Selective Synthesis of Acetic Acid in High Pressure Carbon Monoxide Hydrogenation over a Rh–Mn–Ir–Li/SiO$_2$ Catalyst

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A highly efficient catalyst for direct synthesis of acetic acid from synthesis gas (H_2 + CO) has been developed; acetic acid was produced with > 65% selectivity in carbon efficiency and with high space time yield, a typical value being 130 g (dm^3 cat.)$^{-1}$ h^{-1}, over a Rh–Mn–Ir–Li/SiO$_2$ catalyst at 280 °C, with a pressure of 100 kg cm^{-2}, a space velocity of 10^4 h^{-1}, and a ratio of H_2 to CO of 1 : 9.

Direct and selective syntheses of C$_2$-oxygenates from synthesis gas (H_2 + CO) have received much attention from both industrial and academic points of view; the former is of potential and technological importance for the establishment of new synthetic routes to produce C$_2$-oxygenates from synthesis gas in place of petrochemical routes, and the latter is of fundamental interest in studies of catalytic reactions. The pioneering work at Union Carbide Corporation[1] has stimulated numerous studies of direct syntheses of C$_2$-oxygenates such as ethanol and acetic acid over heterogeneous Rh-based catalysts. For example, the selective synthesis of ethanol over a multi-promoted Rh/SiO$_2$ catalyst was reported[2] as well as

Table 1. Catalytic performance of multi-promoted Rh/SiO_2 catalysts.

Catalyst[a]	% Selectivity in carbon efficiency							Space time yield of $MeCO_2H$[e]
	$MeCO_2H$	MeCHO	EtOH	C_2O[b]	$C_{3-4}O$[c]	CH_4	C_{2+}[d]	
Rh(1)–Mn(1/24)/SiO_2	44.2	23.0	0.0	67.2	5.9	5.8	21.0	84
Rh(1)–Mn(1/24)–Li(1/16)/SiO_2	46.0	23.5	0.0	69.5	6.5	4.3	19.7	110
Rh(1)–Mn(1/24)–Ir(1/8)/SiO_2	55.5	23.6	0.0	79.2	3.9	3.9	13.1	194
Rh(1)–Mn(1/24)–Ir(1/8)–Li(1/16)/SiO_2	61.6	23.6	0.0	85.2	3.2	2.8	8.8	191
Rh(1)–Mn(1/48)–Ir(1/8)–Li(1/16)/SiO_2	65.4	21.8	0.7	87.9	2.5	2.9	6.7	129
Rh(1)–Mn(1/48)–Ir(1/4)–Li(1/4)/SiO_2	67.2	18.7	2.5	88.3	2.2	2.4	6.0	95

[a] Catalyst: Rh content, 5.0 wt%; 10 ml of catalyst was charged. Conditions; T 280 °C, P 100 kg/cm^2; G.H.S.V. = 10^4 h^{-1}; H_2:CO = 1:9. Data were obtained after 4 h on stream. The numbers in parentheses show atomic ratio of additives to Rh supported on SiO_2. [b] Sum of acetic acid, acetaldehyde, and ethanol. [c] Sum of propionaldehydehyde (C_3O) and butyraldehyde (C_4O). [d] Sum of higher hydrocarbons such as ethane, ethylene, propane, and propene. [e] g (dm^3 cat.)$^{-1}$ h^{-1}.

