

# Overview of the Hydrogen-Rich Gas Catalyst Mounted on Gasoline Engine

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**Abstract**— Fossil energy is an important source of raw materials and has played a key role in many activities from life to production for many decades. Currently, fossil fuels such as coal, crude oil and natural gas provide nearly 80% of global energy demand. However, the use of this resource causes many negative effects on production, human health and other living things, directly causing long-term damage to the environment. With current fuel consumption, crude oil reserves are predicted to be exhausted within the next 50 years. Therefore, scientists around the world are working to improve fuel consumption and reduce harmful emissions caused by engines. The application of hydrogen fuel or the use of a hydrogen-rich gas mixture to replace fossil fuels in addition to internal combustion engines is considered as a promising secondary energy source that can meet the needs of energy use. world and reduce harmful emissions into the environment through advanced production technologies and methods.

**Keywords**— Hydrogen gas, fossil energy, toxic emissions, fuel, engine.

## I. INTRODUCTION

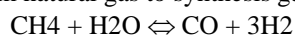
Hydrogen is the lightest element and exists in the gas state, with an atomic weight of 1.00794 C. It mainly exists as atomic hydrogen in the upper layers of the Earth's atmosphere. Its molecular formula is H<sub>2</sub>, it is colorless, odorless, easily flammable, with a boiling point of 20.27 K (-252.87°C) and a melting point of 14.02 K (-259.14°C). Hydrogen crystal has a hexagonal structure, with a valency of 1 and can react with most other chemical elements. Hydrogen can also be directly burned in internal combustion engines or used in fuel cells to produce electricity through the reaction between H<sub>2</sub> and O<sub>2</sub> (in contrast to the electrolysis of water). When hydrogen is burned in an internal combustion engine, the main combustion product is water vapor, so using hydrogen as a fuel for transportation is one of the best ways to reduce emissions that cause environmental pollution.

There are three common methods for producing hydrogen.

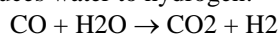
**Electrolysis of water:** Hydrogen only accounts for 10% of the water's mass and can be separated after electrolysis. However, to produce the necessary amount of hydrogen, a large amount of electricity is required. Moreover, the expensive materials used as electrodes increase the cost of producing hydrogen significantly. The solution is to use alternative energy sources for electrolysis, such as hydroelectric power, tidal power, wind power, and solar energy.

**Chemical reaction:** In this method, the raw materials are natural gas, petroleum gas, crude oil, or biogas. For example, when using natural gas with 95% methane, the reaction mechanism is as follows:

Conversion from natural gas to synthesis gas (syngas):



CO reaction reduces water to hydrogen:



**Gasification:** The gasification process is the conversion of fuel (heavy oil, coal, and biomass fuel) into hydrogen by oxidizing the fuel. These fuels require a sufficient amount of oxygen to complete the combustion process underground to produce CO and H<sub>2</sub> gas.

## II. IMPROVING THE EFFICIENCY OF HYDROGEN-RICH GAS CATALYSTS

### 2.1. Current status of catalysts for producing hydrogen-rich gas

The Mo<sub>2</sub>C catalyst system for the iso-octane thermolysis reaction is depicted in Figure 2.1, which illustrates the effect of gas flow rate and steam-to-carbon (S/C) ratio on the Mo<sub>2</sub>C catalyst at 850°C [1]. The gas flow rate is the velocity of gas passing through the reaction volume (the unit of gas flow rate is 1/h). The results indicate that the S/C ratio and gas flow rate have a significant impact on the conversion efficiency of hydrocarbons to hydrogen-rich gas. At low gas flow rates, the conversion efficiency is relatively high, ranging from 75-100%. However, increasing the gas flow rate to over 1.8h<sup>-1</sup> tends to decrease the conversion efficiency. Furthermore, the results show that an S/C mole ratio ranging from 0.8 to 1.1 provides the highest conversion efficiency. The conversion efficiency is the percentage of fuel converted into hydrogen-rich gas by the catalyst from the supplied fuel.

