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Direct Catalytic Conversion of Biogas Methane to Formaldehyde

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Abstract: Efficient Solid waste utilization is a challenging task. In rural areas organic wastes like cattle waste is available in abundant, which is not utilized in the valuable forms and in urban areas it is disposed off in an improper manner. In this study biogas primarily from cattle waste was generated by using a fabricated anaerobic biogas digester. The methane is easily separated from biogas by removal of CO_2 using 40% KOH solution in three steps. After purification, direct conversion of methane to formaldehyde, which is a useful organic chemical using various metal oxide catalysts like SiO_2, V_2O_5/SiO_2, MoO_3/SiO_2 was investigated in a tubular reactor. The yields of methane conversion using various prepared catalysts was studied at varying temperature (from 400 ^oC to 850 ^oC) and at constant pressure (one atmospheric) over different catalyst beds. Among the various catalysts that were studied for methane conversion, the results showed that the V_2O_5/SiO_2 catalyst favours the maximum formaldehyde conversion.

Keywords: Solid waste, Biogas, Metal oxide catalyst, Formaldehyde

1. Introduction

The solid waste like cow dung is not only a source of biomass energy but is also a source of methane and CO_2, which are the main components of greenhouse gases. Improper disposal of these wastes create pollution of different kinds. Cow dung can disintegrate itself in CH_4, CO_2 and H_2O biologically. Although cow dung is used as organic manure but the rate of its production is faster than the disposal rate. These problems lead to deterioration of the environment and increment in green house gases. Digestion is a biological process that occurs in the absence of oxygen and in the presence of anaerobic organism at ambient pressure and temperature of 35 ^oC. Cow dung is supplied to the anaerobic digester as water slurry where it is converted into biogas, containing CH_4, CO_2 and H_2O. The biogas is easily purified to synthetic natural gas (CH_4) by removal of CO_2 by using 40% KOH solution in three to four steps.The single step oxidation of methane to formaldehyde is an economically attractive process because in last decades as researchers search for alternates to the energy intensive steam reforming process [16,18, 24]. The catalyst used by previous investigators for the reaction includes mostly vanadium, tungsten and molybdenum oxides on silica support. The reaction temperature normally employed is very high in the range of 400 °C to 850 °C and sometimes the reaction pressure is on the higher side in the range of 15 atm [3,4,10,19,22]. A considerable effort has been made to study catalysts which are active and selective for the partial oxidation of methane because of the need to convert surplus natural gas mainly methane to value added products [12, 17].

Formaldehyde is currently manufactured from methane via synthetic gas and methanol. Process for the production of formaldehyde directly from methane would potentially reduce both capital and operating costs, and therefore be of considerable industrial importance [6, 14, 18]. Kinetic analyses indicate that the methane is directly oxidized to CO_2 and HCHO. High HCHO selectivities were observed at low CH_4 conversions and HCHO selectivity decreased monotonically with increasing conversion [21]. Another observed trend was that the HCHO selectivity increased with increasing temperature at a fixed CH_4 conversion [2,13]. Unfortunately, at temperatures above 923 K and high CH_4 conversions, selectivity to HCHO continued to increase only slightly, due to the undesirable side reactions (such as gas-phase HCHO oxidation, oxidative coupling reaction etc) [1]. The catalytic activity tests were performed in a fixed bed continuous flow micro reactor [23, 20]. The analyses of the reactant and product streams were done using an online gas chromatograph. The aim of present paper is to identify suitable catalysts which could convert methane directly into formaldehyde (in a single step) at atmospheric pressure and reduced temperature conditions.

2. Material and methods

2.1 Biogas generation

A stainless steel anaerobic digester of volume 30 litre was used for biogas generation. In this digester, only two third volume of cow dung slurry was filled. Nitrogen to phosphorous ratio was fifteen. The temperature of the anaerobic digester was maintained at 35 °C. Time taken to start the gas production was 25 days after first feeding with cow dung (slurry).

