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Suppression of carbon deposition in CO_2-reforming of methane on metal sulfide catalysts

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The catalytic performance of metal sulfides of Mo and W was studied for the CO_2-reforming of methane by comparing with that of Ni/SiO_2. The sulfide catalysts have lower activity than the Ni/SiO_2 catalyst for this reaction, however, no deactivation due to carbon deposition was observed on the sulfide catalysts. The activity for direct decomposition of CH_4 was much smaller on the sulfides than on supported Ni. The rate equation suggested that, during steady-state reaction, the surface was abundant in adsorbed CO_2 on sulfides, by which direct decomposition of CH_4 should be retarded in addition to their lower activity for this reaction.

Keywords: carbon deposition; CO_2-reforming; methane; metal sulfide; supported Ni

1. Introduction

The reduction of CO_2 with CH_4 has become a fashionable reaction because the reacting gases are both contributing significantly to the greenhouse effect [1,2]. The CO_2-reforming of CH_4 is an appropriate reaction, because this reaction can convert these two harmful gases to useful syngas. Supported Ni is known as a typical catalyst for this reaction. During steady-state reaction, carbon deposition often accompanies the reaction, by which a catalyst is deactivated and continuous flow of reactant gases is disturbed. Therefore, a high performance catalyst must be developed, on which carbon deposition is suppressed completely.

In a conventional catalyst system, carbon deposition has been controlled by the presence of excess amount of carbon dioxide [4,5] or by the addition of alkaline metal salts to supported Ni catalysts [6,7]. Partial poisoning of supported Ni catalyst with sulfur compounds, SPARG process [8], is reported as another way to suppress carbon deposition.

It was reported that the activity for the methanation of CO significantly decreased with time on Ni and Fe, however, not so significantly on MoS_2 [9]. The metal sulfide catalyst may also exhibit high performance for the CO_2-reforming of CH_4 without accompanying carbon deposition, although the origin of carbon deposition may be different between these two reactions. In this paper, the catalytic performance of MoS_2 and WS_2 was studied for CO_2-reforming of CH_4 by comparing with that of a supported Ni catalyst.

2. Experimental

MoS_2 and WS_2 catalysts were prepared by decomposing the respective precursors ($(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$; both from Aldrich) in a stream of hydrogen. XRD patterns of the prepared catalysts showed broad diffraction peaks of molybdenum and/or tungsten disulfide. For comparison, the Ni/SiO_2 catalyst (metal loading, 20 wt%) was prepared by impregnating SiO_2 with an aqueous solution of $Ni(NO_3)_2$, followed by drying and subsequent calcination at 773 K for 3 h. Before use, it was reduced with flowing hydrogen.

The CO_2-reforming of CH_4 was carried out by using a conventional flow type microreactor. After reducing a catalyst in a stream of hydrogen (40 ml min^{-1}) at 723 K for 3 h, helium (40 ml min^{-1}) was flowed over the catalyst at 723 K for 30 min. Then an equimolar mixture of CH_4 and CO_2 (28 ml min^{-1}) was introduced on the catalyst. The catalyst weight was 5.1 mg, 305.1 mg, and 359.0 mg for Ni/SiO_2, MoS_2, and WS_2, respectively. The reaction was carried out under the condition of a differential reactor. Effluent gases were analyzed by gas chromatography.

Dependence of reaction time was investigated at 873 K for 6 h. After reducing a catalyst (catalyst weight, 93.5 mg for Ni/SiO_2 and 500 mg for MoS_2) with flowing hydrogen at 873 K for 3 h, helium was flowed over the catalyst at 873 K for 30 min. Then, an equimolar mixture of CH_4 and CO_2 (total flow rate, 28 ml min^{-1} and 60 ml min^{-1} for MoS_2 and Ni/SiO_2, respectively) was introduced onto the catalyst.

Dependence of reaction rate on partial pressures was investigated under the condition of a differential reactor. After reducing a catalyst with flowing hydrogen at 973 K for 3 h followed by purging with helium at 973 K for 30 min, a mixture of CH_4, CO_2, and helium (total flow rate, 54 ml min^{-1}) was introduced onto the catalyst. The catalyst weight was 5.1 mg for Ni/SiO_2, 305.1 mg for MoS_2, and 280.3 mg for WS_2.

