Iron Oxide Dehydrogenation Catalysts supported on Magnesium Oxide

Part 3.—But-1-ene Dehydrogenation Activity[†]

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The catalytic behaviour of iron oxide catalysts supported on magnesium oxide in the non-oxidative dehydrogenation of but-1-ene to buta-1,3-diene has been studied. Under dehydrogenation conditions the magnesium ferrite phase of the fresh catalyst was found to be reduced to FeO in the bulk of the ferrite particles, where FeO is strongly stabilized by the formation of a solid solution with MgO. At the surface of the particles magnesium ferrite is reduced to Fe₃O₄. In the reduced state a catalyst containing *ca*. 3 wt.% Fe shows a but-1-ene conversion of 26% combined with a buta-1,3-diene selectivity of 65% at 873 K. The activation energy for dehydrogenation was found to be 47 kcal mol⁻¹.

The (unpromoted) catalyst gradually deactivates owing to carbon deposition. Under dehydrogenation conditions the catalyst surface is completely covered by a layer of amorphous carbon within 20 h.

Industrially, ethylbenzene is catalytically dehydrogenated over an unsupported alkali-metal-promoted iron oxide catalyst in the presence of steam.¹ But-1-ene can be dehydrogenated to buta-1,3-diene using the same catalyst.^{2,3} Lee has published a review on the research performed in the field of ethylbenzene dehydrogenation with particular reference to unsupported alkali-metal-promoted iron oxide.⁴

Major problems arising with this type of catalyst are caused by potassium migration due to temperature gradients, and reduction of the iron oxide phase under process conditions.^{5–7} Owing to the endothermic character of the dehydrogenation process, temperature gradients are present in the catalyst bed, both in radial direction within the individual catalyst bodies and lengthwise in the catalyst bed. Potassium migrates to the colder centre within the catalyst pellets and to the colder end of the catalyst bed. This leads to a local potassium depletion, causing an increase in porosity coupled with a decrease in mechanical strength and a less effective suppression of catalyst coking. Reduction of the iron oxide phase to Fe₃O₄ causes a lattice transformation from a corundum structure to a spinel structure. Since iron oxide is the bulk material, this transformation leads to a degradation of mechanical strength and, eventually, to disintegration of the catalyst bodies. The disintegration causes a large pressure drop over the reactor, which may be unfavourable for high styrene selectivity and yield. These problems are expected to be obviated by the use of finely divided iron oxide on a support, ensuring the retention of mechanical strength during operation.

To meet with the problems of the present bulk iron oxide dehydrogenation catalyst, an (alkali-metal-promoted) iron oxide catalyst supported on magnesium oxide has been developed. The preparation and characterization of iron oxide supported on magnesium oxide have been reported elsewhere.⁸⁻¹⁰ The catalyst is prepared by incipient-wetness impregnation of preshaped magnesium oxide support bodies with organometallic complexes. Upon decomposition of the iron precursors, highly dispersed magnesium ferrite particles supported on magnesium oxide are formed. In order to determine the effect of the potassium promoter on the supported iron oxide catalyst,^{11,12} the catalytic performance of the unpromoted supported iron oxide catalysts in the dehydrogenation is dealt with in this paper. Kearby^{13,14} has reported on catalysts supported on powder magnesium oxide earlier. However, these catalysts were not autoregenerative in the presence of steam and were strongly deactivated within the first few hours of operation, in spite of the presence of the potassium promoter.

Dehydrogenation of ethylbenzene and but-1-ene are comparable processes.^{2,3} Based on this comparability and on the experimentally less complicated procedure involved with the analysis of the reaction products, dehydrogenation of but-1ene to buta-1,3-diene is preferred as a test reaction. First, the activity and selectivity of the catalysts as a function of the time on stream were measured. Phase changes within the catalysts, which are expected to occur during dehydrogenation,^{4,7} have been examined using magnetic measurements and X-ray diffraction. Several authors have reported the growth of carbon on unpromoted iron oxides in butene atmospheres.^{15,16} After being used in the dehydrogenation, the catalysts were therefore investigated for carbon deposition using temperature-programmed oxidation (TPO). Thermodynamic calculations were made predicting growth or gasification of carbon as a function of the pressure, the temperature, and the composition of the gas phase. Subsequently, the activation energy and the pre-exponential factors of fresh and deactivated catalysts were established.

Experimental

Catalyst Preparation

Unpromoted iron oxide catalysts supported on magnesium oxide were prepared by incipient-wetness impregnation of preshaped magnesium oxide support bodies (Engelhard, Mg-0601 T 1/8'') using poorly crystallizing complexes.⁸ Pure ammonium iron(III) citrate (Bakergrade) and ammonium iron(III) EDTA (Merck, Fotopur) were used. After impregnation the catalysts were dried in air first at room temperature and next at 393 K, at both temperatures for 16–24 h. Finally, the catalysts were calcined in air at 973 K for 24 h to decompose the organometallic precursors. The actual iron loading

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of a catalyst, as determined by titration, is expressed as the calculated weight percentage metallic iron on the magnesium oxide support. For various tests the catalyst bodies were fragmented into particles of sizes between 0.50 and 0.85 mm.

