

Carbon-Supported Fe-Mn and K-Fe-Mn Clusters for the Synthesis of C₂-C₄ Olefins from CO and H₂

II. Activity and Selectivity Maintenance and Regenerability

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Highly dispersed carbon-supported Mn-Fe and K-Mn-Fe catalysts were prepared which showed activity stabilization after a loss of approximately 50% of the initial activity during 24-110 h on-stream. The deactivation was attributed to carbon deposition, rather than sintering, and could be reversed by a treatment in hydrogen at reaction temperatures. Precursors with Fe/Mn = 2 optimized the olefin selectivity, and mixed-metal clusters of this type gave higher selectivities than their coimpregnated counterparts. A low reduction temperature (473 K) for the unpromoted NET₄ [Fe₂Mn(CO)₁₃] catalyst gave a high selectivity to olefins which remained stable during the 24-h period the catalyst was maintained under reaction conditions. The particularly high C₂-C₄ olefin yields obtained with the K[Fe₂Mn(CO)₁₃] catalyst were sustained throughout the 26-h activity maintenance run. © 1987 Academic Press, Inc.

INTRODUCTION

In the preceding paper, the preparation, chemisorption behavior, and initial kinetic properties were described for a family of Fe-Mn/C and K-Fe-Mn/C catalysts prepared from stoichiometric carbonyl clusters (1). Certain compositions showed an ability to produce hydrocarbon products from CO and H₂ containing only C₂-C₄ olefins (85-90 wt%) and CH₄, and the pretreatment given to these clusters had a significant effect on their catalytic properties. The iron spinel—magnetite or Fe₃O₄—has been shown to have higher olefin selectivity than metallic iron at low pressure (2), and bulk Fe-Mn catalysts with stable high olefin selectivities frequently contain a mixed-spinel structure with a stoichiometry near Fe₂MnO₄ (3, 4). This observation is consistent with our previous results and their interpretation (1). The olefin content frequently has a strong dependence on conversion, and many dif-

ferent phases can exist in Fe catalysts in the presence of H₂, CO, and their reaction products (5); therefore, it was of importance to examine the effects of CO conversion and temperature on catalytic behavior and to see if the selectivities and high activities (compared to other Fe-Mn catalysts) were maintained over long periods of continuous operation. In addition, if some deactivation were observed, information pertaining to the cause of this loss of activity and the regenerability of these catalysts would be useful. Finally, the thermodynamics related to the stability of different phases, such as Fe₂MnO₄, FeO, MnO, and Fe, under different pretreatment and reaction conditions could indicate whether the proposed compounds could be stable over long periods under the reaction conditions employed. These results are discussed in this paper.

EXPERIMENTAL

The catalysts examined in detail are listed in Table 1 and were selected from the

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family of carbon-supported clusters described in the preceding paper (1). The reactor system has been described previously, and all kinetic runs were conducted at 0.1 MPa (1 atm) after either a low-temperature reduction (LTR) at 473 K in H₂ or a high-temperature reduction (HTR) at 673 K for 16 h in H₂. Details are given in Ref. (1).

RESULTS

Activity Maintenance and Regeneration

In order to elucidate the factors influencing the high olefin/paraffin ratios (OPRs) observed for some of the cluster-derived

catalysts, activity maintenance experiments were conducted on selected catalysts, namely, FeMn/C, Fe₂Mn/C, FeMn₂/C, KMnFe₂/C, and a 2Fe/Mn/C catalyst derived from the nitrate salts. The catalysts with an Fe/Mn ratio of 2 typically reached a stable activity after about 24 h on-stream, as shown in Fig. 1. During this period of time the activity decline was always observed to be 50 ± 10% of the initial value. A much longer period was required for the FeMn/C catalyst to stabilize (Fig. 2) and steady state was not achieved after 110 h on-stream. Almost none of this decrease in activity appears to be a consequence of sintering because a regeneration procedure

TABLE 1

Selectivities and Activities of Carbon-Supported Fe-Mn Clusters: *P* = 0.1 MPa, H₂/CO = 3

