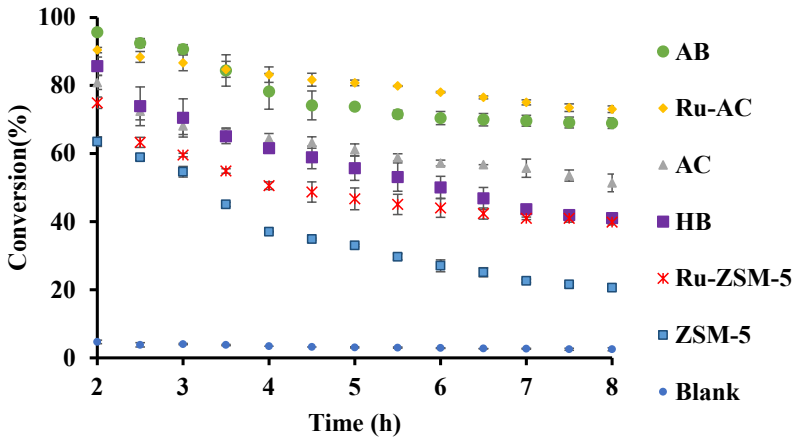

Figure S9: Methane conversion using different catalysts at 800 °C and 0.1 WHSV.

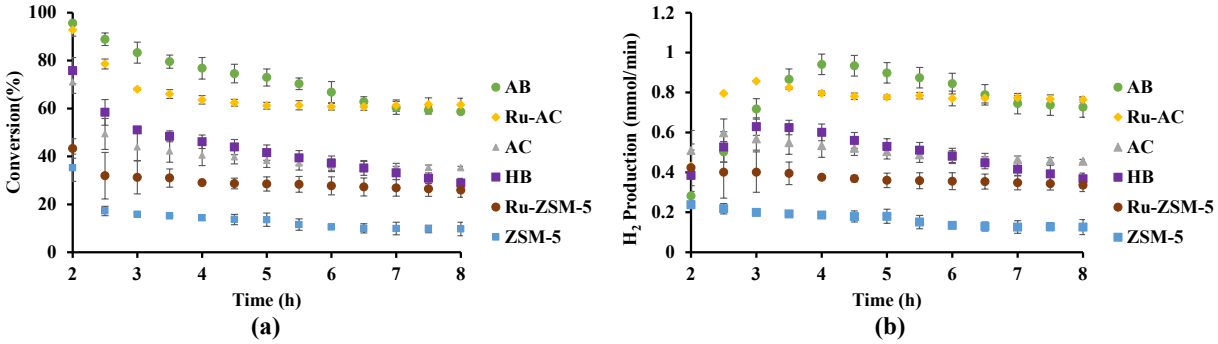

Figure S10: Reaction results for different catalysts at 800 °C and 0.4 WHSV: (a) methane conversion versus time, (b) H_2 production (mmol/min)