But-1-ene Dehydrogenation Activity Testing

The activity of the catalysts for the dehydrogenation of but-1ene was determined with an automated flow apparatus, which is shown schematically in Fig. 1. The catalyst (ca. 1 g) was packed into a quartz fixed-bed flow reactor with an internal diameter of ca. 8 mm. The apparatus was equipped with facilities to provide but-1-ene, nitrogen, hydrogen and oxygen. The gases were used without further purification. But-1-ene (99.9% pure) was obtained from Phillips Petroleum, while other gases were provided by Hoekloos. For the dehydrogenation experiments a mixture of 5 vol.% but-1ene and 30 vol.% water vapour in 65 vol.% nitrogen at atmospheric pressure was used, which is equivalent to a so-called steam : oil ratio of 6.0 (mol/mol). Water vapour was introduced using a saturator containing distilled water, which was held at 343 K using a thermostat. To prevent condensation of water vapour, the tubing was heated at 413 K. Table 1 shows the typical test conditions. The feed was led upstream through the catalyst bed. The reactor temperature was controlled using an Eurotherm 820 temperature controller. The actual temperature was measured in the centre just below the catalyst bed.

The reactor feed and effluent were analysed on-line by two gas chromatographs. For this purpose samples were taken regularly using three heated sample valves. As well as buta-1,3-diene, methane, ethane, ethene, propene and carbon dioxide were formed. No carbon monoxide was detected. Furthermore, but-1-ene was rapidly isomerized to (E)- and (Z)-but-2-ene. Carbon dioxide was separated from the hydro-

Table 1 Standard but-1-ene dehydrogenation test conditions

feed	5 vol.% but-1-ene
	30 vol.% water
	65 vol.% nitrogen
water : but-1-ene	6 mol/mol
pressure	1 bar
feed rate	$50 \text{ cm}^3 \text{ min}^{-1}$
weight hourly space velocity	0.35 g but-1-ene $g_{catalyst}^{-1}$ h ⁻¹
temperature range	723–898 K

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carbons on a Porapack Q column (1/8", 2.5 m) at 433 K using helium as the carrier gas (Hewlett-Packard 5710 gas chromatograph). CO₂ was detected using a thermal conductivity detector (TCD). Other products and but-1-ene were separated using a capillary Al₂O₃/KCl plot column at 353 K using nitrogen as a carrier gas (Packard 427 gas chromatograph). For detection a flame-ionization detector (FID) was used. Since the capillary column used is not resistant to water vapour, samples were dried using a Perma Pure minidryer. Gas chromatograms were integrated using two computing integrators (CI-10B, Milton Roy) and data were collected on a 20 MB hard disk. Temperature control, sampling and data processing were performed using an IBM-AT compatible computer.

Since but-1-ene rapidly isomerized to (E)- and (Z)-but-2ene, and since the dehydrogenations of but-1-ene and but-2enes are comparable,¹⁴ (E)- and (Z)-but-2-ene are not considered as products, but as reactants together with but-1-ene. For the calculations, the three components are therefore added and referred to as 'butenes'. Owing to the pressure drop over the reactor varying with the temperature and a slightly unstable water-vapour concentration inherent to the use of a saturator, the analysis of the feed could not be used for calculations of conversion, selectivity and yield. The following definitions for the conversion, the selectivity to product (i), and the yield of product (i) have therefore been used:

conversion (%) =
$$\frac{\sum n(i) \text{prod.}(i)}{\sum n(i) \text{prod.}(i) + \text{butenes}(\text{after})} \times 100\%$$
 (1)

selectivity i (%) =
$$\frac{n(1)\text{prod.(1)}}{\sum n(1)\text{prod.(i)}} \times 100\%$$
 (2)

yield i (%) =
$$\frac{n(i)\text{prod.}(i)}{\sum n(i)\text{prod.}(i) + \text{butenes}(after)} \times 100\%$$
 (3)

prod.(i) refers to the concentration of product (i) expressed in mol dm⁻³; n(i) refers to the ratio between the number of carbon atoms in product (i) and the number of carbon atoms in butene. The term butenes(after) expresses the total amount of unreacted butenes. Then the term $\sum n(i)$ prod.(i) + butenes(after) is equal to the concentration of butene in the feed expressed in mol dm⁻³. In these calculations carbon deposited on the catalyst is not considered. Unless specified otherwise, kinetic data are always expressed per gram of catalyst.



Fig. 1 A schematic representation of the dehydrogenation apparatus. (a) Pressure regulators (Porter), (b) mass flow controllers (High-Tech Instr.), (c) valve (Whitey), (d) saturator (H₂O, 343 K), (e) bypass, (f) quartz fixed-bed reactor with catalyst, (g) oven, (h) chromel/alumel thermocouple, (i) heated sampling chamber at 413 K, (j) six-port sampling valve, (k) Perma-Pure minidryer MD-125P, (l) cold trap (273 K), (m) vent

Other Characterization Techniques

X-Ray diffraction measurements were performed in a Philips powder diffractometer mounted on a Philips PW 1140 X-ray generator with Fe-K $\alpha_{1,2}$ radiation ($\lambda = 1.93735$ Å).

High-field magnetic measurements were performed using a modification of the Weiss extraction technique, as described by Selwood.¹⁷ The apparatus has been described elsewhere.¹⁸ A reactor was constructed which allowed for the pretreatment of a catalyst in the but-1-ene dehydrogenation apparatus, prior to the magnetization measurements in the modified Weiss extraction apparatus, without intermediate exposure to air. After pretreatment in the but-1-ene-steam feed the reactor was purged with nitrogen at 673 K. Thermomagnetic analyses (TMA) were performed at a field strength of 0.39 MA m⁻¹ in helium. Before use, the helium was purified over activated carbon at liquid-nitrogen temperature.