Carbonyls	Temperature (°C)	% Conversion (CO to HC)	OPR (C ₂ ⁻ + C ₃ ⁻)/(C ₂ + C ₃)	Initial activity at 548 K ((μmole CO reacted/μ mole Fe · s) × 10 ³)		
				CO ₂	HC	CH ₄
LTR^a						
Mn ₂ (CO) ₁₀	327	0	—	0.004	—	—
Mn ₂ Fe(CO) ₁₄	300	0.06	—	0.036	0.042	0.042
NEt ₄ [MnFe(CO) ₉]	306	0.21	1.6	0.033	0.013	0.003
NEt ₄ [MnFe ₂ (CO) ₁₃]	275	1.3	6.4	0.27	0.24	0.059
Fe ₃ (CO) ₁₂	249	2.7	1.3	0.76	0.86	0.16
K[MnFe(CO) ₉]	302	1.3	High	0.52	0.18	0.06
K[MnFe ₂ (CO) ₁₃]	250	0.8	High	1.29	0.50	0.07
K[HFe ₃ (CO) ₁₁]	280	2.2	High	1.11	0.44	0.05
2Mn/Fe; carbonyls	300	0.8	3.5	0.18	0.15	0.05
2Fe/Mn; nitrates	—	—	—	—	—	—
2Fe/Mn; carbonyls	284	1.0	3.9	0.18	0.22	0.10
HTR^b						
Mn ₂ (CO) ₁₀	348	0	—	0.006	—	—
Mn ₂ Fe(CO) ₁₄	314	0.52	1.0	0.06	0.06	0.02
NEt ₄ [MnFe(CO) ₉]	309	1.3	1.6	0.38	0.17	0.03
NEt ₄ [MnFe ₂ (CO) ₁₃]	251	2.4	1.0	0.75	0.91	0.20
Fe ₃ (CO) ₁₂	225	2.0	1.4	1.06	1.17	0.23
K[MnFe(CO) ₉]	290	1.4	High	1.06	0.41	0.04
K[MnFe ₂ (CO) ₁₃]	250	1.7	High	1.68	0.78	0.10
K[HFe ₃ (CO) ₁₁]	285	1.9	15.7	1.15	0.77	0.12
2Mn/Fe; carbonyls	300	1.8	1.2	0.36	0.34	0.09
2Fe/Mn; nitrates	279	2.2	0.8	0.56	0.52	0.13
2Fe/Mn; carbonyls	260	2.2	0.7	0.49	0.50	0.10

^a Low-temperature reduction at 473 K.

^b High-temperature reduction at 673 K.

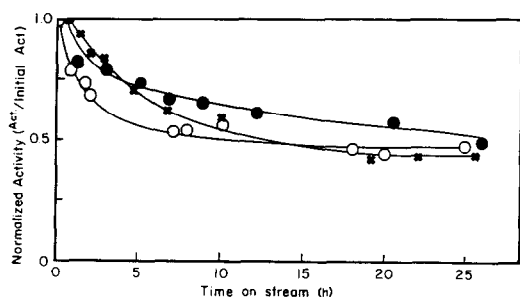


FIG. 1. Activity (CO to Hydrocarbons) maintenance runs for carbon-supported clusters: ●, $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ at 572 K after LTR; ○, $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ at 534 K after HTR; ×, $\text{K}[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ after HTR at 554 K. (Initial activities obtained after 20 min on stream.)

consisting of an HTR step completely restored the activity of this catalyst, as indicated in Fig. 2. During this regeneration treatment in H_2 , significant CH_4 formation occurred; therefore, we attribute this deactivation to the build-up of carbonaceous material on the catalyst surface, which is a well-known phenomenon for iron catalysts (6-11). This interpretation is further sub-

