



Feature Article

Reaction mechanism analysis for molybdenum-based water-gas shift catalysts

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ARTICLE INFO

Article history:

Received 29 September 2016

Received in revised form

23 December 2016

Accepted 29 December 2016

Available online 29 December 2016

Keywords:

Water-gas shift reaction

Sulfur-tolerant catalyst

Elementary reaction

Progression rate

Ni/Mo/Ti

ABSTRACT

The reaction mechanism of molybdenum-based shift catalysts, which are sulfur-tolerant water-gas shift catalysts (sour-shift catalysts), were examined by elementary-reaction analysis. The elementary-reaction progression rate for a nickel/molybdenum/titanium (Ni/Mo/Ti) compound catalyst (as a low-temperature reactive catalyst) and cobalt/molybdenum/aluminum (Co/Mo/Al) compound catalyst (as a conventional catalyst) were investigated. The results of this investigation show that the elementary-reaction progression rate of the Ni/Mo/Ti catalyst is higher than that of the Co/Mo/Al catalyst at 200 °C (which is representative of the low-temperature region). This tendency accorded with that of shift activity. This result suggests that the shift activity depends on improved dispersibility of active sites by the support effect of TiO₂ and the strong electron-withdrawing effect of the nickel promoter.

Moreover, separately from the reaction mechanism of the sour-shift catalyst proposed up to now, a new mechanism, by which H₂S in reaction gas contributes to the progress of the shift reaction in the elementary reaction process, is proposed, and as a result of elementary-reaction analysis, we confirmed this new mechanism must be progressed.

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1. Introduction

The water-gas shift (WGS) reaction is an industrial organic reaction that generally accompanies coal gasification and steam reforming, in which steam and hydrocarbons react at high temperature to generate hydrogen (from steam) and carbon monoxide (CO) in so-called “synthesis gas” (syngas) [1–5] according to the following equation:



As catalysts to promote the WGS reaction, iron-chromium (Fe-Cr)-based catalysts can be used at temperatures of 300 °C or higher, while copper-zinc (Cu-Zn)-based catalysts can be used below 300 °C [6–8]. In the syngas process flow, the reactants must be desulfurized before they reach the catalyst reactor because the above-mentioned catalysts are contaminated by sulfur. Alternatively, sulfur-tolerant shift catalysts (sour-shift catalysts), such as iron-cerium (Fe-Ce)-based [9–12] as well as cobalt-molybdenum

(Co-Mo)-based and nickel-molybdenum (Ni-Mo)-based catalysts [13–24], have been developed. In particular, Mo-based catalysts can be used over a wide temperature range, although they are active only when the reaction gas contains hydrogen sulfide (H₂S). Previously, we developed a Ni-Mo-based catalyst with higher shift activity under conditions of low temperature and low-flow-rate steam supply than a proven Co-Mo-based commercial catalyst [25]. However, we did not clarify the reaction mechanism by which the developed Ni-Mo-based catalyst acts. Moreover, considering the elementary reactions of a reaction system, we did not clarify the elementary-reaction process that contributes to the higher shift activity of Ni-Mo-based catalysts at low temperature.

The elementary shift reaction that is promoted by a sour-shift catalyst has been extensively researched. However, the mechanism proposed by many researches does not consider H₂S, which is said to be an essential component in maintaining the activity of the sour-shift catalyst [22–24]. In various researches, H₂S coexistence (at concentrations of several-hundred ppm) in reaction gas has been shown to be a requirement for actively maintaining a sour-shift catalyst [26,27]. Therefore, we supposed that another reaction mechanism in which H₂S participates must be present in an elementary reaction process.

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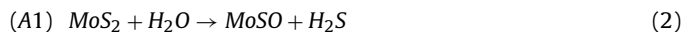
In this study, we intended to clarify the two following points by elementary-reaction analysis of a sour-shift catalyst using a laboratory-scale apparatus. First, we examined the reason that the low-temperature activity of the developed Ni-Mo-based catalyst is higher than that of a conventional Co-Mo-based catalyst. Second, we examined the possibility that a new mechanism, in which H₂S contributes to the progression of the shift reaction in elementary reactions, is taking place. In addition, before clarifying those two points, we examined the dependences of CO-conversion activity on temperature and H₂S concentration. The objective of evaluating the temperature dependence was to clarify the difference between shift activities of Ni-Mo-based and Co-Mo-based catalysts under the same experimental conditions. Moreover, the objective of evaluating the H₂S-concentration dependence was to confirm whether the shift activity of the developed sour-shift catalyst depends on H₂S concentration as reported in many studies on Ni-Mo-based catalysts.

2. Method

2.1. Assumed reaction mechanism

The shift-reaction mechanism proposed to date consists of three elementary reactions described by Eqs. (2)–(4) [22–24]. Hereafter, the overall mechanism is called “mechanism A” and each elementary reaction is respectively identified as “A1”–“A3.” As for mechanism A, MoS₂ formed after sulfiding (which is a catalyst pretreatment) is a starting reagent. In A1, H₂S is generated by a reaction with MoS₂ and H₂O, and MoS₂ becomes MoSO. In A2, CO₂ is generated by the reaction of the oxygen atoms in MoSO and CO in gas phase, and MoSO becomes MoS. In A3, H₂ is generated by the reaction of MoS and H₂O at the same time as MoSO is formed. The shift reaction progresses afterwards by repeating A2 and A3.

