JOURNAL OF CATALYSIS **100**, 507–511 (1986)

Effect of Iron Manganese Oxide Solid Solutions on Selectivity for Lower Hydrocarbons from Carbon Monoxide Hydrogenation

INTRODUCTION

There exists considerable current interest in the study of catalysts that demonstrate high selectivities for C_2–C_4 hydrocarbons from carbon monoxide hydrogenation. In this respect iron manganese matrix catalysts have been well studied by a number of authors (*1–4*) since Kölbel (*5*) initially disclosed that these catalysts could give high yields of C_2–C_4 hydrocarbons with a corresponding very low methane selectivity. Such a product distribution was in disagreement with the expected Schulz–Flory distribution (*6*). The effect of manganese oxide as a catalytic component has been observed with elements other than iron and in particular similar effects have been observed for Co : Mn (*7*) and Ru : Mn (*8*) catalysts. More recently it has been shown (*9*) that non-Schulz–Flory distributions are only observed under restricted experimental conditions and as such these catalysts may have limited industrial applicability. However, Barrault (*10*) has shown that at low catalyst activity high yields of C_2–C_4 alkenes can be observed for ca. 100 h, but the mechanism by which the manganese component causes these product distributions is at present poorly understood. Recently Jensen and Massoth (*11*) have proposed that small iron particles are supported on and electronically promoted by MnO. However, a number of other workers (*12–15*) have shown that there is considerable interaction between iron and the manganese oxide, and solid solutions have been shown to be present at most stages of the catalyst lifetime. In particular Maiti *et al.* (*13*) have shown that these solid solutions are present in freshly reduced catalysts. Although these oxide solid solutions have been identified there have been no reported studies that have investigated the effect of these catalyst components on catalyst selectivity. Oxide solid solutions are known to be important as catalysts of a number of reactions involving carbon monoxide (*16, 17*). In this note we present our initial findings for the effect of iron manganese oxide solid solutions on catalyst selectivity in carbon monoxide hydrogenation.

METHODS

Catalyst preparation and testing. Aqueous solutions of manganese(II) nitrate ($Mn(NO_3)_2 \cdot 4H_2O$, Merck P.A., 0.2 *M*) and iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck P.A., 0.15 *M*) were mixed in the required ratio and heated to 70°C. Aqueous ammonia (25% m/v) was then slowly added with stirring to the mixed nitrate solution until a pH of 9.5 was attained. The precipitate was collected by filtration, washed with distilled water, and then dried at 110°C and 10 kPa. All catalysts prepared and tested did not contain any alkali promoter.

Catalysts were pelleted, ground, and sieved to give particles (2.7–3.3 mm) which were then reduced with hydrogen *in situ* in the catalytic reactor at 400°C for 18 h at a gas hourly space velocity (GHSV) of 200 h^{-1}. Following CO hydrogenation the catalysts were cooled to 20°C in dry nitrogen and were removed from the reaction and stored in a dry-nitrogen atmosphere prior to subsequent analysis. The iron manganese concentrations of the catalysts were determined using X-ray fluorescence spectroscopy and the Fe : Mn ratios are quoted as mass ratios. Surface areas were determined by nitrogen adsorption according to the

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BET method and total carbon was determined using a Leco C, H, and N analyzer.

The bulk catalyst structure was determined by X-ray powder diffraction. Diffraction traces were recorded on a Philips 1410 powder diffractometer using (graphite monochromated) Cu*Kα* radiation, at a scan speed of 2° 2θ per minute. Similar masses of the different samples were used in the same cell holder. Pure MnO and Fe_3O_4 (Cerac 99.99%) were used as control standards. Carbide impurity lines, identified from standard ASTM patterns, were subtracted out from the observed traces and all remaining lines were indexed for cubic unit cells on the basis of regular increase in $\sin^2 \theta$ values.

Catalyst testing. CO hydrogenation was carried out using a fixed bed laboratory reactor which is shown in Fig. 1. The reactor was constructed of 316 stainless steel with an internal diameter of 34 mm and a catalyst mass of 20 g was used. Premixed synthesis gas (CO/H_2 = 1 v/v) was fed to the reactor after preheating to 200°C. Liquid products were condensed and analyzed by off-line gas chromotography and the gases were analyzed by on-line chromatography. Satisfactory mass balances between 95 and 105% were obtained for the data quoted. Test experiments showed that blank thermal reactions in the absence of catalysts were negligible for the reaction conditions studied.

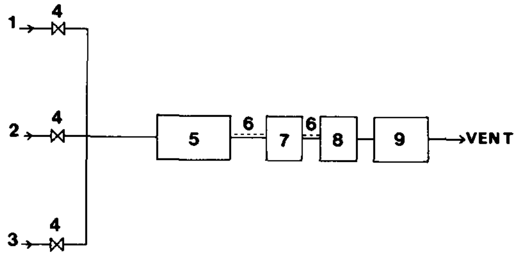

FIG. 1. Experimental apparatus. (1) CO/H_2, (2) H_2, (3) N_2, (4) rotameter needle valve, (5) reactor with built-in preheater section, (6) electrically heated line, (7) condensation vessel, (8) back-pressure regulator, (9) gas chromatograph.

