Novel catalytic properties of Rh sulfide for the synthesis of methanol from $CO + H_2$ in the presence of H_2S

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Received 27 June 2001; accepted 5 October 2001

Rh sulfide yielded 800 g kg-cat^{-1} h^{-1} of methanol at 593 K and 5.1 MPa from $CO + H_2$ (syngas) even in the presence of H_2S 100 ppm in concentration. The obtained space-time yield of methanol was comparable with that obtained with a commercial Cu/Zn/Al catalyst at a conventional reaction condition (523 K and 5.1 MPa) from a feed containing both syngas and CO_2.

KEY WORDS: Rh sulfide; methanol synthesis; sulfur tolerant catalyst; Cu/Zn/Al catalyst

1. Introduction

It has been generally assumed that CO hydrogenation catalysts such as Fischer–Tropsch synthesis (FTS) and methanol synthesis catalysts are poisoned by a small amount of sulfur compounds in the feed [1,2]. For example, Cu/Zn/Al catalyst loses its methanol synthesis activity even in the presence of H_2S 1.6 ppm in $CO/H_2/CO_2$ feed [2]. H_2S content in the syngas is seriously high especially when the syngas is derived from coal, heavy oil, biomass or waste materials. To avoid the sulfur poisoning, conventional plants are equipped with huge desulfurizer units that remove the sulfur compounds almost completely from the feed (usually below 1 ppm). Alternatively, the development of a sulfur tolerant catalyst that works without the desulfurizer unit could overcome this problem. Especially, to develop a novel process producing liquid fuels from small-scale dispersed carbon resources such as remote gas fields, biomass or waste materials, it is desirable to simplify the conventional (huge and complex) process by omitting some units (*e.g.*, huge desulfurizer unit).

Several attempts have been made to improve the sulfur tolerance of the CO hydrogenation catalysts. Both nitriding pretreatment [3] and addition of Mn oxide [4] effectively decrease the deactivation rates of reduced iron FTS catalysts in the presence of gaseous H_2S. Recently, a boric acid has been reported to moderate the poisoning by a pre-added ammonium sulfide of a reduced Co/TiO_2 FTS catalyst [5].

In contrast to reduced metallic catalysts mentioned above, an alkaline-metal-promoted Mo sulfide catalyst preserves its initial activity for the synthesis of mixed alcohol for a long period even in the presence of H_2S 50 ppm in concentration [6]. However, the performance of Mo-sulfide-based catalysts is not adequate since a higher reaction pressure (usually above 10 MPa) is required to attain a high activity and selectivity. Considering the situation mentioned above, we think that the application of transition metal sulfides is a promising way of developing the CO hydrogenation catalyst with sulfur tolerance. Up to the present, however, the CO hydrogenation activity of the metal sulfides, except for Mo and W sulfides, has never been investigated yet.

As concerns the sulfur tolerance of the CO hydrogenation catalysts, interesting results have been reported by Brandreth and Winstanley [7]. They found that pre-adsorbed COS enhances the total activity of a reduced Rh/SiO_2 as well as the selectivity for C_2 oxygenates. Their results suggest that the CO hydrogenation activity of surface Rh species is not necessarily poisoned by sulfur compounds. Thus, the present work investigated the activity and selectivity of Rh sulfides for the CO hydrogenation reaction. Sulfur tolerance of Rh sulfide was also investigated in the presence of H_2S. The obtained activity and selectivity were further compared with that of the commercial Cu/Zn/Al catalyst at the same reaction pressure.

2. Experimental

2.1. Preparation of Rh sulfide

Rh sulfide was prepared by a modified manner reported by Pecoraro and Chianelli [8]. $RhCl_3$ (Aldrich, 98%) and Li_2S (Aldrich, 98%) powder were stirred in an ethyl acetate solution (Wako Pure Chemicals, 98%) at room temperature. The obtained precipitate was treated in a stream of H_2S 5%/H_2 at 673 K for 2 h, which yielded fine black powder. The powder was then washed with an acetic acid solution (Wako Pure Chemicals, 98%) and treated again in a stream of H_2S 5%/H_2 at 673 K for 2 h. BET surface area of Rh sulfide thus prepared was 14 m^2 g^{-1}.

