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Deactivation and Regeneration Method for Ni Catalysts by H$_2$S Poisoning in CO$_2$ Methanation Reaction

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Abstract: The carbon dioxide (CO$_2$) methanation reaction is a process that produces methane (CH$_4$) by reacting CO$_2$ and H$_2$. Many studies have been conducted on this process because it enables a reduction of greenhouse gases and the production of energy with carbon neutrality. Moreover, it also exhibits a higher efficiency at low temperatures due to its thermodynamic characteristics; thus, there have been many studies, particularly on the catalysts that are driven at low temperatures and have high durability. However, with regards to employing this process in actual industrial processes, studies on both toxic substances that can influence catalyst performance and regeneration are still insufficient. Therefore, in this paper, the activity of a Ni catalyst before and after hydrogen sulfide (H$_2$S) exposure was compared and an in-depth analysis was conducted to reveal the activity performance through the regeneration treatment of the poisoned catalyst. This study observed the reaction activity changes when injecting H$_2$S during the CO$_2$ + H$_2$ reaction to evaluate the toxic effect of H$_2$S on the Ni-Ce-Zr catalyst, in which the results indicate that the reaction activity decreases rapidly at 220 °C. Next, this study also successfully conducted a regeneration of the Ni-Ce-Zr catalyst that was poisoned with H$_2$S by applying H$_2$ heat treatment. It is expected that the results of this study can be used as fundamental data in an alternative approach to performance recovery when a small amount of H$_2$S is included in the reaction gas of industrial processes (landfill gas, fire extinguishing tank gas, etc.) that can be linked to CO$_2$ methanation.

Keywords: methanation; CO$_2$ utilization; CO$_2$ conversion; deactivation; regeneration; H$_2$S poisoning
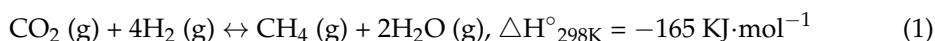
1. Introduction

Many abnormal climate phenomena, which have been recently occurring globally due to global warming, are causing various problems associated with the survival of mankind and preservation of the ecological environment. According to the 6th Report of the International Panel on Climate Change (IPCC), the current climate conditions revealed that the global surface temperature has increased by 1.09 °C between 2011 and 2020 compared to pre-industrialization (1850–1900s) [1], thereby resulting in extreme weather changes. In addition, countries around the globe exert to establish countermeasures to reduce global warming based on the expectation that the frequency and intensity of extreme weather changes will worsen when the average temperature rises further by 0.5 °C. For instance, various policies are being introduced to implement carbon-neutral solutions that can alleviate the situation from deteriorating, and a carbon-neutral approach, in particular, is being developed in the field of energy production where large amounts of carbon are discharged [2,3].
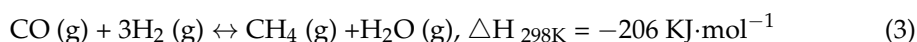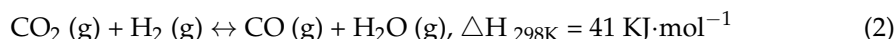
CO$_2$ methanation is one of the methods of CO$_2$ applications for carbon-neutral solutions. It is a process that produces methane by reacting CO$_2$ with H$_2$. This process is mainly used as part of the Power-to-Gas (PtG) technology, which produces methane by reacting the CO$_2$ emitted from industrial activities with H$_2$, produced via electrolysis.

The advantage of this process enables the synthetic methane to interface directly with the existing natural gas infrastructure [4–6].

CO$_2$ methanation has been generally well-known as the Sabatier reaction, in which CO$_2$ generates heat while being converted to CH$_4$ and is operated at 200–550 °C depending on the catalyst (Equation (1)) [7–9].

$$CO_2 \text{ (g)} + 4H_2 \text{ (g)} \leftrightarrow CH_4 \text{ (g)} + 2H_2O \text{ (g)}, \triangle H°_{298K} = -165 \text{ KJ·mol}^{-1} \tag{1}$$

This reaction (Equation (1)) is assumed to be the mechanism of the two-step reaction (Equations (2) and (3)), according to Stangeland et al. [10]:

$$CO_2 \text{ (g)} + H_2 \text{ (g)} \leftrightarrow CO \text{ (g)} + H_2O \text{ (g)}, \triangle H_{298K} = 41 \text{ KJ·mol}^{-1} \tag{2}$$

$$CO \text{ (g)} + 3H_2 \text{ (g)} \leftrightarrow CH_4 \text{ (g)} + H_2O \text{ (g)}, \triangle H_{298K} = -206 \text{ KJ·mol}^{-1} \tag{3}$$

The CO$_2$ methanation reaction mainly uses Vlll group metal-based materials such as Ni, Pt, Pd, and Ru, and catalysts are prepared by various methods, such as impregnation, solution combustion, and plasma decomposition (Supplementary Table S1) [11–18]. Among them, the Ni catalyst is known for its low price and high reactivity in commercial processes [19].