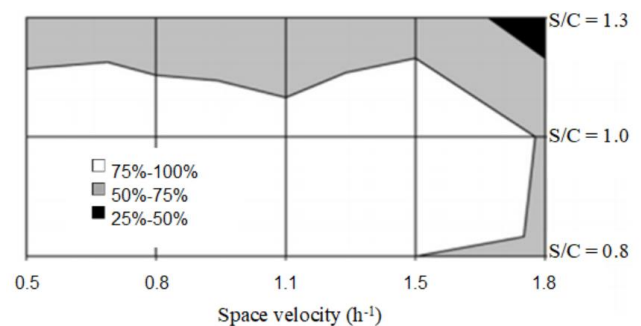


Figure 2.1 shows the conversion efficiency of iso-octane as a function of space velocity

Figure 2.2 illustrates the product distribution as a function of space velocity for the Mo<sub>2</sub>C catalyst system at 850°C [1]. The results indicate that hydrocarbons account for 60-70%, CO for over 20%, and CH<sub>4</sub> and CO<sub>2</sub> for approximately 5-10%. The amount of hydrocarbons increases at higher space velocities

exceeding  $1h^{-1}$ .

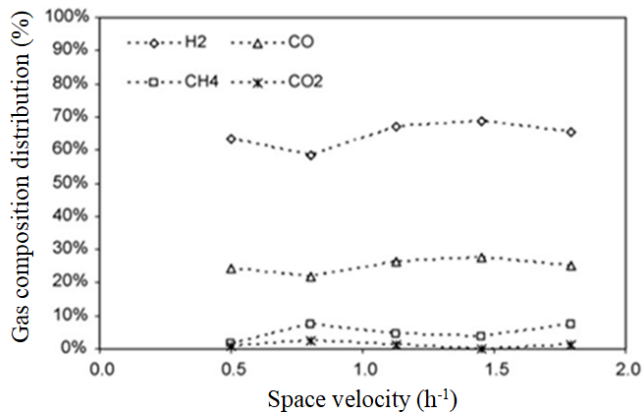


Figure 2.2. The product of the  $Mo_2C$  catalyst system as a function of space velocity at a temperature of  $850^{\circ}C$

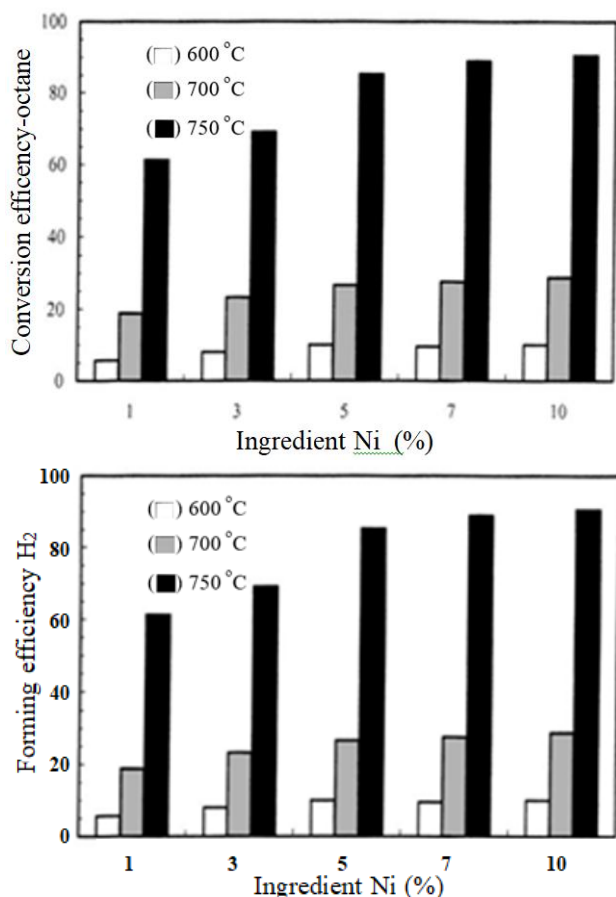


Figure 2.3. Conversion efficiency of n-octane and  $H_2$  yield in the product at  $H_2O/C=3.0$

#### *Ni/Al<sub>2</sub>O<sub>3</sub> catalyst system*

Jinchang Zhang et al. [2], with n-octane replacing gasoline to increase the experimental accuracy. The catalytic efficiency was measured from  $500-750^{\circ}C$ . During the efficiency measurement, the gas product after the reaction was analyzed for its gas components using gas chromatography. At the same temperature, the conversion efficiency of n-octane in the exothermic reaction and the  $H_2$  ratio in the product increased with the increasing weight ratio of Ni in the catalyst system. In addition, with the same Ni ratio, as the reaction temperature

increased, the conversion efficiency also increased. For example, with a 5%  $Ni/Al_2O_3$  catalyst system, the conversion efficiency could reach 85%, with a hydrogen distribution ratio in the product of 75%.

