Overview of Catalytic Methanation in Hot Mixing Asphalt Plants Towards Greenhouse Gas Emissions

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Abstract. Road works mainly involve the use of asphalt for pavement construction. Among Hot-Mix asphalt (HMA) production processes, HMA plants are the most commonly used for asphalt production in world. HMA is shown as an industrial activity in which energy consumption can reach 60% of the total energy consumed by the construction and the maintenance of a road during 30 years of service life. Rate of production, bitumen temperature, burner flow rate and type of fuel consumption are the parameters which directly link to energy consumption and greenhouse gas (GHG) emission during HMA plant operation. Carbon dioxide (CO₂) in GHG has increased the temperature of the earth. Introduction of catalytic methanation as a new method in the HMA production was introduced as an effective way to convert CO₂ released from HMA plants to methane (CH₄). The optimum parameters were found through the experimental result which showed that Ru/Cr/Mn (5:10:85)/Al₂O₃ calcined at 700°C with 10 g of catalyst dosage gave 100% of CO₂ conversion, determined using FTIR, and yielded about 80% of CH₄ at reaction temperature of 300°C. Field Emission Scanning Electron Microscope (FESEM) show the presence of dispersed particles with undefined shape covering the catalyst surface. EDX analysis revealed that the mass ratio of Mn was high compared to the other elements. Thus, this study has proven that the catalytic methanation technology as the new effective method in HMA production plants can convert CO₂ in GHG emission to methane (CH₄). In conclusion, it is highly advisable to adapt these alternatives as the green roads and highways industry.

1. Introduction

Nowadays, injection moulding technology has been widely used in modern industry activity to In HMA plants, two main sources that produce organic emissions at the chimney are coming from...
combustion and Hot-Mix asphalt [1]. From the environmental aspect, the HMA plants (i.e. drum mixer process) can be classified by five parts which are (Figure 1): (1) energy flame, (2) material resources (i.e. aggregate and bitumen), (3) coating process, (4) HMA manufactured, and (5) emissions to the atmosphere.

The warming and drying of aggregates move into the upper part of the drum using the main conveyor belt. The bitumen is put into the remaining half of the drum, which is the flame end, to avoid excessive oxidation [2]. The final HMA mixture is produced after the aggregates are mixed with hot asphalt cement, then the HMA is loaded into trucks for hauling to the job site. The primary emission sources associated with HMA production are the dryers, hot bins, and mixers, which emit a variety of gaseous pollutants. HMA plant’s emissions are not constant over time. There are fluctuations due to the process used, under or out of control [1, 3, 4]

![Figure 1. HMA plant operation][1].

Various methodologies and technologies have been developed by the road pavement industry to reduce the environmental impact: the use of warm mix asphalt (WMA) are considered as a cleaner practice than traditional HMA[5] due to the lower production and application temperatures (100-140°C) incorporating between asphalt plants various percentage of reclaimed asphalt pavement (RAP) blended together with virgin aggregate to conserve the natural aggregate resources [6] and use of by product material (i.e. slag, rubber) to prolong the service life of a pavement [7, 8]. Those techniques are focused more on sustainable environment during road construction. However, GHG emissions from asphalt production cannot be stopped.

In this paper, a chemical conversion technique known as catalytic methanation has been studied to convert CO$_2$ emissions to the higher value-added product, which is natural gas of methane (CH$_4$) [9]. This process does not only create a green and sustainable environment in HMA production but produced valuable methane gas that can also be used as a fuel to run turbine for electricity [10]. Thus, this study has two (2) main objectives, which are to determine the gas composition produced in HMA production plant and to develop the catalyst which can convert CO$_2$ in GHG emission from HMA plants to the natural gas of methane.