The CO$_2$ used in CO$_2$ methanation can be obtained from various industrial processes, power plants using fossil fuels, and emissions from biogas plants [20–22]. Of these, the exhaust gas from the biogas industry is generally composed of 50–75% CH$_4$, 50–25% CO$_2$, 0–10% N$_2$, and 0–3% H$_2$S, including gases that are deactivated by the catalytic activity [23,24]. Although the catalysts used in the industrial process are not consumed and can be used repeatedly, when used for a long time, some problems occur, such as decreased durability and reduced activity caused by pollutants. The most severe issue is a toxicity phenomenon that reduces the activity and lifespan of a catalyst. In a recent investigation on CO$_2$ methanation based on H$_2$S gas exposure, David et al. compared the activity performance after adding Mo, Fe, Co, and Cr to the Ni catalyst to enhance its sulfur resistance [23]. Gac et al. tested the activity by exposing 8 ppm H$_2$S using a Ni catalyst supported by alumina, and their study reported that once exposing H$_2$S to a reactant, the Ni activation sites, which activate CO$_2$ and H$_2$ and are continuously converted into the carbonyl and formate species, are blocked [25]. As such, recent studies have been conducted on either the production of catalysts to enhance the sulfur resistance or the mechanism that deactivates the catalysts using Ni-based catalysts [26]. However, studies considered measures to cope with the actual process are not sufficiently available among the measures to regenerate the poisoned catalysts with H$_2$S for a long time. In addition, no sufficient studies are available regarding dynamic activity changes in temporary driving condition changes.

This study employed a Ni-Ce-Zr catalyst with excellent performance attained through precedent studies and observed the activities of CO$_2$ conversion for each reaction temperature under H$_2$S exposure according to concentration. Moreover, this study verified the activity when exposed for a long period of time at a specific temperature and observed whether the performance is recovered by selecting an appropriate regeneration method for the poisoned catalyst.

2. Results and Discussion

2.1. Activity Evaluation of a Poisoned Catalyst

In this study, the CO$_2$ methanation reaction was observed while injecting H$_2$S by adjusting its concentration in the range of 0~100 ppm at temperatures of 180–350 °C (Figure 1). Results of the experiment indicate that fresh catalysts with no H$_2$S injection exhibited a high CO$_2$ conversion of 90~85% at 350–240 °C, and a minor decrease in the CO$_2$ conversion occurred from 220 °C and was measured to be 76%. In contrast, when H$_2$S gas was injected at 25~100 ppm, the decrease in the conversion was not significant compared with the case of the fresh catalyst up to 350–260 °C; however, the performance decrease was observed from 240 °C and measured 14% at 220 °C. The reduction rate of

the CO_2 conversion did not significantly differ with H_2S concentrations between 25 and 100 ppm, but decreased significantly at 220 °C.
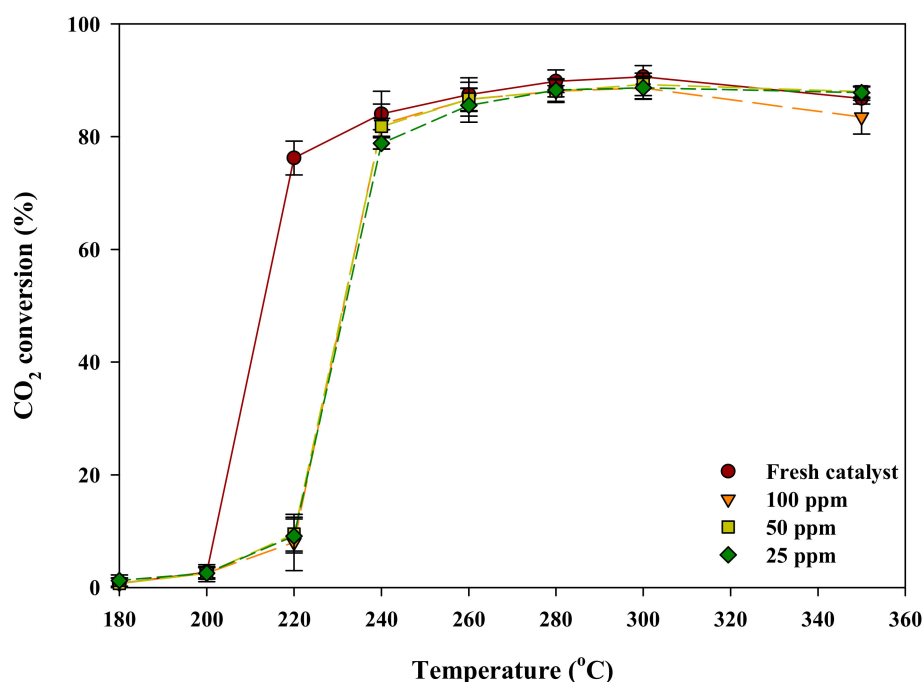

