Selective Synthesis of Methanol from $CO + H_2$ over Pd Sulfide in the Presence of H_2S

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Both bulk and SiO_2-supported Pd sulfides were found to show methanol synthesis activity from $CO + H_2$ (syngas). SiO_2-supported Pd sulfide yielded 120 g kg-cat^{-1} h^{-1} of methanol at 613 K, 5.1 MPa and 20 m^3 (STP) kg-cat^{-1} h^{-1}. In the presence of H_2S 120 ppm in concentration, it preserved 40% of the activity that was obtained under the sulfur-free conditions.

It is widely accepted that Cu/Zn-type methanol synthesis catalyst is susceptible to a sulfur poisoning. A commercial Cu/Zn/Al catalyst is reported to deactivate even in the presence of H_2S 1.6 ppm in concentration.[1] H_2S content in the syngas is seriously high especially when the syngas is derived from a coal, heavy oil, biomass or waste materials. To avoid the sulfur poisoning, conventional plants are equipped with a huge desulfurizer unit that removes the sulfur compounds almost completely from the syngas. Alternatively, developments of a sulfur tolerant catalyst that works without the desulfurizer unit could overcome this problem.

Although Cr/Zn-type methanol synthesis catalyst is known to be more tolerant toward H_2S than Cu/Zn-type catalyst, even this type of catalyst loses its activity gradually in the presence of small amount of H_2S (1.5 ppm).[1] In contrast to these catalysts, alkali metal-promoted Mo sulfide preserves its initial activity for mixed alcohol synthesis for a long period in the presence of H_2S 50 ppm in concentration.[2] However, the performance of Mo sulfide based catalyst is not adequate since the higher reaction pressure (usually above 10 MPa) is required to attain a higher activity and selectivity. Considering these situations, we think that the application of metal sulfides is a promising way of developing the sulfur tolerant catalyst. Although CO hydrogenation activity of the sulfides except for Mo and W sulfides has never been investigated yet, some of sulfides are expected to catalyze CO hydrogenation reaction since $[Rh_{10}Se]/TiO_2$ yields ethanol from $CO_2 + H_2$.[3] The formation of C–C bond is suggested to proceed via the insertion of adsorbed CO_x into adsorbed CH_y that is formed by the hydrogenation of adsorbed CO derived from CO_2. Recently, authors found that Rh sulfide yields methanol from the syngas and H_2S has little influence on its activity.[4] Since reduced Rh and Pd catalysts are known to yield methanol from the syngas,[5–20] our results imply that Pd sulfide also shows methanol synthesis activity in the presence of H_2S. Thus, the present work investigated the activity and selectivity for CO hydrogenation reaction of Pd sulfide. Sulfur tolerance of the sulfide was also examined.

Bulk Pd sulfide ($Pd_{16}S_7$) was prepared by sulfiding $PdCl_2$ powder (Wako Pure Chemicals, 99%) in a stream of H_2S 5%/H_2 at 673 K for 2 h. $Pd_{16}S_7$ was then passivated in a stream of O_2 1%/He at room temperature and stored in the air. BET surface area of $Pd_{16}S_7$ thus prepared was less than 1 m^2 g^{-1}. Before the reaction, $Pd_{16}S_7$ was sulfided in the stream of H_2S 5%/H_2 at 673 K. The cumulative amount of H_2S fed during the sulfiding treatment was 2 mol-H_2S mol-Pd^{-1}. SiO_2-supported Pd sulfide was prepared by sulfiding an oxidic precursor, which had been prepared by impregnating SiO_2 powder with an aqueous $Pd(NH_3)_4(NO_3)_2$ solution (Aldrich) followed by drying and calcination. Two kinds of SiO_2 supports, SiO_2-A (Fuji Davison, ID gel, 192 m^2 g^{-1}) and SiO_2-B (Fuji Silysia, CARiACT Q-3, 560 m^2 g^{-1}), were used for the preparation of the precursor. A weight ratio of Pd (as metal) to SiO_2 support was 0.045. The cumulative amount of H_2S fed during the sulfiding treatment was 160 mol-H_2S mol-Pd^{-1}. CO hydrogenation reaction was carried out using a conventional fixed bed reactor in the absence and presence of the gaseous H_2S.[4] H_2S concentration was determined with a sulfur chemiluminescence detector (SCD). Cu/Zn/Al catalyst supplied by ICI Corp. was used as a reference. A sulfur-free apparatus was also used for the activity measurements of Cu/Zn/Al catalyst in the absence of H_2S.

