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Hydrogen production by steam reforming (SR) of DME over Cu catalysts and de-NOx performance of a combined system of SR + LNT

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ABSTRACT

This study was performed to develop a DME SR catalyst with high H_2 selectivity using a heat source and water in the exhaust emissions of vehicles. The final goal of the research is to develop a combined system of SR + LNT for improving the de-NOx performance of the catalyst system in a DME engine. The scope of this research encompasses the optimization of the Cu concentration for the SR catalyst, evaluation of the NOx conversion efficiency of the LNT catalyst according to the kind of reductant (H_2, CO, and DME), and evaluation of the de-NOx performance of the LNT catalyst and a combined system of SR + LNT. As a result of experiments concerning DME SR catalysts manufactured through the sol–gel method, the Cu20%/γ-Al_2O_3 catalyst showed the highest DME conversion and H_2 selectivity. The combined system of SR + LNT using a Cu20%/γ-Al_2O_3 SR catalyst increased the NOx conversion by about 20% compared to the LNT catalyst alone at temperatures over 300 °C. In the combined system of SR + LNT, a supply of 1% of DME results in a higher NOx conversion than a supply of 0.75%, but results in NH_3 slip and higher fuel consumption; therefore, supplying 0.75% of DME is favorable.

1. Introduction

DME has the appearance of an excellent and efficient alternative fuel for use in a diesel engine. It promises smoke-free combustion because of a high oxygen content of 34.8% and cetane number of 55 [1]. A DME engine has slightly lower NOx (nitrogen oxide) emissions than a diesel engine. It can reduce NOx emissions further through EGR (Exhaust Gas Recirculation). However, excessive use of EGR results in output reduction due to the lower combustion enthalpy; therefore, the EGR rate is limited. Thus, the reduction of NOx is an important challenge when DME is applied to diesel engines [2,3]. Various NOx reduction methods such as LNT (Lean NOx Trap), Urea-SCR (Selective Catalytic Reduction) [4,5], and HC-SCR are well known as after-treatment systems. Urea-SCR is the most effective among these techniques, and is employed mainly to reduce NOx in the case of heavy-duty diesel engines [4,5]. On the other hand, LNT can effectively remove the adsorbed NOx using reductants (H_2, CO and HC) that can be obtained through the post-injection of fuel without a separate device after the adsorption of NOx in a lean condition [6]. However, LNT also uses fuel as a reductant that worsens its fuel consumption. Thus, it is necessary to supply an optimal reductant with a high NOx conversion efficiency. H_2 is an optimal reductant for LNT with fast reactivity; therefore, it has excellent activity at low temperature [7]. Several researchers have investigated a DME SR (Steam Reforming) reaction to generate H_2 by reacting DME with H_2O followed by a partial oxidation reaction to produce H_2 and CO by reacting DME with O_2 [7–10]. Currently, research is underway on the generation of H_2 using low-temperature plasma and diesel fuel cracking catalysts to enhance the selectivity of H_2 [11]. Copper (Cu) is a relatively cheap transition metal for the DME SR catalyst and precious metals are also being developed for the DME SR catalyst [12]. The DME SR reaction has high H_2 selectivity but it is an endothermic reaction; therefore an external heat source and H_2O have to be supplied for the reaction. If DME is directly injected into the exhaust pipe in front of the DME SR catalyst, it can efficiently use the heat source and water vapor from the exhaust gas, which are necessary for the SR reaction [13–15]. However, these studies have not considered the heat source and water vapor in the exhaust emission for the DME SR reaction. Especially, there is no research on the improvement of the NOx conversion of the LNT catalyst using the H_2 or CO that is generated by the DME SR catalyst as a reductant. This study was conducted to develop a DME SR catalyst with high H_2 selectivity using the heat source and water in the exhaust emission of vehicles. The final goal of the research is to develop a combined system of SR + LNT to improve the performance of the de-NOx catalyst system in a DME engine. As of now, the SR catalyst produces H_2 and CO for use as reductants for the LNT catalyst.

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Table 1
Specifications of the catalyst.

Catalyst	Composition (wt%)	BET (cm^2/g)	Pore volume (cm^3/g)
SR	Cu20/γ-Al_2O_3	32.05	0.077
LNT	1Pt/0.03Rh/0.02Pd	39.88	0.125

2. Experimental details

2.1. Preparation of catalysts

The DME SR catalysts were directly manufactured through the sol–gel method [7,16], and a commercialized LNT catalyst (Ordeg Co.) was used. The loaded quantities of Cu in the SR catalysts manufactured by the sol–gel method were 10, 20, and 30 (Cu metal, wt%) of the washcoat. Aluminum isopropoxide ($Al[OCH(CH_3)_2]$, Sigma–Aldrich, 99.9%) was dissolved in 100 ml of H_2O at 70 °C for 20 min. A proper amount of Cu precursor ($[Cu(NO_3)_2 2.5H_2O]$, Sigma–Aldrich) was put in; then, 10 ml of ethylene glycol was injected. The mixture was stirred for an hour, followed by the addition of HNO_3 to adjust the pH to two. The solution was washed, and then dried for 24 h at 130 °C. The washcoat was milled for 2 h, and then calcined for 5 h at 500 °C. A calcined Cu-washcoat was mixed with H_2O for preparing the slurry, stirred for 2 h, and then repeatedly dipped in a substrate. All the Cu catalysts were calcined at 500 °C for 2 h; then, they were reduced with 10% H_2/N_2 at 300 °C for 4 h. The detailed specifications for the DME SR catalysts and the LNT catalyst are shown in Table 1.