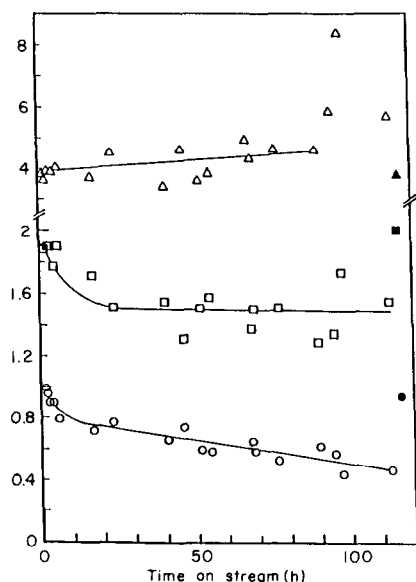


FIG. 2. Variation of catalytic behavior with time on-stream for $\text{NEt}_4[\text{FeMn}(\text{CO})_9]$ after HTR: $T = 587 \text{ K}$, $P = 100 \text{ kPa}$, $\text{H}_2/\text{CO} = 3$, CO conv. to HC = 0.3-0.7%. Δ, Olefin/paraffin $[(\text{C}_2^- + \text{C}_3^-)/(\text{C}_2 + \text{C}_3)]$ ratio. □, moles CO_2 /moles CO reacted to HC; ○, normalized activity (CO conv. to HC) (see Fig. 1). Closed symbols are values after regeneration in H_2 at 673 K for 16 h.

stantiated by the results in Fig. 3 for the FeMn_2/C catalyst, which show that a 20-h exposure to pure H_2 at only 593 K (the reaction temperature) restored half of the initial loss in activity. Again CH_4 was observed in the exit stream during this regeneration period, and experiments showed that in neither case was the CH_4 due to gasification of the carbon support. After the H_2/CO feed was reintroduced, the catalyst activity quickly dropped to its stable level which was near half of its initial value. At that point, the catalyst was exposed to pure He for 20 h at 593 K, during which time no CH_4 was detected, and this treatment produced little increase in activity. A subsequent treatment in H_2 again increased the activity but the gain was not as pronounced as before. This behavior is very consistent with previous work which has shown that amorphous or carbidic carbon that reacts with H_2 can convert slowly to an unreactive graphitic form of carbon (or iron carbide) (7-11). Consequently, we conclude that these Fe-containing clusters form small, well-dispersed Fe particles that are quite resistant to sintering, and essentially all the deactivation is due to the deposition of carbonaceous material on the catalyst surface or within the carbon pore structure.

Finally, CO_2 formation over the unpromoted clusters during continuous operation routinely lined out to give CO_2/CO ratios [moles CO_2 formed/moles CO reacted to

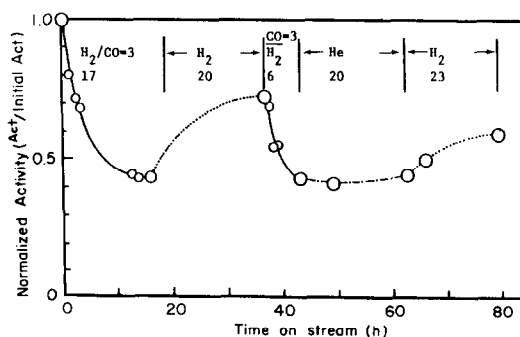


FIG. 3. Activity (CO to hydrocarbons) maintenance, regeneration, and effect of He on regeneration for $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ after HTR: $T = 593 \text{ K}$, $P_{\text{total}} = 100 \text{ kPa}$; —, reaction with H_2/CO ; ···, regeneration in H_2 ; - - -, heating in He.

hydrocarbons (HCs)] near or below 1, as shown in Figs. 2 and 4. This was not the situation with the K-containing catalysts, and a higher CO_2 make was obtained in all cases, as shown in Fig. 4. Alkali metals are known to catalyze CO dissociation on iron (8, 12) and the CO_2/CO ratios well above unity, indicative of CO disproportionation, show that this reaction must occur. Even though ratios of 1 or lower can be explained by invoking a subsequent water gas shift reaction only, a concomitant CO disproportionation reaction to produce surface carbon and CO_2 is also possible.

