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A Striking Effect of H_2S Treatment of Catalyst on the Improvement of Acetic Acid Selectivity in High Pressure CO Hydrogenation over $Rh-Ir-Mn-Li/SiO_2$

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A selective synthesis of acetic acid from syngas was investigated. Acetic acid was produced with nearly 70% selectivity in carbon efficiency over H_2S-modified $Rh-Ir-Mn-Li/SiO_2$ catalyst at the expense of the activity. The role of H_2S modification was also studied.

We have been developing highly efficient catalysts for selective conversion of syngas into acetic acid.[1)] A $Rh-Ir-Mn-Li/SiO_2$ catalyst was proved to show an excellent activity and selectivity for the acetic acid synthesis from syngas.[2)] In order to increase acetic acid selectivity further, we attempted the surface modification of catalyst by H_2S treatment because it is known that sulfur treatment of catalyst changes the catalytic behavior significantly in some cases.[3)] Here, we wish to report the striking effect of H_2S-modified $Rh-Ir-Mn-Li/SiO_2$ catalyst for improving acetic acid selectivity.

Multi-promoted $Rh-Ir-Mn-Li/SiO_2$ catalyst was prepared by the conventional impregnation method. Silica-gel(Davison #57, 9-16 mesh) was impregnated with an aqueous solution containing a definite amount of $RhCl_3 \cdot 3H_2O$ and additive salts such as $IrCl_4 \cdot H_2O$, $MnCl_2 \cdot 4H_2O$ and LiCl. An impregnated sample was dried slowly up to 80 °C and was kept for 20 h under air circulation. Then the catalyst was reduced in a H_2 stream at 450 °C for 2 h. A catalyst includes 7wt% of rhodium as metal. The atomic ratio of employed additives to rhodium(Rh:Ir:Mn:Li) is 1:1/8:1/48:1/16. The procedure of H_2S treatment of the catalyst was carried out as follows. The catalyst(20 ml) was charged in a rotating glass flask and it was reduced again with a H_2 stream(333 ml min^{-1}) at 350 °C for 30 min. The catalyst was treated with a CO stream(333 ml min^{-1}) for 30 min and finally treated with a H_2S stream(95 ppm in N_2, 333 ml min^{-1}) at 350 °C. The H_2S/Rh ratio of modified catalyst was controlled by the feeding amount of H_2S. For example, the stream was fed for 1 h in the case of $H_2S/Rh=0.04$. High pressure reaction was conducted with a flow type fixed-bed micro-reactor under the conditions of pressure=100 kg cm^{-2}, temperature=300 °C, GHSV=10000 h^{-1}, and $CO/H_2=9/1$. A steady state was achieved about 4 h from initiation. Products were analyzed by GC which was equipped with both a Chromosorb 101 column for oxygenates such as acetic acid and an activated alumina column for hydrocarbons(C_1-C_4). An in-situ FT-IR(JEOL JIR-100) spectroscopy[4)] was employed for the observation of CO species adsorbed on the modified catalyst. An electronic state of H_2S-modified Rh on SiO_2 was determined by the ESCA(SHIMADZU ASIX-1000) analysis.

Table 1. Influence of H_2S treatment of the catalyst on the reaction behavior

H_2S/Rh atomic ratio	CO conv.	Selectivity in carbon efficiency / %					STY of CH_3COOH
	%	CH_3COOH	CH_3CHO	C_3^+ Oxygenates[a)]	CH_4	C_2-C_6 Hydrocarbons	g l^{-1} h^{-1}
0.000	6.4	55.4	19.1	9.5	3.2	11.1	450
0.004	4.5	63.9	20.4	5.3	3.0	5.9	359
0.006	3.0	67.2	20.2	4.2	2.8	3.8	260
0.011	1.9	69.4	19.9	3.4	2.8	2.3	171

Catalyst: 7.0 wt%Rh(1)-Ir(1/8)-Mn(1/48)-Li(1/16)/SiO_2, Catalyst charge: 10 ml
Reaction conditions; temperature: 300 °C, pressure: 100 kg cm^{-2}, GHSV: 10000 h^{-1}, CO/H_2: 9/1. a) Sum of C_2H_5CHO, C_3H_7CHO, and C_2H_5COOH.

