JOURNAL OF CATALYSIS 69, 506–510 (1981)

The Effect of Additives to Iron Oxide in the Selective Oxidative Dehydrogenation Reactions[1]

Iron oxide, in the form of Fe_2O_3, has long been used as a major component in the catalysts for the selective dehydrogenation of ethylbenzene to styrene (*1, 2*). More recently, it has also been used in catalysts for the selective oxidative dehydrogenation of butene to butadiene (*3–6*). In these catalysts, components such as Cr_2O_3, ZnO, MgO, and K_2O are often added to enhance their activity and selectivity, and to prolong their useful life. For example, in the oxidative dehydrogenation of butene, it was reported that the addition of Cr, Mg, or Zn to Fe_2O_3 resulted in a catalyst of improved activity and selectivity (*4, 5*). However, the details of the improvement depend on the exact nature of the additives. Furthermore, it has also been reported that γ-Fe_2O_3 of spinel structure is more active and selective than α-Fe_2O_3 of corundum structure (*3, 6*). Therefore, it appears that for the benefit of future catalyst development, it is of interest to understand the function of these additives. The present note aims at this direction by providing a phenomenological explanation of the effect of additives and crystal structure in this particular reaction.

Table 1 shows the typical data which indicate the effect of Cr and Zn additives to α-Fe_2O_3 in the production of the oxidation products butadiene and carbon dioxide in the oxidative dehydrogenation of *cis*-2-butene. The data were gathered in a pulse reactor described earlier (*7, 8*). The catalysts were pretreated by first heating in O_2 at 400°C for 0.5 h, then in He at 300°C for 0.5 h. Pulses of *cis*-2-butene were introduced in a He carrier in the absence of oxygen. The small amounts of catalysts used made the reactor a single-pass reactor. Although the reaction was run in the absence of O_2, the activity and selectivity patterns on the different catalysts as a function of temperature agree well with the reported steady-state measurements made in the presence of oxygen (*5*).

Several points are to be noted from the data: (i) At all temperatures, Cr addition increases the production of CO_2 in the first pulse but not in the subsequent pulses. (ii) At 210°C, the C_4H_6 production decreases rapidly on Fe_2O_3 and $FeCrO_3$, but more slowly on $ZnFe_2O_4$. (iii) At higher temperatures, the C_4H_6 production decreases slowly in subsequent pulses on $ZnFe_2O_4$ and $FeCrO_3$. The rate of decrease on Fe_2O_3 decreases with increasing temperature until eventually the production increases in subsequent pulses. This behavior on Fe_2O_3 has also been reported by Misono *et al.* (*6*). (iv) The production of C_4H_6 in the first pulse increases by about 100% on going from 210 to 350°C on $ZnFe_2O_4$, about 80% on Fe CrO_3, but only 30% on Fe_2O_3. (v) The production of CO_2 increases rapidly with increasing temperature on Fe_2O_3, but much more slowly on $ZnFe_2O_4$ and $FeCrO_3$, except for the first pulse on $FeCrO_3$. Points (iii) and (v) together suggest that the selectivity for butadiene decreases rapidly with increasing temperature on Fe_2O_3, but more slowly on $FeCrO_3$ and on $ZnFe_2O_4$ as was observed under steady-state reaction conditions (*5*). Disregarding the CO_2 production on $FeCrO_3$ in the first pulse for the

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[1] Work supported by the Department of Energy, Basic Energy Sciences Division.

0021-9517/81/060506-05$02.00/0

TABLE 1

Oxidation Products of *cis*-2-Butene[a]

