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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<sub>2</sub>

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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<sub>2</sub> 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.<sup>1)</sup> A Rh-Ir-Mn-Li/SiO<sub>2</sub> catalyst was proved to show an excellent activity and selectivity for the acetic acid synthesis from syngas.<sup>2)</sup> 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.<sup>3)</sup> Here, we wish to report the striking effect of  $H_2S$ -modified Rh-Ir-Mn-Li/SiO<sub>2</sub> catalyst for improving acetic acid selectivity.

Multi-promoted Rh-Ir-Mn-Li/SiO, 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<sub>3</sub>·3H<sub>2</sub>O and additive salts such as IrCl<sub>4</sub>·H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O 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<sub>2</sub> 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<sub>2</sub>S 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<sub>2</sub> stream(333 ml min<sup>-1</sup>) at 350 °C for 30 min. The catalyst was treated with a CO stream(333 ml min<sup>-1</sup>) for 30 min and finally treated with a  $H_2S$  stream(95 ppm in N<sub>2</sub>, 333 ml min<sup>-1</sup>) at 350 °C. The H<sub>2</sub>S/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  $\rm cm^{-2}$ , temperature=300 °C, GHSV=10000  $h^{-1}$ , and CO/H<sub>2</sub>=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<sup>4</sup>) was employed for the observation of CO species adsorbed on the modified catalyst. An electronic state of  $H_2$ S-modified Rh on SiO<sub>2</sub> was determined by the ESCA(SHIMADZU ASIX-1000) analysis.

H <sub>2</sub> S/Rh	H <sub>2</sub> S/Rh CO conv. mic ratio	Selectivity in carbon efficiency / %					STY of
atomic ratio		снзсоон	сн <sub>3</sub> сно	C3 <sup>+</sup> Oxygenates <sup>a)</sup>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>6</sub> Hydrocarbons	$\frac{CH_3COOH}{a^{-1}h^{-1}}$
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0.000	6.4	55.4	19.1	9.5	3.2	11.1	450
0.004	4.5	<u>63.9</u>	20.4	5.3	3.0	5.9	359
0.006	3.0	<u>67.2</u>	20.2	4.2	2.8	3.8	260
0.011	1.9	<u>69.4</u>	19.9	3.4	2.8	2.3	171

Table 1. Influence of H<sub>2</sub>S treatment of the catalyst on the reaction behavior

Catalyst: 7.0 wt&Rh(1)-Ir(1/8)-Mn(1/48)-Li(1/16)/SiO<sub>2</sub>, Catalyst charge: 10 ml Reaction conditions; temperature: 300 °C, pressure: 100 kg cm<sup>-2</sup>, GHSV: 10000 h<sup>-1</sup>, CO/H<sub>2</sub>: 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.

H <sub>2</sub> S/Rh	CO adsorbed	Binding energy of Rh(3d5/2) <sup>a)</sup>	B-CO/L-CO <sup>b</sup> B-CO/L-CO <sup>C</sup>	
atomic ratio	mlSTP g-cat <sup>-1</sup>	eV		
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

Table 2. Characterization of H<sub>2</sub>S modified Rh-Ir-Mn-Li/SiO<sub>2</sub> catalyst

Catalyst: 7.0 wt%Rh(1)-Ir(1/8)-Mn(1/48)-Li(1/16)/SiO<sub>2</sub>, 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<sub>2</sub> support.
- b) IR spectra were taken under the condition of 1 atm, 20 °C, 200 ml min<sup>-1</sup> flow of syngas(CO/H<sub>2</sub>=9/1).
- C) IR spectra were taken under the condition of 20 kg cm<sup>-2</sup>, 300 °C, 200 ml min<sup>-1</sup> flow of syngas (CO/H<sub>2</sub>=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<sub>2</sub>S 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<sup>-1</sup> flow of syngas  $(CO/H_2=0/1)$ , and 20 kg cm<sup>-2</sup>, 300 °C, 200 ml min<sup>-1</sup> 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.<sup>5)</sup> 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.<sup>6)</sup> 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.

In conclusion, a selective synthesis of acetic acid was attained by  $H_2S$  treatment of Rh-Ir-Mn-Li/SiO<sub>2</sub> 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"<sup>7)</sup> in the case of metal alloy catalyst are greater than that of "ligand effect"<sup>7)</sup> as the role of  $H_2S$  modification.

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