Table 1 shows the reaction behavior of H_2S-modified catalysts. This reaction behavior was approximately stable, that is, significant deactivation and the change in the selectivity were not observed during the reaction at least for 10 h. The striking effect of H_2S modification on the catalyst performance was revealed. By the treatment with a small amount of H_2S, the acetic acid selectivity of catalysts increased with more than 10%. However, the total activity decreased. It is obvious that the increase of acetic acid selectivity is attributed not to the decrease of CH_4 and acetaldehyde selectivity, but to the decrease of C_2^+-hydrocarbons and C_3-C_4 oxygenates such as propionaldehyde. This means that the chain propagation of surface CH_x species are suppressed by the H_2S treatment of catalysts.

Table 2. Characterization of H_2S modified Rh-Ir-Mn-Li/SiO_2 catalyst

H_2S/Rh atomic ratio	CO adsorbed mlSTP g-cat^{-1}	Binding energy of Rh(3d5/2)[a)] eV	B-CO/L-CO[b)]	B-CO/L-CO[c)]
0.000	4.6	307.2	0.61	0.65
0.018	4.2	307.4	0.47	0.54
0.180	1.4	307.3	0.04	0.09

Catalyst: 7.0 wt%Rh(1)-Ir(1/8)-Mn(1/48)-Li(1/16)/SiO_2, Average particle size of Rh on catalyst: 36 Å.

a) Normalized by the use of 103.4 eV as a standard binding energy of Si(2p) of SiO_2 support.

b) IR spectra were taken under the condition of 1 atm, 20 °C, 200 ml min^{-1} flow of syngas(CO/H_2=9/1).

C) IR spectra were taken under the condition of 20 kg cm^{-2}, 300 °C, 200 ml min^{-1} flow of syngas(CO/H_2=9/1).

To determine the location of H_2S, CO chemisorption on H_2S-modified catalyst was measured. These data are shown in Table 2. The amount of adsorbed CO decreased with the increase in the H_2S/Rh ratio. This suggests that H_2S is present on the Rh surface of catalyst.