Temp. (°C)	First Pulse		Second Pulse		Third Pulse	
	C_4H_6 ($\times 10^{17}$)	CO_2 ($\times 10^{17}$)	C_4H_6 ($\times 10^{17}$)	CO_2 ($\times 10^{17}$)	C_4H_6 ($\times 10^{17}$)	CO_2 ($\times 10^{17}$)
α-Fe_2O_3 (0.0552 g)[b]						
210	5.60	0.02	0.83	0.07	0.93	0.59[c]
210	4.84	0.01	1.61	0.03	1.33	0.02
300	5.69	2.04	4.54	1.27	5.14	0.84
300	5.14	1.88	4.51	0.91	4.60	0.84
350	6.00	7.87	10.01	6.27	11.50	5.80
350	5.92	6.51	11.56	5.64	11.04	5.50
350	7.06	6.48	8.54	5.06	10.01	5.47
$FeCrO_3$ (0.0159 g)[b]						
210	2.46	0.73	0.51	0.05	0.05	0.02
210	2.72	0.86	0.67	0.06	0.05	0.03
300	3.63	5.06	2.22	0.29	1.60	0.10
300	3.96	5.23	2.29	0.23	1.71	0.08
350	4.36	7.36	2.60	0.33	2.20	0.26
350	4.79	8.01	2.53	0.40	2.46	0.30
$ZnFe_2O_4$ (0.0601 g)[b]						
210	5.95	0	4.06	0	1.74	0
210	6.47	0	3.70	0	2.10	0
210	6.58	0	4.21	0	2.68	0
300	13.55	0.74	—	0.79	5.18	0.63
300	10.69	0.21	5.13	0.08	4.06	0.20
350	11.13	2.79	6.31	1.44	5.64	0.82
350	14.26	3.34	7.45	1.77	5.23	1.04

[a] *cis*-2-Butene pulse size: 2.6 × 10^{18} molecules; He flow rate 40 ml/min; other products were *trans*-2-butene and 1-butene; numbers in the table are number of molecules.

[b] Surface area of Fe_2O_3, 8.5 m^2/g; $FeCrO_3$, 30 m^2/g; $ZnFe_2O_4$, 7.8 m^2/g.

[c] This number is exceptionally high, and is not representative.

moment, the observations suggest that Fe CrO_3 behaves like Fe_2O_3 at low temperature, but like $ZnFe_2O_4$ at high temperature. There are two other related observations reported in the literature that we shall discuss together with those above: (vi) At a low temperature of 200°C on γ-Fe_2O_3, the production of C_4H_6 in subsequent pulses decreases only slowly, similar to $ZnFe_2O_4$ (*6*). (vii) Under comparable conditions, the production of CO_2 from α- and γ-Fe_2O_3 is comparable, although the production of C_4H_6 from the γ form is much higher (*3*).

Since it has been established that the two oxidation products are being produced on two independent sites (*7, 8*), we shall attempt to explain the above observation by the effect of structure and additives on the production of the individual products.

The production of CO_2 in pulse experiments is not affected by the presence or absence of gaseous oxygen. Since 12 O atoms are needed for the combustion of each butene, it is reasonable to expect that CO_2 production involves lattice oxygen in the near-surface region. Indeed it has been shown that up to about three monolayers of lattice oxygen participate directly in this oxidation reaction (*3, 9 ,10*). Thus the reduction in CO_2 production at high temperatures by Zn and Cr additives must be because these additives increase the resistance to reduction in the near-surface region, which is a result of the fact that both ZnO and Cr_2O_3 are more resistant to reduction than Fe_2O_3. This is similar to that suggested earlier for Zn (*8*). At low temperatures, CO_2 is not observed in any of the catalysts because its rate of production is too low (*7, 8*).

The above argument is only valid if Zn and Cr exist to a relatively significant extent at and near the surface. The surface cation densities had been measured for a number of $(Fe, Cr)_2O_3$ solid solutions that were equilibrated in air (*11*). It was found that on all the samples, Cr constitutes a significant fraction of the surface cation. Although the measurements were made on oxidized samples, they are relevant because under steady-state conditions, the gas-phase reactant mixture of oxygen and butene forms an oxidizing atmosphere, and the steady states of the ferrite catalysts are near their fully oxidized forms as determined by X-ray diffraction and electrical conductivity (*3, 12*). Similar surface cation density measurement has not been made on $ZnFe_2O_4$. However, Zn is not expected to be depleted near the surface as it is a constituent of a stable spinel structure. The large quantity of CO_2 produced in the first pulse at high temperature on $FeCrO_3$ is due to the excess surface oxygen present on the sample after the pretreatment that is associated with Cr(VI) species at the surface (*11*). Such oxygen species are very reactive (*13*). Once they are consumed in the first pulse, production of CO_2 rapidly decreases.