The activity and selectivity for CO hydrogenation reaction of $Pd_{16}S_7$ were examined at 613 K, 5.0 MPa and 20 m^3 (STP) kg-cat^{-1} h^{-1}. Under these reaction conditions, CO conversion was 0.9%. Products were mainly composed of methanol with a small amount of methane. Methanol selectivity of $Pd_{16}S_7$ is 95 mol% as shown in Figure 1. Since the equilibrium CO conversion for methanol formation from the syngas feed is 7.2% at 613 K and 5.1 MPa, CO conversion of $Pd_{16}S_7$ is 12% of the equilibrium one. Figure 1 also shows the STY of methanol obtained with $Pd_{16}S_7$. $Pd_{16}S_7$ yields 77 g kg-cat^{-1} h^{-1} of methanol. In the case of

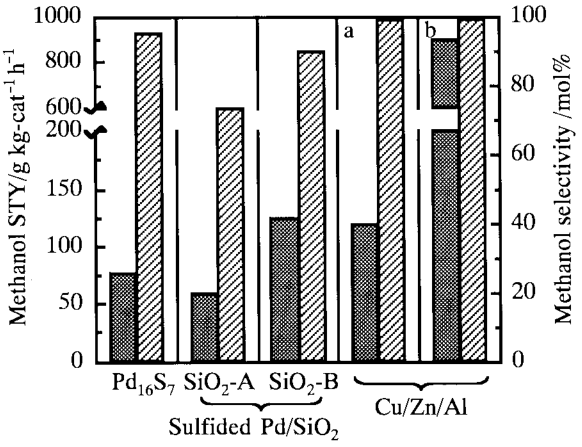

Figure 1. Methanol STY (left side) and methanol selectivity (right side) obtained with $Pd_{16}S_7$ and sulfided Pd/SiO_2 from the syngas feed in comparison with those of the commercial Cu/Zn/Al catalyst from the syngas (a) and $CO/H_2/CO_2$ feed (b); reaction conditions, CO 33%/H_2 62%/Ar, 613 K, 5.1 MPa, 20 m^3 (STP) kg-cat^{-1} h^{-1} for Pd sulfides and CO 33%/H_2 62%/Ar or CO 30%/H_2 60%/CO_2 5%/Ar, 513 K, 5.1 MPa, 6.0 m^3 (STP) kg-cat^{-1} h^{-1} for the Cu/Zn/Al catalyst.

SiO_2-supported Pd sulfide (Figure 1), a higher STY of methanol is obtained when SiO_2 support having the higher surface area (SiO_2-B) is used for the preparation of the precursor. The STY of methanol obtained with sulfided Pd/SiO_2-B is 1.6 times higher than that obtained with $Pd_{16}S_7$. It is also noted that Pd content of sulfided Pd/SiO_2-B is much lower than that of $Pd_{16}S_7$. The yield of methanol obtained with sulfided Pd/SiO_2-B normalized to the total amount of Pd atoms is 30 times higher than that obtained with $Pd_{16}S_7$. Thus, the enhanced activity of sulfided Pd/SiO_2-B may be attributed to the highly dispersed state of Pd sulfide supported on SiO_2-B. Many studies showed that reduced Pd catalysts containing alkali metal,[9–13] alkaline-earth metal[13–16] or lanthanoid[13,12–20] oxides as a support or additive yield methanol selectively from the syngas feed. Metallic Pd particles supported on SiO_2 containing impurities in sub-ppm level yield mainly methane.[13] Among the catalysts reported so far, the maximum STY of methanol is obtained with reduced Pd/CeO_2. This catalyst yields 310 g kg-cat^{-1} h^{-1} of methanol at 473 K and 2.0 MPa,[20] which is 2.6 times higher than that obtained with sulfided Pd/SiO_2-B at 613 K and 5.1 MPa. It is also worthy to note that $Pd_{16}S_7$ yields methanol selectively without the metal oxides mentioned above. This suggests that Pd species having Pd–S bonds play a certain role in the formation of methanol.