Figure 1. Activity influence of the Ni-Ce-Zr catalyst by H_2S concentration in the CO_2 methanation reaction (total flow of 120 cc/min, GHSV 2880 h^{-1}, H_2: CO_2 = 4:1, CH_4 selectivity 1).

When observing the CO_2 methanation reaction by exposure to the H_2S gas shown in Figure 1, it can be observed that the effects of H_2S are different at high (300 °C) and low (220 °C) temperatures. Therefore, CO_2 conversion was observed for 300 min under H_2S exposure at specific temperature ranges. As shown in Figure 2, the toxicity influence of the H_2S gas was not observed during the CO_2 methanation reaction, demonstrating a conversion rate of 89–90% at 300 °C. However, it was verified that the CO_2 conversion decreased from 14% to 8% as the H_2S exposure time increased at 220 °C (Figure 3). It is believed that the deposition of impurities at the activation point increases according to the exposure time of H_2S at low temperatures, thereby lowering the conversion rate. These results agree well with those of a precedent study that demonstrated that the sulfur compounds, which are the impurities, retard the reduction of CO_2 during the reaction by blocking the pores on the surface of a catalyst, and the catalyst is deactivated due to the very strong adsorption of H_2S to Ni [27].

2.2. Regeneration Effects

In this study, the catalyst poisoned with H_2S was regenerated through the heat treatment of H_2 gas, and the performances of the catalyst before and after toxicizing are compared and illustrated in Figure 4. First, it was verified through the previous experiment whether the CO_2 conversion, which rapidly decreased at 220 °C, recovers to the initial CO_2 conversion by blocking the H_2S injection. The results showed an increase of only 2–3%. Based on the above, it is deemed that the substances generated from the reactants or products during the reaction process accumulate on the surface of the solid catalyst to reduce the catalytic efficiency rather than degrade the performance by the reaction with the reactant (H_2 + CO_2 + H_2S) during the CO_2 methanation. Therefore, it is necessary to eliminate the toxic composition that degrades the reaction performance or to supplement the active catalyst component that reacts with the toxic composition. In this study, the catalyst was regenerated at 350 °C for 1 h using H_2 gas (100 cc/min), which is a CO_2 methanation reactant, as one of the regeneration methods, under the condition that the poisoned catalyst

in the actual process was installed. As a result, it was found that the catalyst performance was recovered to the result before being poisoned, which is approximately 76% at 220 °C.
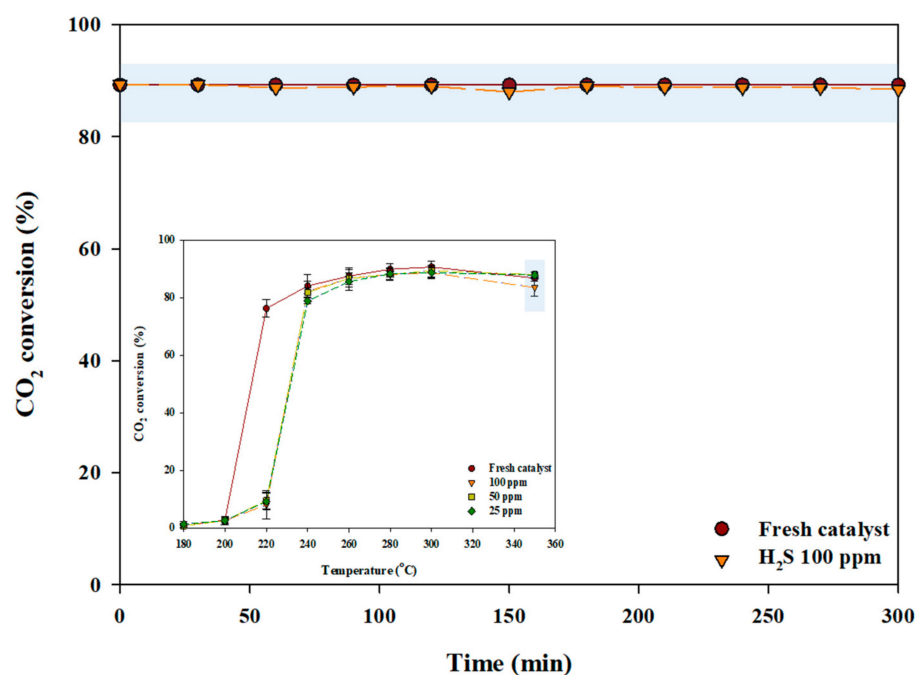

