STUDIES ON TRANSFORMATION OF CO_2 AND CO_2-RICH NATURAL GAS INTO FUELS AND CHEMICALS AT PVPro/VPI: INITIAL RESULTS AND FUTURE WORKS

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Summary

This paper summarises some initial research results of CO_2 and CO_2-rich natural gas transformation into fuels and chemicals at VPI. Our results showed that CO_2 conversion by either direct or indirect routes to fuel or chemical is feasible. The improved catalyst performance by optimisation of catalyst formulation, structure, and catalyst preparation methods will greatly contribute to the overall economics of the process. On the other hand, application of new catalytic reactor technology such as membrane reactor also enhances the process efficiency. These promising results will pave the way for further investment of research activities, aiming to develop new catalysts and technologies that ultimately could help to efficiently utilise CO_2 and CO_2-rich natural gas in Viet Nam.

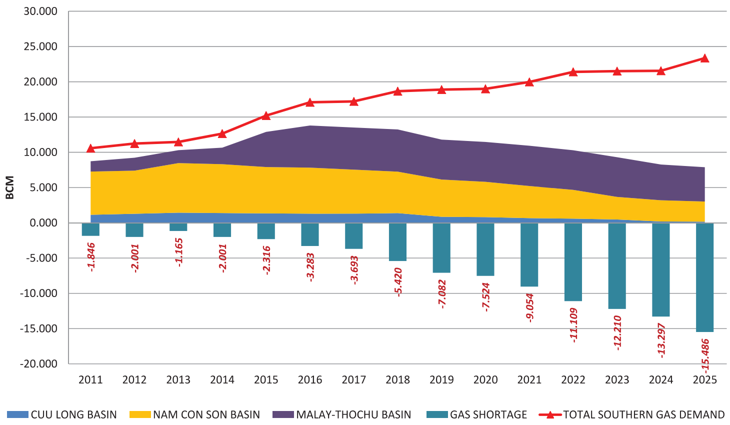
I. Introduction

It is believed that natural gas is the most important energy source for the future where natural gas should gradually take over from oil and become the most important fossil fuel by the middle of the 21st century [1]. The abundance of natural gas coupled with its environmental soundness and multiple applications across all sectors means that natural gas will continue to play an increasingly important role in meeting demand for energy as well as being a feedstock for the chemical industry.

Proven natural gas reserves had reached about 196 trillion standard m^3 in 2011 [2] without counting the enormous methane reserves trapped in the form of hydrates at the bottom of the oceans. Currently, the majority of natural gas is used for power generation, however, in the longer term it will be increasingly used to produce liquid motor fuels and intermediates for the chemical industry.

Most of the world's natural gas reserves contain some amount of CO_2, which could be as high as 70 - 80% in volume. With current technology, natural gas is economically viable only when the CO_2 content is less than 10 - 15% of the total volume. If the CO_2 content is higher, then the removal process is prohibitively expensive, therefore leaving these natural gas reserves uneconomical to develop. To be marketable and pipeline ready, the CO_2 content must be reduced at the wellhead to a content level of approximately 2.5%.

Unfortunately, most of the CO_2 that is removed at the wellhead by the gas producers is simply released into the atmosphere. According to the U.S. Energy Information Agency, the production of natural gas is the second largest source of CO_2 emissions in the country. These conditions create a dual economic challenge for the natural gas industry. First, how can we monetise the vast amounts of high CO_2 content as a potential feedstock to produce fuel or chemicals? Second, how can all resource holders, irrespective of the level of CO_2 concentration in their gas, deal with the inevitable need to discontinue the practice of emitting CO_2 during processing?



Source: Forecast PVN, PVGAS

Fig.1. *The supply-demand balance in the South of Vietnam*

Vietnam has a total natural gas reserve of approximately 228 billion m^3, which mostly locate in the South and central areas, with the CH_4 and CO_2 content in the range of 58 - 81% and 0.1 - 30% respectively. The production capacity is about 8.24 billion m^3/year by 2012, which is expected to increase to 13.52 billion m^3/year in 2020. Fig.1 shows the balance of gas demand-supply in the South of Vietnam, indicating that there is always a gas shortage in the region [3].

On the other hand, the expected natural gas supply capacity of the central part of Vietnam is 2 - 4 billion m^3/year from 2018 of which 1.3 billion m^3/year is reserved for power generation making 0.7 - 2.7 billion m^3/year of natural gas available for processing. However, the CO_2 content of the natural gas in this area could be as high as 30% in volume, which imposes some technical difficulties in processing. Furthermore, effective utilisation of CO_2 in some natural gas field could improve the economics as well as environmental protection of the natural gas production in Vietnam. Therefore, the two above-mentioned questions are also important issues for the natural gas industry in Vietnam.