2.2. CO hydrogenation reaction

Rh sulfide was pretreated before the reaction in a stream of H_2S 0.5%/H_2 at 673 K. The cumulative amount of H_2S

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fed during the pretreatment was 3 mol-H_2S mol-Rh^{-1}. The CO hydrogenation reaction was carried out using a conventional fixed-bed reactor equipped with two on-line gas chromatographs. A feed containing a syngas (CO 33%/H_2 62%/Ar) or a feed containing both a syngas and CO_2 (CO 30%/H_2 60%/CO_2 5%/Ar) was used for the reaction. A Cu/Zn/Al catalyst supplied by ICI Corp. was also used as a reference. The Cu/Zn/Al catalyst was pretreated in the same feed as that employed for the reaction. Both Rh sulfide and Cu/Zn/Al catalyst were subjected to the CO hydrogenation reaction in the presence of H_2S 100 ppm in concentration. A sulfur-free apparatus was also used for the activity measurements of the Cu/Zn/Al catalyst. The space-time yield (STY) of methanol was determined by analyzing liquid products condensed with an ice trap using an off-line gas chromatograph. The concentration of H_2S in the gas-phase was determined with a sulfur chemiluminescence detector.

2.3. X-ray powder diffraction

To determine the crystalline structure of Rh sulfide, the X-ray powder diffraction pattern was measured using a Rigaku diffractometer (Mini Flex) equipped with a variable divergence slit. Cu K_α radiation was used as X-ray source operating at 30 kV and 15 mA. Intensity data were recorded by a step-scan mode in a 2θ range from 10° to 120° with an interval of 0.04°. The sampling time at each step was set 4 s to get the maximum intensity of around 6000 counts.

3. Results

3.1. Crystalline structure of Rh sulfide

Figure 1(A) shows the X-ray powder diffraction pattern of a fresh Rh sulfide. Four diffraction peaks are visible at 2θ values of 30°, 41°, 48° and 52°. The d-spacing of these peaks are 0.300, 0.220, 0.191 and 0.175 nm, respectively. In the Rh–S system, single-crystal $Rh_{17}S_{15}$ [9], Rh_3S_4 [10] and Rh_2S_3 [11] were synthesized and their structures were investigated by the X-ray diffraction method. To identify the crystalline structure(s) of the fresh Rh sulfide, intensity profiles of the single crystal Rh sulfides were calculated from their structural parameters. Results are shown in figures 2 (A)–(C), respectively. Since the 2θ values and relative intensities of the main peaks in the pattern of the fresh Rh sulfide are closer to those in the profile of $Rh_{17}S_{15}$, it is reasonable to assume that the crystalline structure of the fresh Rh sulfide is the $Rh_{17}S_{15}$ structure.

Careful inspections of the diffraction pattern, however, show that the relative intensities of the peaks in figure 1(A) do not completely fit with those in figure 2(A), *i.e.*, the relative intensity of the peak at the 2θ value of 30° in figure 1(A) is weaker. Since the $Rh_{17}S_{15}$ structure is not a layered structure [9], it is not likely that a preferential orientation occurs during preparation of the sample for the XRD measurements. The authors calculated the intensity profile of $Rh_{17}S_{15}$ using the structural parameters of the sample, which had been prepared by exposing a metallic Rh powder to S vapor at a temperature above 1273 K [9,12]. In contrast, Rh sulfide was prepared in a stream of H_2S 5%/H_2 at 673 K. Such differences may cause differences of the relative growth rate of each crystal surface. Thus, it is suggested that the difference of the relative intensities of the peaks arises from the difference of preparation conditions employed for Rh sulfide and $Rh_{17}S_{15}$.