In the above-described reaction system, although H₂S coexistence is supposed to be required when a sour-shift catalyst is used, H₂S does not participate in the elementary reactions. As mentioned above, H₂S coexistence in the reaction gas (at a concentration of several-hundred ppm) is required to maintain the sour-shift catalyst. Therefore, we propose a new mechanism in which H₂S contributes to the progress of the shift reaction in the elementary-reactions. This elementary reaction mechanism, hereafter designated as “B,” is described by Eqs. (2), (3), and (5). Mechanism B assumes elementary reaction B3 instead of A3; in other words, MoS reacts with H₂S, not H₂O. As for mechanism B, as the shift reaction progresses by repeating elementary reactions A1, A2, and B3, H₂S participates in the elementary-reaction process. In the following, we examine the progression of the elementary reactions involved in mechanism A (which has been previously proposed) and mechanism B (which is newly assumed in this study).



2.2. Catalyst

The reaction mechanisms of a Ni/Mo/TiO₂ catalyst (Ni/Mo/Ti, hereafter), which is active at low temperature, and for a Co/Mo/Al₂O₃-MgO catalyst (Co/Mo/Al hereafter), which has widely reported reaction characteristics [28–30], were examined first. Both catalysts were prepared by kneading and extrusion molding. Their compositions (wt%) are as follows: in Ni/Mo/Ti, NiO 5.0 ± 1.0, MoO₃ 20.0 ± 1.0, and TiO₂ 75.0 ± 1.0; and in Co/Mo/Al, CoO

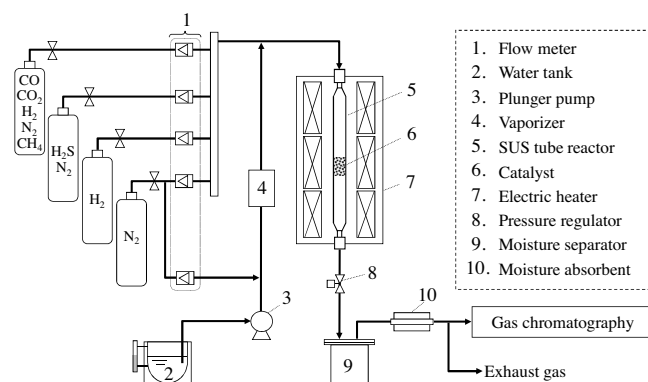
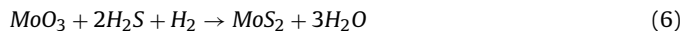


Fig. 1. Schematic drawing of experimental apparatus.

5.0 ± 1.0, MoO₃ 15.0 ± 1.0, Al₂O₃ 60.0 ± 1.0, and MgO 20.0 ± 1.0. The particle sizes of both catalysts were 2.0 mm in diameter and 3–10 mm in length.

2.3. Catalyst pretreatment

Sulfiding is a necessary pretreatment for a sour-shift catalyst [31,32]. Although the molybdenum contained in the catalyst after preparation is present as an oxide (MoO₃), MoO₃ must be converted into MoS₂ before it is used to the shift reaction. The reaction that converts MoO₃ to MoS₂ is expressed as Eq. (6). The catalyst was pretreated by the following procedure. After the catalyst-bed temperature was increased to 200 °C under N₂ flow, H₂ and H₂S were added to produce H₂ at 7 vol% and H₂S at 3 vol%. After H₂S at 1 vol% or higher was detected at the catalyst-bed exit, the gas temperature was increased to 300 °C at a rate of 1 °C/min. The pretreatment ended after the catalyst bed had been kept at 300 °C for 45 min.



2.4. Experimental equipment

A schematic drawing of the experimental apparatus used for elementary-reaction analysis is shown in Fig. 1. This apparatus is composed of a gas-supply system (labelled 1), a steam-supply system (2–4), a stainless-steel (SUS) tube reactor (5), an electric furnace (7), a pressure regulator (8), and moisture-removal devices (9 and 10). The reaction gas was a mixture of CO, CO₂, H₂, N₂, and CH₄ supplied from one cylinder and H₂S and N₂ supplied together from another cylinder. These gases simulated coal-gasification gas. The reaction gas flow was adjusted to 830 mL/min by the flow meter (1) and supplied into the top of the tube reactor (with outside diameter of 21.3 mm, inside diameter of 15.8 mm, and length of 500.0 mm). Steam was generated by supplying water to the vaporizer (4) from the water tank (2) with the plunger pump (3). The tube reactor was filled with catalyst (6). The pressure was adjusted by a pressure regulator installed under the tube reactor. After the shift reaction, a large amount of water vapor that had not been used in the reaction remained in the gas, and the moisture-removal devices removed it so it would not contaminate the analysis-gas sample. The concentrations of CO, CO₂, H₂, N₂, and CH₄ were determined by gas chromatograph analyzer, i.e., a Hitachi G-5000 TCD (thermal-conductivity detector). The concentrations of H₂S and COS were determined by gas-chromatograph analyzer, i.e., a Shimadzu GC-2014 FPD (flame ionization detector). CO conversion rate was calculated from the catalyst inlet and outlet concentrations as follows:

$$\text{CO conversion rate (\%)} = \frac{\text{CO}_{in} - \text{CO}_{out}}{\text{CO}_{in}} \times 100 \quad (7)$$

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