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EFFECT OF MOLECULAR SIEVE 4A ON THE CATALYTIC HYDROGENATION OF CARBON DIOXIDE FOR SUSTAINABLE TRANSPORT

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1. ABSTRACT

Carbon dioxide emissions have become the subject of much government incentives and sparked major clean-up process initiatives throughout the motoring world. Although CO_2 emissions are not solely from transportation, this sector contributes the most, with gasoline being the major sub-division. The development of electric and hydrogen cars have provided evidence that vehicles can be manufactured to achieve low emissions, while still providing the car with sufficient power. The combination of the Zero Emission Petrol Vehicle (ZEPV) concept, catalytic hydrogenation of CO_2 and methanol to gasoline (MTG) process gasoline is not only zero emission but also sustainable through the use of carbon recycling, via renewable energy sources.

However the low methanol yields, both selectivity and conversion, is the main problem in the methanol synthesis. The research showed that Molecular Sieve 4A could increase the CO_2 conversion significantly. The objectives of this research are to develop a mathematical model for representing the effect of Molecular Sieve 4A on methanol synthesis and to analyse the feasibility study for re-syn fuel refinery from recycled CO_2.

2. INTRODUCTION

CO_2 emissions are one of the main causes of the greenhouse effect. These emissions have, over the past decade, become the subject of many government incentives and sparked major clean-up process initiatives throughout the motoring world. Although CO_2 emissions are not solely from transportation, this sector produces approximately 24% of the UK's total carbon emissions and road transport contributes 85% of this. From 1995 to 2005, CO_2 emissions from transport sector increased by approximately 6.5% (Foster and Ramaswamy, 2007). If there are no new initiatives, these emissions will continuously increase. Catalytic hydrogenation of CO_2, such as methanol synthesis and methanation, could play an important role in reducing these emissions. By using a combination of the Zero Emission Petrol Vehicle (ZEPV) concept, catalytic hydrogenation of CO_2 and methanol to gasoline (MTG) process gasoline can be re-synthesised from recycle CO_2. The low methanol yields, both selectivity and conversion, is the main problem in the methanol synthesis. Methanation could be considered as another alternative process, because recent research showed that the yield in methanation process is high, the conversion of CO_2 to CH_4 was nearly 100% (Qijian and Qiming, 2003).

Several investigations have been undertaken regarding the specific use of copper-based catalyst on suitable supports, with promoters and appropriate preparation methods to find an effective catalyst for methanol synthesis from CO_2/H_2. Although all the proposed catalysts can enhance the conversion of CO_2 to CH_3OH and yield of CH_3OH, but the values are relatively still too low. One of the major reasons was the presence of H_2O. It was adsorbed on the active site of the copper catalyst and inhibited the adsorption of CO_2 and H_2 for the next catalytic reaction (Joo et al,1999). Therefore, the objectives of this study are to design and examine the behaviour of methanol synthesis in a lab scale tubular catalytic reactor and in particular to investigate the effect of a water removal desiccant (molecular sieves 4A, MS 4A) on the reversible methanol synthesis and to develop a mathematical model for presenting the effect of MS 4A.

3. EXPERIMENTAL WORKS

The objectives of these experiments were to design and examine the lab scale tubular catalytic reactor for methanol synthesis behaviour and in particular to investigate the effect of a water removal desiccant on the methanol synthesis. For this, different composition of $CuO/ZnO/Al_2O_3$ catalyst and molecular sieve 4A (MS 4A) were used.

All experiments in this study were carried out in the stainless steel catalytic tubular reactor, with dimension 0.10 m in length, 3/8 inch outside diameter and 0.006 m inside diameter, at 190 – 220°C and 1 bar. The performances of the $CuO/ZnO/Al_2O_3$ commercial catalyst and the effects of MS 4A, as a desiccant, on the conversion of CO_2 were investigated. The indicator of this performance is conversion of CO_2. The effluent of the tubular reactor was analysed by in-line GC, making use of a Poraplot Q column and TCD. The conversion of CO_2 to methanol as a function of H_2/CO_2 ratio, feed flow rate (GHSV = gas hourly space velocity) and temperature was investigated. The highest conversion value (1.12 %) was reached at 3600 h^{-1}, 190°C and $H_2/CO_2 = 4$. This conversion is lower than the equilibrium conversion, 1.74%.