2.2 Purification of Biogas

A 10 litre glass gas collection bottle was filled with water up to 7 litres. The upper inlet of the bottle was connected to biogas generator through three consecutive conical flasks filled with 40% KOH solution in three flasks and fourth with water. When Biogas is passed through KOH solution flasks, total CO_2 was absorbed by the KOH solution and more than 99 % pure methane was obtained. During the experiments the water was fed at a desired rate at the bottom of the bottle so that liquid entering displaces the methane out in the required flow rate to be used in the reactor. Since the air in the desired quantity was already present in the collection vessel, a CH_4/O_2 ratio of 12:1 was directly obtained for the use in the reactor. The schematic diagram is shown in Figure1.

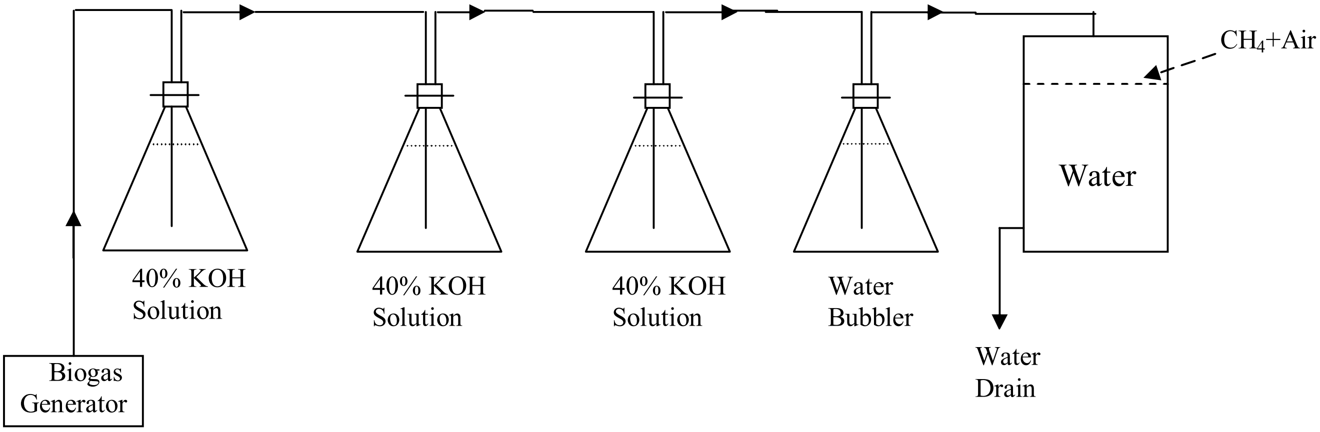

Figure 1: CO_2 Free-Biogas (i.e. Methane) Collection System

2.3 Catalyst Preparation

The metal oxide catalysts were prepared by wet impregnation method. Respective metal nitrates in desired quantity were dissolved in the distilled water. Silica was taken as a support in desired quantity and mixed with nitrate solution of the active metals. The mixture was heated at 60 °C under constant stirring for 4 hour and left for 15 hour. The mixture was dried in an oven at 110 °C for 12 hour. Finally, it was calcined at 450 °C for 3 hour. The powdered catalyst has been pelletized at 7.5 tonne/cm^2 pressure and broken to small particles and sieved in size ranges of 425 to 500 micron. A sieved catalyst was used for the test of catalytic activity in the tubular reactor.

3. Experimental Setup

A schematic diagram of the experimental setup for the test of catalytic activity is shown in Figure 2. Mixture of methane and air was passed through the catalyst bed, approximately 1 inch in length around 30mg to 150 mg of fresh catalyst of particle size range from 425 to 500 micron was used in the experimental runs. The catalyst bed was supported by glass wool on both sides to prevent it from being displaced from its position during the runs. The pre and post heating zones in the reactor tube ensured the heating as well as uniformity of flow of gases in the reactor. The experiments were carried out on SiO_2, V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts.

