Promoting Role of Fe in Enhancing Activity and Selectivity of MeOH Production from CO and H_2 catalysed by SiO_2-Supported Ir

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Addition of Fe to Ir/SiO_2 catalysts used in CO hydrogenation improves the yield of and selectivity towards MeOH (90% carbon efficiency), owing to suppression of methanation.

Recent studies show that noble metals, *e.g.*, Pd[1] and Rh[2] are good catalysts for the selective synthesis of C_1 and C_2 oxygenates from CO and H_2 under high pressure conditions. Additionally, oxygenate selectivities in CO hydrogenation are markedly influenced by the nature of oxide supports employed to disperse Rh,[3] Pt,[4] and Pd.[5,6] In particular, supported Pd, lanthanoid oxides, *e.g.* La_2O_3, Nd_2O_3,[5,6] and MgO[5,16] provide a marked promoting effect: they enhance the selectivity and activity of MeOH formation. On the other hand, addition of Fe to Rh modifies the oxygenate distribution in CO hydrogenation and promotes the formation of MeOH and EtOH.[7] Thus, it is of interest to study the effect of adding Fe to other noble metal catalysts such as Ir,[1,8] Pt, and Pd, and its possible influence on the selectivity and activity of oxygenate production in CO hydrogenation.

In this communication, we report on the specific and relevant role of Fe, when it is added to Ir, in improving the MeOH selectivity to over 90% c.e. (carbon efficiency) and dramatically enhancing the activity of MeOH production to over fifty times as much as that on non-promoted Ir.

The kinetic measurements on the high pressure reaction were carried out using an open-flow reactor (Ti tubing; 14 mm inner diameter, 500 mm length). Product analysis was conducted by g.c. (flame-ionization detector), as described elsewhere.[5,9]

Ir and Fe were coimpregnated from $IrCl_4 \cdot H_2O$ and $FeCl_3 \cdot 6H_2O$ in EtOH on Davison Grade 57 silica gel (10—24 mesh, surface area = 280 m^2/g). The impregnated catalysts were reduced in flowing H_2 (100 ml/min) by raising the temperature from 25 to 400 °C and holding at 400 °C for 6 h prior to the CO–H_2 reaction. For a series of Ir–Fe and Ir catalysts, CO conversion, yields of products (space–time yield STY, g/l-cat./h), and selectivities based on CO consumed

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Table 1. Catalytic performances of SiO_2-supported Ir and Ir–Fe catalysts.[a]

Atomic ratio Fe/Ir	CO conv. (%)	Selectivity[b] (%)				Space–time yield (g/l-cat./h)			
		MeOH	EtOH	CH_4	C_{2+}	MeOH	EtOH	CH_4	C_{2+}
4.4 wt% Ir	0.024	67.0	4.1	19.2	—	0.45	0.02	0.07	—
0.02	0.15	86.2	2.7	8.4	0.4	3.57	0.08	0.17	+
0.1	0.50	89.1	2.2	6.1	0.5	13.0	0.23	0.44	0.05
0.2	0.94	93.9	2.6	9.9	1.1	22.7	0.51	1.34	0.16
0.3	0.81	74.2	4.4	14.5	5.2	16.8	0.71	1.65	0.83
0.6	0.97	50.2	8.3	25.8	11.7	14.2	1.69	3.67	1.58
1.0	1.06	22.4	10.1	34.8	27.9	6.69	2.18	5.21	3.79
2.6 wt% Fe (Fe/Ir 10)	0.23	13.0	7.9	38.4	38.0	0.88	0.38	1.30	1.28

[a] Temperature 250 °C, pressure 20 kg/cm^2 (gauge), $CO/H_2 = 0.5$ vol. ratio, cat. = 5 ml, space velocity = 6000 h^{-1}, data were obtained at time-on-stream of 4 h. [b] Based on CO consumed (c.e.).

