

Cobalt Manganese Oxide: A Novel High Activity Water Gas Shift Catalyst

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A stable Co/MnO water gas shift catalyst with high activity particularly suited to coal derived synthesis gas feedstocks has been prepared.

The water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) is used extensively to produce hydrogen for the industrial synthesis of ammonia. It is used to decrease the concentration of CO

present in synthesis gas ($\text{CO} + \text{H}_2$) generated either from coal gasification or hydrocarbon steam reforming. At present most production units operate a two stage process involving an iron chromium high temperature shift catalyst¹ which reduces the CO concentration from *ca.* 40 mole % of *ca.* 3 mole % and a copper zinc oxide low temperature shift catalyst² which

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Table 1.

Expt. ^a	Catalyst	T/°C	Reaction time/h	CO conversion (%)	CH ₄ production (mole %)
1	Co:Mn = 3:1	400	117	98.4	0.01
	Co:Mn = 3:1	400	677	98.4	0.02
	Co:Mn = 3:1	350	300	98.7	0.06
2	Co:Mn = 1:1	400	119	97.8	0.25
	Co:Mn = 1:1	400	185	92.0	0.25
	Co:Mn = 1:1	400	672	89.9	0.25
	Co:Mn = 1:1	350	285	90.3	0.35
	Co:Mn = 1:1	300	350	83.7	0.14
3	Co:Mn = 1:1 ^b	400	118	97.0	0.01
	Co:Mn = 1:1 ^b	400	185	96.9	0.01
	Co:Mn = 1:1 ^b	300	150	93.1	0.01
4	Co	400	119	97.8	0.50
	Co	400	597	58.0	0.50
5	Fe:Cr:O ^c	400	117	69.3	0
	Fe:Cr:O ^c	400	390	70.3	0
	Fe:Cr:O ^c	350	300	33.6	0
6	Co:Mo:O ^d	400	113	3.6	0
	Co:Mo:O ^d	400	286	2.9	0

^a CO:N₂:H₂O = 1:1:4.5 mole ratio, CO feed rate 510 ml/ml catalyst/h, catalyst particle size *ca.* 1 mm diameter. ^b Promoted by addition of 1% K by mass. ^c Commercial iron–chromium oxide high temperature shift catalyst. ^d Unsulphided commercial cobalt–molybdenum hydrodesulphurisation catalyst.

further reduces the CO to *ca.* 0.3 mole %. Owing to the sensitivity of the Cu/ZnO catalyst to low concentrations of sulphur (*e.g.* > 1 p.p.m. H₂S or COS) this catalyst cannot be successfully operated with coal derived synthesis gas, and consequently yield losses can be incurred in such a process. Cobalt is known to be a highly active water gas shift catalyst³ but is unstable and produces significant byproduct hydrocarbons. Cobalt–molybdenum catalysts⁴ give stable high activity but only when the catalyst is totally sulphided, and unfortunately most coals contain insufficient sulphur to enable this to be readily achieved. To date the identification of a high temperature shift catalyst specifically suited to a one stage high conversion [*ca.* 98%, *i.e.* CO (exit) = 0.5 mole %] of coal derived synthesis gas has received scant attention. Here we report our initial studies involving the modification of cobalt with manganese oxide which gives a catalyst with significantly improved activity when compared with current industrial formulations.

Co and Co/Mn (3:1 and 1:1 mole ratio respectively) catalysts were prepared by co-precipitation from the metal nitrates at a constant pH of 8.3 and 70 °C. The resulting solids were washed with distilled water, dried *in vacuo* at 110 °C, and calcined in air (500 °C; 16 h). In a typical experiment the catalyst (2 g) was reduced with H₂ *in situ* 400 °C, 16 h in a fixed bed stainless steel reactor of internal diameter 14 mm. A mixture of CO–N₂–H₂O (1:1:4.5 mole ratio) was allowed to react over the reduced catalyst at a CO gas hourly space velocity [g.h.s.v., volumetric gas flow rate (s.t.p.) per unit volume of catalyst] = 510 h⁻¹. The unreacted aqueous effluent

was collected in a trap held at 20 °C and the residual gaseous products were analysed using on-line gas chromatography; satisfactory mass balances were obtained for all data presented. Blank thermal reactions in the absence of catalyst were negligible as was carbonyl formation in the stainless steel reactor.

The results for reaction of CO–N₂–H₂O over the Co and Co/Mn (1:1 and 3:1) catalysts are shown in Table 1 (expts. 1,2,4). It is apparent the ratio of Co to Mn is crucial in determining catalyst stability and activity. Analysis of unreduced catalyst before and after calcination using powder X-ray diffraction indicated that the catalysts consisted of a solid solution with a spinel structure: Co_xMn_{3-x}O₄, and calcination improved the crystallinity of the catalyst. Following reduction, then reaction for *ca.* 600 h the catalysts contained Co metal and a solid solution of Co in the cubic MnO structure: Co_yMn_{1-y}O. The degree of solid solution varied according to the Co/Mn mole ratio. Unreduced and reduced catalysts were found to have low total surface areas, typically 10–14 m² g⁻¹. However, after reaction for 600 h the catalyst surface area was greatly increased: Co:Mn = 1:1, 45 m² g⁻¹; Co:Mn = 3:1, 64 m² g⁻¹, and the surface area of the active catalyst was generally proportional to the cobalt content. Although the Co only catalyst gives initially a very high activity this decreases irreversibly and steadily with reaction time owing to catalyst sintering (*c.f.* expts. 1 and 4). Addition of manganese oxide stabilises the high activity of Co and also reduces the by-product methane formation. Addition of a potassium promoter to the Co/Mn catalyst further enhances the catalyst activity and stability whilst significantly reducing the by-product methane formation (*c.f.* expts. 2 and 3). Comparison of the catalyst performance with that of an industrial iron–chromium high temperature shift catalyst (expt. 5) and an unsulphided cobalt–molybdenum catalyst (expt. 6) indicates that the Co/Mn catalysts demonstrate significantly improved catalyst activity. It must be emphasised that the catalyst formulation (Co:Mn mole ratio and K⁺ concentration) has yet to be optimised but the results presented here are indicative of the high catalyst activities for this system. In particular since the CO concentration of coal derived synthesis gas is significantly higher than that derived from steam reforming of hydrocarbons,^{5,6} the enhanced activity of the Co/Mn catalysts will be of particular value in the operation of a one stage coal based process.

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