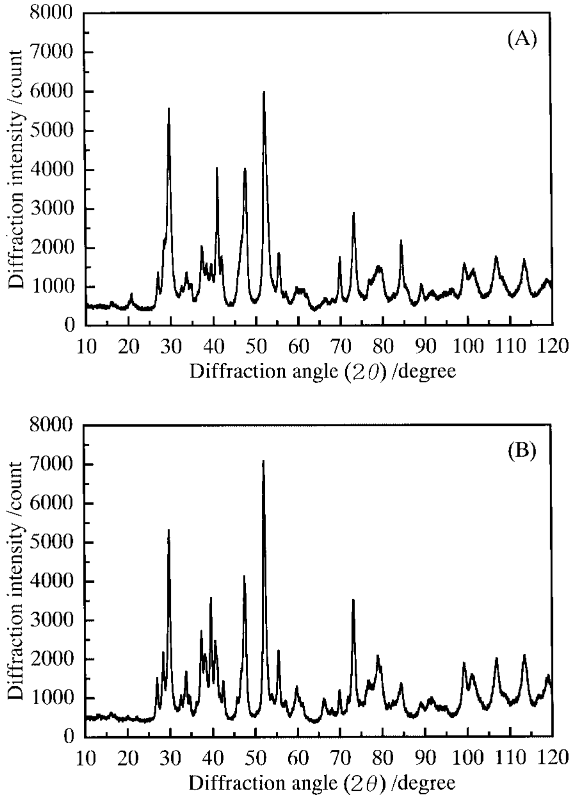

Figure 1. X-ray diffraction patterns of the fresh Rh sulfide (A) and Rh sulfide after the CO hydrogenation reaction (B).

Figure 1(B) shows the XRD pattern of Rh sulfide after the CO hydrogenation reaction. Since the 2θ values and relative intensities of the main peaks in the pattern of Rh sulfide after the reaction are identical to those in the pattern of the fresh Rh sulfide, the crystalline structure of Rh sulfide after the reaction is the $Rh_{17}S_{15}$ structure also.

3.2. Activity and selectivity of Rh sulfide for the CO hydrogenation reaction

The activity and selectivity of Rh sulfide for the syngas were investigated in a temperature range from 523 to 613 K at 5.0 MPa and 30 m^3 kg-cat^{-1} h^{-1}. Under these reaction conditions, methanol was mainly produced. Methanol selectivity at 523 K was 98 mol%. With increasing reaction temperature, methanol selectivity decreased 70 mol% at 613 K. CH_4 and CO_2 were also observed in the effluent gas. Figure 3 shows the STY of methanol obtained with Rh sulfide at each reaction temperature. The STY of methanol increases linearly with increasing reaction temperature from 523 to

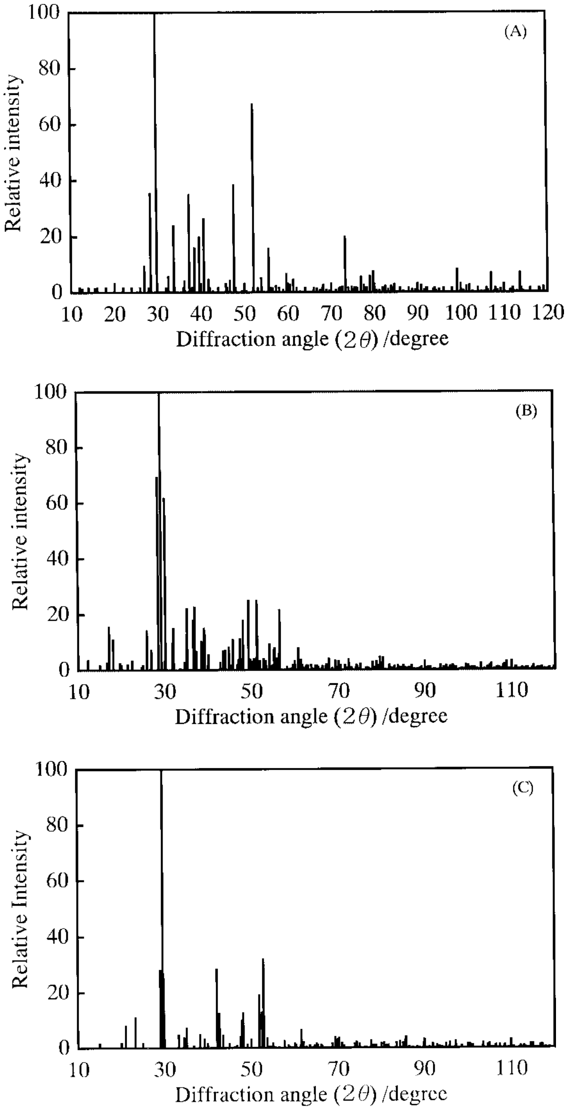

Figure 2. Calculated intensity profiles of X-ray diffraction patterns of $Rh_{17}S_{15}$ (A), Rh_3S_4 (B) and Rh_2S_3 (C). Structural parameters of these sulfides are adapted from [9] for $Rh_{17}S_{15}$, [10] for Rh_3S_4 and [11] for Rh_2S_3.

593 K and reaches 800 g kg-cat^{-1} h^{-1} at 593 K. At this temperature, CO conversion was 6% with methanol selectivity of 80 mol%.

