# Highly Selective Synthesis of $C_2$-Oxygenates in CO Hydrogenation on $SiO_2$-supported Rh–Ir and Rh–Ti–Ir Catalysts

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The addition of Ir to $Rh/SiO_2$ and $Rh–Ti/SiO_2$ CO hydrogenation catalysts substantially suppresses methanation and enhances $C_2$-oxygenate formation; consequently high selectivities for $C_2$-oxygenates such as MeCHO and EtOH are achieved.

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Among other group 8 metals, Rh is unique in its ability to catalyse the formation of $C_2$-oxygenates directly from CO + $H_2$. In view of the value of these oxygenate products, a large number of studies have been made in recent years since the pioneering work at Union Carbide in 1975.[1] Some metal additives appear to improve the activity and/or selectivity of Rh in comparison with unpromoted $Rh/SiO_2$. One of us has shown that promotion of highly dispersed Rh, prepared by decomposing carbonyl clusters on $ZrO_2$, $TiO_2$, and $La_2O_3$,[2] was particularly effective. Recent studies demonstrated that early transition metals such as Mn,[3] Ti, and Zr[4] (existing most likely as oxides in the reduced Rh catalysts) provide a significant enhancement of CO conversion (*ca.* 10—50 times that with $Rh/SiO_2$), whereas the selectivities are still for $C_2$-oxygenates. In contrast to these oxophilic metal additives the addition of Fe[5] to $Rh/SiO_2$ does not influence CO conversion but does affect the oxygenate selectivities, *i.e.* changing from a mixture of MeCHO and $MeCO_2H$ to a mixture of EtOH and MeOH. Nevertheless, the total selectivity of formation of $C_2$-oxygenates remains basically unchanged by the addition of Fe to Rh.

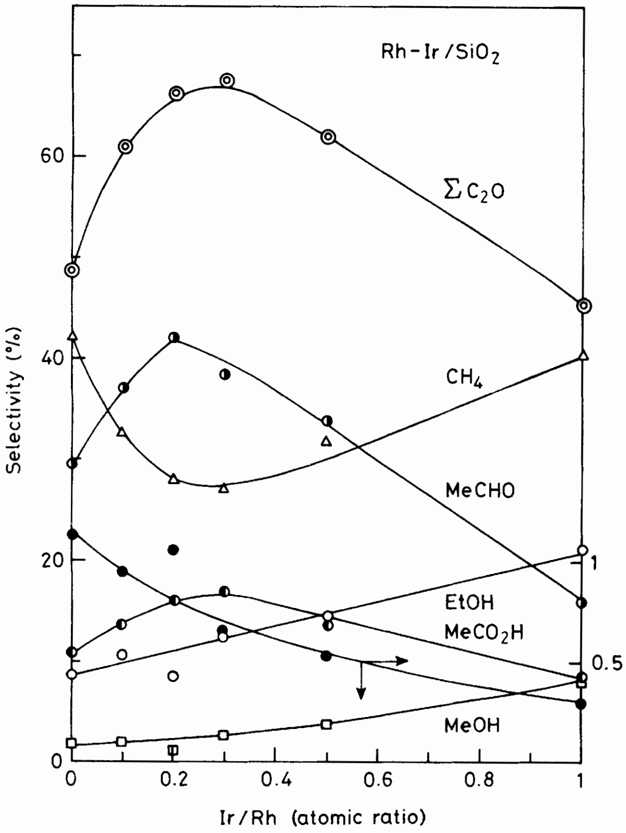

**Figure 1.** Product selectivities and CO conversion in CO hydrogenation on $Rh–Ir/SiO_2$ *vs.* Ir content in terms of Ir/Rh atomic ratios. Rh 4.0 wt% loading, 5 ml catalyst charged, 20 kg/cm$^2$ (gauge) syngas, $CO/H_2$ 0.5 v/v, 250 °C, space velocity 6000 h$^{-1}$.

In a study of the lesser known metals, we have found that Ir, when added to Rh catalysts, exerts a modifying effect, suppressing the hydrocarbon formation and improving the selectivities for $C_2$-oxygenate formation (70% carbon efficiency, c.e.) in CO hydrogenation. In this communication, we report the unique and relevant role of Ir in improving the $C_2$-oxygenate selectivities in CO hydrogenation on $Rh–Ir/SiO_2$ and $Rh–Ti–Ir/SiO_2$. We briefly relate these findings to the promoting role of Ir, which makes a bimetal alloy with Rh, in terms of the proposed mechanism of $C_2$-oxygenate formation from CO + $H_2$.