The amount of carbon deposited on a catalyst was determined using TPO. Carbon was oxidized in a flow of 10% oxygen in helium. The oxygen consumption was determined as a function of the temperature using a thermal-conductivity detector. Ca. 500 mg of catalyst were oxidized. The temperature was raised linearly at a rate of 0.11 K s⁻¹. CO₂ formed during the oxidation was frozen out using a cold trap (pentane₁/pentane_s, 143 K).

Catalysts were also characterized using transmission electron microscopy (Philips EM420).

Results and Discussion

Activity and Selectivity of the Catalysts

Non-oxidative dehydrogenation catalysts are commonly operated at temperatures between 850 and 900 K. To determine the catalytic behaviour of the supported iron oxide catalyst as a function of time, the catalysts were exposed to dehydrogenation conditions isothermally at 873 K. The butene dehydrogenation activity of an unpromoted 1.0 wt.% Fe/MgO catalyst (ex citrate) at this temperature during the first 20 h is shown in Fig. 2. As can be seen, the yield and especially the selectivity of buta-1,3-diene strongly increase during the first hour, whereas the conversion remains constant. At the same time the colour of the catalyst changes from beige to grey. An optimum in the catalyst performance is reached after 2 h. Beyond this period, the conversion and the selectivity slowly decrease. In Fig. 3 the product distribution is shown as percentage yield. Initially, a considerable amount of CO₂ is produced as well as buta-1,3-diene, other products being methane, ethene and propene. Ethane is pro-



Fig. 2 But-1-ene dehydrogenation activity for a 1.0 wt.% Fe/MgO catalyst (ex citrate) at 873 K in 5 vol.% but-1-ene and 30 vol.% H_2O in N_2 . (a) But-1-ene conversion, (b) buta-1,3-diene yield, (c) buta-1,3-diene selectivity



Fig. 3 Product distribution of butene dehydrogenation for a 1.0 wt.% Fe/MgO catalyst (ex citrate) at 873 K in 5 vol.% but-1-ene and 30 vol.% H₂O in N₂. (a) CO₂, (b) methane, (c) ethene, (d) propene, (e) buta-1,3-diene

duced only in extremely small amounts. The initially high CO_2 yield of 9% strongly diminishes with time. After *ca.* 12 h CO_2 is no longer detected. The formation of such large amounts of CO_2 points to a reduction of the catalyst by hydrocarbons during the first few hours of operation. This is consistent with the change in colour.

For catalysts with higher iron loadings the dehydrogenation activity shows identical behaviour. However, a catalyst containing more iron requires a longer period of time to become active and selective. This agrees with what is expected if the initial increase in selectivity and yield is caused by reduction of the catalysts. Fig. 4 shows the buta-1, 3-diene yields at 873 K for catalysts with different iron loadings ranging from 1–3 wt.% Fe. Remarkably, after the initial increase of the yield, all catalysts reach an equal maximum yield of buta-1,3-diene of *ca.* 17%, in spite of the difference in free surface area of the magnesium ferrite.¹⁰ As dehydrogenation proceeds, the catalyst with only 1.0 wt.% Fe is deactivated more rapidly than the catalyst with 3.1 wt.% Fe.

The results of Fig. 4 show that the buta-1,3-diene yield of the catalysts does not depend significantly on the iron



Fig. 4 Buta-1,3-diene yield for different catalysts (ex citrate) at 873 K in 5 vol.% but-1-ene and 30 vol.% H_2O in N_2 . (a) 1.0 wt.% Fe/MgO, (b) 2.1 wt.% Fe/MgO, (c) 3.1 wt.% Fe/MgO

loading of the magnesium oxide. Since the free surface area of the active component may also not vary significantly with the loading it is important to establish the free surface area of the active component. The free surface area of the magnesium ferrite phase was calculated from the amount of oxygen taken up with surface oxidation of the previously reduced catalysts.¹⁰ A reliable assessment of the free surface area of the magnesium ferrite calls for a complete reduction of the magnesium ferrite to iron(II). Earlier, the iron-containing phase of the thus reduced catalyst was described $(FeO)_x \cdot (MgO)_{1-x}$. The thus obtained free surface area of the magnesium ferrite phase of the catalyst containing 1.0 wt.% Fe is 1.12 m² per gram of catalyst, while that for the catalyst containing 3.1 wt.% Fe is 3.22 m² g⁻¹. ¹⁰

Apparently, the activity of the catalyst does not depend simply on the free surface area of the magnesium ferrite. It seems logical that intraparticle transport of reactants could account for the lack of a relation between catalyst activity and the free surface area of the magnesium ferrite. However, the effectiveness factor η , as calculated using the Thiele modulus ϕ , is practically unity.^{12,19} The activity is therefore not influenced by internal diffusion phenomena. The lack of a relation between catalyst activity and the free surface area of the magnesium ferrite could, however, be explained by the fact that the catalyst is in a reduced state, which was concluded from the initially high CO₂ production rate. In that case, the surface area of the active phase in the reduced catalyst should not be corresponding with the free surface area of the magnesium ferrite. Accordingly, the extent of reduction of the catalyst under dehydrogenation conditions should be different from the above mentioned $(FeO)_x \cdot (MgO)_{1-x}$ phase. This is conceivable, as in earlier experiments the FeO has appeared to disproportionate to Fe_3O_4 and metallic iron upon severe thermal treatment.⁹ The nature of the active phase of the catalyst after dehydrogenation of but-1-ene will be investigated using X-ray diffraction and thermomagnetic analysis.