The possibility of MS 4A, as a desiccant, to lower the effect of water upon active site reaction was examined. After being ground to 250 – 425 µm particle size, typically 0.3 – 0.5 gram of MS 4A was physically mixed with 0,5 gram catalyst and then this mixture was activated, reduced and flushed for one hour under Helium at 290°C. Then after being cooled to 190°C under Helium, this mixture was ready to use for methanol synthesis. The synthesis was carried out for 20 hours with the $H_2/CO_2 = 4$, GHSV = 3600h^{-1} and 190°C. The product was analysed every 50 minutes by on-line Gas Chromatograph (GC).

The mixture catalyst performance was further compared to the $CuO/ZnO/Al_2O_3$ catalyst under the same reaction conditions, see Figure 1.

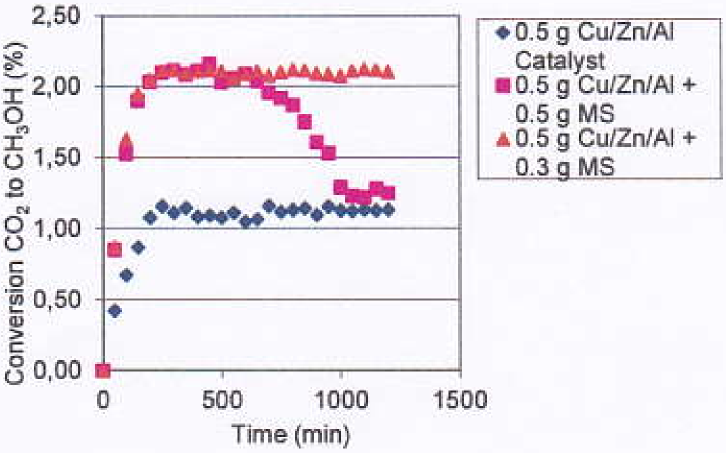

Figure 1: CO_2 Conversion with Different Compositions of MS 4A

4. MODEL DEVELOPMENT FOR METHANOL SYNTHESIS USING DESICCANT

The conversion of CO_2 (X_{CO2}) profile for methanol synthesis using desiccant can be derived from mass balance in the fluid and solid/desiccant phases. Mass balance in the fluid phase as follows :

$$(input)+\begin{pmatrix}rate\ of\\ reaction\end{pmatrix}+\begin{pmatrix}rate\ of\\ adsorption\end{pmatrix}=(output)+\begin{pmatrix}accumulation\\ in\ fluid\ phase\end{pmatrix}+\begin{pmatrix}accumulation\\ in\ solid\ phase\end{pmatrix} \quad (1)$$

or

$$v\,C_O + W_{ct}\,r_D + W_{ct}\,(r_D\,X_D) = v\,C + V\frac{dC}{dt} + W_d\,\frac{dW}{dt}$$

or

$$v\,C_O + W_{ct}\,r_D\,(1 - X_D) = v\,C + V\frac{dC}{dt} + W_d\,\frac{dW}{dt} \tag{2}$$

At the initial condition Co = 0, Equation (2) can be written as

$$W_{ct}\,r_D\,(1 - X_D) = v\,C + V\frac{dC}{dt} + W_d\,\frac{dW}{dt} \tag{3}$$

Mass balance in the solid/desiccant phase can be written as the equation below,

$$\frac{dW}{dt} = k_a\,(W^* - W) \tag{4}$$

The expression for the concentration of water (C_D) or conversion of CO_2 (X_{CO2}) profile is obtained from the Laplace transform of these equations. For 30% molecular sieve (30% MS 4A)