The amount of CO adsorbed on the catalyst was measured by a conventional pulse technique at 298 K in a flow of helium as a carrier gas: 41.0 μmol g^{-1} for Ni/SiO_2, 15.0 μmol g^{-1} for MoS_2, and 38.6 μmol g^{-1} for WS_2.

The rate of carbon deposition on the catalyst was investigated by using thermal gravimetric analysis. After the reduction of a catalyst with hydrogen followed by purging with helium at 773 K, CH_4 (40 ml min^{-1}) was flowed over the catalyst and the catalyst weight was continuously measured. The catalyst weight was 25.5 mg for Ni/SiO_2, 16.5 mg for MoS_2, and 50.7 mg for WS_2.

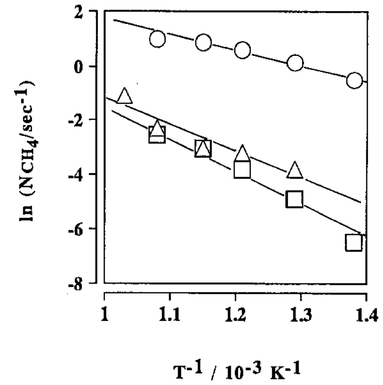

Fig. 1. Arrhenius plots for CH_4–CO_2 reaction on Ni/SiO_2 (○), MoS_2 (△), and WS_2 (□) using the continuous flow technique.

3. Results and discussion

Fig. 1 shows the rates of methane conversion on the sulfide catalysts and the Ni/SiO_2 catalyst in the initial period of time. The rates can be compared with each other on the basis of turnover frequency (N_{CH_4}/s^{-1}). As shown, the sulfide catalysts exhibited lower activity than the Ni/SiO_2 catalyst for this reaction. Of the sulfide catalysts, MoS_2 showed a little higher activity than WS_2, while the apparent activation energy seemed to be a little larger on WS_2 than on MoS_2.

Fig. 2 shows the decay of catalyst activity for CO_2-reforming of CH_4. Due to carbon deposition, supported Ni lost its activity significantly. On MoS_2, on the other hand, no deactivation was observed, although the activity was smaller than on supported Ni. Fig. 3 summarizes the dependence of the reaction rate on partial pressures. The rate equation was expressed by

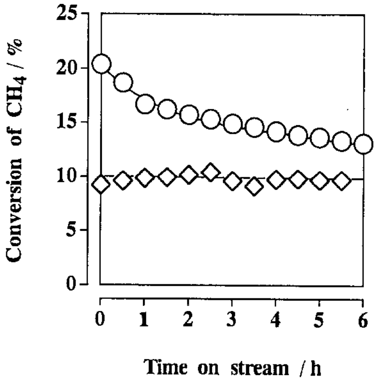

Fig. 2. Decay of catalyst activity for the CO_2-reforming of CH_4 on Ni/SiO_2 (○) and MoS_2 (◇). Reaction temperature = 873 K. $W/F = 0.582$ g h mol^{-1} for Ni/SiO_2 and 6.67 g h mol^{-1} for MoS_2.