Reduction of the Catalyst during Dehydrogenation

XRD

intensity (arb. units)

70

60

To establish the nature of the reduced state of the catalyst under dehydrogenation conditions, a 4.4 wt.% Fe/MgO catalyst (ex citrate) was studied with X-ray diffraction both before and after use in the dehydrogenation of but-1-ene. The diffractograms are shown in Fig. 5. As can be seen in Fig. 5(a)the iron oxide in the fresh calcined supported catalyst is present as magnesium ferrite. After use in the dehydroge-

(a)

(b)

20

nation, the magnesium ferrite diffractions disappeared, confirming the assumption that the catalyst has been reduced. Since no other iron diffractions appeared in the diffractogram of Fig. 5(b), it is assumed that the magnesium ferrite is reduced to FeO, which is stabilized by the MgO support. The diffractions of FeO coincide with those of MgO owing to the similarity of the cell parameters.

The lack of observable FeO diffractions prohibits a final assessment of the reduced state. Fe or Fe_3O_4 may also result upon reduction. If Fe or Fe_3O_4 is present as small or non-crystalline particles, it will not show up in the X-ray diffraction pattern. Using magnetic measurements, however, the presence of different iron species can be more accurately established.

TMA

A 5.6 wt.% Fe/MgO catalyst was studied with high-field magnetic measurements using a modified Weiss extraction technique before and after use under dehydrogenation conditions. For this purpose *ca.* 1 g of catalyst was treated in a flow of 5 vol.% but-1-ene and 30 vol.% water in nitrogen at 873 K for 4 h. Subsequently, the catalyst was cooled to 673 K and purged with nitrogen for 1 h to remove the feed. Next, the catalyst was cooled to room temperature in nitrogen. The reactor was transferred to the Weiss extraction apparatus without intermediate exposure to air, after which a TMA was performed in helium. The TMA diagram of the catalyst after use in the dehydrogenation is shown in Fig. 6(*b*). The magne-



Fig. 5 X-Ray diffractograms of a 4.4 wt.% Fe/MgO catalyst (ex citrate) before (a) and after (b) use in the dehydrogenation of butene. \times , MgFe₂O₄; \triangle , MgO

2θ/°

50

40

30

tization of the catalyst is plotted against the temperature. The profile has been recorded first at a linearly increasing temperature and subsequently at a linearly decreasing temperature. In the figures also the TMA profile of the empty reactor is shown, indicated by the solid line. The fresh catalyst in Fig. 6(a) shows a magnetization of 4050 a.u. at 298 K relative to the empty reactor. The magnetization decreases strongly with increasing temperature. The profile shows a Curie temperature, T_c , of 595 K, which is characteristic of MgFe₂O₄. From the fact that the profiles measured under increasing and decreasing temperature conditions are identical, it can be concluded that the fresh catalyst is thermostable at least up to 900 K. Identical magnetic behaviour has been observed earlier.^{8,9}

After use of the catalyst in the dehydrogenation, the TMA profile of the catalyst changes, as can be seen from Fig. 6(b). At 298 K the magnetization is only 2050 a.u. relative to the empty reactor and, furthermore, the catalyst has $T_c = 790$ K. This Curie temperature can be attributed to the presence of Fe_3O_4 . Pure Fe_3O_4 has $T_c = 848$ K. However, the Curie temperature of the species within the used catalyst is lowered by the presence of some Mg²⁺ ions substitutionally dissolved in the Fe₃O₄ lattice.⁹ The profile measured at decreasing temperature runs slightly below that measured at increasing temperature. The lower magnetization can be attributed to the fact that at high temperatures some water is released from the magnesium oxide support, which causes slight reoxidation of the Fe₃O₄ to antiferromagnetic α -Fe₂O₃. Comparing the saturation magnetizations of bulk $MgFe_2O_4$ and Fe_3O_4 at room temperature, 110 and 480 G, respectively,⁹ it becomes evident that the $MgFe_2O_4$ in the catalyst was not reduced to Fe₃O₄ entirely. From the magnetizations measured at room temperature before and after use in the dehydrogenation, it can be calculated that only 17 wt.% of the $MgFe_2O_4$ is reduced to Fe_3O_4 under hydrogenation conditions at 873 K. Evidently, the remaining 83 wt.% of the magnesium ferrite was reduced to antiferromagnetic FeO dissolved in the magnesium oxide support. This is in agreement with earlier observations.⁹

To determine whether the reduction of the magnesium ferrite is indeed responsible for the initial increase of selectivity and yield of buta-1,3-diene, the 1.0 wt.% Fe/MgO catalyst was subjected to a reduction pretreatment after which the dehydrogenation activity was measured. The catalyst was pre-reduced in a nitrogen gas flow containing 60 vol.% H_2 and 30 vol.% H_2O at 873 K for 4 h. In Fig. 7 the catalyst activity is shown after the reduction pretreatment. Now, the

100

80



(c)