Olefin Formation

Those factors which influenced the olefin/paraffin ratio (OPR) were of particular interest. Compared to the Fe-Mn clusters, initial kinetic measurements had shown that the K-containing clusters typically had high OPRs along with comparable or higher activities, as shown in Table 1. The only unpromoted cluster to exhibit high initial

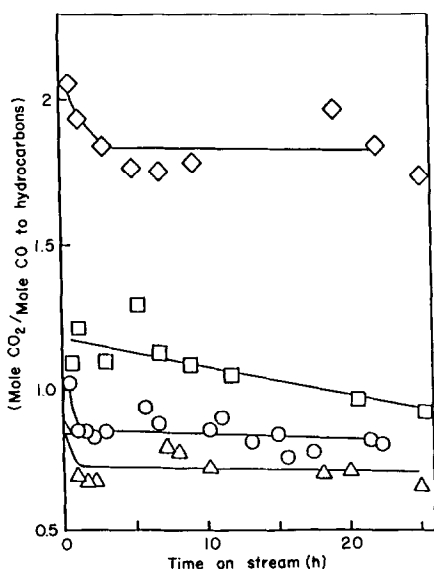


Fig. 4. Variation of CO_2 formation with time on stream: $P = 100$ kPa, $\text{H}_2/\text{CO} = 3$. \diamond , $\text{K}[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ after HTR, $T = 554$ K, CO conv. = 0.4–1.4%; \square , $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ after LTR, $T = 571$ K, CO conv. = 1.4–4.0%; \circ , 2Fe/Mn (from carbonyls) after HTR, $T = 548$ K, CO conv. = 1.5–3.8%; \triangle , $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ after HTR, $T = 543$ K, CO conv. = 1.4–2.9%.

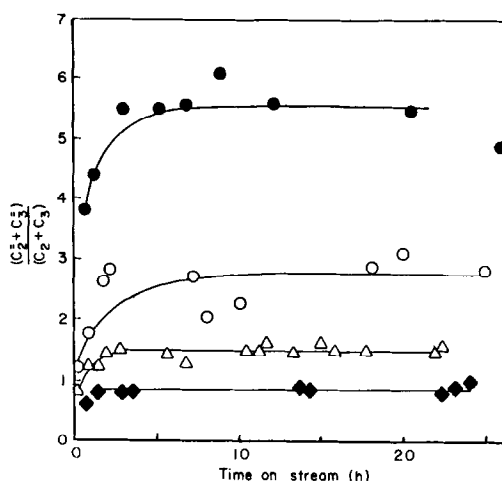


Fig. 5. Variation in the olefin/paraffin ratio with time on stream for catalysts with $\text{Fe}/\text{Mn} = 2$, $P = 100$ kPa, $\text{H}_2/\text{CO} = 3$. \bullet , $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ after LTR, $T = 572$ K; \circ , $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ after HTR, $T = 534$ K; \triangle , 2Fe/Mn (from carbonyls) after HTR, $T = 547$ K; \blacklozenge , 2Fe/MN (from nitrates) after HTR, $T = 544$ K.

olefin formation was the $\text{Fe}_2\text{Mn}/\text{C}$ catalyst, although the FeMn/C sample gave an OPR above 4 after 2 h of continuous operation as shown in Fig. 2. The addition of potassium to iron catalysts is known to enhance olefin formation (6, 12); therefore, the high selectivity of the catalyst derived from the $\text{NEt}_4[\text{Fe}_2\text{Mn}(\text{CO})_{13}]$ cluster in the absence of K is very intriguing. The OPRs versus time on stream for the three catalysts with an Fe/Mn ratio of 2 are shown in Fig. 5. These results lead to the following conclusions: (1) the LTR pretreatment is much more beneficial for olefin formation than the HTR step, and much higher OPRs were obtained over the entire range of conversion; (2) these dependencies on conversion are not so severe as those reported by Butt and co-workers for Fe/SiO_2 (13, 14); and (3) the high OPR provided by the Fe_2Mn cluster cannot be mimicked by coimpregnation of separate Fe and Mn carbonyl clusters or nitrate salts—the initial bonding within the Fe-Mn cluster appears to be critical.

