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# Catalytic hydrogenation of carbon monoxide over silica-supported Ir–Mo–Rh catalyst

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We present here some results on Ir–Mo–Rh metallic catalysts for the synthesis of $C_2-C_4$ alcohols from syngas. It was found that Ir–Mo–Rh supported on silica containing small amounts of Rh exhibited much higher activity for CO hydrogenation than Ir–Mo bimetallic catalyst. The selectivity to various alcohols did not change very much upon the addition of Rh. The activity was greatly affected by the impregnation procedure of the metals in the catalyst preparation.

**Keywords:** Catalytic hydrogenation of CO; $C_2$–$C_4$ alcohols; Ir–Mo–Rh/$SiO_2$

## 1. Introduction

It is well known that Rh catalysts are effective for the synthesis of ethanol from syngas [1–4]. However, Rh catalysts may not be necessarily optimum for commercial use because of their high price and poor resources. Therefore, we have been investigating the reduction of Rh content in the catalysts.

For the synthesis of $C_2-C_4$ alcohols, catalysts must activate CO both dissociatively and nondissociatively [5]. One of the authors previously found that some $C_2-C_4$ alcohols from syngas were yielded over bimetallic catalysts composed of Ir on which CO adsorbed nondissociatively and Mo on which CO adsorbed dissociatively [6]. Monometallic catalysts, Ir/$SiO_2$ [7,8] and Mo/$SiO_2$ [9], were extremely low in activity and yielded hydrocarbons as main products. On the other hand, $Ir^*Mo/SiO_2$ bimetallic catalyst exhibited an activity about 500 times as high as each monometallic one [6]. The selectivity of the bimetallic catalyst to the products was quite different from that of the monometallic ones. The synergy of an increase in the selectivity to the higher alcohols ($C_{2+}$ alcohols) was observed on the bimetallic catalyst.

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Recently, we have found that the addition of Rh to Ir–Mo catalysts increases the catalytic activity. The Ir–Mo–Rh/$SiO_2$ catalyst system is considered an attractive one to reduce the Rh content in catalyst.

In this work, the catalytic performance of Ir–Mo–Rh/$SiO_2$ catalyst was investigated.

## 2. Experimental

The catalysts were prepared by impregnating silica gel (Fuji-Davison Cariact-50 10–20 mesh) with the aqueous solutions of $IrCl_4 \cdot H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $RhCl_3$ and then by reducing in $H_2$ at 450°C for 3 h. The impregnation procedures of the catalyst were as follows: simultaneous impregnation and stepwise impregnation. The simultaneous impregnation catalyst, Ir*Mo*Rh/$SiO_2$, was prepared by loading all the metals at the same time. Among stepwise catalysts, for example, Ir*Rh//Mo/$SiO_2$ catalyst was prepared by loading firstly Mo, and then both Ir and Rh, and the Ir//Mo*Rh/$SiO_2$ catalyst was prepared by loading firstly both Mo and Rh, and then Ir. The other stepwise catalysts were as follows; Ir*Mo//Rh/$SiO_2$, Mo*Rh//Ir/$SiO_2$, Mo//Ir*Rh/$SiO_2$, Rh//Ir*Mo/$SiO_2$.

Reactions were carried out at 20 kg/cm$^2$ of syngas (CO : $H_2$ : Ar = 3 : 6 : 1) with a fixed-bed flow reactor. The effluent gas was directly introduced into gas-chromatographs for analysis.

Table 1
Hydrogenation of CO over various Ir–Mo–Rh/$SiO_2$ catalysts [a]

| Catalysts | CO conv. (%) | Alc.STY (g/ℓh) | Product selectivity (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | alcohols | | hydrocarbons | | $CO_2$ |
| | | | $C_1$ | $C_2$–$C_4$ | $C_1$ | $C_{2+}$ | |
| Ir*Mo*Rh | 5.0 | 8.5 | 18.5 | 11.3 | 35.0 | 14.3 | 19.3 |
| Ir*Rh//Mo | 39.9 | 48.7 | 11.0 | 10.5 | 28.6 | 9.6 | 40.4 |
| Ir//Mo*Rh | 30.8 | 31.7 | 10.4 | 7.7 | 32.3 | 13.0 | 36.6 |
| Ir*Mo//Rh | 18.8 | 25.7 | 11.6 | 12.5 | 24.2 | 12.0 | 36.8 |
| Mo*Rh//Ir | 12.7 | 18.9 | 13.3 | 12.9 | 23.9 | 12.4 | 34.7 |
| Mo//Ir*Rh | 6.0 | 6.5 | 7.8 | 11.2 | 34.0 | 23.2 | 20.8 |
| Rh//Ir*Mo | 2.3 | 2.8 | 12.0 | 9.7 | 35.5 | 17.8 | 23.4 |
| Ir*Mo | 2.2 | 2.3 | 10.3 | 8.1 | 35.0 | 23.5 | 19.7 |
| Rh [b] | 0.8 | 1.6 | 14.9 | 21.1 | 39.8 | 3.6 | 0 |