2. PVPro/VPI's initial results

There are two ways to convert CO_2 and CO_2-rich natural gas to useful fuels or chemical. One is direct conversion of CO_2 into fuels and chemicals, and the other is conversion of CO_2-rich natural gas into syngas, using CO_2 as a carbonaceous feedstock, followed by other chemical synthesis processes to produce fuels and chemicals. At PVPro/VPI, both of these approaches are adopted to solve challenges in effective utilisation of CO_2 and CO_2-rich natural gas. The following sections described the initial results of our research projects in these areas.

2.1. Direct conversion of CO_2 to methanol

In order to directly convert CO_2 to methanol, the $CuO/ZnO/Al_2O_3$ catalyst system was studied. The objectives are to achieve high yield and selectivity of methanol and to suppress the formation of H_2O and higher alcohols by the reverse water gas shift (RWGS) reaction to improve the efficiency of the process as well as the catalyst stability. For that, a new procedure for $CuO/ZnO/Al_2O_3$ catalyst preparation and modification by CeO_2 addition was studied. Furthermore, the performance of membrane reactor was compared with traditional reactor in CO_2 hydrogenation into methanol to evaluate the possibility to improve CO_2 conversion and methanol yield by using catalytic membrane reactor technology.

2.1.1. New procedure for preparing highly effective catalysts

$CuO\text{-}ZnO/Al_2O_3$ catalysts prepared by co-precipitation method using nitrates of Cu, Zn, and Al have been widely used in methanol synthesis with H_2/CO_2 [4]. In our first study, 30%CuO - 30%ZnO 40%Al_2O_3 model catalysts were prepared by parallel-slurry-mixing method based on [5, 6] with some modifications in 3 different procedures.

Differences of these procedures were the order of mixing $\gamma\text{-}Al_2O_3$ (prepared in-house) with precipitation of $Cu^{2+}\text{-}Zn^{2+}$ and use of different precipitation agents. The catalyst prepared by procedure 1 (P1) has the longest contact time between Cu and Zn phases and procedure 2 (P2) ensures the maximum deposition of Cu and Zn on Al_2O_3. Procedure 3 (P3) is combination of the others. The catalysts were symbolised as CZ/Al P1, CZ/Al P2, CZ/Al P3.

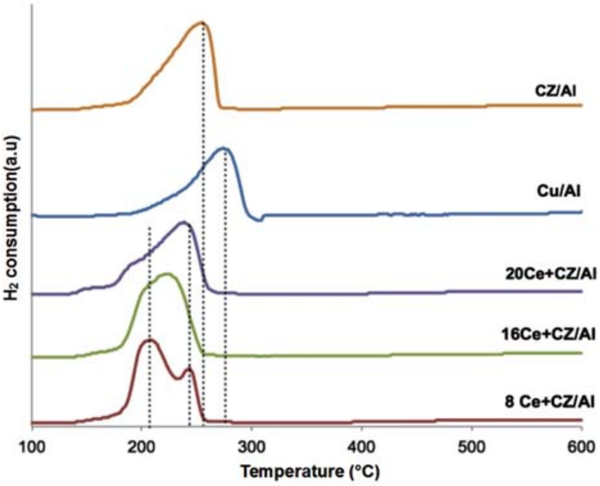


Fig.2. *TPR profiles of CZ/Al, Cu/Al, 20Ce + CZ/Al, 16Ce + CZ/Al and 8Ce + CZ/Al catalysts*

Table 1. *Methanol yield and product selectivity (250°C; 5 bar; 0.5g, GHSV = 36,000h^{-1}), d_{CuO} and S_{BET} of the catalysts*

Catalysts	MTY (m_{CH3OH}(g).Kg_{cat}^{-1}.h^{-1})	% CH_3OH	% DME (dimethyl ether)	% CO	dCuO (nm)	S_{BET} (m^2/g)
CZ/Al P1	9.1	9.4	4.0	86.6	21	70
CZ/Al P2	14.4	11.1	0.0	88.9	12	65
CZ/Al P3	25.9	12.5	0.0	87.5	27	66

Table 2. *Methanol yield and product selectivity (250°C; 5 bar; 0.5g, GHSV = 36,000h^{-1}), d_{CuO}, d_{CeO2} and S_{BET} of the catalysts*