RESULTS

Two catalysts with high concentrations of manganese were prepared by precipitation and the CO hydrogenation activity was studied at 800 kPa and 300°C. The results (shown in Table 1) indicate that at this elevated pressure and catalyst bed size the principle products were alkanes. The results obtained at 100 kPa by previous workers for high manganese-containing catalysts are shown for comparison in Table 1. It is evident that at the reduced pressure the proportion of alkenes in the products is greatly enhanced at the reduced level of catalyst activity. In particular, the yield of methane is significantly enhanced at the higher reaction pressure. This effect of reaction pressure was confirmed by a further set of experiments conducted for the Fe : Mn = 1 : 8.3 catalyst at various reaction pressures. As the reaction pressure is raised so does the catalyst activity but the selectivity to alkanes is significantly increased, and this effect has also been noted by Schulz (*2*). At the lower reaction pressures selectivity is relatively stable whereas for the higher pressure studies the proportion of methane present in the product increases with time-on-stream. Considerable yields of CO_2 are observed, particularly during the initial reaction stages. This could be caused by (a) high water-gas shift activity, and recently it has been indicated that manganese based catalysts may exhibit considerable shift activity (*18*), (b) CO acting as a primary O acceptor, and (c) carbon deposition on the catalyst via the Boudard reaction:

$$2CO = CO_2 + C$$

Subsequent analysis of catalysts indicated that during the initial period of reaction studied considerable catalyst carbiding occurred at all pressures indicating that (c) is possibly a dominant process during the initial reaction stages. Barrault (*10*) has also considered that carbide formation reduced catalyst lifetime.

Determination of catalyst structure and performance for a wide range of Fe : Mn ratios at two reaction times is shown in Table

TABLE 1

Effect of Reaction Pressure on Catalyst Activity and Selectivity

	Fe : Mn								
	1 : 19.1[a]		1 : 11.8		1 : 8.3				
Time on-line (h)	10	30	1[b]	17[b]	Initial[b]	17[b]	25[c]	50[c]	75[c]
GHSV (h^{-1})	500	500	1000	1000	1000	1000	600	600	600
T (°C)	270	290	300	300	300	300	300	300	300
P (kPa)	100	100	800	800	800	800	250	500	750
Activity (10^{-2} mole CO converted · h^{-1} · g Fe^{-1})									
To all products	0.75	0.32	4.1	10.1	12.2	5.3	3.4	4.3	5.4
To CO_2	0.45	0.17	1.8	5.6	7.2	2.6	0.5	0.6	0.7
Hydrocarbon selectivity (mass %)									
C_1	9.2	10.8	33.2	56.8	22.9	54.2	44.4	41.2	46.7
C_2	18.3	28.7	30.7	18.2	30.5	19.6	8.2	7.9	7.9
C_3	31.2	25.5	9.8	9.5	22.9	8.1	9.4	10.0	10.1
C_{4+}	38.3	35.0	26.3	15.5	23.7	18.1	38.0	41.0	35.5
% Alkene C_2–C_4	70	94	24	17	23	31	75	64	56
$(C_2 + C_3)/(C_1 + C_{4+})$ mole ratio	1.1	1.3	0.52	0.22	0.84	0.23	0.17	0.17	0.16

[a] Data taken from Ref. (*10*).

[b] Reactor (34-mm diameter), 20 g catalyst.

[c] Reactor (14-mm diameter), 1 g catalyst, steady-state data for each condition.

2. Catalysts were used for the time specified and then the reaction was stopped and the catalyst rapidly cooled in dry N_2 and the bulk structure was determined by X-ray powder diffractometry. In this way the catalyst performance data obtained are considered to be representative of the bulk composition obtained.

The catalysts were found to contain cubic solid solutions of iron in MnO, which we represent as $Fe_xMn_{1-x}O$, and mixed spinel structures in which manganese is present as a solid solution in Fe_3O_4, which we represent as $Mn_yFe_{3-y}O_4$. Based on the cell parameters obtained it is clear that a significant amount of incorporation of these metal ions occurs and the values of x and y can approach 0.5. At the short reaction time these solid solutions represent the major crystalline phase present in the catalyst.

DISCUSSION

The comparison of catalyst structure and performance for the range of iron manganese catalysts indicates that initially catalysts containing significant quantities of the solid solutions $Fe_xMn_{1-x}O$ and/or $Mn_y Fe_{3-y}O_4$ are the most selective for the formation of C_2 and C_3 hydrocarbons. As the reaction time is increased the relative proportion of these solid solutions decreases and in particular the degree of incorporation of iron into the MnO lattice is decreased since the cell parameter in all cases is increased at the longer reaction time (Table 2, Fig. 2).