Catalysts were prepared by a conventional co-impregnation method. $SiO_2$ (gel granule, 10—24 mesh, Davison Grade 57,

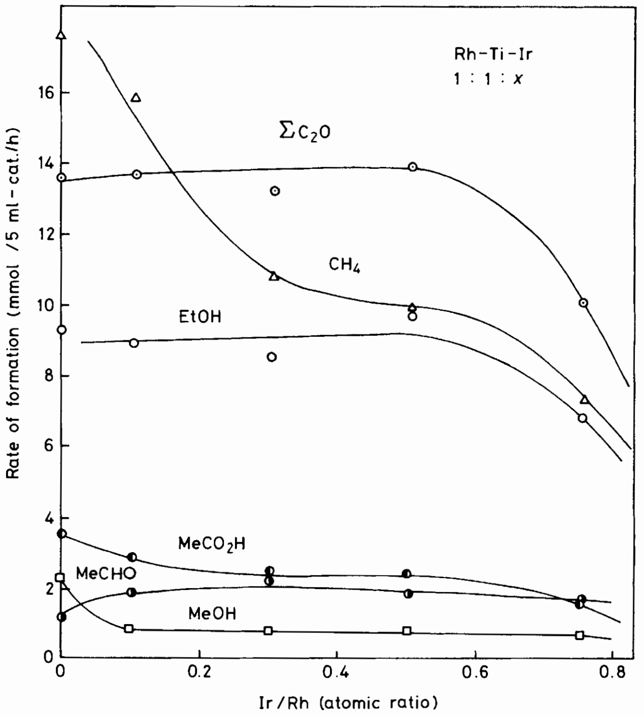

**Figure 2.** Dependency of the product yields (mmol/5 ml of catalyst/h) in CO hydrogenation on $Rh–Ti–Ir/SiO_2$ on varying the Ir content. Rh 4.0 wt% loading, Rh : Ti : Ir 1 : 1 : *x* atomic ratios, 20 kg/cm$^2$ (gauge) syngas, $CO/H_2$ 0.5 v/v, 250 °C, space velocity 6000 h$^{-1}$. Data at Ir/Rh 0 are the results obtained on 4.0 wt% Rh–Ti (1 : 1)/$SiO_2$ under similar reaction conditions.

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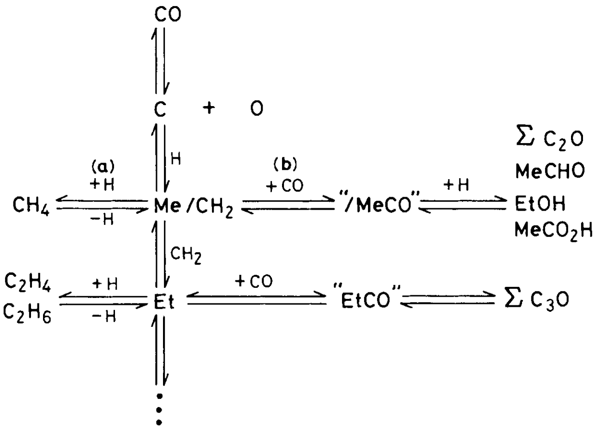
surface area 280 $m^2/g$) was impregnated with $RhCl_3 \cdot 3H_2O$, $IrCl_4 \cdot H_2O$, and $TiCl_4$ from EtOH solutions. After removal of solvent, the impregnated catalysts were subsequently reduced by flowing $H_2$ (1 atm, 100 ml/min) while the temperature was raised from 20 to 400 °C, and then for 6 h at 400 °C. High pressure CO–$H_2$ reactions [20 kg/$cm^2$ (gauge), 250 °C] were conducted with a flow-type Ti-reactor (14 mm inner diameter, 500 mm length). The oxygenated products such as MeOH, EtOH, MeCHO, and acetates, which were dissolved in a water trap by bubbling the effluent gas through, were analysed by g.c. (flame-ionisation detector) using a Chromosorb 101 column (4 m) at 135 °C. The effluent gas was also analysed by g.c. (chemical deionisation) with an $Al_2O_3$–dimethylformamide, DMF, (38 wt% loading DMF, 4 m) column for $C_2$—$C_5$ hydrocarbons and an active carbon column (1 m) for $CH_4$, CO, and $CO_2$. For a series of Rh–Ir, Rh–Ti–Ir, Rh, and Ir catalysts, CO conversions, yields of products (space–time yield, g/l-cat./h), and selectivities based on CO consumed were measured at a standard set of operating conditions, and are summarized in Table 1.