We now turn to the production of butadiene. It appears that the difference in the behavior at 210°C between $ZnFe_2O_4$ (and γ-Fe_2O_3) and α-Fe_2O_3 in repeating pulses, the higher rate of production on γ- than on α-Fe_2O_3, and the higher rate of increase in production with increasing temperature on $ZnFe_2O_4$ than on α-Fe_2O_3 are all associated with the difference between a spinel and a corundum structure. There are two structural differences between the two structures. A spinel surface possesses sites not present on a corundum surface. For example, on an ideal (100) surface of a normal spinel (Fig. 1), the interstices between rows of oxygen atoms, which represent truncation of close-packed oxygen layers, are filled with alternate rows of 3+ ions and 2+ ions in the manner shown with the 2+ ions recessed into a subsurface position between the topmost and the second atomic layers. On an equivalent surface of corundum, the interstices between rows of oxygen atoms are two-thirds filled by 3+ ions. Clearly cation vacancy sites such as those denoted by A are not present on a corundum surface. Perhaps the participation of these cation vacancy sites in the active center for butadiene production accounts for the higher activity and the stronger temperature dependence of spinel catalysts. The participation of cation vacancy in selective oxidation of propene to acrolein has been demonstrated on scheelite catalysts of Pb–Bi–Mo–O (*14, 15*). It was proposed in these studies that a cation vacancy is electron rich and makes the surrounding oxygen ions more basic. These more basic oxygen ions can abstract a proton more easily from an adsorbed olefin, thus enhancing the rate. Such a mechanism can participate in the butadiene production.

The possible importance of a cation vacancy associated with a spinel structure

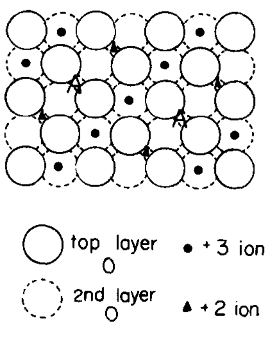

Fig. 1. Model of a normal spinel (100) surface.

also explains the increase in C_4H_6 production in subsequent pulses on α-Fe_2O_3 at high temperatures. Reactions due to the first butene pulse reduce the α-Fe_2O_3 surface to one probably close to that of Fe_3O_4. However, rapid migration of lattice oxygen to the surface, which is possible at high temperature reconverts the surface to one in between Fe_3O_4 and γ-Fe_2O_3, and the surface atomic arrangement is converted to a spinel. Such a surface now is more active in producing C_4H_6. If such a surface rearrangement to spinel is inhibited, for example, by the addition of Cr, such an increase in the activity will not be observed.

The second structural difference is that in a spinel there are rows of cations (solid circles in Fig. 1) at the centers of octahedrons sharing edges. Charge delocalization along these uninterrupted rows of cations is probably more efficient than that along the interrupted ones in corundum. This would facilitate the redox mechanism involved in dehydrogenation reactions (*4, 9*). The effective charge delocalization also permits more sustained production of butadiene in the pulse experiments. Such uninterrupted rows of cations may not be present on γ-Fe_2O_3, but effective charge delocalization may be accomplished by the high density of oxygen vacancies in the compound (*16*).

The fact that Cr exists as Cr(VI) in the surface of $FeCrO_3$ after preparation may have another implication. In addition to the presence of excess oxygen to balance the excess charge on Cr(VI), this excess charge can also be balanced by extra cation vacancies. If so, the addition of Cr also results in a higher density of cation vacancies at the surface which then has a higher activity and a stronger temperature dependence in butadiene production. This increase in activity, however, may be offset by a lower density of Fe ions at the surface. The temperature dependence of the rate, however, will still reflect the participation of the vacancy. This can be used to explain the data observed.

While the discussion is centered on the addition of Zn and Cr, the effect of Mg addition, which also results in the formation of a spinel (*4*), can similarly be explained.

Thus we have advanced a phenomenological explanation for the effect of Cr and Zn additives on the behavior of a ferrite catalyst in the selective oxidation reactions. In addition to the generally accepted effect of bulk structural stabilization, these additives also stabilize the near-surface region which results in a reduction in CO_2 production. The conversion into a spinel structure by adding Zn generates surface cation vacancy sites and more effective charge delocalization, which result in improved butadiene production activity. The better performance of γ-Fe_2O_3 than α-Fe_2O_3 can likewise be explained. Addition of Cr may also generate surface cation vacancies that have a similar effects.

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Received August 15, 1980; revised December 22, 1980

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