Longer reaction time also increases the relative proportion of iron carbides present in the catalyst as determined by powder X-ray diffraction and confirmed by the total

TABLE 2

Comparison of Fe : Mn Catalysts at Constant Reaction Conditions, T = 300°C, GHSV = 1000 h^{-1}, P = 800 kPa

	Fe : Mn							
	1 : 2.28		1 : 0.992		1 : 0.357		1 : 0	
Time on-line (h)	0.7	17	1	17	1	17	1	17
Products (10^{-5} mole · m^{-2} · h^{-1})								
C_1	7.4	2.4	2.6	4.9	6.6	7.1	9.9	6.3
C_2	6.4	0.8	0.7	1.4	2.2	1.6	2.6	1.7
C_3	1.9	0.2	0.2	0.5	0.4	0.5	0.3	0.3
C_4+	1.5	0.5	0.3	1.0	0.6	1.3	0.6	1.6
CO_2	16.3	6.6	3.8	5.5	15.8	12.0	24.8	13.1
(C_2 + C_3)/(C_1 + C_{4+}) mole ratio	0.93	0.34	0.31	0.32	0.36	0.25	0.28	0.25
Carbon[a] (% by mass)	3.8	18.4	0.04	1.1	12.5	21.6	20.5	46.8
Catalyst structure[b]	$Fe_xMn_{1-x}O$ a_0 = 4.412 Fe_5C_2 trace	$Fe_xMn_{1-x}O$ a_0 = 4.437 Fe_5C_2	$Fe_xMn_{1-x}O$ a_0 = 4.366 Fe_5C_2 trace	$Fe_xMn_{1-x}O$ a_0 = 4.406 Fe_5C_2	$Mn_yFe_{3-y}O_4$ a_0 = 8.4470 Fe_5C_2 $Fe_xMn_{1-x}O$ a_0 = 4.393	Fe_5C_2 $Fe_xMn_{1-x}O$ a_0 = 4.420	Fe_5C_2 Fe_3O_4	Fe_5C_2 Fe_3O_4 trace

[a] Total carbon, i.e., carbon in carbide and as carbon.

[b] X-Ray powder diffraction study; phases listed in relative order, cell parameter a_0 given in Ångstroms; pure phase literature values of cell parameter (Å): MnO a_0 = 4.445, FeO a_0 = 4.307, Fe_3O_4 a_0 = 8.396, $MnFe_2O_4$ a_0 = 8.499. X-Ray powder diffraction data of Fe_5C_2 given in Refs. (*23*, *24*).

carbon analysis. As the degree of carbiding increases the relative selectivity to C_2–C_3 hydrocarbons, based on the mole ratio to other products, decreases relative to other hydrocarbon products. At the longer reaction time catalyst selectivity appears to be independent of Fe : Mn ratio, and the catalyst activity is proportional to the total iron content of the catalyst. This evidence indicates that the selectivity for C_2–C_3 hydrocarbons decreases with increasing catalyst carbide content, whereas the selectivity for C_2–C_3 hydrocarbons is higher for catalysts containing increased contents of the iron manganese oxide solid solutions. Hence it is considered that the high selectivities to C_2 and C_3 hydrocarbons observed by other workers for iron manganese catalysts may be due to the presence of significant quantities of these oxide solid solutions. Although Jensen and Massoth (*11*) attribute the catalyst action to small iron particles supported on MnO, it is apparent from the X-ray powder data they present that the MnO is also an iron manganese oxide solid solution and hence the catalytic effects noted in their studies may also be due to iron manganese oxide solid solutions.

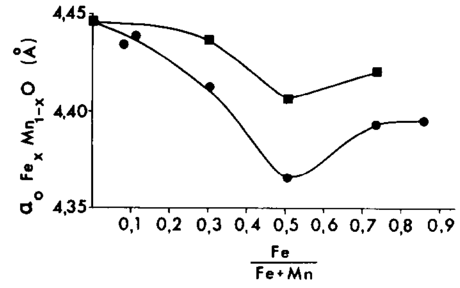

FIG. 2. Effect of reaction time and Fe : Mn ratio on the observed cell parameter for $Fe_xMn_{1-x}O$. Reaction time (●) 1 h, (■) 17 h.

The results presented in this study indicate that iron manganese oxide solid solutions may play a major role in controlling product selectivity for Fe : Mn CO hydrogenation catalysts. Under the conditions examined in this study these solid solutions do not appear to be particularly stable and in the presence of CO/H_2 they break down to form iron carbide and a solid solution with a decreased iron content. This process is accompanied by an increase in the methane yield and other workers (*19*) have also noted that carbiding of an iron catalyst in the early stages of reaction leads to an increase in the methane yield. It is interesting to note that other oxide (*20*) and sulfide (*21*, *22*) catalysts have also been shown to be associated with non-Schulz–Flory product distributions, in particular giving high C_{2-4} selectivities. Further studies are now required to investigate the mechanism of action of these iron manganese solid solutions and to determine possible methods of stabilizing them under reaction conditions.

ACKNOWLEDGMENTS

We gratefully acknowledge the Foundation for Research Development for comprehensive support and the Research Department, AECI Limited, for the X-ray diffraction spectra.

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Received October 29, 1985

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