#### 2.2. Research on improving the efficiency of hydro-rich gas catalysts worldwide.

The above research results have shown that the conversion efficiency of traditional catalysts and the ratio of hydrocarbon formation are high when the catalyst temperature is above  $750^{\circ}C$ . Therefore, many studies have focused on improving the catalyst efficiency at lower temperatures. A common solution is to use traditional metal catalysts combined with other metal catalysts. In the following section, the authors will evaluate the effectiveness of some previous studies as a basis for selecting catalysts.

#### *Ni-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst system*

To enhance the efficiency of the Ni catalyst, Jinchang Zhang added a small amount of Palladium into the catalyst sample. The results showed that the catalytic activity increased significantly with the addition of a small amount of Pd, reaching 100% at  $750^{\circ}C$ . In addition, the  $H_2$  ratio in the product reached 92% at  $750^{\circ}C$  with a  $H_2O/C$  mole ratio of 3.0 (Figure 2.3). The major role of adding Pd was to prolong the catalyst system's activity maintenance time, which reached up to 500h (Figure 2.5), much longer than the  $Ni/Al_2O_3$  catalyst system.

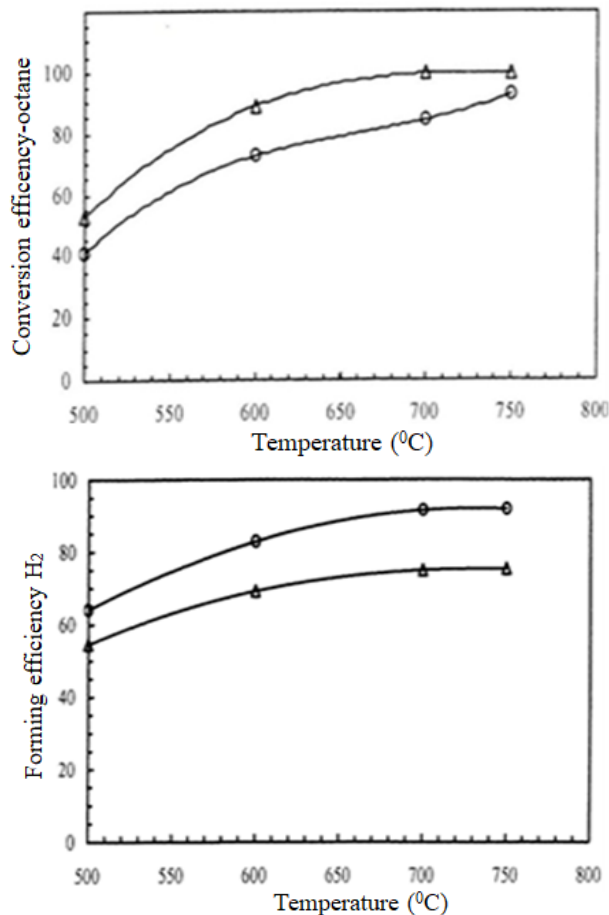


Figure 2.4. Conversion efficiency of n-octane and  $H_2$  yield in the product of  $Pd-Ni/Al_2O_3$  catalyst system when: ( $\Delta$ )  $O_2/C_8H_{18} = 1.0, H_2O/C = 3.0$ ; ( $\circ$ )  $O_2/C_8H_{18} = 2.0, H_2O/C = 3.0$  [2]

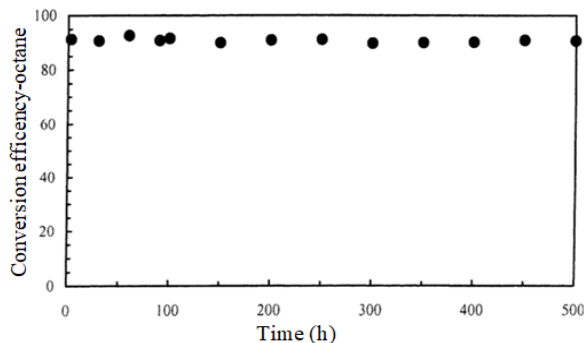


Figure 2.5. Catalytic durability of Ni-Pd/Al<sub>2</sub>O<sub>3</sub> sample [2].

*Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalytic system*

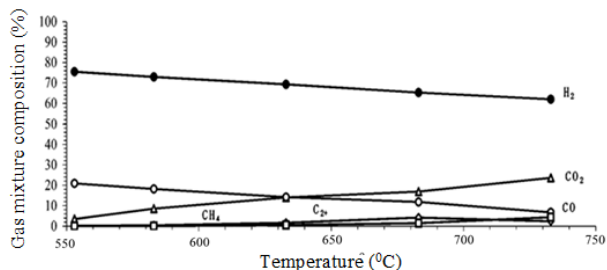


Figure 2.6 shows the efficiency of converting gasoline into a hydrocarbon-rich gas mixture using the Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst at a temperature where the carbon (S:C) ratio is 1.7:1 and the space velocity is 12 h<sup>-1</sup> [3].

Ahmed and M. Krumpelt [3] studied the fuel pyrolysis of gasoline containing 75% MCH (methylcyclohexane) and 25% toluene with steam on the Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst in the temperature range of 550-750°C, as indicated in Figure 2.7. The H<sub>2</sub> concentration decreased from 75% to 68% as the temperature increased from 550°C to 750°C, while CO<sub>2</sub> increased significantly and the gas components CH<sub>4</sub> and C<sub>2</sub> + decreased.

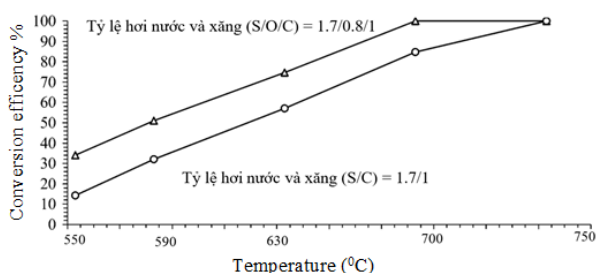


Figure 2.7. Conversion efficiency as a function of temperature and S/O/C and S/C ratios of Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst system at a space velocity of 3 h<sup>-1</sup> [3].

Figure 2.7 shows the conversion efficiency of the Ni-Re catalyst system for gasoline. The results indicate that the addition of Re decreases the conversion efficiency, which can only be improved by the addition of oxygen to the catalyst system, indicating that incomplete oxidation (IO) has been promoted.

*Ni-Ce and Ni-Mo catalyst systems.*

Praveen K. Cheekatamarla et al. [4] studied the Ni-Ce and Ni-Mo catalyst systems, showing that they achieve the best catalytic performance at 550°C. The catalytic performance is described in Tables 2.1 and 2.2.

Table 2.1 shows the conversion efficiency of gasoline to gas

mixtures at a temperature of 550°C and a WHSV of 4 h<sup>-1</sup>, with the fuel consisting of 75% MCH and 25% C<sub>7</sub>H<sub>8</sub> and an S/C/O ratio of 1.7/1/0.3. The results show that the hydro-creation efficiency of the catalyst materials is in the following order: Ni/CeZSM-5>NiMo/ZSM-5>Ni/ZSM-5>NiRe/ZSM-5>Ni/MgZSM-5>Ru/ZSM-5. Ce added to the catalyst system accelerates the catalytic performance and thermal stability of the catalyst.

TABLE 2.1. Efficiency of catalyst materials for gas mixture synthesis at a temperature of 550°C and a space velocity of 4 h<sup>-1</sup>, S/C/O = 1.7/1/0.3 [4].