2.2. Experimental apparatus

In order to evaluate the performance of the DME SR catalysts and the NOx conversion of a combined system of SR + LNT, a laboratory-scale normal-pressure fixed-bed model gas catalyst reactor was set up, as shown in Fig. 1 [7]. A cylindrical quartz tube of 19 mm inner diameter and 350 mm length was used as the catalytic reactor, and the catalysts were fixed to the center of the reaction tube. The experiment used a catalyst of 18 mm diameter and 30 mm length (600 cpsi, Cordierite, Cu/γ-Al_2O_3) for the DME SR catalyst and 18 mm diameter and 15 mm length (400 cpsi, Cordierite) for the LNT catalyst. The hydrocarbons and DME were measured by a GC (Gas Chromatograph, HP 6890) with an FID (Flame Ionization Detector) and a TCD (Thermal Conductivity Detector). A PLOT U column and a Molecular Sieve 5A column, respectively, were used to measure the DME, H_2, CH_4 and CO with Ar carrier gas. A Horiba 554JK was used for CO_2 analysis. The combined system of SR + LNT had the DME SR catalyst at the front and the LNT catalyst at the rear, and the interval between the catalysts was 5 mm. The catalyst temperature of the front of the SR catalyst (T1 point), between the rear of the DME SR catalyst and front of the LNT catalyst (T2 point), and the rear of the LNT catalyst (T3 point) were measured using a 1.6 mm K-sheath thermocouple. FTIR (Fourier Transform Infrared Spectroscopy, MIDAC) was used for the measurement of NOx. A heat exchanger was installed to prevent the DME gas temperature from decreasing due to the latent heat of evaporation. The H_2O necessary for reactions was supplied while the water temperature was kept constant via a saturated steam pressure and N_2 was passed through water, whereby the water vapor was separated from GC before measurement.

2.3. Experimental method

The experimental conditions to evaluate the H_2 selectivity of the DME SR catalysts and the NOx conversion using the combined system of SR + LNT are shown in Table 2. The evaluation of the H_2 selectivity of the DME SR catalysts used 14,000 h^{-1} as the SV (space velocity). The SR catalyst temperature was T1 and varied in 50 °C intervals from 200 °C to 500 °C in steady conditions. Before reaction, all catalysts were reduced with 10% H_2 at each

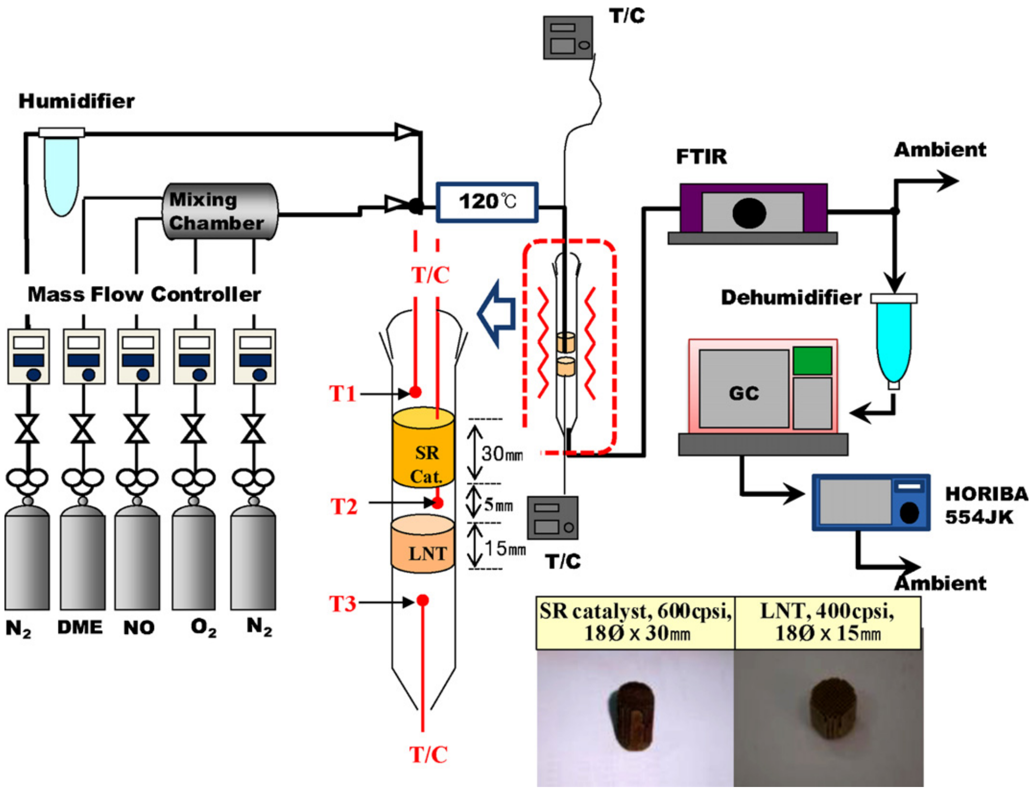

Fig. 1. Experimental apparatus and catalysts.