**Scheme 1**

It is apparent from Table 1(a) and Figure 1 that, when iridium was added to Rh/$SiO_2$, the rates and selectivity of methane formation as the major product in hydrocarbons formed dropped remarkably and the selectivities for $C_2$-oxygenates, mainly as MeCHO, increased. Besides the $C_2$-oxygenates, only very small amounts of $C_{2+}$ hydrocarbons, methanol, and $C_{3+}$ alcohols (less than 5% c.e.) were formed. The optimum selectivity of $C_2$-oxygenates (70% c.e.) was obtained on addition of 30% (atomic ratio) Ir to Rh under similar conditions. It is of interest that the addition of iridium had little influence on the total yields or the distributions of oxygenates in CO hydrogenation, compared with those on Rh/$SiO_2$. Addition of a large amount of Ir to Rh suppressed the CO conversion as shown in Table 1(a). The metal surface areas of the Rh–Ir/$SiO_2$ catalysts, which were estimated by transmission electron microscopy, suggested that the metal particle sizes were almost constant at 20—40 Å, and hence the rates of CO conversion in terms of turnover frequency seem to remain basically unchanged over a range of Ir content from Ir/Rh atom ratios 0 to 0.3. On the other hand, the 4.4% Ir/$SiO_2$ catalyst gave a much lower CO conversion and provided only a mixture of MeOH and $CH_4$ with a slight selectivity for $C_2$-oxygenates. This result is characteristic of the Ir based catalysts as described in previous reports.[6]

Similarly, when Ir was added to Rh–Ti (1:1 atom ratio)/$SiO_2$, the formation of $CH_4$ and higher hydrocarbons was dramatically suppressed, whereas the yields of total $C_2$-oxygenates (mainly as EtOH) were constant over a wide range of Ir added, *i.e.*, Ir/Rh atomic ratios 0—0.5, as shown in Figure 2. Consequently, the selectivities for $C_2$-oxygenates as well as EtOH were substantially improved [Table 1(b)]. As previously reported,[4] on addition of Ti to Rh/$SiO_2$ the CO conversion was increased to 8.5%, which is 8 times that on Rh/$SiO_2$, but the selectivities for $C_2$-oxygenates were lower (*ca.* 40% c.e.) with an increase of hydrocarbons such as $CH_4$. The use of Ti and Ir together with Rh provided a composite catalyst which gave higher selectivities for $C_2$-oxygenates such as EtOH as well as higher CO conversion.

As we have suggested following $^{13}C$-labelling studies[7] and

**Table 1.**

(a) Catalytic performance of Rh–Ir catalysts.[a]

| Atomic ratio Ir/Rh | CO conversion (%) | Space–time yield (g/l-cat./h) | | | | | | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | MeOH | MeCHO | EtOH | $MeCO_2H$ | $\Sigma C_2O$ | $CH_4$ | MeOH | MeCHO | EtOH | $MeCO_2H$ | $\Sigma C_2O$ | $CH_4$ |
| 0.0 (4.0 wt% Rh) | 1.12 | 0.5 | 6.2 | 1.9 | 3.1 | 11.1 | 6.5 | 1.7 | 29.4 | 8.6 | 10.7 | 48.8 | 42.2 |
| 0.1 | 0.94 | 0.4 | 6.4 | 1.9 | 3.2 | 11.4 | 4.1 | 1.7 | 36.9 | 10.4 | 13.5 | 60.8 | 32.7 |
| 0.2 | 0.83 | 0.2 | 6.8 | 1.3 | 4.2 | 12.2 | 3.1 | 1.3 | 42.5 | 7.7 | 19.2 | 69.4 | 26.2 |
| 0.3 | 0.66 | 0.5 | 4.7 | 1.6 | 2.8 | 9.0 | 2.4 | 2.6 | 38.3 | 12.5 | 16.8 | 67.6 | 27.0 |
| 0.5 | 0.53 | 0.5 | 3.4 | 1.5 | 1.9 | 6.7 | 2.3 | 3.6 | 33.8 | 14.2 | 13.6 | 62.0 | 31.8 |
| 1.0 | 0.29 | 0.7 | 0.9 | 1.2 | 0.7 | 2.7 | 1.6 | 9.1 | 15.8 | 21.3 | 8.6 | 45.6 | 40.3 |
| (4.4 wt% Ir) | (0.024) | (0.45) | (trace) | (0.02) | (trace) | (0.47) | (0.07) | (67.0) | (trace) | (4.1) | (trace) | (4.1) | (19.2) |