Catalyst	Efficiency		Metabolic rate (μmols <sup>-1</sup> g <sup>-1</sup> )			
	HC	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>	C1-C3
Ni/ZSM-5	48,9	12,1	66,0	7,0	23,1	9,6
Ni/CeZSM-5	59,3	16,7	83,9	10,9	26,5	10,4
NiMo/ZSM-5	58,9	10,0	57,2	27,8	10,0	5,3
NiMg/ZSM-5	24,6	2,5	17,5	5,5	11,2	2,8
NiRe/ZSM-5	37,3	6,8	44,4	9,4	15,0	5,5
Ru/ZSM-5	23,4	1,1	14,4	5,5	9,4	4,0

T=550°C; The space velocity of the fuel is 4 h<sup>-1</sup>; The fuel is 75%.  
MCH = 25% C-H8; S/C/O = 1.7/1/0.3

The catalytic activity of Ni/CeZSM-5 increases with increasing oxygen in the reaction and reaches the highest conversion efficiency to hydrocarbons (90.8 μmol<sup>-1</sup>g<sup>-1</sup>) corresponding to S/O/C = 1.7/1/0.8 (Table 2.2). In the absence of oxygen in the reaction, the conversion efficiency to hydrocarbons is only 65.6 μmol<sup>-1</sup>g<sup>-1</sup>, corresponding to S/C/O = 1.7/1/0. Therefore, the presence of Ce accelerates the fuel oxidation reaction, thereby promoting the catalytic conversion of CO<sub>2</sub>, CO with fuel and water to release hydrocarbons.

TABLE 2.2. The effect of S/C/O ratio on the fuel conversion efficiency of Ni/CeZSM-5 catalyst at a temperature of 550°C and a WHSV of 4h<sup>-1</sup> [4].

Tỷ S/O/C	lệ	Efficiency		Metabolic rate (μmols <sup>-1</sup> g <sup>-1</sup> )			
		HC	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>	C1-C3
1.7/1/0		38,3	26,7	65,6	7	14,8	8,3
0/1/0.8		39,1	-11,5	25,5	12	14,2	4,8
1.7/1/0.3		42,3	16,4	57,3	7,6	17,6	8
1.7/1/0.5		59,3	16,1	83,9	10,9	26,5	10,4
1.7/1/0.8		69,1	2,8	90,8	12,8	32,8	9,3
1.7/1/1.4		67,5	-12	54,4	10,2	35,7	7,4

T=550°C; The space velocity of the fuel is 4 h<sup>-1</sup>; The fuel is 75%.  
MCH = 25% C-H8; S/C/O = 1.7/1/0.3

*Cu/CeO<sub>2</sub> and Ni-Cu catalyst system*

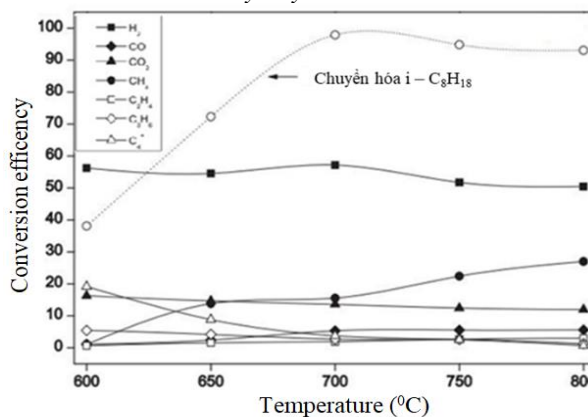


Figure 2.8. Change of reaction efficiency and product selectivity of Cu/CeO<sub>2</sub>

catalyst system with temperature ( $p_i-C_8H_8=1.5$  kPa,  $p_{H_2O}=36$  kPa,  $m_{cat}=250$ mg,  $F_t=150$  cm<sup>3</sup>/min) [5]

Hoang Dinh Long, Chan Siew Hwa and Ding Ovi Lian [5] studied and showed that with Cu/CeO<sub>2</sub> catalyst system, to achieve high efficiency, relatively high temperature is still required. When the reaction temperature reaches over 700°C, the gasoline conversion efficiency can reach over 90%. The product selectivity of the Cu/CeO<sub>2</sub> catalyst system is also relatively stable. In the surveyed temperature range (600-700°C), the percentage of H<sub>2</sub> in the product always reaches 50-60% and the percentage of harmful CO gas is very low, less than 5% (Figure 2.8). This can be explained by the catalytic ability of Cu for the CO oxidation reaction to generate CO<sub>2</sub>, reducing the amount of CO in the product.