4. Results and discussion

Figure 3 to Figure 5 represents the performance of silica based catalysts as a function of reaction temperature. The nature of curves shows an increasing trend in the percent methane conversion as a function of reaction temperature from 450 °C to 850 °C. In the case of pure silica as catalyst, the HCHO selectivity is increasing with increasing reaction temperature up to 650 °C and there after it declines (Figure3). With V_2O_5/SiO_2 as a catalyst, the HCHO selectivity is increasing with increasing reaction temperature up to 600 °C and decreases with the further increases in temperature (Figure 4). Same trend is also observed in Figure 5, for MoO_3/SiO_2 as a catalyst, the HCHO selectivity is increases with increasing reaction temperature up to 800 °C and then a decrease in selectivity is recorded from 40.2 to 10.12. It was observed that for all three catalysts, HCHO selectivity increases with temperature up to certain range and beyond that range it starts decreases .It was also observed that no definite trend in the variation of percent HCHO selectivity with reaction temperature has been observed with the three catalysts and it declines with the increase in the temperature from around 650 °C with SiO_2, 600 °C with V_2O_5/SiO_2 and 800 °C with MoO_3 catalysts. The reason in the decline in the HCHO selectivity at high temperatures by these catalysts may be attributed to the decomposition of HCHO in to CO and H_2. The highest percent of HCHO selectivity were found at 650 °C for pure SiO_2, 600 °C for V_2O_5/SiO_2 and 800 °C with MoO_3/SiO_2 respectively.

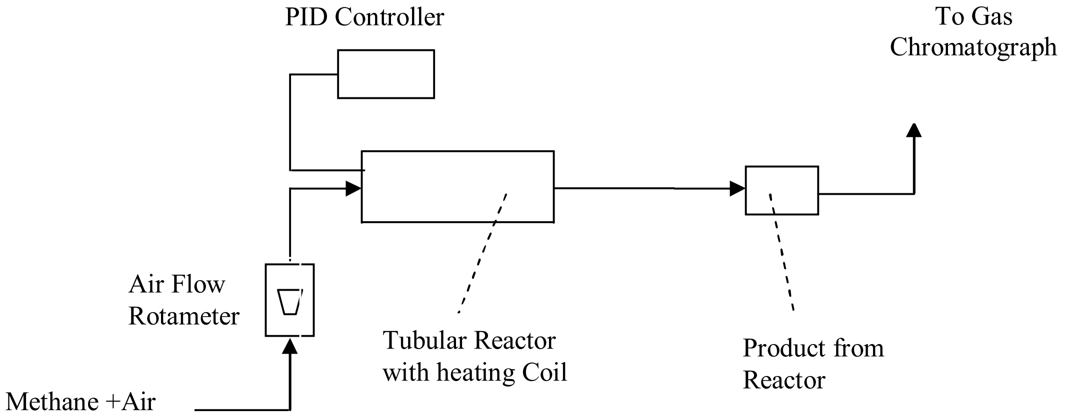

Figure 2: Experimentation setup for catalytic conversion of methane

V_2O_5/SiO_2 gives highly selective catalyst for HCHO formation from methane at low conversion. However this system suffers from a rapid falloff in HCHO selectivity as methane conversion increases. Similar behaviour was observed by other researchers [5,7,9,11] have also reported that silica itself appears to catalyse the partial oxidation of methane to formaldehyde. Partial oxidation of methane over silica supported vanadia catalyst has also been reported [15]. A similar catalyst 4% V_2O_5/SiO_2 used by these investigators reported a 2.6 % CH_4 conversion and 45% HCHO selectivity at 580 ^oC and at one atmospheric pressure. Methane to oxygen ratio has been maintained at 10, catalyst weight has been taken 200 mg and a total flow rate of 150 cm^3 per minute. The corresponding value in our case 5% V_2O_5/SiO_2 were 7.1 % methane conversion with 35.8 % HCHO selectivity at 600 ^oC. The variation in the two results may be attributed to the source of silica obtained and its physical properties. The MoO_3/SiO_2 system was also studied using O_2 as the oxidant [8].