Figure 2. CO_2 methanation activity evaluation of the Ni-Ce-Zr catalyst under the conditions of 100 ppm H_2S at 300 °C (total flow of 120 cc/min, GHSV 2880 h^{-1}, H_2: CO_2 = 4:1, CH_4 selectivity 1).
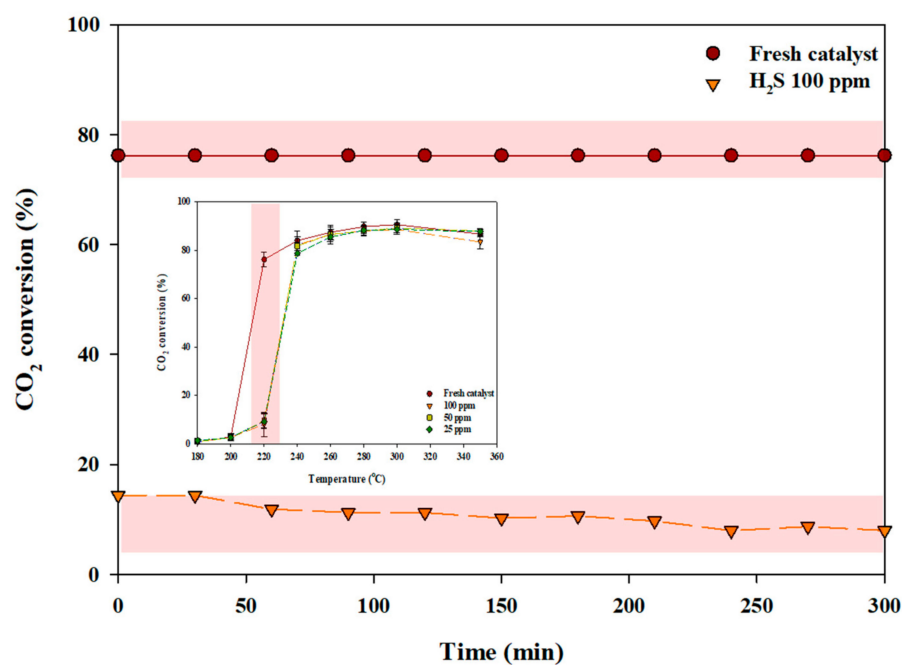