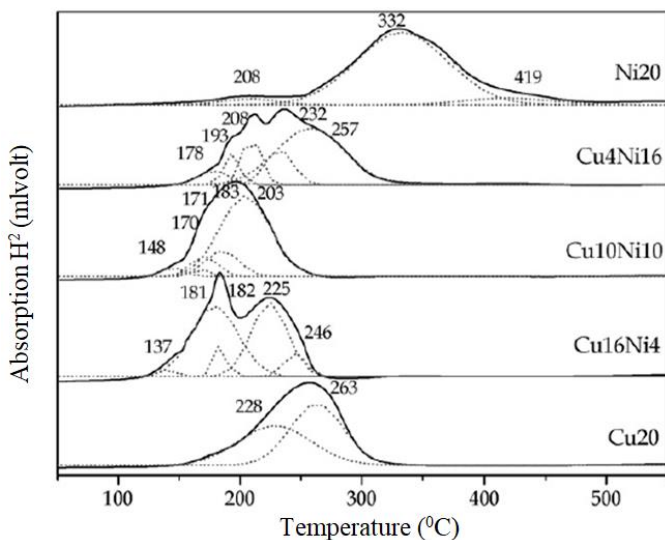


Figure 2.9. Temperature-dependent reduction characteristics of Ni-Cu catalyst samples [5]

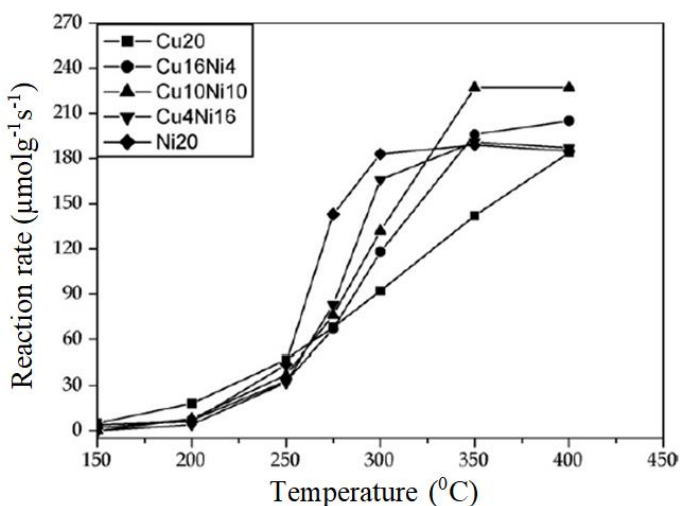


Figure 2.10. Reaction rate of Ni-Cu catalyst samples [6]

Jiann-Hong Lin [6] conducted a study and demonstrated the performance of the Ni-Cu/CeLaOx catalyst system for ethanol fuel reforming. The results indicated (Figure 2.9) that the Ni/CeLaOx catalyst system achieved efficient reduction reaction at temperatures ranging from 200-400°C, with a

reduction peak appearing at 332°C. When Cu was added to the catalyst system, the reduction reaction temperature decreased. With the Cu<sub>4</sub>-Ni<sub>16</sub> catalyst system, the reduction peak appeared at temperatures ranging from 178-257°C. As the Cu content was further increased to Cu<sub>16</sub>-Ni<sub>4</sub>, the reduction temperature decreased to 137-246°C. When using the Cu/CeLaOx catalyst system alone, the reduction temperature increased (228-263°C), but still remained lower than that of the Ni/CeLaOx catalyst system (Figure 2.10).

Figure 2.10 illustrates the results of the reaction rate of catalyst samples. The Cu<sub>20</sub> catalyst sample showed efficient reaction at low temperatures ranging from 150-200°C [6]. Several other studies [7-9] also showed the effectiveness of reducing the reaction temperature of ethanol reforming when using Ni-Cu catalyst systems.