2. GAS COMPOSITION FROM HMA PLANT

GHG emissions have been monitored and controlled under binding environmental regulations and legislation. Operating of HMA plants require the agreement of local authorities which is given according to pollutants thresholds: CO, SO$_2$, NO$_x$, and total organic compounds (TOC)[1]. Gas/fumes from asphalt plants is a mixture containing different chemicals. The chemicals in asphalt vary depending on the source of the crude oil, the type of asphalt being made, and the process used. Figure

[1]: Figure 1. HMA plant operation[1].
2 shows GHGs emissions that had been collected from HMA plants by using gas analyser (GA). Based on GA reading, hydrocarbon, carbon dioxide (CO$_2$), nitrogen oxides (NO$_x$), carbon monoxide (CO) and Air fuel oil have been detected from HMA plants. The amount of CO$_2$ released was about 6% because the type fuel was already filtered by following the Environment Act (Figure 3). Generally, CO$_2$ was produced from the type of fuel used and at the same time, the energy consumption needed for the heating process of the mineral aggregates and bitumen tanks. Other CO gas released was due to the combustion process in the dryer and was strongly influenced by the fine content of the mineral, and the water vapour content in the drum. Usually, NO$_x$ emission depends on the nitrogen content of the fuel and was originated from the burner in the drying drum[11].

Figure 2: HMA plant and Gas analyser (GA).

Figure 3: GHGs gas composition of HMA plants from Gas Analyser (GA).
3. Experimental
In this study, catalytic methanation system was used to utilize the GHG emissions from HMA plants. The methanation reaction is the catalytic reaction where carbon dioxide reacts with hydrogen to produce methane and water as described in Equations 1 and 2.

\[
\begin{align*}
\text{CO}_2(g) + 4\text{H}_2(g) & \rightarrow \text{CH}_4(g) + 2\text{H}_2\text{O}(l) \\
\text{CO}(g) + 3\text{H}_2(g) & \rightarrow \text{CH}_4(g) + \text{H}_2\text{O}(l)
\end{align*}
\]

The catalytic methanation conversion system uses rare earth oxides. Rare earth oxides are expected to adsorb significant amount of the acidic CO$_2$ gases on the catalyst surface. Catalyst act as the conversion towards CO$_2$ that is released from asphalt production to form methane (CH$_4$) which is one of the components of natural gas. Methane gas production is an environmentally friendly approach for purification of natural gas [12]. Natural gas is an extremely important source of energy for reducing pollution and maintaining a clean and healthy environment [13].

3.1. Preparation of Chemical and Catalysts
Manganese (Mn) was used as the base in this study. Meanwhile Chromium (Cr), Nickel (Ni) and Cobalt (Co) were used as dopants and Ruthenium (Ru) as co-dopant. In addition, aluminium oxide beads (Al$_2$O$_3$) were used as the support materials for the preparation of catalysts. All the catalysts were prepared by aqueous incipient wetness impregnation method. 85 wt% 5 g of Manganese (Mn) salts was dissolved in small amount of distilled water, then mixed with a dopant and co-dopant solution in a beaker, according to the desired ratio. A homogeneous mixture was obtained by electromagnetic stirring at room temperature for 30 minutes. Alumina beads with diameter of 3 mm were used as support material in this study. The support was immersed into the catalysts solution until the solution was evenly absorbed on the surface of the support. It was then aged inside an oven at 90˚C for 24 h followed by calcinations using a furnace in the air atmosphere at 400˚C, 700˚C and 1000˚C for 5 h using a ramp rate of 10˚C/min to remove all the metal counter ions and water present in the catalyst.

3.2. Catalytic Activity Measurement
The catalytic CO$_2$ methanation reaction was performed under atmospheric pressure in a fixed microreactor and analysed via online FTIR Nicolet Avatar 670 DGTs. 10 g of supported catalyst was placed in the middle of a Pyrex glass tube of diameter 10 mm and length 520 mm. It was then secured with glass wool at both ends. The reaction gas mixture (inlet) consisting of CO$_2$, Hydrogen (H$_2$), Nitrogen (N$_2$), (10/40/39 mL/min) was passed continuously through the catalyst and was heated in an isothermal tube furnace. The feed gas flow rate was adjusted with a mass flow controller and the reaction temperature was performed from 50˚C up to 400˚C with the increment temperature rate of 5˚C/min (Figure 4).

![Figure 4. Catalytic Methanation System](image-url)
4. Results

4.1. Catalytic Performance Of Mn Based Catalyst Over Various Dopant

Table 1 illustrates the catalytic performance of Mn based catalysts, which were calcined at 700 °C for 5 h. According to the results, a Mn (100%)/Al₂O₃ catalyst gives only 22.36% conversion of CO₂ at a reaction temperature of 400°C. Three types of chemical, which are Chromium (Cr), Nickel (Ni) and Cobalt (Co), were used as a dopant catalyst.