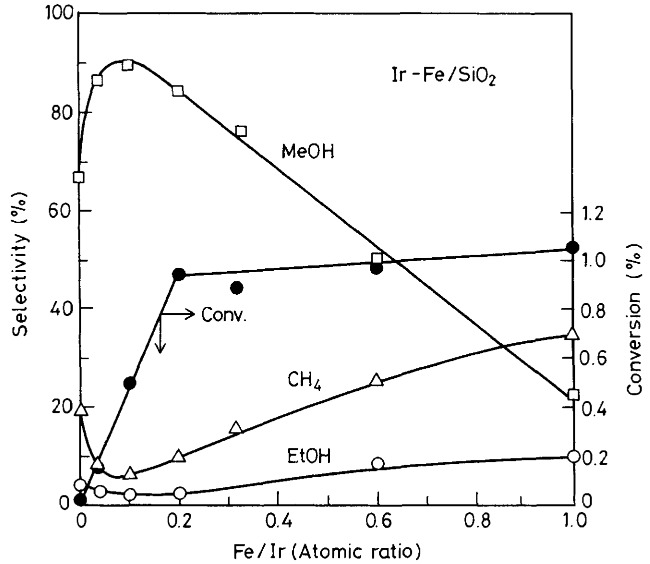

Figure 1. Product selectivities and CO conversion in CO–H_2 reaction on Ir–Fe/SiO_2 *vs.* Fe/Ir atomic ratios. 4.0 wt% Ir loading, 5 ml catalyst charged: 20 kg/cm^2 (gauge) of syngas, $CO/H_2 = 0.5$ v/v, 250 °C, and space velocity = 6000 h^{-1}.

(c.e.) were measured at a standard set of operating conditions [20 kg/cm^2 (gauge), 250 °C], and the results are summarized in Table 1. 4.4 wt% Ir on SiO_2 provided MeOH in low yield and selectivity, with CH_4 and a small amount of EtOH. MeOH selectivity was decreased down to 20% c.e. with an increase of CH_4 and higher hydrocarbons as by-products for 1% CO conversion at 300 °C.

When Fe was added to 4 wt% Ir/SiO_2, the rates of MeOH formation were enhanced (eventually to over fifty times that on Ir/SiO_2) under similar reaction conditions; an MeOH selectivity of over 90% c.e. was achieved. CO conversion increased almost linearly with the increase of Fe content up to 0.2 Fe/Ir atomic ratio, as shown in Figure 1. The selectivities for CH_4 and EtOH appear to be substantially suppressed by addition of Fe to Ir/SiO_2. Addition of an excess of Fe (more than 0.2 Fe/Ir atomic ratio) caused a decrease in MeOH selectivity due to an increase in CH_4 production, while the CO conversion remained almost unchanged.

As shown in Figure 1, we found that optimum MeOH production occurred at 0.1—0.2 Fe/Ir atomic ratios. The yield of MeOH per unit volume of catalyst obtained on 4 wt% Ir–Fe (1 : 0.2)/SiO_2 was five times larger than that on 4 wt% Pd/SiO_2 under similar syngas reaction conditions [*e.g.*, 20 kg/cm^2 (gauge) and 250 °C].

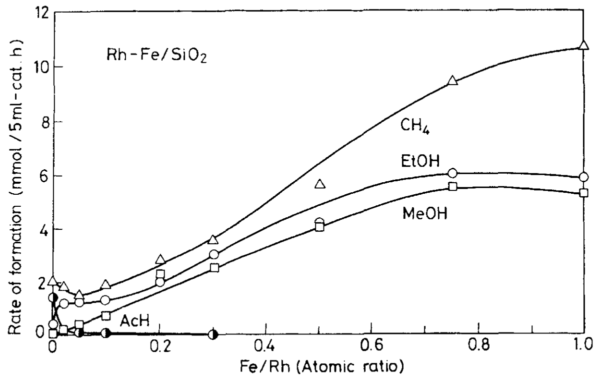

Figure 2. Dependency of rates of formation (based on CO) of CH_4, MeOH, and EtOH in CO hydrogenation on Rh–Fe/SiO_2 on the Fe content. 4.0 wt% Rh loading, 5 ml catalyst, 20 kg/cm^2 (gauge) of syngas, CO/H_2, 250 °C, and space velocity = 6000 h^{-1}. Rh : Fe = 1 : *x* (atomic ratio).

Generally, iron-based catalysts, *e.g.*, Fe, Fe–Co, and Fe–Mn[10] are characterized by hydrocarbon synthesis, over 50% c.e. of consumed CO going to CH_4 and C_{2+} hydrocarbons and several % c.e. to oxygenate mixtures consisting of MeOH and other higher alcohols. Thus, the Fe added to Ir would be associated with the generation of selective sites for MeOH formation.

Sinfelt *et al.*[11] and Guczi[12] used Mössbauer techniques to show that the Fe in Ir–Fe/SiO_2 after H_2 reduction at 400—500 °C exists as either Fe^{3+} or Fe^0 in clusters with Ir particles. Minai *et al.*[13] suggested for the same Ir–Fe/SiO_2 systems that Fe mostly exists as Fe^{3+} in catalysts of less than 0.3 Fe/Ir atomic ratio. It is thus conceivable that Fe clustering with Ir would result in a decrease in the amount of adjacent Ir atoms which are required for multi-bonded chemisorption of CO. This is reflected in the depression of methanation and production of C_2-oxygenates such as EtOH because CO dissociation on large metal ensembles is an essential elementary step for these reaction processes.[14] On the other hand, Fe^{3+} in Ir–Fe/SiO_2, which may reside at the interface of an Ir particle,[13] will provide Ir–Fe^{3+} ensembles containing partially oxidised Ir. This is expected to catalyse MeOH synthesis preferentially, as Ponec *et al.*[16] suggested for Pd/MgO. They claimed that partially oxidised Pd in contact with MgO is catalytically active for MeOH synthesis, rather than Pd^0 for methanation. Also, it has been recently demonstrated[15,17,18] that the Fe in Rh–Fe/SiO_2 with less than 0.3 Fe/Rh atomic ratio (mostly existing as Fe^{3+}), exerts a significant promoting effect: it enhances the conversion of MeCHO into EtOH besides increasing MeOH formation.