Figure 3. CO_2 methanation activity evaluation of the Ni-Ce-Zr catalyst under the conditions of 100 ppm H_2S at 220 °C (total flow of 120 cc/min, GHSV 2880 h^{-1}, H_2: CO_2 = 4:1, CH_4 selectivity 1).
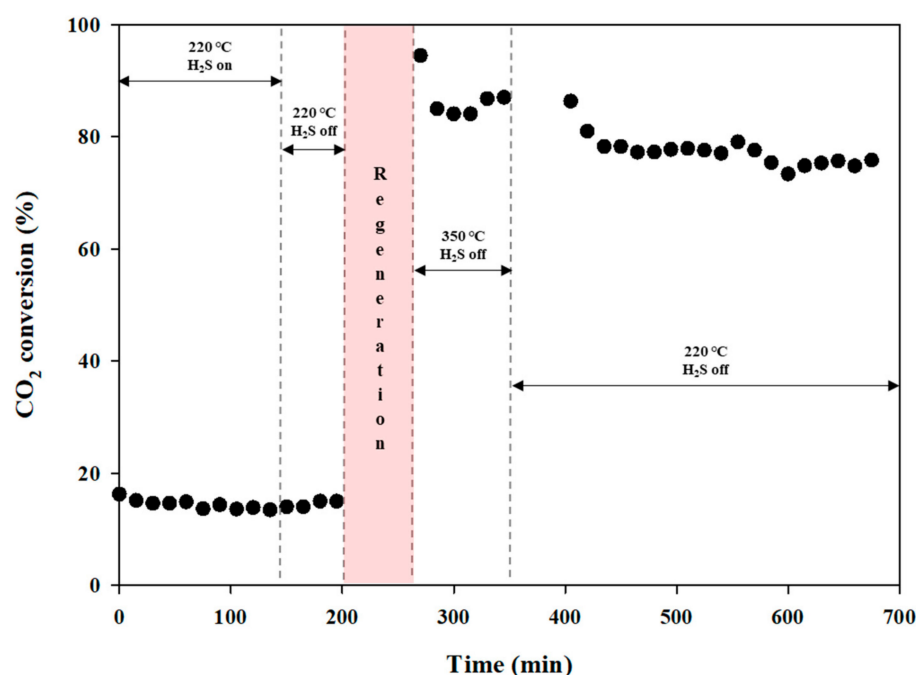
Figure 4. Activity analysis of both the poisoned and regenerated catalysts for a consecutive timeframe (total flow of 120 cc/min, GHSV 2880 h^{-1}, H_2: CO_2 = 4:1, H_2S 100 ppm).

According to a study by Gac et al., H_2S arriving at the surface of a metal catalyst is dissociated and adsorbed to form sulfides on the nickel (Ni) surface in accordance with the reaction Equation (4):

$$H_2S + xNi \rightarrow Ni_xS + H_2 \tag{4}$$

The sulfides on the Ni surface exhibit much more stability than bulk sulfides, and such stability decreases as the temperature increases. Moreover, their study reported that the adsorption of sulfur could be regarded as an irreversible process at low temperatures [25]. Therefore, it was verified that the result of this experiment, i.e., the regeneration was successful through H_2 heat treatment at high temperatures, agrees well with the results of the precedent study.

In addition, whether a decrease would occur in the performance through the repetition of continuous poisoning and regeneration was evaluated, as shown in Figure 5. The experiment was conducted continuously for more than 2700 min, and no decrease in performance was observed as a result of poisoning and regeneration 3 times. Through these results, it is believed that it is appropriate as a regeneration method for repeated poisoning.