The differences in the OPR cannot be attributed to the reaction temperatures utilized, but the effect of pretreatment is again

clearly demonstrated in Fig. 6. The HTR step changes the catalyst such that a lower OPR is obtained which is very similar to other unpromoted Fe/carbon catalysts (15, 16). Finally, the variations in the olefin/paraffin ratio with CO conversion, obtained by cross-plotting the results in Figs. 1 and 5, are shown in Fig. 7. Stable values were obtained, within experimental error, after 2–3 h on-stream. Although most of this increase can be attributed to a decline in conversion, as discussed the next section, the possibility of phase changes cannot be discounted at this time. Similar plots are not shown for the K-containing catalysts because the detectable products consistently contained *only olefins and methane* during the entire period on-stream, even at CO conversions to HCs up to 4.1% and total conversions (including CO₂ formation) up to 13.4%.

DISCUSSION

The principal purpose of this paper is to demonstrate that the high olefin/paraffin ratios and activities achieved with specific Fe-Mn and K-Fe-Mn clusters are not due

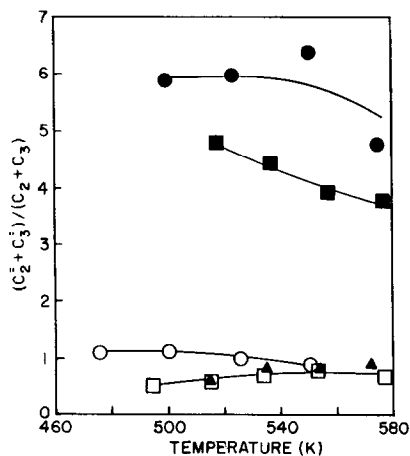


FIG. 6. Influence of temperature on the olefin/paraffin ratio for catalysts with Fe/Mn = 2, $P = 100$ kPa, $H_2/CO = 3$. ●, $NEt_4[Fe_2Mn(CO)_{13}]$ after LTR, CO conv. = 0.4–3.3%; ○, $NEt_4[Fe_2Mn(CO)_{13}]$ after HTR, CO conv. = 0.5–5.6%; ■, 2Fe/Mn (from carbonyls) after LTR, CO conv. = 0.2–1.8%; □, 2Fe/Mn (from carbonyls) after HTR, CO conv. = 1.1–6.3%; ▲, 2Fe/Mn (from nitrates) after HTR, CO conv. = 0.2–4.0%.

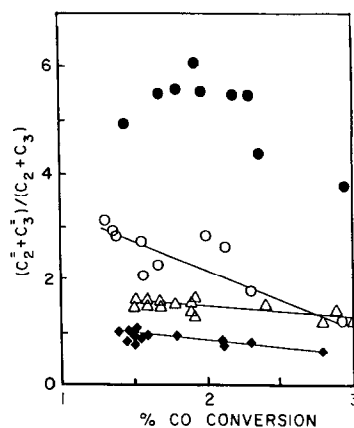


FIG. 7. Variation of the olefin/paraffin ratio with CO conversion to hydrocarbons for catalysts with Fe/Mn = 2, $P = 100$ kPa, $H_2/CO = 3$. ●, $NEt_4[Fe_2Mn(CO)_{13}]$ after LTR, $T = 572$ K; ○, $NEt_4[Fe_2Mn(CO)_{13}]$ after HTR, $T = 534$ K; △, 2Fe/Mn (from carbonyls) after HTR, $T = 547$ K; ◆, 2Fe/Mn (from nitrates) after HTR, $T = 544$ K.

to differences in conversion and temperature and are retained after long periods of continuous operation. As shown in Fig. 1, these cluster-derived catalysts usually attain stable activity within 24 h and lose about half their initial activity during this period. More importantly, the high OPRs typically stabilize after only 2–3 h on-stream. For comparison, Kuznetsov *et al.* observed a 90% loss in activity over various oxide-supported Fe_2Mn clusters after 20 h on-stream (17). Activity maintenance was not reported for other Fe-Mn cluster catalysts (18). In addition, the high OPR obtained with the Fe_2Mn/C catalyst after the LTR pretreatment was previously shown not to be due to artifacts such as higher reaction temperatures or CO conversion levels. There was no large effect of pretreatment on the K-containing catalysts; however, for the Fe-Mn catalysts with no potassium, the LTR pretreatment typically gave higher OPRs and lower specific activities while the HTR step induced behavior similar to that of Fe-only catalysts (15, 16).