V_2O_5 has been reported to posses hetrolytic oxygen exchange mechanism similar to MoO_3. It has been predicted that V^{5+} exhibit dehydrogenation and oxygen insertion properties which are important factors for selective methane oxidation. If the performance of these three catalysts are compared towards percent HCHO selectivity, V_2O_5/SiO_2 may be adjudged best due to its activity at a much reduced reaction temperature. A comparison of percent yields of HCHO for different catalysts is shown in Figure 6. It shows that percent yield for V_2O_5/SiO_2 is 2.54 at 600 ^oC and percent yield for MoO_3/SiO_2 is 3.18 at 800 ^oC. From above discussion it is clear that V_2O_5/SiO_2 is performing better at reduced reaction temperature.

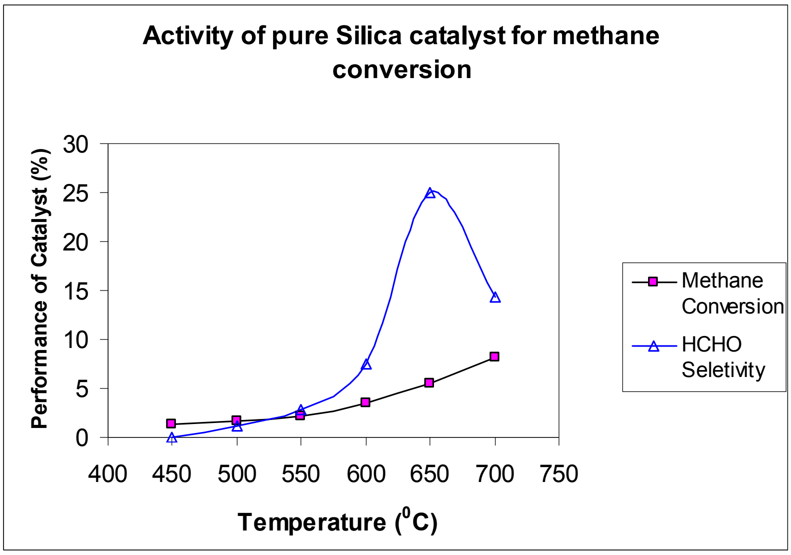

Figure 3: Performance of pure silica catalyst

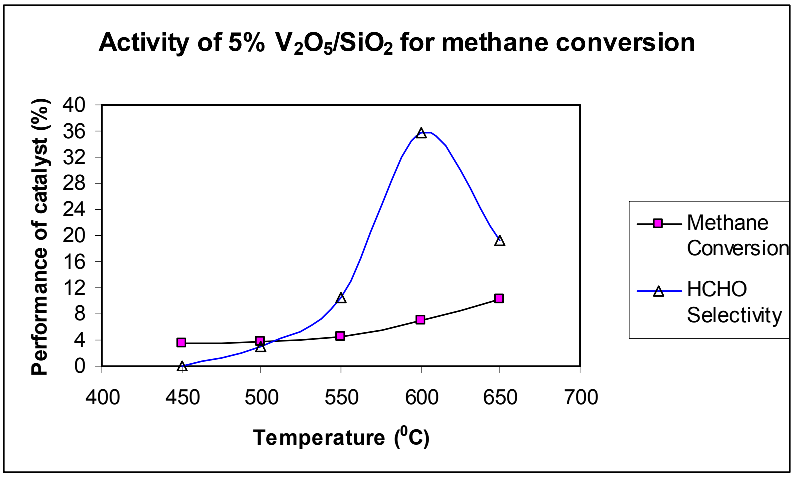

Figure 4: Performance of V_2O_5/SiO_2 catalyst

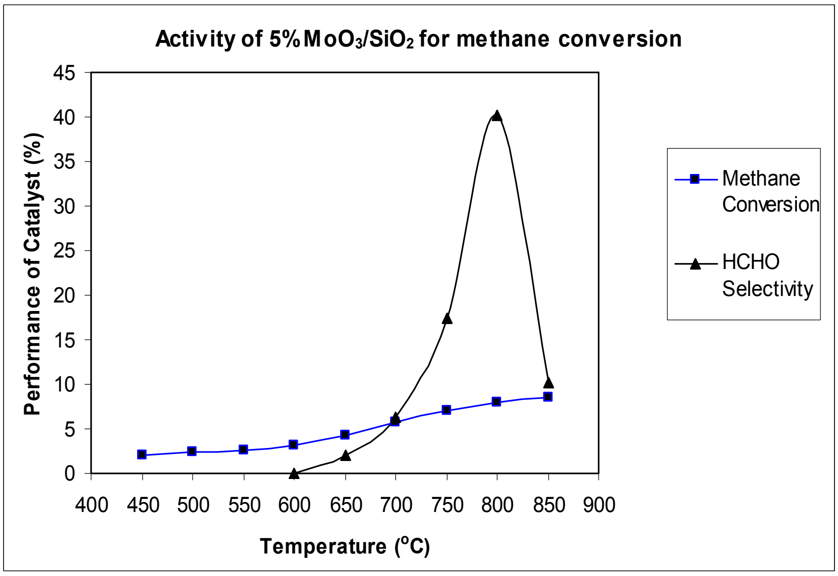

Figure 5: Performance of MoO_3/SiO_2catalyst