Fig. 7 But-1-ene dehydrogenation activity of a 1.0 wt.% Fe/MgO catalyst (ex citrate) at 873 K after pre-reduction for 4 h in 60 vol.% H_2 and 30 vol.% H_2O in nitrogen. (a) But-1-ene conversion, (b) buta-1,3-diene yield, (c) buta-1,3-diene selectivity

selectivity and the yield immediately start off at their highest values without showing any signs of increasing yield and selectivity. As was concluded from the initially high CO₂ yield during the dehydrogenation of a 5 vol.% but-1-ene and 30 vol.% water in nitrogen flow, the catalyst is reduced not only by the hydrogen formed in the dehydrogenation, but also by the hydrocarbons present in the gas phase. If the reduction were brought about by hydrogen alone, then the reduction has to proceed already in a 5 vol.% H₂ and 30 vol.% H₂O in N₂ gas flow at 873 K. However, such a treatment does not affect the 1.0 wt.% Fe/MgO catalyst at all. It can therefore be concluded that the initial stabilization period can be ascribed to the reduction of the magnesium ferrite phase in the MgO-supported catalyst to Fe_3O_4 and FeO by the hydrocarbons in the feed. Evidently, the reduced state is more active and selective to buta-1,3-diene than the oxidized state of the catalyst.

Carbon Deposition within the Catalysts

After the reduction pretreatment a gradual deactivation of the catalyst is observed. When in Fig. 8 the activity of a 0.9 wt.% Fe/MgO catalyst (ex EDTA) is considered on a longer timescale than has been done thus far, it can be seen that the deactivation is practically complete within the first 20 h. After this period, the conversion and yield of buta-1,3-diene remain constant at *ca.* 8 and 4%, respectively. The buta-1,3-diene selectivity decreases further slowly from ca. 60% to 54%. At this stage the performance of the catalyst is comparable with that of the bare magnesium oxide support. Several authors have reported the formation of carbon on unpromoted iron oxide in butene atmospheres.^{15,16} Therefore, the deactivation is expected to be caused by carbon deposition. Carbon deposition or coking can lead to both pore blocking and covering of sites that are active for the dehydrogenation.²⁰

Fig. 9 shows transmission electron micrographs of the 0.9 wt.% Fe/MgO catalyst after 200 h of dehydrogenation at 873 K. As expected, both the magnesium oxide support and the reduced magnesium ferrite particles have been encapsulated by a layer of carbon after dehydrogenation for 200 h. In the micrograph on the left-hand side the small encapsulated ferrite particles are clearly visible. In the micrograph on the right-hand side the carbon layer on the magnesium oxide support is shown. According to these micrographs, the average thickness of the carbon layer on both the support and the ferrite particles is ca. 100 Å.

To determine the amount of carbon deposited under dehydrogenation conditions at 873 K for 20 h, the catalysts were



Fig. 8 But-1-ene dehydrogenation activity for a 0.9 wt.% Fe/MgO catalyst (ex EDTA) at 873 K in 5 vol.% but-1-ene and 30 vol.% water in nitrogen. (a) But-1-ene conversion, (b) buta-1,3-diene yield, (c) buta-1,3-diene selectivity



Fig. 9 Transmission electron micrographs of a 0.9 wt.% Fe/MgO catalyst (ex EDTA) after 200 h of dehydrogenation at 873 K. The arrows indicate the carbon layers

analysed afterwards using TPO. For this purpose the coked catalysts were treated in a flow of $10\% O_2$ in He, while the temperature was raised linearly. Oxidation of the coke to CO_2 occurred at *ca.* 673 K. It has been determined that the amount of oxygen required for reoxidation of the catalyst during TPO was negligible compared with the amount required for the oxidation of the deposited carbon. The amount of carbon formed during 20 h of dehydrogenation is plotted against the catalyst loading in Fig. 10. As can be seen, the bare magnesium oxide support after 20 h showed *ca.* 1 wt.% of carbon, which is indicated at an iron loading of 0 wt.% in Fig. 10. When the support was loaded with iron, *ca.* 1.5–2 wt.% carbon was found after 20 h of dehydrogenation.



Fig. 10 Carbon content as determined using TPO after 20 h of dehydrogenation plotted against catalyst iron loading. \bigcirc , ex citrate; +, ex EDTA; \triangle , MgO support



Fig. 11 Carbon-deposition boundaries at 700, 800, 873, 900 and 1000 K at total P_{CHO} of 0.35 atm. Dehydrogenation conditions, expressed as molar water : but-1-ene ratios, are indicated as: A, 6; B, 8.2; C, 10

The amount of carbon deposited seems to be more or less independent of the catalyst loading. The rather low values of the carbon content found for the catalysts containing *ca.* 3 wt.% Fe cannot be readily accounted for. For the catalyst containing 0.9 wt.% Fe (ex EDTA), the deactivation of which is shown in Fig. 8, a carbon content of no less than 15 wt.% is found after 200 h of dehydrogenation. From the carbon content and the B.E.T. surface area of this catalyst of *ca.* 9 m² g⁻¹, it is calculated that the average carbon layer thickness must have been 83 Å after 200 h of dehydrogenation. This value is in good agreement with the value of 100 Å derived from the electron micrographs shown in Fig. 9.