2.3. Catalyst Characterization

An X-ray diffraction (XRD) analysis was conducted, and the resulting patterns are shown in Figure 6 to observe the structural changes in the catalyst and the existence of substances other than the catalyst component before and after the H_2S gas exposure. The peaks of Ni, ZrO_2, and CeO_2 can be observed on the surfaces of both fresh (before exposure) and spent (after exposure) catalysts, and no structural changes are observed. In addition, it was expected that substances in the sulfate species would be identified in the case of the spent catalysts, but nothing was detected through the XRD analysis. Therefore, the difference between fresh and spent catalysts could not be identified by XRD analysis.
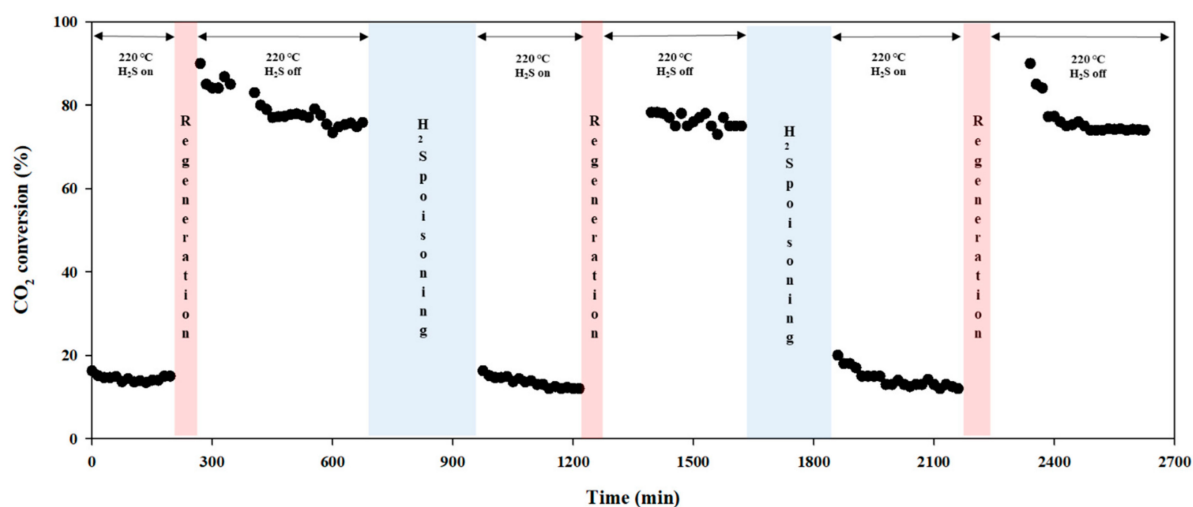
Figure 5. Activity evaluation of poisoned and regenerated catalysts for a consecutive timeframe (total flow of 120 cc/min, GHSV 2880 h^{-1}, H_2: CO_2 = 4:1, H_2S 100 ppm).
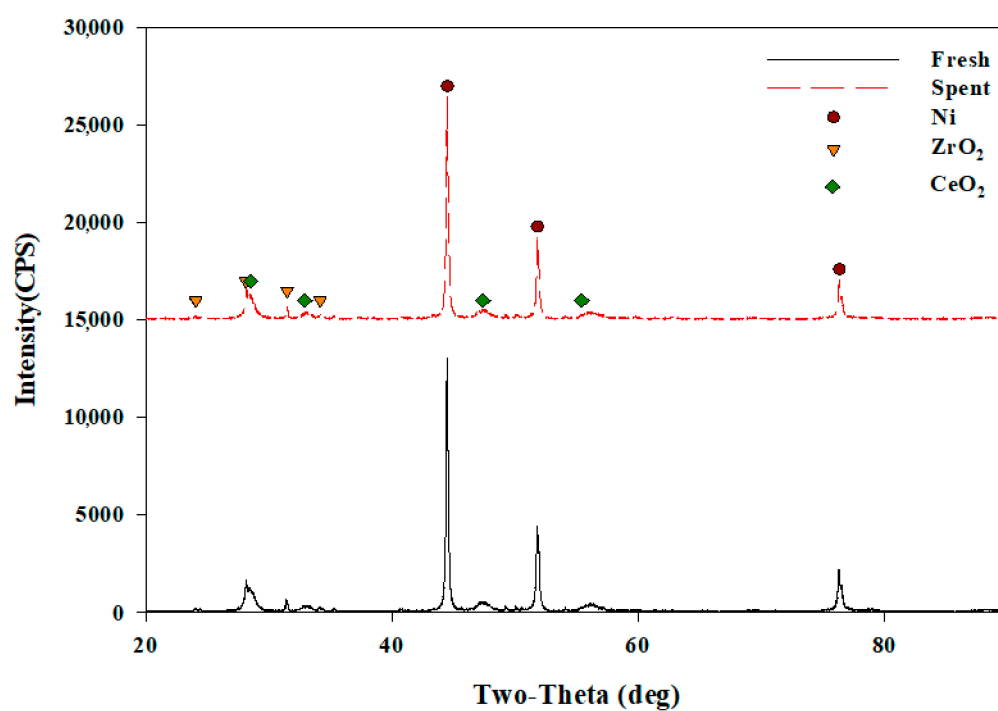

Figure 6. XRD patterns of fresh and spent catalysts.

In this regard, according to the results of the precedent experiment, it was determined that sulfides were formed on the surface of the catalyst by sulfate species, and EDS analysis was performed to verify this (Table 1).

Table 1. EDS analysis results of the catalysts before and after exposure to H_2S as well as the regeneration catalyst.

Element	Fresh (before Exposure)	Spent (after Exposure)		Regeneration
		300 °C	220 °C	
	wt.%	wt.%	wt.%	wt.%
C	9	8	9.4	13.9
O	8.1	6.1	3.3	10
Ni	61.4	61.1	59.3	53.3
Zr	5.2	6.5	2.4	5.6
Ce	16.3	18.4	5.4	17.3
S	-	-	20.2	

This study analyzed the surfaces of both the fresh catalyst before the exposure to H_2S and the catalysts poisoned with H_2S for more than 5 h at 300 and 220 °C, respectively. Through the corresponding analysis, it was verified that approximately 20% of S existed at 220 °C, whereas S was not identified on the surface of the fresh catalyst and the catalyst exposed to H_2S at 300 °C. It is deemed that the S is adsorbed on the catalyst surface to block the activation point, thereby lowering the efficiency, which agrees well with the CO_2 methanation results shown in Figures 2 and 3. In addition, S was not found on the catalyst of which the performance was recovered through the H_2 heat treatment. Through this, this was considered as an appropriate regeneration method.