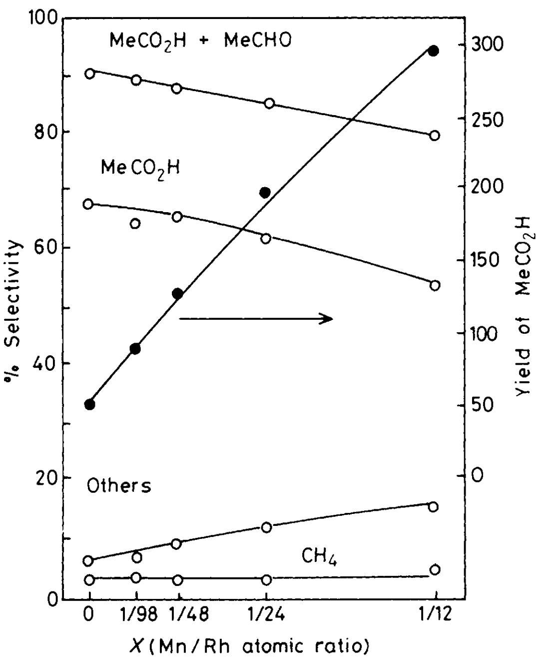

Figure 1. Influence of Mn additive amount (x) on product selectivities and space time yield of acetic acid in CO hydrogenation over Rh(1)–Mn(x)–Ir(1/8)–Li(1/16)/SiO_2. Reaction conditions are shown in footnotes of Table 1. For all Figures, % selectivity is in terms of carbon efficiency, and the yield of $MeCO_2H$ is the space time yield in g (dm^3 cat.)$^{-1}$ h^{-1}.

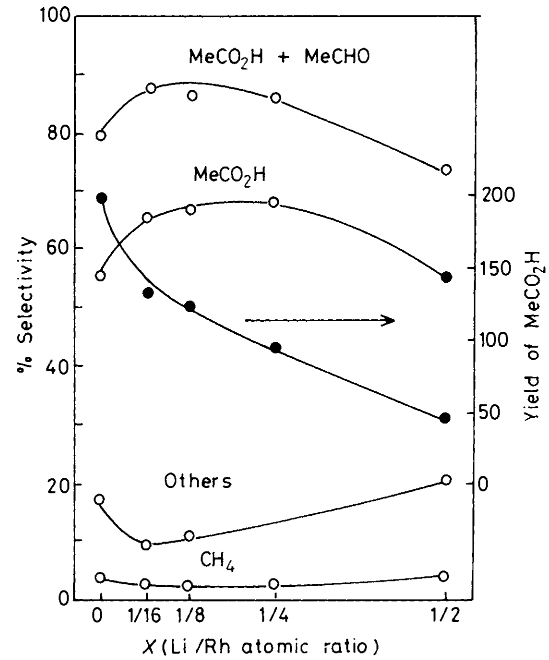

Figure 2. Influence of Li additive amount (x) on product selectivities and space time yield of acetic acid in CO hydrogenation over Rh(1)–Mn(1/48)–Ir(1/8)–Li(x)/SiO_2. Reaction conditions are shown in footnotes of Table 1.

the influence of Rh dispersion,[3] support effects,[4] and promotion effects of additives such as Mn,[5] Ti,[6] Fe,[7] and Ir.[8] However, there have been few studies on the selective synthesis of acetic acid. We now report a high performance catalyst for the selective synthesis of acetic acid from synthesis gas directly.

Multi-promoted catalysts, Rh–Mn–Ir–Li/SiO_2, were prepared by a conventional co-impregnation method. Silica-gel (Davison grade 57, 10—24 mesh) was impregnated with an aqueous solution containing $RhCl_3 \cdot 3H_2O$, $MnCl_2 \cdot 2H_2O$, $IrCl_4 \cdot H_2O$, and LiCl. The impregnated catalysts were dried in a circulating air atmosphere at up to 80 °C for 20 h, followed by reduction with a hydrogen stream at up to 450 °C for 2 h. High pressure synthesis gas reactions were carried out using a flow type reactor at a temperature of 280 °C, a pressure of 100 kg cm^{-2}, a flow rate (G.H.S.V.) of 10^{-4} h^{-1}, and a synthesis gas ratio (H_2 : CO) of 1 : 9. This ratio is one of the most important factors for the selective synthesis of acetic acid,[9] and the 1 : 9 ratio was selected. The effluent gas was directly introduced to a g.c. instrument and analysed with three columns: Chromosorb-101 for oxygenates, alumina–Apiezon for hydrocarbons, and activated carbon for inert gases. The main products were acetic acid and acetaldehyde, together with hydrocarbons, ethanol, propionaldehyde, and butyraldehyde as by-products.