Evidently, ca. 2 wt.% carbon is sufficient to deactivate a catalyst containing 1.0 wt.% Fe almost completely. In Fig. 4 it was already shown that after an initial increase of the yield a catalyst containing only 1.0 wt.% Fe shows the same activity as a catalyst containing 2.1 or 3.1 wt.% Fe, but is deactivated more rapidly. This can be understood by the fact that the 2.1 and 3.1 wt.% Fe/MgO catalysts may contain larger active surface areas and therefore do not show signs of deactivation due to coking as fast as a catalyst containing only 1.0 wt.% Fe. The low carbon content of the 3.1 wt.% Fe/MgO catalyst in Fig. 10 is an additional reason for the lower rate of deactivation compared with the catalysts with 1.0 and 2.1 wt.% Fe (ex citrate) in Fig. 4.

Thermodynamic Carbon-deposition Boundaries

Several authors working in the field of catalyst research have reported on the deposition and the gasification of carbon.^{15,16,21,22} Whether carbon deposition or gasification occurred, it was always determined empirically, and not predicted thermodynamically. Cairns et al.23,24 and Broers and Treijtel,²⁵ however, both working in the field of fuel-cell research, published a simplified model to calculate thermodynamic equilibria in the ternary carbon-hydrogen-oxygen system. With this model so-called carbon-deposition boundaries (c.d.b.) can be calculated, which indicate the boundary in the C-H-O system between carbon deposition and gasification. According to this model, the only stable species to be considered in the temperature range between 400 and 1500 K and pressures of the order of 1 atm are at equilibrium: C (graphite), H₂, CO₂, H₂O, CO and CH₄. Since it is a thermodynamic model, kinetic effects are not taken into account. In principle, the c.d.b. follows from the fact that the twophase system is fixed uniquely when, at given T and total pressure P, the remaining degree of freedom is specified. For this purpose Cairns et $al.^{23,24}$ have chosen the O: H ratio. But, since it is much simpler and more straightforward, Broers and Treijtel²⁵ chose the partial pressure p_i at equi-

librium of one of the gaseous species *i*, such as, CO or H_2 . When p_i is varied, the other partial pressures follow from the three hypothetical reactions describing the equilibrium:

$$H_2 + CO_2 \xrightarrow{K_s} CO + H_2O$$
 (water-gas shift) (4)

$$4H_2 + CO_2 \xrightarrow{K_b} CH_4 + 2H_2O$$
 (methane-steam) (5)

$$C + CO_2 \longrightarrow 2CO$$
 (Boudouard) (6)

From these values a c.d.b. can be constructed in a triangular C-H-O diagram for any given temperature and pressure. In Fig. 11 the c.d.b.s for a set of temperatures in the range 700–1000 K calculated for a total pressure of carbon, hydrogen or oxygen containing gases, P_{CHO} , of 0.35 atm are shown. Above a c.d.b., graphite will be formed, whereas below a c.d.b. graphite will be gasified. In Fig. 11 the but-1-ene dehydrogenation conditions as applied here (molar water : but-1-ene ratio = 6) are indicated by the point A, situated below the c.d.b. at 900 and above the one at 873 K. From this triangular diagram it can therefore be deduced that carbon deposition is indeed thermodynamically expected at 873 K at the water : but-1-ene molar ratio of 6 applied here.

Kinetic Parameters of the Catalysts

Thus, far, the unpromoted iron oxide catalysts supported on magnesium oxide have been studied under dehydrogenation conditions isothermally at 873 K. It also is very important to establish kinetic parameters of the unpromoted catalysts, such as the activation energy for dehydrogenation. The influence of an alkali-metal promoter on the supported catalyst can be established more quantitatively later if the kinetic parameters of the unpromoted catalysts are known. However, a reliable determination of the activation energy requires that the catalyst is not deactivated during the measurements. This implies that carbon deposition should not occur, in contrast to what we have seen thus far. In Fig. 11 it can be seen that when the water : but-1-ene molar ratio is raised (shifting from point A to C), the dehydrogenation conditions shift well below the carbon deposition boundary at 873 K and even below that at 700 K. Consequently, at higher water vapour pressures no carbon deposition is expected to occur. To check the effect of water vapour on the deposition of carbon, the dehydrogenation activity of a 1.0 wt.% Fe/MgO catalyst was determined as a function of time for feeds with different molar water : but-1-ene ratios. The results are represented in Fig. 12. The logarithm of the reaction rate is plotted against the time on stream. The reaction rate R is defined as $YP_{but-1-ene} \tau^{-1}$, where Y is the buta-1,3-diene yield, $P_{but-1-ene}$ is the partial pressure of but-1-ene in the feed and τ is the residence time in the catalyst bed. As was shown above, the catalysts are rapidly deactivated in 5 vol.% but-1-ene-30 vol.% water (molar ratio = 6). Lowering the but-1-ene concentration to 3.64 vol.% (molar ratio = 8.2) results in a slower deactivation. The effect is even more evident for 3 vol.% but-1-ene (molar ratio = 10). Additionally, the amount of carbon deposited after 20 h of dehydrogenation was determined using TPO. The carbon content is plotted against the but-1-ene concentration in the feed for the 1.0 wt.% Fe/MgO catalyst in Fig. 13. Agreeing with the lower rate of deactivation, a higher water : but-1-ene ratio clearly leads to lower carbon deposition rates. Lowering the but-1-ene concentration even further should lead to total cessation of carbon deposition. However, using too high water : but-1-ene ratios may cause the catalyst not to become reduced. Below the calculated c.d.b. some carbon is still found. This is attributed to the fact that in the calculations graphite is considered, and no other types of (more amorphous) carbon of a different ther-



Fig. 12 Logarithmic buta-1,3-diene formation rate of a 1.0 wt.% Fe/MgO catalyst (ex citrate) plotted against time for different water : but-1-ene mixtures in nitrogen. Molar water : but-1-ene ratio is given in parentheses: (a) 30 vol.% water : 5.0 vol.% but-1-ene (6), (b) 30 vol.% water : 3.64 vol.% but-1-ene (8.2), (c) 30 vol.% water : 3.0 vol.% but-1-ene (10)

modynamic potential. Furthermore, it is a thermodynamic model, and, hence, kinetic effects have not been taken into account.