Many studies show that reduced Rh catalysts yield methanol from syngas in the presence of some metal oxides [13–18]. Among these catalysts, the maximum STY of methanol is obtained with the reduced Rh/SiO_2 promoted with Fe oxide, which yields 170 g kg-cat^{-1} h^{-1} of methanol at 573 K, 6.9 MPa and 39 m^3(STP) kg-cat^{-1} h^{-1} [16]. Since the STY of methanol obtained with the present Rh sulfide at 573 K, 5.1 MPa and 30 m^3(STP) kg-cat^{-1} h^{-1} is 600 g kg-cat^{-1} h^{-1}, the methanol synthesis activity of Rh sulfide is much higher than that of the reduced Rh/SiO_2 promoted with Fe oxide.

As concerns the CO hydrogenation reaction on the transition metal sulfides, the activity and selectivity of only Mo and W sulfides have been reported. Stevens [6] claimed that K-promoted MoS_2 (K/MoS_2) yields C_1–C_5 alcohol in the presence of H_2S 50 ppm in concentration. The obtained STY of methanol is 48 g kg-cat^{-1} h^{-1} at 538 K, 10.5 MPa and 1200 ml ml-cat^{-1} h^{-1}. In the absence of H_2S, Klier *et al.* [19] reported that the higher STY of methanol (190 g kg-cat^{-1} h^{-1}) is obtained with Cs/MoS_2 at 568 K, 8.2 MPa and 7.8 m^3(STP) kg-cat^{-1} h^{-1}. Thus, much higher STY of methanol is obtained with the present Rh sulfide even at the lower reaction pressure.

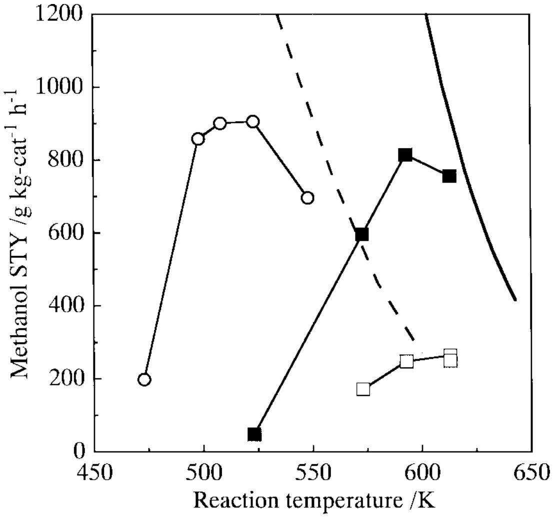

Figure 3. STY of methanol obtained with Rh sulfide from the syngas (■) and CO/H_2/CO_2 (□) feed in comparison with the commercial Cu/Zn/Al catalyst (○) from CO/H_2/CO_2 feed. Reaction conditions: 5.1 MPa, 30 m^3(STP) kg-cat^{-1} h^{-1} for Rh sulfide and 5.1 MPa, 6.0 m^3(STP) kg-cat^{-1} h^{-1} for the Cu/Zn/Al catalyst (the equilibrium yields of methanol at 5.1 MPa, 30 m^3(STP) kg-cat^{-1} h^{-1} (—) and 5.1 MPa and 6.0 m^3(STP) kg-cat^{-1} h^{-1} (- - -) are also plotted in the figure).

Figure 3 also includes the STY of methanol obtained with the Cu/Zn/Al catalyst from CO/H_2/CO_2 feed. The activity measurements were performed using a sulfur-free apparatus. The STY of methanol obtained with the Cu/Zn/Al catalyst at 523 K is 900 g kg-cat^{-1} h^{-1}. Methanol selectivity at this temperature was 99.9 mol%. Since Chinchen *et al.* [20] reported that a commercial Cu/Zn/Al catalyst yields 1090 g kg-cat^{-1} h^{-1} of methanol at 513 K and 5.1 MPa from CO/H_2/CO_2 feed, the methanol synthesis activity of the Cu/Zn/Al catalyst observed here is comparable with the reported value. The present Rh sulfide yields methanol of 90% of that obtained with the Cu/Zn/Al catalyst from CO/H_2/CO_2 feed at the higher reaction temperature and gas-hourly space velocity.