At high Fe : Ir ratios, reduced Fe^0 may cover the Ir particle surface, likewise on Rh–Fe/SiO_2.[17,18] This is reflected in the increase of hydrocarbons at the expense of MeOH, as shown in Figure 1. We can compare the trends of product yields depending upon Fe content for Ir–Fe/SiO_2 (Figure 1) and Rh–Fe/SiO_2 (Figure 2). In contrast to Ir–Fe, it is of interest to find that rates of MeOH and EtOH as well as CH_4 formation increased almost linearly with Fe content even above 0.3 Fe/Rh atomic ratio. We suggest that this different behaviour for oxygenate production due to addition of an excess of Fe is associated with the different miscibility of Fe into these two noble metals. In fact, the phase diagrams of Rh–Fe and Ir–Fe indicate[19] that Fe forms a miscible alloy with Rh much more readily than with Ir over a wide range of metal composition.

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References

1 M. L. Poutma, L. F. Elek, P. A. Risch, and J. A. Rabo, *J. Catal.*, 1978, **52**, 157.

2 P. C. Ellgen, W. J. Bartley, M. M. Bhasin, and T. P. Wilson, *Adv. Chem. Ser.*, 1979, **178**, 147.

3 M. Ichikawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2273; *Chemtech*, 1982, 674.

4 M. Ichikawa and K. Shikakura, *Stud. Surf. Sci. Catal.*, 1981, **7**, 925.

5 M. Ichikawa and K. Shikakura, *Shokubai*, 1979, **21**, 253; M. Ichikawa, K. Shikakura, and T. Matsumoto, *Nippon Kagakukai Zashi*, 1982, 213; M. Ichikawa, U.S.P. 4393144, 1982.

6 Yu. A. Ryndin, R. F. Hicks, and A. T. Bell, *J. Catal.*, 1981, **70**, 287.

7 M. M. Bhasin, W. J. Bartley, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, 1978, **54**, 120.

8 M. Ichikawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2268.

9 M. Ichikawa, T. Fukushima, and K. Shikakura, Proceedings of the 8th International Congress on Catalysis, Berlin, 1984, vol. II, p. 69.

10 M. D. Schlesinger, H. E. Benson, E. M. Murphy, and H. H. Storch, *Ind. Eng. Chem.*, 1956, **46**, 1322; J. Barrault and C. Renard, *Appl. Catal.*, 1985, **14**, 133.

11 J. H. Sinfelt, G. H. Via, and F. W. Lytle, *J. Chem. Phys.*, 1981, **75**, 5527; J. H. Sinfelt, *J. Catal.*, 1980, **62**, 127.

12 L. Guczi, *Catal. Rev.-Sci. Eng.*, 1981, **23**, 329.

13 Y. Minai, T. Fukushima, M. Ichikawa, and T. Tominaga, *J. Radioanal. Nucl. Chem. Lett.*, 1984, **87**, 189; Y. Minai, T. Fukushima, M. Ichikawa, T. Tominaga, and S. Ogasawara, unpublished work.

14 M. Ichikawa and T. Fukushima, *J. Chem. Soc., Chem. Commun.*, 1985, 321.

15 J. W. Niemansverdrit, A. M. van der Kraan, J. J. van Loef, and W. N. Delgass, *J. Phys. Chem.*, 1983, **87**, 1292; J. W. Niemansverdrit, A. M. van der Kraan, and W. N. Delgass, *J. Catal.*, 1984, **89**, 138.

16 J. M. Driesse, E. K. Poels, J. P. Hinderman, and V. Ponec, *J. Catal.*, 1983, **82**, 26.

17 M. Ichikawa and T. Fukushima, *J. Phys. Chem.*, 1985, **89**, 1564.

18 Y. Minai, T. Fukushima, M. Ichikawa, and T. Tominaga, 'Industrial Applications of Mössbauer Effects,' eds. G. L. Long and J. G. Sterns, Plenum, New York, 1985.

19 O. Kubascheskoviski, 'Iron-Binary Phase Diagram,' Springer–Verlag, Berlin, 1982.