(b) Catalytic performance of Rh–Ti–Ir/$SiO_2$ catalysts (Rh : Ti : Ir = 1 : 1 : $x$ atomic ratio).[a]

| Atomic ratio Ir/Rh | CO conversion (%) | Space–time yield (g/l-cat./h) | | | | | | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | MeOH | MeCHO | EtOH | $MeCO_2H$ | $\Sigma C_2O$ | $CH_4$ | MeOH | MeCHO | EtOH | $MeCO_2H$ | $\Sigma C_2O$ | $CH_4$ |
| 0.0(4.0 wt% Rh) | 8.47 | 7.0 | 5.5 | 41.7 | 21.9 | 65.9 | 52.8 | 3.1 | 3.6 | 25.8 | 10.4 | 39.8 | 47.0 |
| 0.1 | 8.16 | 5.3 | 8.5 | 40.8 | 17.7 | 63.8 | 51.3 | 2.4 | 5.7 | 26.1 | 8.7 | 40.5 | 47.2 |
| 0.3 | 6.76 | 4.8 | 9.8 | 39.2 | 14.9 | 61.1 | 34.9 | 2.7 | 8.0 | 30.7 | 8.9 | 47.6 | 39.1 |
| 0.5 | 6.50 | 4.8 | 7.9 | 44.9 | 14.7 | 65.1 | 32.0 | 2.7 | 6.4 | 34.8 | 8.8 | 50.0 | 35.6 |
| 0.75 | 5.00 | 3.9 | 7.6 | 31.4 | 9.8 | 47.2 | 23.8 | 2.8 | 8.0 | 31.8 | 7.6 | 47.4 | 34.5 |

[a] Temperature 250 °C, pressure 20 kg/$cm^2$ (gauge), CO/$H_2$ 0.5, space velocity 6000 $h^{-1}$. Data were obtained after 2 h on stream. Catalyst, Rh 0.912 mmol, 5 ml of catalyst was charged in a Ti-reactor.

high pressure i.r. observation[8] of the promoted Rh catalysts, it is conceivable that $C_2$-oxygenates such as EtOH, MeCHO, and $MeCO_2H$ come from a common precursor, *e.g.*, acyl 'MeCO' which is formed by CO insertion into the $Me/CH_2$ surface species on Rh. As proposed by Sachtler,[9] the chain growth mechanism is identical for hydrocarbons and oxygenates such as aldehydes and alcohols occurring on the same sites, where CO is dissociatively chemisorbed, as depicted in the proposed Scheme 1.

While chain growth is a common elementary step for hydrocarbons and $C_{2+}$-oxygenates, it appears that the two termination processes (a) and (b) are likely to occur on different sites. Likewise, we assume that addition of Ir to the Rh catalysts affects the CO insertion into $Me/CH_2$ species to form $C_2$-oxygenates and/or depresses sites for methanation.

Sinfelt *et al.*[10] found, using Mössbauer and EXAFS techniques, that Ir forms homogeneous alloys with Rh in $Rh-Ir/SiO_2$ catalysts. This suggests that Ir resides between the contiguous Rh atoms on the particle surface. This alloy formation is a plausible reason for the depression of a non-selective Rh site for methanation (a), and consequently, formation of a suitable site for $C_2$-oxygenate formation. Ir appears to improve step (b), the CO insertion into $Me/CH_2$ to form a common precursor for $C_2$-oxygenates. This is reasonably reflected in the evidence that Ir does not influence the distribution of other oxygenate products such as MeOH, which is formed owing to the hydrogenation of non-dissociatively chemisorbed CO.[7,11]

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## References

1 M. M. Bhasin and G. L. O'Connor, Belgian Patent, 824822, 1975.
2 M. Ichikawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2273; *Chemtech.*, 1982, 674.
3 P. C. Ellgen, W. J. Bartley, M. M. Bhasin, and T. P. Wilson, *Adv. Chem. Ser.*, 1978, **178**, 147; T. P. Wilson, P. C. Kasai, and P. C. Ellgen, *J. Catal.*, 1981, **69**, 193.
4 M. Ichikawa, K. Sekizawa, K. Shikakura, and M. Kawai, *J. Mol. Catal.*, 1982, **11**, 167.
5 M. M. Bhasin, W. J. Bartley, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, 1978, **54**, 120.
6 M. Ichikawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2268; M. L. Poutma, L. F. Elek, P. A. Risch, and J. A. Rabo, *J. Catal.*, 1978, **52**, 157.
7 M. Ichikawa and T. Fukushima, *J. Chem. Soc., Chem. Commun.*, 1985, 321.
8 H. Arakawa, T. Fukushima, M. Ichikawa, K. Takeuchi, T. Matsuzaki, and Y. Sugi, *Chem. Lett.*, 1985, 23; T. Fukushima, H. Arakawa, and M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1985, 729.
9 W. M. H. Sachtler, Proceedings of the International Congress on Catalysis, VIII, Berlin, vol. I, 1984, 151.
10 J. H. Sinfelt, G. H. Via, and F. W. Lytle, *J. Chem. Phys.*, 1981, **75**, 5527; G. Meitzner, G. H. Via, F. W. Lytle, and J. H. Sinfelt, *ibid.*, 1983, **78**, 2533.
11 A. Takeuchi and J. R. Katzer, *J. Phys. Chem.*, 1981, **85**, 937.