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Reaction selectivity to hydrocarbons and solid-state carbon over molybdenum sulfide-based shift catalyst

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ABSTRACT

IGCC-CCS process is one application of a cobalt-molybdenum (Co–Mo)-based water-gas shift catalyst (sour shift catalyst). In this process, it is necessary for the shift reaction to progress efficiently with a small amount of steam in order to suppress CO_2 emissions and to increase production efficiency. However, if the amount of steam used in the shift reaction is decreased, there is a possibility that the selectivity of side reactions represented by hydrocarbon production and carbon deposition increases. Therefore, we investigated the effects of various operating parameters regarding the selectivity and reaction mechanism of the side reactions with a reduced steam supply in the shift reaction for Co–Mo-based shift catalyst. Among the side reactions accompanying the shift reaction, the reaction of hydrocarbon production progresses due to the Fischer–Tropsch reaction and increases at a high temperature, high pressure, low steam supply, and long residence time. Moreover, the reaction of carbon deposition in the catalyst progresses due to the Boudouard reaction, which produces carbon directly from the CO source and the deposition increases at a low temperature, high pressure, and low steam supply. Furthermore, the selectivity of the shift reaction of the Co–Mo-based catalyst is high in the co-existing steam conditions, and the shift reaction progresses even if there is a small amount of steam in the reaction gas.

1. Introduction

The water-gas shift (WGS) reaction is an organic industrial reaction (Eq. (1)). It generally accompanies coal gasification and steam reforming, in which steam and hydrocarbons react at high temperature, and it enables the adjustment of the CO and H_2 composition in the synthesis gas. In the fuel reforming process of a fuel cell, this reaction is used to lower the CO concentration to accelerate the electrode reaction of the fuel cell. In addition, during ammonia synthesis in the Haber-Bosch process, CO, which is the catalyst poison contained in H_2, is removed by the WGS reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

As catalysts promoting this reaction, Fe-Cr-based catalysts can be used in a higher temperature region of 300 °C or higher and Cu-Zn-based catalysts can be used in a lower temperature region of 300 °C or lower [1–3]. Desulfurization equipment must be used before the catalysts are introduced into the reaction system because these catalysts are poisoned by sulfur. In addition, sulfur-tolerant shift catalysts (sour shift catalysts) have been developed. Typical examples include Co-Mo-based and Ni-Mo-based catalysts [4–16]. These catalysts have shift activity over a wide temperature region but do not react unless H_2S coexists in the reaction gas. One application of sour shift catalysts is the integrated coal gasification combined cycle with carbon capture and storage (IGCC-CCS) [17–21].

In this process, coal is first gasified in a gasifier. Next, the reaction of CO included in the syngas and steam is promoted by the shift catalyst, and H_2 and CO_2 are produced. Then, after the shift reaction the gas is converted into fuel composed mainly of H_2 by separating and recovering CO_2. By using the fuel, electricity is generated in a gas turbine. Furthermore, electricity is generated in a steam turbine by using the steam produced by the exhaust heat of the gas turbine and gasifier. As a result, electricity can be generated with high efficiency while greatly suppressing CO_2 emissions.

In the IGCC-CCS process, some of the steam for the electric power production in a steam turbine is used for the shift reaction. As a result, the amount of steam supplied to the steam turbine is decreased, which degrades production efficiency. It is necessary for the shift reaction to progress efficiently with a small amount of steam in order to suppress CO_2 emissions and to increase production efficiency.

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There is a wide usage range of catalysts in which molybdenum sulfide is the active ingredient, such as sour shift catalysts. Molybdenum sulfide is also used as a catalyst for synthesizing alcohols and hydrocarbons [22–26] in addition to the shift reaction included in this study. Therefore, if the amount of steam used in the shift reaction is decreased, the hydrocarbon production reaction due to the Fischer–Tropsch (FT) reaction indicated in Eqs. (2)–(4) [22–25] and the alcohol production reaction represented by the methanol synthesis indicated in Eq. (5) [25,26] progress in addition to the shift reaction, and there is a possibility that CO will be converted into a chemical species other than the desired CO_2. In addition, side reactions such as the carbon deposition indicated in Eqs. (6) and (7) [27,28] also progress, and there is a possibility that the catalyst will be deteriorated [29–31].

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O} \tag{2}$$

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \tag{3}$$

$$2n\mathrm{CO} + n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{CO_2} \tag{4}$$

$$\mathrm{CO} + 2\mathrm{H_2} \rightarrow \mathrm{CH_3OH} \tag{5}$$

$$2\mathrm{CO} \rightarrow \mathrm{C} + \mathrm{CO_2} \tag{6}$$

$$\mathrm{CO} + \mathrm{H_2} \rightarrow \mathrm{C} + \mathrm{H_2O} \tag{7}$$

Many reports have been published on reaction selectivity from the viewpoints of the differences in the catalyst composition and the operating conditions in synthetic processes for producing alcohol and hydrocarbons [25,32,33]. However, these reports assumed that there was no steam in the reaction system. There are no reported examples of reaction selectivity as side reactions of the shift reaction in the presence of steam, which this study aimed for. Therefore, in this paper, for a sour shift catalyst of the Co–Mo system, among the side reactions associated with the shift reaction, we examined the hydrocarbon production reaction that influences the CO_2 recovery in the IGCC-CCS process and the carbon deposition on the catalyst, which affects the durability of the catalyst. Specifically, to improve production efficiency in the IGCC-CCS process, we examined the influence of operating parameters such as temperature, total pressure, and residence time on reaction selectivity for when the steam supply is lowered in the shift reaction. In addition, we investigated the reaction mechanism of the side reactions that progress on the sour shift catalyst.