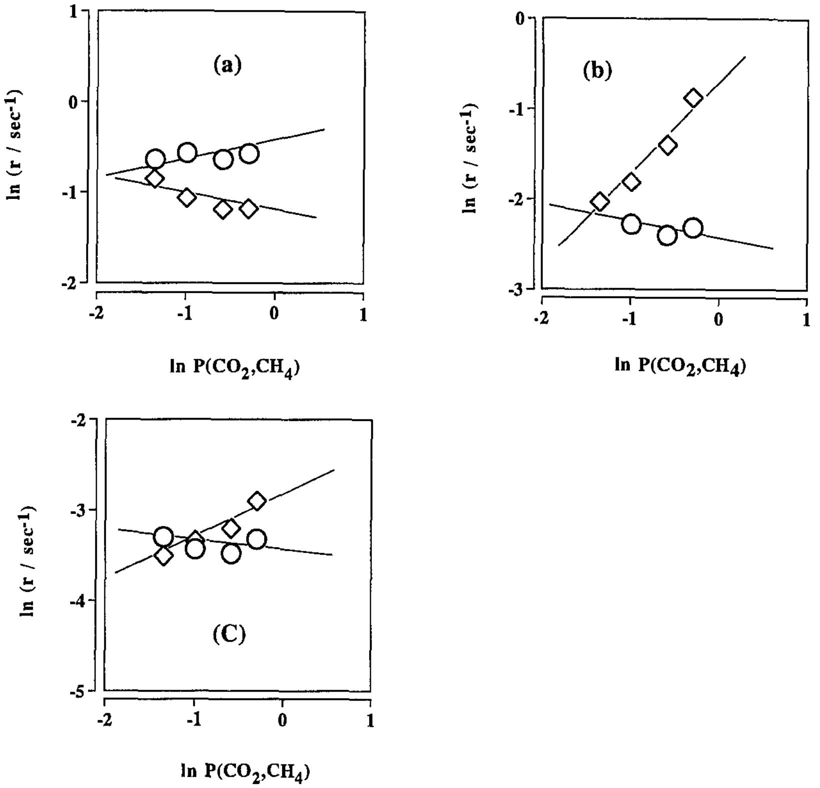

Fig. 3. Dependence of reaction rate on partial pressures for the CO_2-reforming of CH_4 on Ni/SiO_2 (a), MoS_2 (b), and WS_2 (c) at 973 K. log r vs. log P_{CO_2} (○), log r vs. log P_{CH_4} (◇).

$$r_1 = k_1 P_{CH_4}^{0.54 \text{ to } 0.76} P_{CO_2}^{-0.09 \text{ to } -0.10} \qquad \text{for sulfide catalysts,}$$

$$r_2 = k_2 P_{CH_4}^{-0.30} P_{CO_2}^{0.16} \qquad \text{for supported Ni catalyst,}$$

where r_i and k_i are the reaction rate and the rate constant, respectively, and P_j is the partial pressure of reactant gas. The reaction order observed with respect to partial pressure suggested that, under steady-state reaction conditions, the catalyst surface was abundant in adsorbed CO_2 on sulfides, while in adsorbed CH_4 on supported Ni. Since carbon deposition is caused by the decomposition of CH_4, covering the sulfide surface with adsorbed CO_2 should yield a favorable condition for avoiding CH_4 decomposition, which results in no deactivation as shown in fig. 2. Fig. 4 shows the activity for CH_4 decomposition in the absence of CO_2. Sulfide catalysts were much less active than supported Ni, which should be another cause for the absence of deactivation during steady-state CO_2-reforming of CH_4.

Our preliminary experiment showed that alkaline metal salts added to supported Ni changed the reaction order with respect to CH_4 partial pressure from zeroth or negative to positive value and with respect to CO_2 partial pressure from positive to

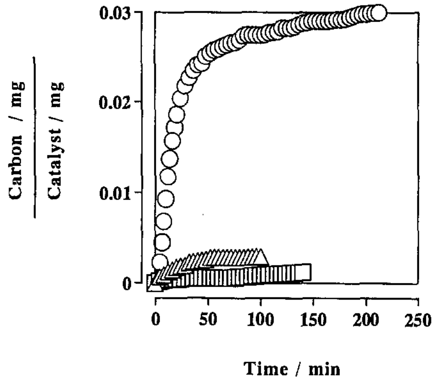

Fig. 4. Decomposition of CH_4 in the absence of CO_2 on Ni/SiO_2 (○), MoS_2 (△), and WS_2 (□) at 773 K.

zeroth or negative value [10]. The addition of alkaline salts also decreased the activity of supported Ni for the direct decomposition of CH_4. These observations were very similar to the present findings on sulfide catalysts, which may allow us to speculate that metal sulfides of Mo and W play the same part as alkali-promoted Ni catalysts. The precise characterization of the sulfide catalysts is now in progress.

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