First, the combination effect of additives on the reaction was investigated, and results are shown in Table 1. Rh–Mn/SiO_2 was used as the base catalyst because it is known that Mn addition to Rh/SiO_2 increases CO conversion markedly.[5] The addition of Li to Rh-Mn/SiO_2 did not have a large influence on the acetic acid selectivity, but it increased the yield. However, the addition of Ir to Rh–Mn/SiO_2 increased both selectivity and yield of acetic acid markedly as a result of the suppression

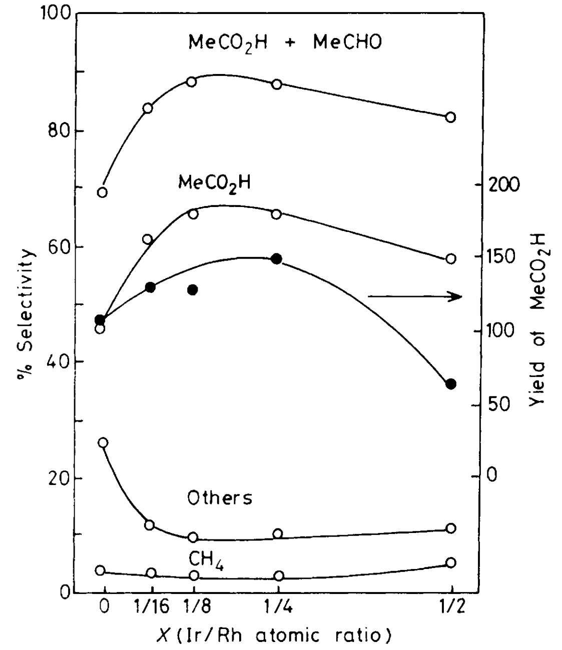

Figure 3. Influence of Ir additive amount (x) on product selectivities and space time yield of acetic acid in CO hydrogenation over Rh(1)–Mn(1/48)–Ir(x)–Li(1/16)/SiO_2. Reaction conditions are shown in footnotes of Table 1.

of hydrocarbon formation, especially hydrocarbons C_{2+}. Moreover, the combination of Ir and Li with Rh–Mn/SiO_2 showed a significant synergistic effect in improving acetic acid selectivity without decreasing its yield. Secondly, the optimization of the amount of additive in this triply promoted catalyst was attempted to improve catalytic performance. Results are shown in Figures. As shown in Figure 1, the addition of Mn to Rh(1)–Ir(1/8)–Li(1/16)/SiO_2 (numbers in parentheses show the atomic ratio with respect to Rh supported) increased the yield of acetic acid as the amount of Mn increased, but the selectivity decreased gradually. In contrast, as shown in Figure 2, the addition of Li to Rh(1)–Mn(1/48)–Ir(1/8)/SiO_2 increased acetic acid selectivity in the region 0—1/4 Li/Rh atomic ratio but the yield was decreased monotonically. In the case of Ir addition to Rh(1)–Mn(1/48)–Li(1/16)/SiO_2, both the yield and selectivity of acetic acid increased in the region 0—1/4 Ir/Rh atomic ratio as shown in Figure 3. On the basis of these results, optimum catalysts for acetic acid synthesis were prepared. Results are also shown in Table 1. High acetic acid selectivity (67% in carbon efficiency) was achieved by using a 5 wt% Rh(1)–Mn(1/48)–Ir(1/4)–Li(1/4)/SiO_2 catalyst. This value is currently the maximum selectivity yet found. In conclusion, a synergistic promoting effect of the three additives, Mn, Ir, and Li to Rh/SiO_2 has been found for the selective synthesis of acetic acid.

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