2. Materials and methods

2.1. Catalyst preparation

The catalyst examined in this study consisted of Mo, which is the principal ingredient, Co, which is the promoter, and a magnesium oxide and alumina ($MgO–Al_2O_3$) support. The preparation procedure was as follows. First, the $MgO–Al_2O_3$ support was prepared. Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$; special grade chemical from Wako Pure Chemical Industries] and boehmite [$AlO(OH) \cdot 1/2H_2O$; Pural SB-1 from Condea chemicals] were mixed so that the weight ratio of MgO and Al_2O_3 provided after calcination was set to 1:3. Then, the mixture was mixed with distilled water, and wet-milling was carried out for 30 min using an automatic mortar. The mixture was dried for 2 h at 120 °C and calcined for 1 h at 500 °C. Next, Mo and Co were added. Ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; special grade chemical from Wako Pure Chemical Industries], cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$; special grade chemical from Wako Pure Chemical Industries], and $MgO–Al_2O_3$ composition support were mixed so that the weight percentages of MoO_3 and CoO provided after calcination were 24 wt% and 6 wt%, respectively. After that, distilled water was added, and wet-milling was carried out for 30 min using the automatic mortar. Next, the mixture was dried for 2 h at 120 °C and calcined for 5 h at 500 °C. The catalyst after calcination was crushed in the mortar and then pressure molded for 2 min at 5 kPa with a pressurization pressing machine. Finally, the molded catalyst was sized to a 10–20 mesh.

2.2. Catalyst pretreatment

Sulfiding is a necessary pretreatment for the sour shift catalyst. Although the Mo contained in the catalyst after preparation is present as an oxide of MoO_3, MoO_3 must be converted into MoS_2 before it is applied to the shift reaction. The reaction that converts MoO_3 into MoS_2 is expressed in Eq. (8). The catalyst was pretreated by the following procedure. After the catalyst bed temperature was increased to 200 °C under a N_2 flow, H_2 and H_2S were added to get H_2 at 7 vol% and H_2S at 3 vol%. Furthermore, the catalyst bed temperature was controlled so as not to exceed 230 °C. If the catalyst bed temperature exceeds 230 °C, the reaction that converts MoO_3 to MoO_2 (Eq. (9)) progresses quickly. Accordingly, the amount of MoS_2, which is the active site of the shift reaction, is decreased and catalytic activity is deteriorated because the reaction that sulfurates MoO_2 to MoS_2 (Eq. (10)) is extremely slow. After it was confirmed that H_2S at 1 vol% or higher was detected in the catalyst bed exit, the gas temperature was increased to 320 °C at 1 °C/min. Finally, the catalyst bed temperature was maintained at 320 °C for 45 min, and the pretreatment was finished.

$$\mathrm{MoO_3} + 2\mathrm{H_2S} + \mathrm{H_2} \rightarrow \mathrm{MoS_2} + 3\mathrm{H_2O} \tag{8}$$

$$\mathrm{MoO_3} + \mathrm{H_2} \rightarrow \mathrm{MoO_2} + \mathrm{H_2O} \tag{9}$$

$$\mathrm{MoO_2} + 2\mathrm{H_2S} \rightarrow \mathrm{MoS_2} + 2\mathrm{H_2O} \tag{10}$$

2.3. Catalytic activity

In this study, the evaluation of catalytic characteristics was carried out by using a fixed bed type experimental apparatus (outline of this apparatus is shown in Supplementary material). This apparatus was composed of a gas supply system, steam supply system, reaction tube made of stainless steel, electric furnace, pressure regulator, and moisture separator. The reaction gas was a mixture of CO, CO_2, H_2, N_2, and CH_4, which were filled in the same cylinder and H_2S/N_2 gas and these were supplied to the reaction tube. These gases simulated coal gasification gases. The composition of the mixed gas was CO at 53 vol%, CO_2 at 5 vol%, H_2 at 23 vol%, CH_4 at 1 vol%, N_2 at 18 vol%, and H_2S at 200 volppm. The reaction gas was adjusted to 830 mL/min with a flow meter and supplied from the top of the reaction tube, which had an outside diameter of 21.3 mm, inside diameter of 15.8 mm, and length of 500.0 mm. The steam was generated by supplying water to a vaporizer from a water tank with a plunger pump. A 5 mL amount of catalyst (dry-GHSV: 10,000 h^{-1}) was placed in the reaction tube. The pressure in the system was adjusted with the pressure regulator installed under the reaction tube. In the gas after the reaction, a large amount of vapor remained, which had not been used in the reaction. Therefore, the moisture in the gas was removed with the moisture separator so that it would not enter the analysis gas sample. The dried gas was collected, and the composition of CO, CO_2, H_2, N_2, and CH_4 was determined by using a G-5000 TCD gas chromatograph analyzer from Hitachi. The CO conversion rate was calculated by Eq. (11), which uses the CO quantity at the inlet and outlet of the catalyst containing tube.

$$\mathrm{Conversion}(\%) = \frac{[\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{out}}}{[\mathrm{CO}]_{\mathrm{in}}} \times 100 \tag{11}$$

$[CO]_{in}$ (mol/h): molar flow rate of the inlet of the catalyst containing tube.

$[CO]_{out}$ (mol/h): molar flow rate of the outlet of the catalyst containing tube.