Because of the lower deactivation rate, a mixture of 3.64 vol.% but-1-ene and 30 vol.% water in nitrogen has been used for the determination of the activation energy. To establish the activation energy the buta-1,3-diene yield was determined, while the reactor temperature was varied. To avoid the initial stabilization period, the catalyst was pre-reduced in a flow of 60 vol.% hydrogen and 30 vol.% water in nitrogen at 873 K. To establish whether catalyst deactivation occurred, the activity at each temperature has been measured twice. Fig. 14 shows a typical Arrhenius plot of a catalyst containing 1.0 wt.% Fe (ex citrate). No systematic deactivation is observed between two measurements at the same temperature. The activation energy was calculated from the differential part of the plot, *i.e.* at yields < 5%. The activation energy thus found is ca. 47 kcal mol⁻¹. Table 2 gives the activation energies and the pre-exponential factors for a few catalysts as well as the free magnesium ferrite surface areas as determined using selective oxygen chemisorption.¹⁰ The activation energy is essentially the same for catalysts containing 1.0 wt.% Fe and 3.1 wt.% Fe. The activation energy is also independent of the type of precursor used in the preparation of the catalysts. The usual slight scattering of the activation energies is reflected in the values calculated for the preexponential factor. Therefore, it is preferable that the preexponential factors of different catalysts are calculated using



Fig. 13 Carbon content of a 1.0 wt.% Fe/MgO catalyst (ex citrate) after 20 h of dehydrogenation as a function of but-1-ene concentration in the feed



Fig. 14 Arrhenius plot of a 1.0 wt.% Fe/MgO catalyst. (a) Fresh after pre-reduction, (b) After 200 h isothermal dehydrogenation at 873 K

the same activation energy.²⁶ The pre-exponential factors of the supported catalysts listed in Table 2 were therefore calculated using 46.5 kcal mol⁻¹ as the average activation energy. The value for the pre-exponential factor of 25.4, thus found for the catalyst containing 1.0 wt.% Fe, is slightly lower than that found for the 3.1 wt.% Fe/MgO catalyst, which is quantitatively in accordance with the lower value of the free surface area of the magnesium ferrite in the 1 wt.% Fe/MgO catalyst. However, a larger difference in $\ln k_0$, viz. ca. 1, would be expected based on the difference in the magnesium ferrite free surface areas. The discrepancy can be explained by the fact that the active state does not comprise the magnesium ferrite itself, but its reduced state with a different free surface area, as explained above. Both catalysts containing ca. 3 wt.% Fe show identical pre-exponential factors. The bare MgO support exhibits a considerably higher activation energy of 64.6 kcal mol^{-1} . The support shows much lower dehydrogenation activity and selectivity to buta-1,3-diene than the supported iron oxide catalysts. The high value of $\ln k_0$, determined using $E_a = 64.6$ kcal mol⁻¹, can be explained by the different activation energy for the MgO support and should therefore not be compared with the value of $\ln k_0$ for the iron oxide catalysts.

As discussed above, the unpromoted catalysts are strongly deactivated by carbon deposition during the first 20 h in a feed with a water : but-1-ene molar ratio of 6. The activation energy and pre-exponential factor of the catalysts were determined both after 20 h and after 200 h of use in the dehydrogenation at 873 K. These kinetic parameters have been obtained at a steam : oil ratio of 8.2 to allow for comparison with the fresh catalysts. Table 3 shows the kinetic data for the fresh and deactivated catalyst containing 1.0 wt.% Fe. After 20 h the activation energy decreased from 46.5 to 40.9 kcal mol⁻¹; ln k_0 also strongly decreased to only 21.1. After 200 h the activation energy decreased only slightly further to 39.3

Table 2 Kinetic data for fresh catalysts

catalyst	E_a /kcal mol ⁻¹	$\ln k_0^a$	$\frac{S_{(MgFe_2O_4)}}{/m^2 g^{-1}}$
1.0 wt.% Fe/MgO (ex.citrate)	46.8	25.4	1.12
3.1 wt.% Fe/MgO (ex citrate)	46.5	25.6	3.22
2.8 wt.% Fe/MgO (ex EDTA)	46.4	25.6	3.68
MgO support	64.6	34.0	_

^a $[k_0] = \operatorname{atm min}^{-1} g_{cal}^{-1}$. For Fe/MgO catalysts, $\ln k_0$ was calculated using $E_a = 46.5$ kcal mol⁻¹.