It is widely accepted that the STY of methanol obtained with the Cu/Zn/Al catalyst is significantly enhanced by the presence of a small amount of CO_2 in the feed [21]. Isotopic labeling experiments [22,23] suggest that methanol is directly formed by the hydrogenation of CO_2. Thus, the present work further investigated effects of CO_2 on the methanol synthesis activity of Rh sulfide. The results are also included in figure 3. The STY of methanol slightly increases with increasing reaction temperature up to 613 K and is 260 g kg-cat^{-1} h^{-1} at 613 K. Methanol selectivity at this

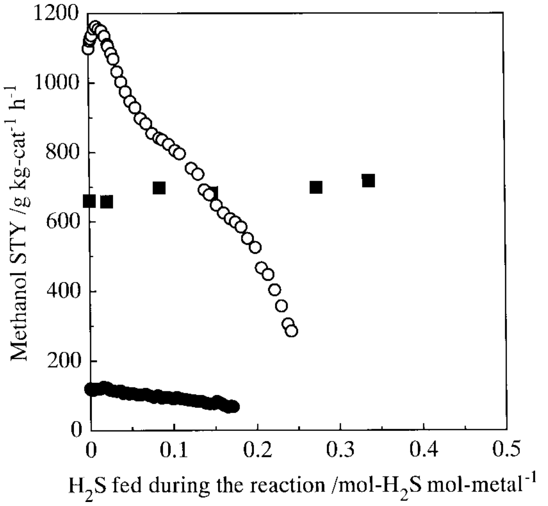

Figure 4. Effects of the gas-phase H_2S (100 ppm) on the STY of methanol obtained with Rh sulfide (■) from the syngas in comparison with the commercial Cu/Zn/Al catalyst from the syngas (•) and $CO/H_2/CO_2$ feed (○). Reaction conditions: 593 K, 5.1 MPa, 30 m^3(STP) kg-cat^{-1} h^{-1} for Rh sulfide and 513 K, 5.1 MPa, 6.0 m^3(STP) kg-cat^{-1} h^{-1} for the Cu/Z/Al catalyst.

temperature was 90 mol%. Thus, contrary to the Cu/Zn/Al catalyst, the presence of CO_2 significantly depresses the STY of methanol.

The much lower STY of methanol obtained with Rh sulfide from $CO/H_2/CO_2$ feed suggests that the mechanism of the methanol formation on Rh sulfide is different from that on the Cu/Zn/Al catalyst. Since CO_2 concentration of the effluent gas was observed to be lower than that of the feed, it is not unreasonable to assume that the reverse water–gas shift reaction occurs on Rh sulfide in the presence of CO_2 in the feed. Thus, one explanation for the much lower STY of methanol for the $CO/H_2/CO_2$ feed is that H_2O formed by the reverse water–gas shift reaction oxidizes the surface of Rh sulfide, which may strongly inhibit the hydrogenation of CO.

3.3. Sulfur tolerance of Rh sulfide

When the syngas is produced from carbon resources containing sulfur compounds, H_2S is a predominant sulfur compound in the syngas. H_2S concentration of the syngas derived from coal or heavy oil is above ten thousand ppm [4,22] while that of the syngas derived from waste materials such as plastics is within several hundred ppm [24]. The present work investigated the sulfur tolerance of Rh sulfide in the presence of H_2S 100 ppm, which is comparable with that of the syngas produced from the waste materials. The Cu/Zn/Al catalyst was also subjected to the reaction in the presence of H_2S for a comparison purpose.

After reaching the steady state activity under the sulfur-free conditions, the syngas or $CO/H_2/CO_2$ feed mixed with H_2S/H_2 was fed to the reactor. The total amount of H_2S fed during the reaction is normalized on the mol-H_2S mol-metal^{-1} basis. The obtained results are shown in figure 4. Even when the molar amount of H_2S fed reaches 40% of the molar amount of Rh, the STY of methanol obtained with Rh sulfide from the syngas preserves its activity under the sulfur-free conditions. In contrast, the STY of methanol obtained with the Cu/Zn/Al catalyst from both the syngas and $CO/H_2/CO_2$ feed decrease with increasing total amount of H_2S fed during the reaction. They drop into less than 50% of that obtained under the sulfur-free conditions when the molar amount of H_2S is 20% of the molar amount of Cu and Zn. Thus, the Rh sulfide prepared in the present work is quite tolerant toward H_2S.