Catalysts	**MTY (m_{CH3OH}(g).$Kg_{cat}^{-1}.h^{-1}$)**	**CH_3OH selectivity (%)**	**CO selectivity (%)**	**d_{CuO}(nm)**	**S_{BET} (m^2/g)**
CZ/Al	25.9	12.5	87.5	27	66
8%Ce + CZ/Al	75.6	37.5	62.5	25	72
12%Ce + CZ/Al	91.2	40.7	59.3	24	75
16%Ce + CZ/Al	105.4	43.9	56.1	27	74
20%Ce + CZ/Al	57.4	47.4	62.6	37	70

Table 3. *The activity (MTY) of the catalysts for methanol synthesis*

Catalyst	**MTY (m_{CH3OH}(g).$Kg_{cat}^{-1}.h^{-1}$)**		**Reaction conditions**	**Ref.**
	Initial activity	Activity after 40h		
16%Ce + CZ/Al powder	105	104	H_2/CO_2 3/1, 250°C; 5 bar; 36,000h^{-1}	This study
16%Ce + CZ/Al tablet	101	98		
$Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ powder	785	-	H_2/CO_2 3/1, 250°C; 50 bar; 36,000h^{-1}	[7]
Cu-Zn-Ga/SiO_2 powder	329	349	H_2/CO_2 3/1, 250 - 270°C; 20 bar; 36,000h^{-1}	[8]
Commercial catalyst ($Cu/ZnO/Al_2O_3$) tablet	626	-	H_2/CO_2 3/1, 250°C; 50 bar; 18,000h^{-1}	[9]
$Cu/ZnO/Ga_2O_3$ powder	738	-	H_2/CO_2 3/1, 250°C; 50 bar; 36,000h^{-1}	[10]
ZrO_2-doped CuZnO powder	780	-	H_2/CO = 2; 210 - 280°C, 50 bar, 4,000h^{-1}	[11]

The results in Table 1 show that catalysts with the same compositions but prepared by different methods have a large difference in their activities. The catalyst prepared by our procedure (P3) has its activity improved by a factor of 1.7 - 3 compared to the others, indicating the importance of not only the catalyst formulation but also the catalyst preparation procedure.

2.1.2. $CuO-ZnO/Al_2O_3$ catalysts promoted by CeO_2

Table 2 shows that Ce addition could enhance the dispersion of active phase Cu without decreasing the S_{BET}. Fig.2 shows TPR-H_2 profiles of catalysts, indicating that Ce addition could increase the reducibility of CuO. By the addition of 8 - 20%CeO_2, catalytic activities of CeO_2-$CuO-ZnO/Al_2O_3$ catalysts are increased by a factor of 1.6 - 3.0 compared to that of the sample without modification. The highest activity can be obtained with the catalyst having CeO_2 loading of 16wt.%. The decrease of catalytic activity with higher CeO_2 loadings could be caused by the increase of d_{CuO}.

2.1.3. Catalyst shaping and stability test

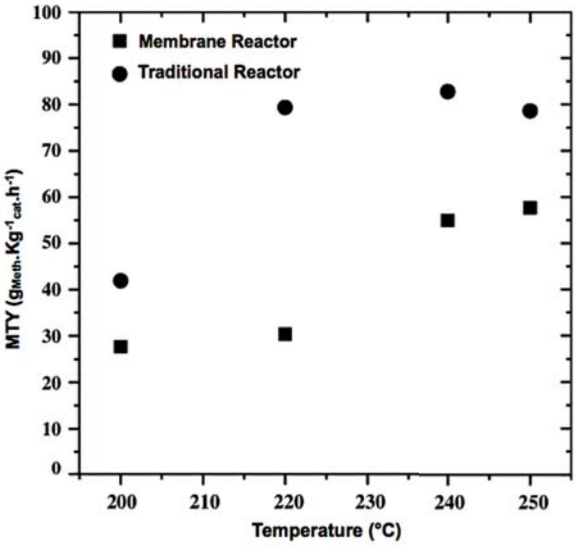


Fig.3. *Methanol yield versus temperature for both membrane and traditional reactors;*

16%Ce + CZ/Al catalyst formulation was chosen to pelletise for industrial application. After the powder has been ground to be suitable for feeding to a pilling machine, it is mixed with a cellulose-typed binder, and then formed into pellets and treated at 280°C. It has been found that treated catalyst pellets still maintain a high BET surface (60m^2/g) and high activity (MTY = 98). Comparisons of CH_3OH productivity of our prepared catalysts with several previous works are given in Table 3. It can be seen that our Ce-based catalyst exhibits a very high stability with time on stream (after 40h on stream).