Figure 1 also includes methanol synthesis activity and selectivity of the commercial Cu/Zn/Al catalyst at 513 K, 5.1 MPa and 6.0 m^3 (STP) kg-cat^{-1} h^{-1}. The STY of methanol obtained with Cu/Zn/Al catalyst from the syngas and CO/H_2/CO_2 feed was 110 and 900 g kg-cat^{-1} h^{-1}, respectively. The latter value is in good accordance with that reported by Chinchen et al.[21] The STY of methanol obtained with sulfided Pd/SiO_2-B is no more than 10% of that obtained with Cu/Zn/Al catalyst from CO/H_2/CO_2 feed. The STY of methanol obtained with sulfided Pd/SiO_2-B and Cu/Zn/Al catalyst from the syngas feed is comparable with each other.

Then, effects of H_2S on methanol synthesis activity of sulfided Pd/SiO_2-B and Cu/Zn/Al catalysts were examined (Figure 2). 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 amount of H_2S fed during the reaction is normalized on the mol-H_2S mol-metal (Pd or Cu)$^{-1}$ basis. By introducing the syngas containing H_2S (120 ppm in concentration), the STY of methanol obtained with sulfided Pd/SiO_2-B decreases to 40% of the initial value. Sulfided Pd/SiO_2-B, however, preserves this activity even when the total amount of H_2S exceeds 6.0 mol-H_2S mol-Pd^{-1}. H_2S 80–100 ppm in concentration was observed in the effluent gas during the experiment. In the case of Cu/Zn/Al catalyst, the activity measurements were performed in the presence of H_2S 100 or 300 ppm in concentration. H_2S concentration was 100 ppm until the total amount of H_2S reached 0.16 mol-H_2S mol-Cu^{-1} while it increased to 300 ppm at above 0.16 mol-H_2S mol-Cu^{-1}. The STY of methanol obtained with Cu/Zn/Al catalyst decreases monotonously with increasing the total amount of H_2S and is nearly 0 at 0.4 mol-H_2S mol-Cu^{-1}. H_2S concentration of the effluent gas was below the detection limit of SCD throughout the experiment. From these results, it is suggested that active species of sulfided Pd/SiO_2-B (possibly having Pd–S bonds) is equilibrated with the gas-phase H_2S in the stream of the syngas feed containing H_2S and shows the constant activity.

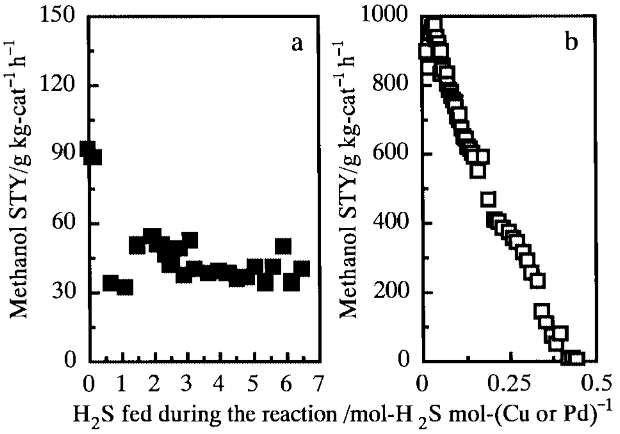

Figure 2. Effects of the gas-phase H_2S on the methanol synthesis activity of sulfided Pd/SiO_2-B (a) from the syngas feed in comparison with that of the commercial Cu/Zn/Al catalyst from CO/H_2/CO_2 feed (b); Reaction conditions, CO 33%/H_2 62%/Ar, 613 K, 5.1 MPa, 20 m^3 (STP) kg-cat^{-1} h^{-1} for sulfided Pd/SiO_2-B and CO 30%/H_2 60%/CO_2 5%/Ar, 523 K, 5.1 MPa, 6.0 m^3 (STP) kg-cat^{-1} h^{-1} for Cu/Z/Al catalyst; H_2S concentration, 120 ppm for sulfided Pd/SiO_2-B and 100 or 300 ppm for Cu/Zn/Al catalyst.

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