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Mechanism of Low-Temperature Oxydehydrogenation of 1-Butene to 1,3-Butadiene over a Novel Pd–Fe–O Catalyst

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The minimum operating temperature for sustainable oxydehydrogenation of butene to butadiene over Fe_2O_3 can be reduced from ca. 300° to ≤150°C by including Pd in the catalyst formulation. This effect would not be predicted on the basis of the widely accepted redox mechanism for selective oxidation, in which transport of the essential oxide ions can become limiting at low temperatures. Temperature-programmed desorption and temporal analysis reveal that the selective oxygen within the Pd–Fe–O catalyst is localised near the surface, and can be replenished easily from the gas phase. The ability of Pd to activate oxygen at low temperatures is critical to the process of oxygen replenishment, but just as important, it promotes the removal of site-blocking species from the surface of the catalyst. We show that whereas unmodified α-Fe_2O_3 is in fact capable of converting 1-butene to 1,3-butadiene at temperatures as low as 150°C, the activity is extremely short-lived because of the buildup of site-blocking carbonaceous species at this temperature. The addition of Pd enables the removal of these undesirable species at low temperatures. © 2001 Academic Press

Key Words: **low temperature; oxydehydrogenation; palladium; Pd–Fe–O.**

INTRODUCTION

Work in this laboratory during the past 10 years has led us to identify two classes of catalyst with activity at remarkably low temperatures (1–4). A common characteristic is that all the catalysts are composed of a metallic phase in intimate contact with a reducible metal oxide, with the most effective preparative route being one in which the phases are coprecipitated. The essential distinction between the two classes is that in one, the materials exhibit unexpected catalytic performance (resulting from an effect that we call *normal-support activation* (3)), whereas the other consists of materials in which known catalytic activity has been deliberately induced at low temperatures by including Pd in the formulation (2).

In the latter class, we have demonstrated that the presence of Pd enhances the catalytic activity of iron(III) oxide for CO oxidation, water–gas shift, and oxydehydrogenation of butene (4)—this effect we call *active-phase enhancement* (3). For example, a coprecipitated 4% Pd–Fe–O catalyst is capable of achieving 70% butadiene selectivity at a butene conversion of 50% at 120°C, whereas the parent Fe_2O_3 catalyst shows no sustainable activity at this temperature. The same approach can be used to influence the oxydehydrogenation of butene over bismuth molybdate catalysts. The operating temperature of the parent Bi–Mo–O catalyst (Bi_2MoO_6) is around 350°C, while the novel Pd–Bi–Mo–O catalyst can operate at 200°C. Although we have observed that the operating temperature of metal oxides can sometimes be lowered by simple impregnation with Pd, the resultant catalyst is not nearly as effective as the coprecipitated analogue (2).

It is generally perceived (see, e.g., (5)) that selective partial oxidation processes (including oxydehydrogenation) involve easily accessible oxide ions near the surface of the catalyst, whereas reaction of adsorbed hydrocarbon with chemisorbed oxygen usually leads to complete combustion. Indeed, Fe_2O_3 reputedly belongs to the family of catalysts that conforms to the Mars–van Krevelen redox cycle (6), in which a high mobility of lattice oxygen is believed to be crucial to achieving selective partial oxidation (7). For such reactions, both Fe_2O_3 and Bi_2MoO_6 catalysts exhibit changes in the rate-determining step as a function of operating temperature. At high temperatures (>350°C), where the mobility of lattice oxide ions is high, the slow reaction step is the initial H-abstraction from the hydrocarbon molecule (6–9). However, as the temperature (and therefore the oxygen mobility) is lowered, the slow reaction step often becomes the reoxidation of the catalyst (8), and then the desorption of products (6).

Since the Pd–Fe–O catalyst operates at temperatures as low as 120°C, it seems unlikely that it functions by a conventional Mars–van Krevelen mechanism. The aim of our study was to establish the nature of the oxygen species responsible for the low-temperature oxydehydrogenation activity of Pd–Fe–O, and hence to provide an understanding of why the inclusion of Pd can lower the operating temperature of a metal oxide catalyst.

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CATALYSTS

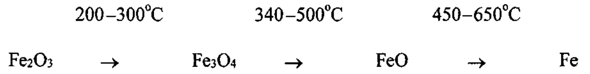
The Pd–Fe–O catalyst (nominal mass composition: 4% Pd/Fe_2O_3) was prepared by adding aqueous precipitant (Na_2CO_3) to a Pd/Fe solution made by mixing crystalline $Fe(NO_3)_3 \cdot 9H_2O$ and aqueous $Pd(NO_3)_2$ in demineralised water. A peristaltic pump was used to add the aqueous precipitant to the stirred Pd/Fe solution at a fixed rate (initially 2 $cm^3\ min^{-1}$). When the suspension became very dark and viscous, the rate of addition of the precipitant was halved, and was finally stopped when the pH reached 8.5. The precipitate was isolated by filtration and was then washed and dried (110°C for 16 h in air). The dry material was catalytically active at low temperatures, even without further treatment. However, for the mechanistic studies, the Pd–Fe–O was calcined at 500°C to ensure thermal stability; the BET surface area of the calcined catalyst was 49 $m^2\ g^{-1}$. Pure α-Fe_2O_3 (Johnson Matthey; maximum total metallic impurities, 10 ppm) was calcined in air at 500°C; the calcined material had a BET surface area of 38 $m^2\ g^{-1}$.

