

Selective Hydrogenation of Carbon Monoxide to Oxygenates by Use of a Novel Iron Catalyst

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We report a novel high-selectivity Fe/Cr₂O₃ catalyst for the title reaction which when unpromoted gives high selectivities for methanol production, and on addition of K⁺ as promoter gives combined selectivities for ethanol and ethanal of ca. 70%.

Hydrogenation of carbon monoxide to produce ethanol, ethanal, and other oxygen-containing molecules (oxygenates) is a commercially attractive reaction¹ that continues to receive attention.²⁻⁴ A number of catalysts have been studied; in particular, considerable interest has been shown in alkali-promoted Rh catalysts, but with these catalysts significant selectivity for hydrocarbon production is invariably observed.⁵ Other workers have shown that supported Pd,⁶ Re,⁷ Ru,⁸ and Ir⁹ catalysts can also give high selectivities for oxygenate production. It has been noted⁴ that higher oxygenate synthesis is normally catalysed by alkali-promoted methanol synthesis catalysts; this approach has recently been exemplified with a potassium-promoted cobalt/copper/chromium oxide catalyst¹⁰ which gives very high yields of C₂-C₄ linear alcohols with no hydrocarbon by-product formation. Alkali-promoted iron catalysts have been known for some time to produce oxygenated products but as yet this

reaction has not been studied in detail. We now report a novel, stable, high-selectivity Fe/Cr₂O₃ catalyst that exhibits high selectivity for methanol or ethanol and ethanal production under appropriate conditions.

K/Fe/Cr and Fe/Cr catalysts were prepared by an incipient wetness technique. Cr₂O₃ (B.D.H.; 99.5%) was impregnated with aqueous iron(III) nitrate (Reidel De Hain AG; reagent grade) and potassium carbonate, and the resulting slurry was dried at 100 °C *in vacuo* and calcined (500 °C; 24 h). In a typical experiment the catalyst (2 g) was reduced with H₂ at 400 °C for 16 h *in situ* in a fixed-bed stainless steel reactor of internal diameter 14 mm. Carbon monoxide and hydrogen (1 : 1 v/v) were introduced over the reduced catalyst at 585 kPa and at a gas hourly space velocity [g.h.s.v.; volumetric gas flow rate (at s.t.p.) per unit volume of catalyst] of 260 h⁻¹. Products were analysed by on-line gas chromatography; satisfactory mass balances were obtained for all data quoted.

The results of reactions over a 5% Fe/Cr₂O₃ catalyst at a range of temperatures are shown in Table 1. At low reaction temperatures this catalyst can give high selectivities for methanol production of ca. 60 mass % at the low reaction pressures utilised. At higher reaction temperatures the

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Table 1. Experimental results.^a

Catalyst	CO		Product selectivity (% by mass)													Total oxygenates (%)	Total hydrocarbons (%)
	Temp. (°C)	conv. (%)	CH ₃ OH	C ₂ H ₅ OH	C ₃ H ₇ OH	C ₄ H ₉ OH	C ₅ H ₁₁ OH	CH ₃ CHO	CH ₄	C ₂	C ₃	C ₄	C ₅	C ₆₊			
K:Fe:Cr ₂ O ₃ , 0.1:5:100	220	5	0	21.4	9.6	3.6	0	48.7	3.3	1.0	0.2	7.0	2.0	3.2	83.4	16.6	
	250	5.5	0	20.6	10.6	7.6	0.5	35.2	2.0	1.4	1.4	6.5	3.5	10.7	74.5	25.5	
	300	15	0	8.8	5.4	5.3	6.1	5.8	6.7	9.2	10.9	7.4	7.4	27.0	31.4	68.5	
	350	20	0	4.9	3.3	2.2	0.1	4.2	22.8	18.1	14.5	8.0	6.4	15.5	14.8	85.2	
Fe:Cr ₂ O ₃ , 5:100	250	5	59.6	15.9	8.0	0	0	0	2.5	2.9	2.6	4.6	1.2	2.7	83.8	16.2	
	300	32	7.2	10.7	7.9	0	0	0.8	15.0	17.3	16.6	7.8	5.9	10.8	26.7	73.3	
	350	56	0.1	12.9	5.3	0	tr	tr	32.5	22.0	18.5	1.9	1.0	5.8	18.3	81.6	

^a CO/H₂ reaction at 585 kPa; g.h.s.v. 260 h⁻¹.

products comprise mainly hydrocarbons, and the high oxygenate selectivity is decreased. However, addition of 0.1% K⁺ to this catalyst dramatically changes the product distributions under comparable reaction conditions: the major products are then ethanol and ethanal (*ca.* 70 mass %) at low temperatures (220 °C). Significantly, no methanol or other C₁ oxygenates were observed as products under any conditions tested with the K⁺-promoted catalyst. An increase in reaction temperature again results in loss of selectivity for oxygenate production, with CH₄ becoming the dominant product at 350 °C. The high selectivity for methanol production with the unpromoted catalyst and the high selectivity for C₂ oxygenates with the promoted catalyst were stable for reaction periods in excess of 680 h. Additionally, the start-up temperature at which the reduced catalysts are stabilised in the CO/H₂ reactant was found to be important for the promoted catalyst, and use of lower initial temperatures produced catalysts with improved selectivity for C₂ oxygenate production.

Detailed studies of catalyst optimisation and the mechanistic role of the alkali promoter are continuing in our laboratories. However, the dramatic change from C₁ oxygenates to C₂ oxygenates observed with alkali-promoted catalysts may be indicative that the C₂ oxygenates are formed *via* a CO insertion pathway; hence these results support the recent observation of Ponec *et al.*³

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