$$\begin{aligned} C_D = {} & 4\,x10^{-7} - 6.1\,x10^{-6}\,\exp(-0.02t) \\ & - 5.4\,x10^{-7}\,\exp(-60.8t) + 2\,x10^{-6}\,\exp(9.74x10^{-4}\,t) \end{aligned} \tag{5}$$

and for 50% MS 4A

$$\begin{aligned} C_D = {} & 2.3\,x10^{-7} - 6.1\,x10^{-6}\,\exp(-0.02t) \\ & - 6.3\,x10^{-7}\,\exp(-60.8t) + 1.7\,x10^{-6}\,\exp(4.98x10^{-5}\,t) \end{aligned} \tag{6}$$

For example, the comparison between experimental and numerical result can be seen in Figure 2. From this figure, the numerical model gives a good fit to the experiment points for the same composition of desiccant (50% MS 4A). This indicates that the model, Equation (6), can be used to predict the conversion of CO_2 profile for methanol synthesis using molecular sieve 4A as a desiccant.

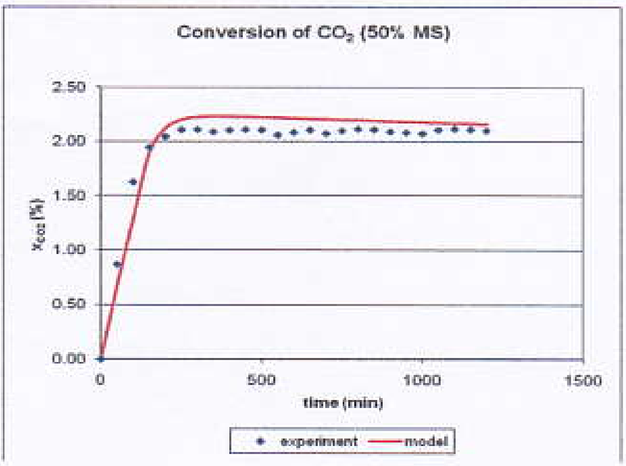

Figure 2. Comparison of CO_2 conversion profile between experimental result and numerical model (50% MS 4A)

5. CONCLUSIONS

The combination of the ZEPV concept, catalytic hydrogenation of CO_2 and MTG process, which is referred to as gasoline re-synthesis from recycled CO_2 (to produce re-syn fuel), is one of the possibilities to eliminate CO_2 emissions from the transportation sector.

The results of experiments clearly show that methanol was produced at the proposed conditions and compares to another technologies, Camere process and membrane reactor, the usage of MS 4A in methanol synthesis to remove the water from the active site of catalyst is very recommended.

The present study has provided useful information to increase the conversion of CO_2 to methanol in the catalytic hydrogenation of CO_2 process by using molecular sieve 4A (MS 4A). However, further studies are still need to be considered to increase the conversion of CO_2 by increasing the pressure and by using different catalyst such as $CuO/ZnO/ZrO_2/Ga_2O_3$ which was used in the Camere process.

The results of model development for the high pressure process indicate that the initial rate of methanol synthesis at pressure around 50 atm will be 35 – 45 times higher than this initial rate at 1 atm and becomes relatively constant at pressures above 50 atmospheres. For the further experiment, it is suggested to design the reactor for high pressure and perform the reaction at pressure around 30 to 50 atm.

Joo et al. (1999) reported that the carbon conversion in methanol synthesis at 27.2 atm over $CuO/ZnO/ZrO_2/Ga_2O_3$ catalyst in direct hydrogenation of CO_2 was 69%. This conversion is higher than the conversion obtained here and predicted from present study and interpolation from numerical model, which is around 50%. Joo et al. (1999) also reported by using a combination of direct hydrogenation of CO_2 and reverse water gas shift (RWGS) reaction, the conversion increased from 69% to 89%. From the present study, it found that the use of MS 4A increased the conversion of CO_2 1.8 times. So, it could be considered to replace the RWGS reaction with MS 4A as a water removal for the further experiment. It would increase the conversion and also reduce the operational cost as no RWSG reactor needed.

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