Incorporating Cr/Mn (15:85)/Al₂O₃, Ni/Mn (15:85)/Al₂O₃ and Co/Mn (15:85)/Al₂O₃ as dopant catalyst have increase the catalytic activity of Mn base to 26.43 %, 4.79% and 33.31 %, respectively, at 400°C reaction temperature. Combination of transition metal (i.e Mn, Cr, Nickel and Co) was found to accelerate the Methanation process [14].

The addition of Ru into Cr/Mn (15:85)/Al₂O₃, Ni/Mn (15:85)/Al₂O₃ and Co/Mn (15:85)/Al₂O₃ as co-dopant catalyst to form Ru/Co/Mn (5:10:85)/Al₂O₃, Ru/Ni/Mn (5:10:85)/Al₂O₃ and Ru/Co/Mn (5:10:85)/Al₂O₃ catalyst coincidentally enhanced catalytic activity for the conversion of CO₂ of the prepared catalysts. The small amounts of Ru addition can play an important role in the improvement of catalyst activity. The presence of Ru as a co-dopant catalyst to Mn based catalyst also has enhanced and eased the chemisorptions of the reactants (CO₂ and H₂) on their surfaces [14]. Combination of Ru/Co/Mn (5:10:85)/Al₂O₃ presented the highest combination of conversion CO₂ between other catalyst, which are fully 100% of CO₂ conversion at reaction temperatures of 300 °C.

Table 1. Percentage conversion of CO₂ from methanation reaction over Manganese based catalysts with various dopant.

| Alumina supported catalyst | Reaction Temperature (°C) |
|----------------------------|---------------------------|
|                            | 50 | 100 | 150 | 200 | 250 | 300 | 350 | 400 |
| Mn (100%)/Al₂O₃            | 6.22 | 6.19 | 6.51 | 4.94 | 7.87 | 6.22 | 9.21 | 22.36 |
| Cr/Mn (15:85)/Al₂O₃       | 6.40 | 10.11 | 12.72 | 16.31 | 22.36 | 22.64 | 23.89 | 26.43 |
| Ni/Mn (15:85)/Al₂O₃       | 5.98 | 12.03 | 14.49 | 25.78 | 29.05 | 31.45 | 30.98 | 41.79 |
| Co/Mn (15:85)/Al₂O₃       | 10.64 | 6.60 | 6.68 | 10.26 | 11.32 | 12.44 | 21.01 | 33.31 |
| Ru/Co/Mn (5:10:85)/Al₂O₃ | 0.40 | 2.41 | 15.70 | 30.50 | 100.00 | 100.00 | 100.00 | 100.00 |
| Ru/Co/Mn (5:10:85)/Al₂O₃ | 8.61 | 14.83 | 23.14 | 46.51 | 78.52 | 80.97 | 80.57 | 80.39 |
| Ru/Co/Mn (5:10:85)/Al₂O₃ | 4.15 | 9.32 | 2.39 | 19.46 | 82.38 | 83.31 | 82.98 | 83.15 |

4.2. Formation of methane (CH₄)

Figure 5 illustrates the detection of the formation of CH₄ after CO₂, hydrogen (H) and Nitrogen (N) (simulate: CO₂, H and N was GHG gas in laboratory) was flowed through to Ru/Co/Mn (5:10:85)/Al₂O₃ catalysts. The Ru/Co/Mn (5:35:60)/Al₂O₃ calcined at 700°C was considered as the potential catalyst for CO₂ methanation reaction since it gave 100% of CO₂ conversion. Based on the results, CH₄ was not produced at initial temperatures of 50°C, 100°C and 150°C. As the reaction temperatures were elevated to 200°C, 250°C, 300°C, 350°C and 400°C, about 19.59%, 58.67%, 80%, 80%, 80% of methane formation were detected, respectively, by using GA. The high formation of methane at high reaction temperature was possibly due to its highly exothermic reaction where the methanation reaction was favored at high temperature [14].

