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SELECTIVE SYNTHESIS OF C_2-OXYGENATED COMPOUNDS FROM SYNTHESIS GAS OVER Ir-Ru BIMETALLIC CATALYSTS

Hideaki HAMADA, Yasushi KUWAHARA, Yoshiaki KINTAICHI, Takehiko ITO, Katsuhiko WAKABAYASHI,* Hitoshi IIJIMA,† and Ken-ichi SANO†
National Chemical Laboratory for Industry,
Yatabe, Tsukuba-gun, Ibaraki 305
†Showa Denko K. K., Nakanosu, Oh-ita 870

Silica-supported Ir-Ru bimetallic catalysts were found to produce C_2-oxygenated compounds from synthesis gas at temperatures from 280 °C to 300 °C under 50 atm. The addition of Li to the bimetallic catalysts brought about improvement in catalytic activity and selectivity

It is well known that C_2-oxygenated compounds such as ethanol, acetaldehyde, and acetic acid are produced selectively from synthesis gas over supported Rh catalysts promoted with Mn, Fe, Zr, etc. However, there have been few reports[1)] relating to the synthesis of these compounds over other catalysts than Rh, although some catalysts are presented in the patents.[2)] We report here the excellence of novel Ir-Ru bimetallic catalysts for the selective formation of C_2-oxygenated compounds.

The catalysts were prepared by impregnating Davison Grade 57 silica (12-20 mesh) with an aqueous solution of chloride salts, followed by reduction in H_2 at 500 °C for 3 h. Reactions were carried out at 50 atm of synthesis gas ($CO:H_2:Ar=3:6:1$) by using a 316 stainless steel flow reactor of 17 mm inner diameter and 300 mm length. The effluent gas was directly introduced into gas chromatographs to analyse. CO conversion was calculated by using Ar in the feed gas as an internal standard, and product selectivity was determined based on CO reacted.

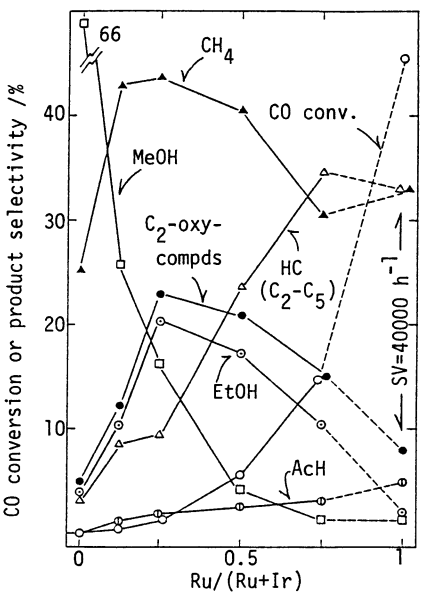

Fig. 1. Effect of Ru molar fraction
Reaction conditions: 50 atm, 300 °C, SV=2000 h^{-1}. Metal content: 0.2 mmol/g-SiO_2.

Figure 1 shows the effect of Ru molar fraction of the catalysts on the reaction. It should be noted that the selectivity to C_2-oxygenated compounds composed mainly of EtOH had a maximum at a 1/4 Ru molar fraction. In contrast, CO conversion and the selectivity to C_2-C_5 hydrocarbons increased with an increase in Ru content, although the selectivity to

MeOH decreased.

Table 1 shows the effect of the addition of alkali metals to the bimetallic catalysts. It is noteworthy that Li has an excellent effect of improving CO conversion and the selectivity to C_2-oxygenated compounds. The selectivity was 29.1% at 300 °C and 38.4% at 280 °C. The following order is obtained as that of the effect of alkali metals for the selectivity to C_2-oxygenated compounds: Li > Na > K > Rb > Cs.

Table 1. Activity and selectivity of alkali-doped Ir-Ru/SiO_2 catalysts

Catalyst	Ir-Ru	Ir-Ru-Li	Ir-Ru-Na	Ir-Ru-K	Rb//Ir-Ru[a]	Cs//Ir-Ru[a]
CO conv./%	5.6	6.5 (2.0)[b]	3.3	3.4	1.6	1.4
Selectivity/%						
CH_4	40.5	30.8 (23.8)	37.7	32.9	37.8	41.2
HC(C_2-C_5)[c]	23.6	24.9 (22.6)	19.4	29.2	23.2	23.8
MeOH	4.2	2.3 (3.6)	7.1	2.4	3.5	2.8
EtOH	17.2	21.6 (22.7)	20.5	12.4	10.7	7.0
PrOH	2.1	2.2 (2.4)	2.1	1.9	1.7	1.2
AcH	2.6	5.7 (10.8)	3.1	7.0	7.8	8.9
AcOH	0.3	0.5 (2.5)	0	0.6	0	0
AcOMe	0.2	0.3 (0.3)	0.4	0.2	0.4	0.3
AcOEt	0.6	1.2 (2.1)	0.7	1.6	1.6	1.8
CO_2	4.5	5.7 (4.0)	5.6	6.2	8.8	8.5
ΣC_2-O[d]	20.9	29.1 (38.4)	24.5	21.7	20.3	18.0

Reaction conditions: 300 °C, 50 atm, H_2/CO=2, SV=2000 h^{-1}. Metal content: 0.1 mmol/g-SiO_2 for each metal. a) Reduced Ir-Ru/SiO_2 was doped with Rb or Cs. b) Values at 280 °C. c) C_2-C_5 hydrocarbons. d) Sum of C_2-oxygenated compounds.

In addition, it was found that H_2/CO ratios of the feed gas affected the product distribution remarkably. Under CO rich reaction conditions, significant amounts of AcOH and AcH were obtained. For example, under the conditions of H_2/CO =1/2, 290 °C, and 75 atm, a Ru-Ir-Li/SiO_2 (3:1:3 molar ratio) catalyst showed the following selectivity: CH_3COOH 12.3%, CH_3CHO 19.6%, C_2H_5OH 2.5% (ΣC_2-O 34.4%).

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