2.1.4. Application of a membrane reactor to improve the methanol synthesis

The experimental performance of a zeolite membrane reactor has been analysed in comparison to a conventional reaction system. The methanol synthesis from CO_2 and H_2 has been considered versus temperature (Fig.3). The results of this work show a better performance of membrane reactor compared with traditional reactor (TR): at the same temperature, CO_2 conversion for MR was higher than the one related to TR, especially at 220 - 240°C. This improvement can be also seen in the sense that the same methanol yield of TR (at 250°C) can be reached by working with MR over less drastic conditions (at 220°C). This should notably reduce the energy demand.

2.2. CO_2 reforming of natural gas

In this direction, the harmful greenhouse gases, namely CH_4 and CO_2, are reformed to produce valuable synthesis gas (syngas). The catalyst based on Ni/Al_2O_3 was developed with some modification to minimise coke formation on the catalyst surface. Our previous study showed that at the optimal active phase concentration of 15wt.%, the conversions of CO_2 and CH_4 were the highest [12]. Therefore, this catalyst formulation was used for our further modification in order to improve catalyst performance.

For that, magnesium oxide was incorporated in γ-Al_2O_3 to enhance the basicity of support because basicity was believed to promote the activation of acidic CO_2 and suppress carbon formation [13]. Cobalt was used as a secondary active component since a small Ni substitution of Co dramatically enhances the catalyst activity and stability by improved resistance to metal oxidation [14, 15]. All catalysts were prepared by co-precipitation method to achieve highly dispersed metallic particles with small crystal sizes.

Catalytic performance of all samples is indicated in Table 4. The addition of MgO could dismiss coke formation on the catalyst surface. The coke deposited on Ni/Al_2O_3-MgO sample was a haft compared to that on Ni/Al_2O_3 sample. The resistance to coking of Ni/MgO-Al_2O_3 catalyst might be assigned for its high sintering-resistance ability and low acidity of support. The results showed that when the cobalt is incorporated in the catalyst, coke formation decreases. The interaction between metallic species Ni^o - Co^o could cause a synergetic effect that contributes to stabilisation of the catalyst and suppressing coke formation [16]. However, the optimal concentration of cobalt should be about 7.5%. At the Co content of 9wt.%, coke formation on this sample was even higher than that on the sample without Co addition. It could be interpreted by the poorer dispersion of Co on the sample and also the large crystallite size of this sample as shown in Table 4. Our in-house prepared catalyst also showed better performance to a commercial catalyst in term of CH_4, CO_2 conversions as well as H_2, CO yields. The low H_2/CO ratio of the syngas product is also suitable for other downstream processes such as methanol or Fischer-Tropsch synthesis.

3. Future works

Our initial results showed that CO_2 conversion by either direct or indirect routes to fuel or chemical is feasible. The improved catalyst performance by optimisation of

Table 4. *Catalytic performance of the catalyst samples (T = 700°C, CH_4/CO_2 = 1.5/1, GHSV = 12,000ml.h^{-1}.g^{-1})*

Catalysts	$S_{B.E.T}$ (m^2/g)	d_{Ni} (nm)	CH_4 conversion (%)	CO_2 conversion (%)	CO yield (%)	H_2 yield (%)	H_2/CO	Coke (%)
15Ni/ Al_2O_3	99	5.0	73.6	73.9	50.3	51.1	1.2	20.5
15Ni / Al_2O_3 - MgO	82	7.0	66	64.2	39.9	45.4	1.3	11.3
9Ni 6Co/ Al_2O_3 - MgO	75	8.5	68.9	61.0	45.9	53.3	1.4	9.8
7.5Ni 7.5Co/ Al_2O_3 - MgO	76	10.3	65.2	62.8	46.5	53.2	1.3	9.68
6Ni 9Co/ Al_2O_3 - MgO	71	11.5	65.7	63.4	40.6	51.0	1.5	13.4
Commercial (Ni/Al_2O_3-MgO) catalyst	47	-	37.7	63.4	42.2	32.6	0.9	-

catalyst formulation, structure, and catalyst preparation methods will greatly contribute to the overall economics of the process. These promising results pave the way for further investment of research activities, aiming to develop new catalysts and technologies that ultimately could help to efficiently utilise CO_2 and CO_2-rich natural gas in Vietnam. Obviously, there are still many issues to be solved technically and economically. In order to tackle such challenges, PVPro/VPI has established a long-term R&D programme for deep processing of natural gas, in which the issues of CO_2 and CO_2-rich natural gas utilisation are of major importance. The objectives of this programme are to be able to identify the suitable technology as well as to develop pilot plants to convert CO_2 or CO_2-rich natural gas to methanol or fuels with the capacity of 10l/h by 2020.

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