[a] Conditions: CO : $H_2$ : Ar = 3 : 6 : 1, 240°C, 20 kg/cm$^2$, $W/F$: 11.2 g-cat. h mol$^{-1}$, mole ratio Ir : Mo : Rh = 1 : 1 : 0.29. Ir, Mo, Rh content: 6.5, 3.2, 1.0 wt%.

[b] 280°C, 50 kg/cm$^2$, Rh content: 1.0 wt%.

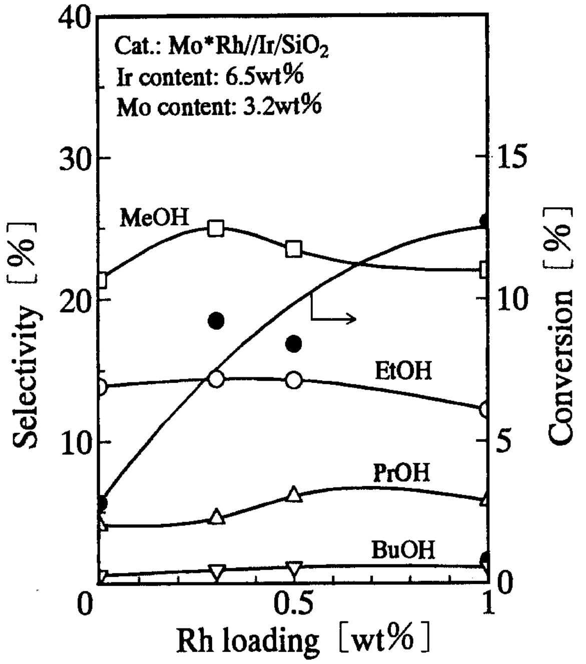

Fig. 1. Effect of the amount of Rh loaded. Pressure 20 kg/cm$^2$, 240°C, SV 2000 h$^{-1}$.

## 3. Results and discussion

The effect of the addition of Rh to Ir–Mo/$SiO_2$ catalyst was investigated. The performance of Ir–Mo–Rh/$SiO_2$ catalyst system for the CO hydrogenation is presented in table 1. It is noteworthy that the various impregnation procedures influenced the performances of Ir–Mo–Rh catalysts. In particular, the catalysts prepared by later Ir-impregnation exhibited a higher CO conversion, whereas the product distribution did not changed considerably.

Fig. 1 shows the conversions and selectivities of the Mo*Rh//Ir/$SiO_2$ catalyst as a function of Rh content. The activity of the Ir–Mo bimetallic catalyst increased remarkably upon the addition of a small amount of Rh, though the CO conversion over the 1wt% Rh/$SiO_2$ monometallic catalyst was extremely low as seen from table 1. The selectivities of the Mo*Rh//Ir/$SiO_2$ catalyst to the products did not remarkably depend on Rh content.

## References

[1] M.M. Bhasin, W.J. Bartley, P.C. Ellgen and T.P. Wilson, J. Catal. 54 (1978) 120.
[2] T.P. Wilson, P.H. Kasai and P.C. Ellgen, J. Catal. 69 (1981) 193.
[3] M. Ichikawa, T. Fukushima, K. Tanala, T. Saito and Y. Onoda, in: *Proc. Symp. $C_1$ Chem.*, Tokyo 1984, p. 7.

[4] Y. Mita, K. Sano, S. Mutsuhira and T. Nakajo, in: *Proc. Symp. $C_1$ Chem.*, Tokyo 1984, p. 7.
[5] G. Borden, T.N. Rhodin, C. Brucker, R. Benbow and Z. Hurych, Surf. Sci. 59 (1976) 593.
[6] Y. Kuwahara, H. Honda, Y. Tanaka, T. Ito and K. Wakabayashi, Chem. Lett. (1985) 205.
[7] M.A. Vannice, J. Catal. 37 (1975) 449.
[8] M.A. Vannice, J. Catal. 50 (1975) 228.
[9] C.B. Murchison and D.A. Murduck, Hydrocarbon Processing 60 (1981) 159.