Table 1. Percentage conversion of CO₂ from methanation reaction over Manganese based catalysts with various dopant.
4.3. Characterization: FESEM-EDX

Characterization: Figure 6 (i,ii,&iii) shows the FESEM micrographs of fresh and spent Ru/Cr/Mn(5:10:85)/Al₂O₃ catalysts, calcined at 700°C for 5 h with magnification of 20000× and 50,000×. The fresh Ru/Cr/Mn(5:10:85)/Al₂O₃ catalyst showed rough surface morphology with a homogeneous spherical shape, and comes with small particle sizes. In this study, it was found that the particle size of fresh Ru/Cr/Mn(5:10:85)/Al₂O₃ catalyst is categorized at the nano (<100 nm) level, which varies from 67 to 147 nm. The smaller particle size plays an important role in exhibiting higher catalytic activity. The morphology of the fresh catalyst changed significantly after the hydrogenation of the methanation reaction, which showed the formation of aggregated and agglomerated undefined shapes on the surface of the spent catalyst (Figure 6(ii)) due to the heat generated during the catalytic reaction and which caused the catalyst to agglomerate [15].

Furthermore, Table 2 shows the EDX analysis for the fresh and spent Ru/Cr/Mn(5:10:85)/Al₂O₃ catalysts. The elemental analysis performed by EDX confirmed the presence of Ru, Cr, Mn, Al and O in the potential catalyst. From EDX analysis, it can be detected that the composition of Mn was higher than the other composition of Ru and Cr on the fresh and spent Ru/Cr/Mn(5:10:85)/Al₂O₃ catalysts, which are 18.1 % and 10.7%. Moreover, the spent Ru/Cr/Mn(5:10:85)/Al₂O₃ catalyst confirms the existence of 3.40% carbon on the surface of the catalyst. The difference of fresh and spent catalyst surfaces was due to the presence of carbon. From the EDX analysis, the weight ratio of Aluminium (Al) was the highest, indicating that the catalyst surface was dominated by the Al from the support. This may be due to the noble metal and Mn being absorbed into the high porosity and high surface area of alumina beads[14].
Figure 6: i) Fresh Ru/Cr/Mn(5:10:85)/Al$_2$O$_3$ catalyst with magnification 20000x, ii) spent Ru/Cr/Mn(5:10:85)/Al$_2$O$_3$ catalysts with magnification 20000x, iii) particle size of fresh Ru/Cr/Mn(5:10:85)/Al$_2$O$_3$ catalyst with magnification 50000x

Table 2. EDX analysis

| Weight ratio (%) | Ru/Cr/Mn (5:10:85)/Al$_2$O$_3$ catalysts, calcined at 700 °C |
|------------------|---------------------------------------------------------------|
|                  | Fresh             | Spent              |
| O                | 35.0              | 42.3               |
| Al               | 32.3              | 29.6               |
| Mn               | 18.1              | 10.7               |
| Cr               | 8.9               | 4.0                |
| Ru               | 3.1               | 1.0                |
| C                | -                 | 3.4                |

5. Conclusion

Gas composition from HMA plants has successfully been detected by using GA. In general, gas that has been released to atmosphere are categorized as GHGs emissions. Therefore, this study tries to convert CO$_2$ emissions to natural gas by applying chemical conversion system. This method can also be called catalytic methanation system. Overall, the catalytic activity studies can achieve almost 100% of CO$_2$ conversion at low reaction temperature and produced 80% yield of methane (CH$_4$) at 300°C of reaction temperature. Catalyst of Ru/Cr/Mn (5:10:85)/Al$_2$O$_3$ calcined at 700°C was assigned as the potential catalyst that had successful been developed due to the contribution of 100% of CO$_2$ conversion at the reaction temperature of 250°C. Field Emission Scanning Electron Microscopy (FESEM) analysis illustrated the surface of the catalysts were covered with small and dispersed spherical particles. Energy Dispersion X-ray (EDX) analysis revealed that the weight ratio composition of Mn was high in the fresh Ru/Cr/Mn (5:35:60)/Al$_2$O$_3$ but reduced after Ru/Cr/Mn (5:35:60)/Al$_2$O$_3$ catalysts was used.

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