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 Table 3
 Kinetic data for deactivated catalysts

catalys	t	E_{a} /kcal mol ⁻¹	ln k _o "
1.0 wt.% Fe/MgO	fresh	46.8	25.4
1.0 wt.% Fe/MgO	coked 20 h	40.9	21.1 (40)
1.0 wt.% Fe/MgO	coked 200 h	39.3	20.1 (40)
MgO support	fresh	64.6	34.0
MgO support	coked 3 h	51.5	26.6 (51)
MgO support	coked 20 h	50.7	27.4 (51)

 ${}^{a}[k_{0}] = \operatorname{atm} \min^{-1} \operatorname{g}_{\operatorname{cat}}^{-1}$. The values for average E_{a} which were used for the extrapolation are shown in parentheses.

kcal mol⁻¹, while ln k_0 dropped to 20.1. The Arrhenius plot of the 1.0 wt.% Fe/MgO catalyst after 200 h is shown in Fig. 14. As has been mentioned above, the catalytic performance of the 1.0 wt.% Fe/MgO catalyst after 200 h of dehydrogenation is about equal to that of the coked magnesium oxide support. To determine whether the value of *ca*. 40 kcal mol⁻¹ is characteristic for dehydration over a coked surface, the activation energy of the coked MgO support was also determined. After 3 h as well as after 20 h of coking of the support, an activation energy of *ca*. 51 kcal mol⁻¹ was found. The difference suggests that the nature of the carbon deposited on magnesium oxide is different from that deposited onto the supported iron oxide particles.

Conclusions

Iron oxide catalysts supported on magnesium oxide showed activity in the dehydrogenation of but-1-ene to buta-1,3diene. At 873 K a maximum butadiene yield of *ca.* 17 vol.% is reached at a buta-1,3-diene selectivity of *ca.* 65%. Under dehydrogenation conditions the catalysts are reduced, which causes a colour change from beige to grey. The iron oxide present as magnesium ferrite in a fresh catalyst is reduced mainly to FeO. However, a considerable part of the iron is present as Fe₃O₄ after dehydrogenation.

MgO can have a stabilizing effect on FeO.⁹ Accordingly, it has been demonstrated earlier that in a 10% H_2/Ar flow at 633 K magnesium ferrite in a magnesia-supported iron oxide catalyst is reduced to a solid solution of FeO in MgO of the type $(FeO)_x \cdot (MgO)_{1-x}$.⁹ During a TMA on the reduced catalyst in helium, it has nevertheless been found that a small part of the FeO, likely located at the surface of the $(FeO)_x \cdot (MgO)_{1-x}$ particles, is less stabilized by MgO. This results in the partial disproportionation of the less stabilized FeO to Fe_3O_4 and metallic iron above 720 K. In the experiments described in this paper, which have been performed in a but-1-ene : steam flow at 873 K, the magnesium ferrite will also be reduced to FeO that is dissolved in magnesium oxide. However, the FeO at the surface of the particles, that is less stabilized by MgO, will immediately disproportionate to Fe_3O_4 and Fe under the experimental conditions, *i.e.* at 873 K. The metallic iron then formed is reoxidized to Fe_3O_4 at the same time owing to the presence of butene, hydrogen and large amounts of steam. As FeO reacts to form Fe₃O₄ on the surface of the particles, the Fe₃O₄ phase thus formed, evidently, is responsible for the higher activity towards buta-1,3diene compared to the oxidized state of the catalyst, as confirmed by Lee.⁴ Assigning Fe₃O₄ as the active phase also explains the lack of a relation between the catalyst activity and the initial free surface area of the magnesium ferrite. Reduction of the iron species in the catalyst is not only driven by hydrogen produced in the dehydrogenation reaction, as is generally considered,^{4,6,7} but is also caused by the presence of hydrocarbons in the feed.

The catalyst that has not been promoted with alkali metal, shows deactivation due to carbon deposition. During the first 20 h of dehydrogenation, the catalyst surface is covered by a thin layer of carbon, leading to complete deactivation. At that stage the catalyst contains ca. 2 wt.% of carbon. Beyond this period of time the carbon layer grows and reaches a thickness of ca. 100 Å after 200 h of dehydrogenation. From the deposition of carbon on the bare support and from the linear rate of deactivation during the first 20 h, it can be concluded that carbon is not present as filamentary carbon. Filamentary carbon should have to be formed via the so-called carbide cycle mechanism, i.e. via a metastable iron carbide phase.^{16,21} Then the bare support would hardly contain any deposited carbon and the amount of carbon would be expected to increase strongly with the iron content of the catalyst. More importantly, reduction of the magnesium ferrite to metallic iron would be required for the formation of a metastable iron carbide. According to the results of the magnetic measurements, metastable iron carbides have not been formed. The catalyst is reduced only to Fe₃O₄ and a solid solution of FeO in MgO. Under the dehydrogenation conditions used here, poorly crystallized carbon deposits are formed covering the catalyst surface, as reported by Buyanov.¹⁵ The electron micrographs and the observed deactivation confirm this. The facts that the amount of coke deposited seems not to be dependent on the catalyst loading and the magnesium oxide also contains considerable amounts of carbon suggest that the coke deposition observed here is not a catalytic but a thermal process.

Under conditions where deactivation is minimized, an activation energy for dehydrogenation to buta-1,3-diene of *ca.* 47 kcal mol⁻¹ was found. After prolonged deactivation the activation energy decreased to *ca.* 40 kcal mol⁻¹. The MgO support material initially shows a high activation energy of 65 kcal mol⁻¹. After coking the activation energy decreased to *ca.* 51 kcal mol⁻¹. The difference between the value for coked MgO and the value for the coked iron oxide catalyst suggests that that the carbon deposited on both materials is of a different nature.

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