To evaluate the difference in physical properties caused by toxicizing, BET characterizations of the fresh and spent catalysts, which were exposed to the H_2S gas for more than 5 h at 220 °C, were measured. The BET surface area decreased from 7.04 to 6.89 m^2/g. The total pore volume and average pore diameter decreased from 0.035 cm^3/g and 19.8 nm to 0.024 cm^3/g and 13.9 nm, respectively (Table 2). It was deemed that the difference between the fresh and the spent catalysts was not considerable because there was no significant difference between the two catalysts, although a decrease in the specific surface area of the poisoned catalyst was identified.

Table 2. BET results of fresh and spent catalysts.

Ni/Ce/Zr	BET (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Fresh	7.04	0.035	19.8
Spent	6.89	0.024	13.9

3. Materials and Methods

3.1. Catalyst Preparation

This study used a Ni-Ce-Zr catalyst for which excellent CO_2 methanation performance was proven in the precedent study [28]. The Ni-Ce-Zr catalyst was prepared using the following reagents: Ni powder (99.7%, Aldrich Chemical Co., St. Louis, MO, USA), Cerium nitrate hexahidrate (Aldrich Chemical, St. Louis, MO, USA), and Zirconium oxide (Aldrich Chemical Co., St. Louis, MO, USA), by the wet impregnation method. The Ni, Ce, and Zr were mixed together into the catalyst by the calculated weight ratio of 1:0.2:0.3, respectively. After stirring the mixed solution in a slurry state for over 1 h, the moisture content in the solution was evaporated using a rotary vacuum evaporator (DAIHAN Scientific Co., Seoul, Korea). Afterward, to eliminate the moisture content contained in the micropores, the solution was dried in a dry oven for 24 h and then calcined at 500 °C.

3.2. Experimental Apparatus and Activity Test

A fixed bed reactor was used in the CO_2 methanation experiment. As shown in Figure 7, it is largely composed of a gas injection part, a main reactor, and a reaction gas analysis device. The flow rates of H_2, CO_2, N_2, and H_2S gases supplied in the gas injection inlet were adjusted constantly through a mass flow controller (MFC, MKS Co., Andovor, MA, USA). The ratio of H_2, CO_2, and N_2 was fixed at the rate of 4:1:1, and H_2S gas was injected by adjusting its amount according to the concentration and reducing the injection amount of N_2 gas. The total flow rate of gases was 120 cc/min. The activity test was conducted at a reaction temperature range between 350 and 180 °C. After the reaction, the moisture component contained in the reaction gas was eliminated by passing the reaction gas though a cold trap before flowing into the analyzer. Afterward, the behaviors and properties of the reaction gas were analyzed using gas chromatography (YL 6500GC).
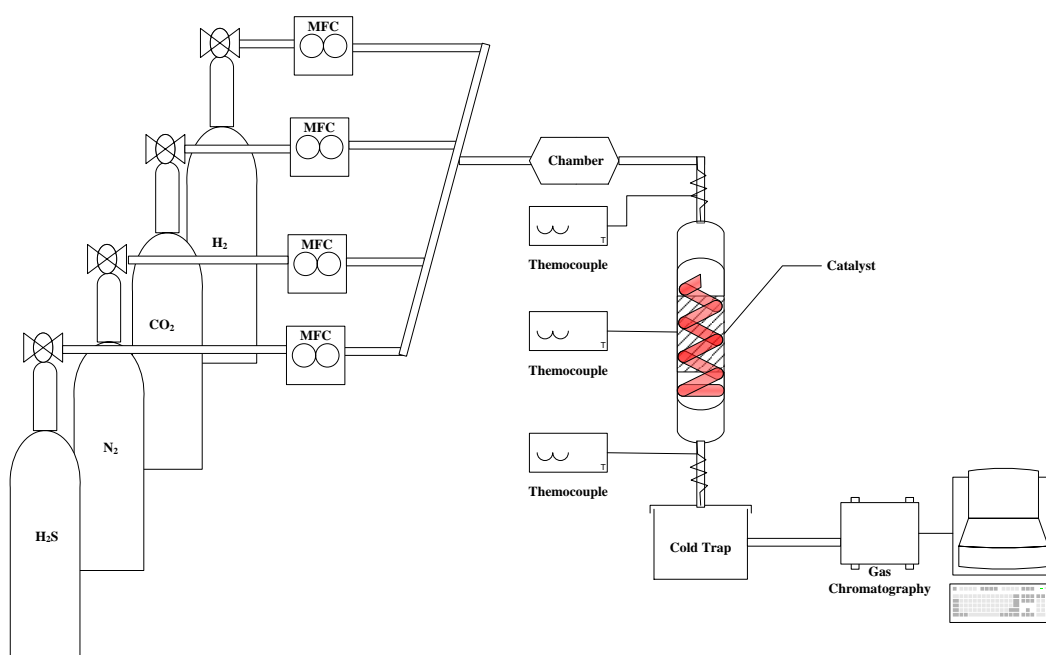