Recent literature indicates that certain general trends can be observed when studying activity maintenance behavior during

CO hydrogenation over iron. Two classes are arbitrarily designated here; namely, class A catalysts for which the activity increases, stabilizes, or decreases only slightly after short times (10–15 h) on-stream, and class B catalysts which show continued, sometimes rapid, deactivation even after 10–15 h on-stream. Examples of class B catalysts have been reported by Niemantsverdriet *et al.* (19, 20), Van Dijk and Van der Baan (21), Butt and co-workers (22), Sommen *et al.* (23), and Kuznetsov *et al.* (17). In contrast, class A behavior was found by El Deen *et al.* (24), Huff and Satterfield (25), Krebs *et al.* (2), and Teichner and co-workers (26–29). One characteristic of the class A Fe catalysts, whether bulk (2, 24, 25, 28, 29) or supported (26, 27), is that they are poorly reduced prior to the initiation of the synthesis reaction, although highly dispersed, well-reduced Fe/C catalysts have also provided very good activity maintenance (16). Class B catalysts tend to be well-reduced bulk (19–21, 28, 29) or poorly dispersed supported Fe systems (16, 22, 23, 26, 27). The Fe–Mn clusters in this study were supported and well dispersed; therefore, class A behavior might be expected, as observed for most of the catalysts and shown in Figs. 1 and 2.

These patterns can be explained by the assumption that a stable oxide phase, even if it is only a surface oxide, can exist under reaction conditions, and iron oxide phases in used Fischer–Tropsch catalysts have been identified (12). Oxides that are initially poorly reduced would not carburize (3, 29) and would more rapidly approach stable behavior (class A), perhaps by providing a lattice to stabilize the presence of very small Fe and Fe carbide clusters, whereas well-reduced Fe catalysts with large Fe crystallites would carburize (19). The activity observed would be very dependent upon the carbide phases present (30–32). This carburization can be quite rapid (29–32) and may impede or prevent the formation of stable oxides. The activity maintenance data on bulk Fe–Mn catalysts ob-

tained by Maiti *et al.* support this hypothesis completely since the very poorly reduced Fe–Mn oxide catalysts increased in activity and the metallic Fe catalyst drastically decreased in activity, whereas the mixed-spinel catalyst showed very little deactivation (4). The unpromoted Fe–Mn catalysts in our study favor the formation of surface spinel because of their high dispersion and oxygen affinity.

High olefin/paraffin ratios have been correlated with the presence of a mixed-spinel structure having a stoichiometry near Fe_2MnO_4 (3, 4), and the behavior of these Fe–Mn/C catalysts without K is consistent with the hypothesis that this phase is primarily responsible for olefin formation (1). Upon the introduction of the syngas feed stream after the LTR step, we postulate a very rapid oxidation of the Fe and Mn to form Fe_2MnO_4 , which is favored by Fe/Mn ratios of 2 and the LTR pretreatment. The formation of separate MnO and reduced Fe phases, which can occur under HTR conditions if trace amounts of oxygen or H_2O are present, will result in catalytic behavior similar to that of iron. The apparent stability of this mixed spinel is consistent with the studies of Teichner and co-workers who found that the Fe spinel, Fe_3O_4 , existed under reaction conditions and gave performance superior to catalysts which had been prerduced to form metallic Fe (26–29).