4. Discussion

Reduced Rh catalysts are well known to show a catalytic activity for the conversion of the syngas. Their activity and selectivity change sensitively depending on the nature of the supports and promoters used. Ichikawa [13] reported that methanol is formed selectively when an alkaline earth metal oxide or ZnO is used as a support while the reduced Rh/SiO_2 yields hydrocarbons exclusively. A further addition of Ti [14], Mn [15], Fe [16] or Zr [14] oxides to the reduced Rh/SiO_2 improves the formation rate of methanol as well as ethanol.

To make clear the active sites for the methanol formation on the reduced Rh catalyst, several authors investigated the correlation between the surface structure and the methanol synthesis activity of the reduced Rh catalysts. *In situ* XPS measurements showed that Rh species supported on SiO_2 after H_2 reduction are in a metallic state while those on ZnO support are in a cationic state [17]. Ponec and his coworkers [18] investigated the amount of cationic Rh species present in various supported catalysts after the reaction by an extracting technique using an acetonitrile solution. They found that the methanol selectivity of the supported catalysts increases with increasing extractable amount of the cationic Rh species. These results led them to the hypothesis that the cationic Rh species are active for the methanol formation [18,25].

XRD measurements presented here show that the crystalline structure of Rh sulfide before and after the CO hydrogenation reaction is the $Rh_{17}S_{15}$ structure. When we consider the previous works on the reduced Rh catalysts, our findings suggest that the cationic Rh sites are stabilized by Rh–S bonds of the $Rh_{17}S_{15}$ structure and are active for the methanol formation. Moreover, the present Rh sulfide shows much higher methanol synthesis activity than the reduced Rh catalysts, which also suggests that the cationic Rh sites of Rh sulfide are much more effective for the methanol formation than those of the reduced Rh catalysts. In the stream of the syngas containing H_2S, the surface cationic Rh species stabilized by the sulfur coordination is equilibrated with the gas-phase H_2S and shows high activity for the methanol formation.

It is also worth noting that Brandreth and Winstanley [7] observed the enhancement of the total activity of the reduced Rh/SiO_2 as well as the selectivity for C_2 oxygenates (mainly acetaldehyde) by the pre-adsorption of COS (20% of monolayer coverage). They also found that a small amount of pre-adsorbed H_2S onto the reduced Rh/SiO_2 (5% of monolayer coverage) enhances its methanol selectivity while a larger quantity of H_2S (20% of monolayer coverage) completely inhibits the methanol formation [7]. Their results and the present result indicate that the CO hydrogenation activity of surface Rh species is not necessarily poisoned by sulfur compounds. However, their results and our results are difficult to explain consistently by assuming that the catalytic activity and selectivity of Rh–S species exclusively depends on the electronic state of Rh sites, *i.e.*, the cationic character of Rh sites imparted by Rh–S bonds. When we consider the difference of the activity and selectivity between the present Rh sulfide and their reduced Rh/SiO_2 modified by COS or H_2S, the difference of dispersion between them should be noted. Such a difference of the dispersion may cause differences of the surface fine structure of Rh–S species, *e.g.*, coordination number of S atoms and interatomic distance between Rh atom and S atom. Highly dispersed Rh species (*i.e.*, Rh/SiO_2) may strongly interact with S atoms, and easily reconstruct to lose its activity for the CO hydrogenation reaction in the presence of full coverage of S. In other words, the sulfur-coordination structure around the Rh atom favorable for the CO hydrogenation reaction may depend on the Rh dispersion and the kinds of reaction.

5. Conclusions

The present work found that Rh sulfide prepared by the reaction between $RhCl_3$ and Li_2S shows the catalytic activity for the conversion of syngas into methanol even in the presence of H_2S 100 ppm in concentration. Rh sulfide yielded 800 g kg-cat^{-1} h^{-1} of methanol with a selectivity of 80 mol% at 593 K and 5.1 MPa, which is 90% of that obtained with the Cu/Zn/Al catalyst at 523 K and 5.1 MPa from $CO/H_2/CO_2$ feed in the absence of H_2S. The results obtained by the present work suggest that Rh sulfide is applicable to the synthesis of methanol from the syngas containing H_2S without the desulfurizer unit when the concentration of H_2S is below 100 ppm.

Acknowledgment

This work was supported by Research for the Future Program of Japan Society for the Promotion of Science under the Project “Synthesis of Ecological High Quality Transportation Fuels” (JSPS-RFTF98P01001).

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