### 2.3. Advanced studies on hydro-rich gas catalysts in Vietnam

Research on hydro-rich gas production on board to supply internal combustion engines has not been extensively studied, and there are no complete studies on this issue. Hoang Dinh Long and Nguyen The Luong [10] conducted a study and equipped a catalyst system to transform fuel thermochemistry. Gasoline is used to reduce emissions from engines, but the impact of installing a catalyst on engine emissions has only been evaluated, and the working characteristics and hydrocarbon content of the catalyst have not been assessed. These catalysts utilize heat, water vapor, and oxygen in the exhaust gas to convert the thermal energy of gasoline; the feedstock includes gasoline and recycled exhaust gas. With this principle, the catalyst does not require an external heat source, oxygen, and water vapor, so it has a compact structure. However, the amount of hydrocarbons produced is limited due to the low amount of water vapor and oxygen in the exhaust gas. On the other hand, the rich hydrocarbon gas product of the catalyst used for the engine is diluted by the exhaust gas with high nitrogen and carbonic levels, resulting in a significant reduction in engine power. Author Pham Ngoc Anh [11] researched using Ni/Al<sub>2</sub>O<sub>3</sub> catalysts to create hydrocarbon-rich gas supplied to the engine by utilizing exhaust gas heat. The author's research only stopped at the catalyst manufacturing and installation on the engine, with no specific evaluation of the catalyst's efficiency. The engine test results showed that at 100% throttle, the engine power did not change significantly while fuel consumption decreased by 11.53%, CO and HC decreased by 74% and 29%, respectively. However, the study also showed that the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst only achieved high efficiency at a catalyst temperature above 700°C or when the engine was operating under heavy load. In contrast, the exhaust gas temperature of the engine during low and medium load conditions was only around 450-550°C, resulting in low hydrocarbon gas production efficiency.

### III. CURRENTLY APPLIED SOLUTIONS

Studies both domestically and internationally have shown that using fuel transformation catalysts to directly provide hydro-rich gas to engines has great potential in increasing the economic and technical performance of engines while reducing emissions. The issue of transporting and storing hydro gas is no

longer a concern. As mentioned above, it can be seen that the single-metal catalyst systems Ni/Al<sub>2</sub>O<sub>3</sub> and Mo<sub>2</sub>C begin to achieve high efficiency when the catalyst temperature is above 700°C, while the exhaust gas temperature of a conventional engine is only about 450-550°C. Therefore, the exhaust gas temperature is not sufficient to provide the traditional hydro-gas catalyst system with high efficiency. Studies have also shown that when adding metals to the single-metal system to form a dual-metal catalyst system, the catalyst efficiency is improved, the reaction temperature is significantly reduced (suitable for the exhaust temperature of the engine), and the activity maintenance time of the catalyst is increased. When Pd is added to the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst system, the results show that the hydro conversion efficiency reaches a very high 92% and the catalyst durability is greatly increased (10 times higher than the traditional Ni/Al<sub>2</sub>O<sub>3</sub> catalyst system). However, Pd is a precious metal and very expensive. Studies have also shown that when adding Ce, Mo to the Ni/Al<sub>2</sub>O<sub>3</sub> and Cu/CeO<sub>2</sub> systems, they have good activity for the catalyst conversion efficiency while achieving high efficiency in the engine working range and reducing the cost of the catalyst. Therefore, in this study, we will evaluate the new catalyst systems Ni-Cu/Al<sub>2</sub>O<sub>3</sub>, Ni-Ce/Al<sub>2</sub>O<sub>3</sub>, Ni-Mo/Al<sub>2</sub>O<sub>3</sub> to determine the appropriate catalyst system to be installed in vehicles for manufacturing and testing purposes.

#### IV. CONCLUSION

Through analyzing solutions to improve the work efficiency and reduce the emission of harmful pollutants from engines, using hydro-enriched gas as a feasible solution can help to reduce the total amount of greenhouse gas emissions into the environment. Hydrogen can entirely be a replacement fuel for gasoline and diesel oil due to its high heat value and unlimited fuel source. Most of the widely published research studies worldwide demonstrate that the thermal efficiency of the engine is improved, the two main emission components of CO and HC are significantly reduced, and NO<sub>x</sub> increases when hydro-enriched gas is added to the intake path. These results are an

important basis for experimental research to assess the potential for improving efficiency and reducing emissions for combustion engines by supplying hydro-enriched gas mixture to the engine.

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