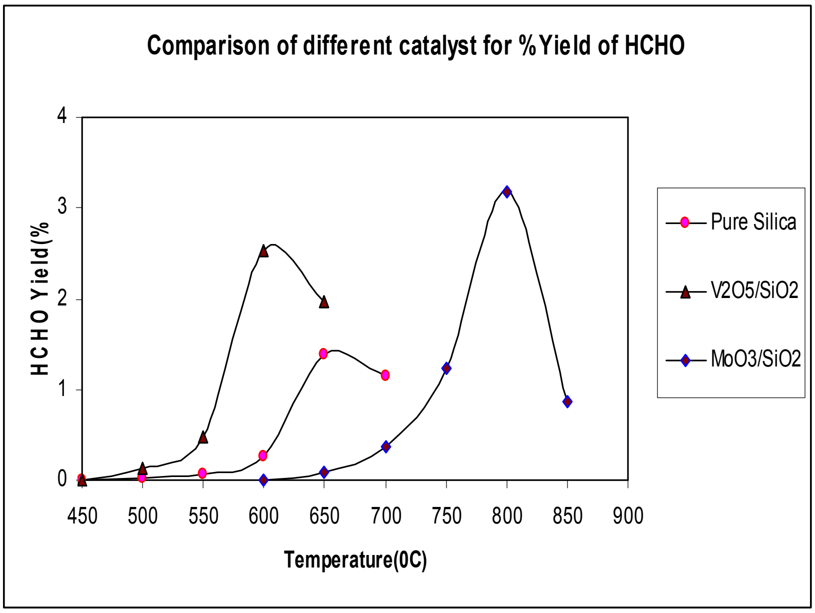

Figure 6: Comparison among tested metal oxide catalysts

5. Conclusion

Catalyst system based on SiO_2 prepared by wet impregnation method with Vanadium and Molybdenum were prepared and tested for methane partial oxidation to formaldehyde. In general, V_2O_5/SiO_2 is selective catalyst for the partial oxidation of biogas methane to formaldehyde. As methane conversion increases, formaldehyde selectivity also increases up to 35.8% (reaction temperature 600 °C) and then decreases because of the decline in the HCHO selectivity at high temperatures by the decomposition of HCHO in to CO and H_2. V_2O_5 shows hetrolytic oxygen exchange mechanism similar to MoO_3. It has been predicted that V^{5+} has better dehydrogenation and oxygen insertion properties than Mo^{+6} which are important factors for selective methane oxidation. Thus V_2O_5/SiO_2 is clearly more active than the MoO_3/SiO_2 catalyst towards formaldehyde selectivity and yield.

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