An examination of the thermodynamics governing the reducibility of various Fe and Mn oxides and mixed-Fe–Mn spinels by H_2 and CO, based on C_p data, standard enthalpies, and free energies for bulk materials (33, 34), showed that although MnO is the most stable Mn phase, the presence of Fe_2MnO_4 is enhanced by LTR in H_2 and only small amounts of H_2O (or O_2) are required to stabilize this phase (35). Under reaction conditions at 500–600 K, the situation is less clear because the formation of H_2O favors the presence of the mixed spinel but the low CO_2/CO ratios indicate that reduction to metallic Fe can occur. However, these thermodynamic consider-

ations imply that it is possible for the mixed spinel to exist among the numerous phases that can be present under dynamic reaction conditions and that the stability of the mixed spinel would be favored by higher conversions (higher H_2O/H_2 ratios) as suggested by Maiti *et al.* (4). If this mixed spinel were to be considered primarily as a surface phase because of the small crystallites present, then the stability of these oxide phases might be expected to be greater than the corresponding bulk phases. For example, Almquist and Black (36) and Brunauer and Emmett (37) reported that a surface iron oxide phase existed even when the H_2O/H_2 ratio was 3 orders of magnitude smaller than the equilibrium value for bulk oxide. More recently, O_2 concentrations in the parts per million range were found to oxidize small Fe crystallites on carbon whereas larger Fe crystallites exhibited little or no detectable oxidation (32).

Based on these considerations, we conclude that the formation of Fe_2MnO_4 is maximized by the use of Fe/Mn ratios of 2, especially when the Fe_2Mn cluster is used, and is favored by the use of the LTR step. The use of the HTR pretreatment can decompose the spinel to iron and MnO, promote phase separation, and result in a catalyst with iron-like behavior. As stated in the previous paper (1), we consider the K-promoted catalysts as a separate group. The addition of a K atom to the $Fe_3(CO)_{12}$, $MnFe(CO)_9$, and $MnFe_2(CO)_{13}$ clusters markedly enhanced olefin formation, but at this time we do not know the interrelationship between K and Mn when they are present together. Future studies using Mössbauer spectroscopy are directed toward determining the iron phases that exist before and during reaction conditions.

The activity maintenance run with the KFe_2Mn/C catalyst showed that the *high selectivity to C_2-C_4 olefins was constant within experimental error for the entire run* although the activity declined by approximately 55% (Fig. 5). During this 26-h period on-stream, the average hydrocarbon prod-

uct distribution (in wt%) was 20% CH_4 , 33% C_2H_4 , 33% C_3H_6 , and 14% C_4H_8 , with no detectable C_{2+} paraffins. The most negative aspect of the K-promoted clusters was the large amount of CO_2 formed, as shown in Fig. 4. Even after extended periods on-stream, the ratio of CO_2 formed to CO reacted (to HCs) remained high and never dropped far below 2. The long-term effects of this carbon deposition have not yet been determined; however, under the reaction conditions used here, it appears to have no more of an effect on activity maintenance than that produced by the smaller extent of carbon formation in the absence of potassium. It is possible that a coimpregnation of a mixture of $NEt_4[Fe_2Mn(CO)_{13}]$ and $K[Fe_2Mn(CO)_{13}]$ clusters could provide an optimum K/Fe ratio which would still give a very high selectivity to C_2-C_4 olefins but with much lower CO_2 production.

SUMMARY

Under continuous reaction conditions, the activity of all these cluster-derived catalysts usually stabilizes within 24 h, and the high OPRs obtained remain essentially unchanged during long periods on-stream. This behavior is acceptable compared to bulk iron and other poorly dispersed Fe catalysts, which typically decline continuously in activity; but very well-dispersed Fe on carbon has been found to exhibit even greater stability on-stream (16). The H_2/CO ratio of 3 used may well be part of the reason. The successful regeneration efforts in H_2 combined with the detection of CH_4 during this period provide overwhelming evidence that the observed deactivation is due to the deposition of carbonaceous species and not to sintering of the small Fe or Fe_2MnO_4 particles. Thus these well-dispersed, carbon-supported, cluster-derived Fe-Mn systems are active, highly selective catalysts for the production of light olefins, and because they are stable for long periods on-stream, they offer the potential of commercial application.

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