Figure 7. Configuration diagram of the CO_2 methanation reaction device.

The GHSV of the catalyst was calculated using Equation (5) and the experiment was performed at 2880 h^{-1}. The reaction activity of the catalyst is represented by conversion to CO_2, which is a reaction gas, and was calculated using Equations (6) and (7):

$$\text{GHSV (Gas Hour Space Velocity)}\left(\text{hr}^{-1}\right) = \frac{Q_{in}}{V_{cat.}} \tag{5}$$

$$\text{CO}_2 \text{ conversion (\%)} = \frac{\text{CO}_{2\text{IN}} - \text{CO}_{2\text{OUT}}}{\text{CO}_{2\text{IN}}} \times 100 \tag{6}$$

$$\text{CH}_4 \text{ selectivy} = \frac{\text{CH}_{4\text{OUT}}}{\text{CH}_{2\text{IN}} - \text{CH}_{2\text{OUT}}} \tag{7}$$

3.3. Catalyst Characterization

The physical and chemical characteristics of the catalysts used in this study were analyzed through XRD, EDS, and BET. To obtain information regarding the crystalline substances on the surface of the catalysts, the XRD was analyzed with a high-power X-ray diffractometer (HR-XRD) (Rigaku co., Tokyo, Japan). The radiation source was Cu (40 kV, 150 mA) and the measurement was conducted in the range of 2θ = 20–50°. To verify the presence of S on the surface of the catalysts, EDS was analyzed using a field-emission scanning electron microscope/energy dispersive X-ray spectrometer (FE-SEM/EDS) (JEOL

co., Tokyo, Japan). The analysis was performed on the catalysts before and after the exposure to H_2S as well as the regenerated catalyst. The BET was analyzed using a Tristar II Surface Area and Porosity Analyzer (Micromeritics, Norcross, GA, USA) to measure the specific surface area of the catalyst particle.

4. Conclusions

This study observed the CO_2 methanation reaction activity by H_2S toxicizing of a Ni-Ce-Zr catalyst and the successful regeneration of the catalyst through an H_2 gas heat treatment. The following section presents the conclusions of this study.

During the CO_2 methanation reaction, the conversion rates of 95–76% were demonstrated in the temperature range of 220–350 °C in the case of a fresh catalyst with no H_2S injection, whereas the conversion rate dramatically dropped from approximately 70% to approximately 10% when injecting H_2S gas at 25–100 ppm at 220 °C. No significant difference in the activity performance was observed based on H_2S concentration (range between 25 and 100 ppm) at this time.

When exposed to H_2S, changes during long-term activity were observed in both the case at 300 °C with no performance decrease and the case at 220 °C with a rapid performance decrease by mixing 100 ppm H_2S with each of the two reactants. As a result, no activity change was observed for 5 h for the case at 300 °C, whereas the activity gradually decreased from 14% to 8% as the exposure time to H_2S grew for the case at 220 °C.

The poisoned catalyst was regenerated using H_2 gas at 350 °C. The results confirmed that the performance was recovered to 76%, which is the performance efficiency of the catalyst before being poisoned, at 220 °C. In addition, it was confirmed that the CO_2 conversion recovered without a performance decrease despite the continuous and repeated poisoning and regeneration process. Results of the BET analysis indicate that S was observed on the surface in the case of the poisoned catalyst, whereas no S was found on the catalyst of which the performance was recovered through H_2 gas heat treatment. This is a method to regenerate a catalyst at the temperature range close to an actual operating temperature using H_2 gas that is a CO_2 methanation reactant, and from the results thus far, it is believed that this method can be applied to actual industrial processes to regenerate poisoned catalysts in the simplest way.

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