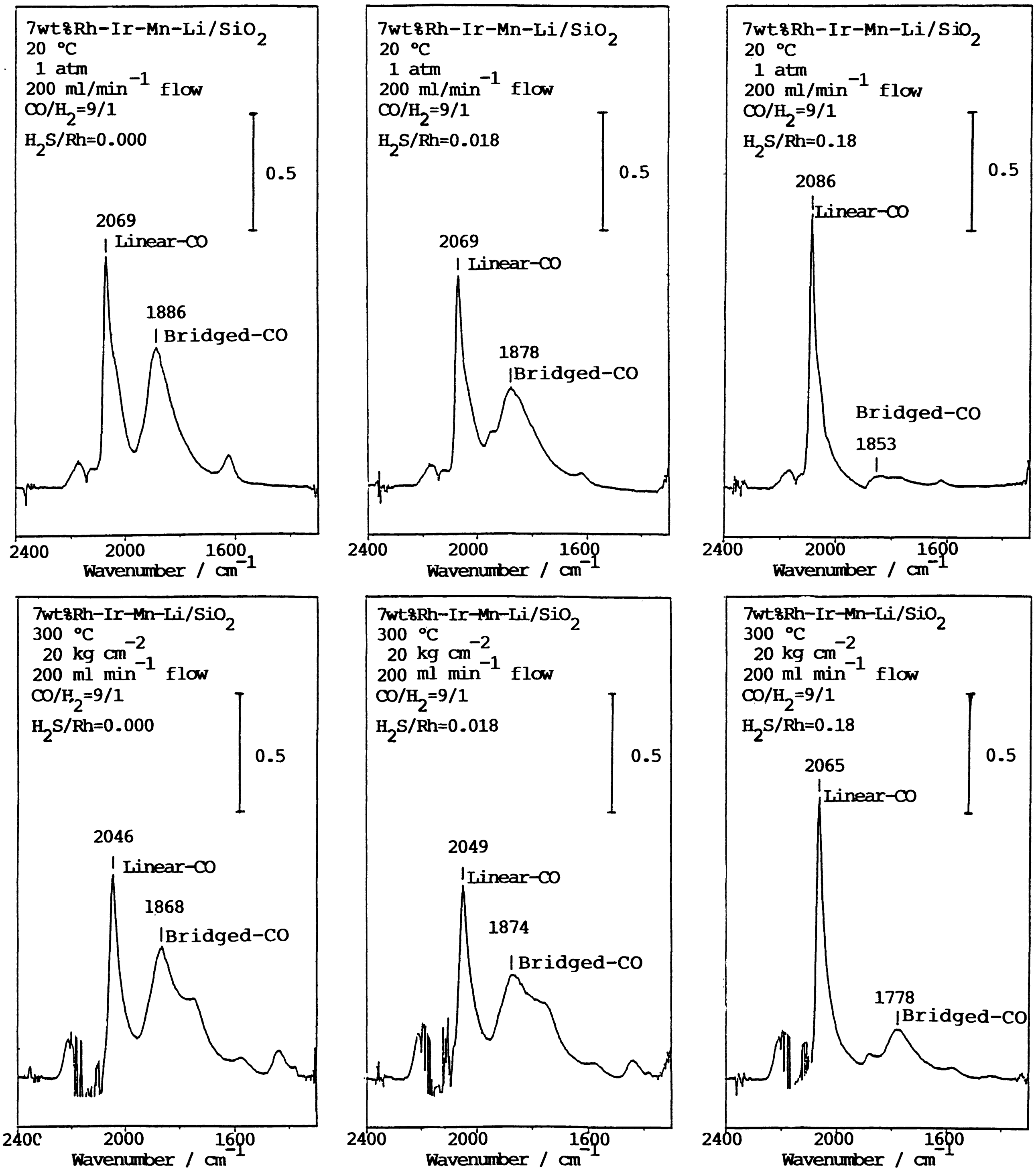

Fig. 1. In-situ FT-IR spectra of adsorbed CO species on H_2S modified catalyst.

The electronic state of Rh particle on SiO_2 measured by ESCA is also shown in Table 2. There is almost no difference of Rh binding energy between the H_2S-modified catalyst and the non-modified catalyst. This result shows that the electronic state of Rh particle of catalyst is not much influenced by H_2S treatment.

Figure 1 shows the in-situ FT-IR spectra of adsorbed CO species under the conditions of both 1 atm, 20 °C, 200 ml min^{-1} flow of syngas(CO/H_2=0/1), and 20 kg cm^{-2}, 300 °C, 200 ml min^{-1} flow of syngas(CO/H_2=9/1). Two kinds of adsorbed CO species were observed on every catalyst and they were assigned as linear-CO species and bridged-CO species.[5)] The bridged-CO species almost disappeared under the conditions of 1 atm and 20 °C in the case of H_2S/Rh=0.18. A similar phenomenon on Rh/Al_2O_3 was observed previously by Fujimoto et al.[6)] However, the realtionship between the amount of treated H_2S and catalytic behavior was not discussed satisfactorily. The ratio of bridged-CO absorbance to linear-CO absorbance(B-CO/L-CO) is shown in Table 2. This ratio decreased with the increase in the H_2S/Rh ratio. This shows that H_2S blocks mainly the bridged-CO adsorption site on Rh of catalyst. In addition, it is clear that CO conversion decreased dramatically with the decrease of bridged-CO absorbance. These results suggest that H_2S treatment reduces the amount of bridged-CO species which contributes to increase CO conversion as well as higher hydrocarbon formation. Thus, the chain propagation of surface CH_x species to C_2^+-hydrocarbons and C_3-C_4 oxygenates was suppressed. Consequently, the acetic acid selectivity increased.

In conclusion, a selective synthesis of acetic acid was attained by H_2S treatment of Rh-Ir-Mn-Li/SiO_2 catalyst. The H_2S on Rh particle controls the adsorbed CO species by its geometric modification of Rh surface principally. In other words, the effects of "ensemble effect"[7)] in the case of metal alloy catalyst are greater than that of "ligand effect"[7)] as the role of H_2S modification.

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