Characterisation of the unmodified α-Fe_2O_3 by either conventional (i.e., starting from ambient temperature) or subambient (starting close to the boiling point of nitrogen) temperature-programmed reduction (TPR) in 10% H_2/N_2 showed the expected (10) three-step profile (Scheme 1), with the second and third steps giving rise to a single broad-shouldered peak. During conventional TPR, the Pd–Fe–O catalyst began to reduce at room temperature. By starting at subambient temperatures, however, it was possible to discern that the reduction of PdO to Pd and Fe_2O_3 to Fe_3O_4 (Scheme 2) was occurring at much lower temperatures than expected for these phases.

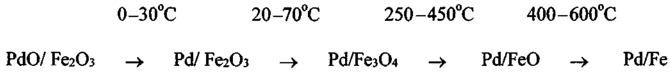
TEMPORAL ANALYSIS OF PRODUCTS (TAP)

The TAP apparatus and technique have been described in detail by the inventors (11), so only the most relevant features are mentioned here. Basically, the system comprises (i) a valve assembly which facilitates the introduction of either a continuous stream of gas or discrete, very narrow gas pulses, (ii) a small stainless steel catalytic reactor (length, 12.5 mm; internal diameter, 6.4 mm), which was filled with 0.25 g of sieved catalyst (particle size, 500–710 μm) held in place by a stainless steel mesh, (iii) a high vacuum system, and (iv) a quadrupole mass spectrometer detector.

Two fast-acting pulsing valves are incorporated into the valve assembly. These deliver narrow gas pulses containing between 10^{13} and 10^{20} molecules with a FWHH (full width at half height) of approximately 200 μs. These two pulsing valves enable the operator to carry out "pump/probe" experiments, in which the catalyst is first exposed to a pulse from the first valve, and is later "probed" by a pulse of a different gas from the second valve. Within this study, the pump/probe capability of the TAP reactor was used to investigate the nature of the selective oxygen species on the Pd–Fe–O catalyst. This was done by loading the catalyst with an oxygen pulse and then probing it *dt* seconds later with a butene pulse; the butadiene yield was monitored as the time interval, *dt*, was gradually increased from 0.01 s to 10 s. In this way, the lifetime of the selective oxygen species was investigated, allowing us to determine whether the selective species was a molecular oxygen species (i.e., short-lived on the catalyst surface), or whether it was an atomic oxygen species (i.e., long-lived on the catalyst surface).



SCHEME 1. Steps in the reduction of Fe_2O_3 by hydrogen.



SCHEME 2. Steps in the reduction of Pd–Fe–O by hydrogen.

Within the continuous flow mode of operation, a stream of gas is passed over the catalyst, either isothermally or as a function of temperature, and the corresponding product distribution is monitored using the mass spectrometer. The same mode was also used to pretreat the catalyst prior to temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) experiments. These experiments were performed by heating the catalyst, either under vacuum—the TAP reactor needs no carrier gas for TPD experiments—or under a flow of oxygen, at a rate of 10°C min^{-1}. The temperature ramp was perfectly linear over the range 25–375°C but deviated at higher temperatures. For this reason, our figures for TPD experiments show a maximum temperature of 375°C, even though in reality the samples were heated to 400°C and allowed to dwell there until desorption was complete.

Within the experiments reported here, butene was monitored on the mass spectrometer at 56 amu, and butadiene at 54 amu. Control experiments revealed that the cracking fragment of the butene molecule at 54 amu was approximately 7% as intense as the parent fragment at 56 amu. As will be seen, this did not interfere significantly with the analysis of the butadiene at 54 amu within the continuous flow experiments. However, for the pulsing experiments it was necessary to subtract the contribution of the butene fragment at 54 amu from the raw 54-amu trace, to enable us to obtain the true profile of the butadiene response to the butene pulse.

Oxygen (Air Products, 99.999%), 1-butene (BOC, 99.0%), and 1,3-butadiene (BOC, 99.0%) were all used without additional purification.

RESULTS AND DISCUSSION

A. Butene and Butadiene TPD Experiments: 4% Pd–Fe–O and Fe$_2$O$_3$

Apart from the ability to activate oxygen, a potential low-temperature selective partial oxidation catalyst must be capable of adsorbing the reactant hydrocarbon and desorbing both the desired product and water. We, therefore, investigated the interaction of the reactant (butene) and product (butadiene) with the Pd–Fe–O and α-Fe$_2$O$_3$ catalysts using TPD. Figure 1 shows the relevant TPD traces obtained following the room-temperature adsorption of butene onto oxidised 4% Pd–Fe–O. It is apparent that a small amount of butene desorbs at ~100°C, while a small quantity of butadiene is generated and released at ~125°C. The dominant reaction during this TPD run, however, is the total combustion of the adsorbed hydrocarbon to generate CO$_2$ and H$_2$O. The H$_2$O trace looked very similar to the CO$_2$ trace and is omitted from Fig. 1 for clarity.

After this experiment, the sample was cooled to room temperature under vacuum, and butene was again adsorbed. Figure 2 shows the TPD spectra obtained following this procedure. It is clear that far more butadiene is generated and released during the second run. Significant levels of butene are also desorbed at low temperatures. In addition, during the second run, the amount of CO$_2$ released is 65% less than in the first run, indicating that the surface is now far less active towards total combustion. It is important to note that butadiene starts to desorb from the Pd–Fe–O catalyst at temperatures of the order of 100°C, which is consistent with activity tests (2) that show that sustainable butadiene formation is possible at this temperature.

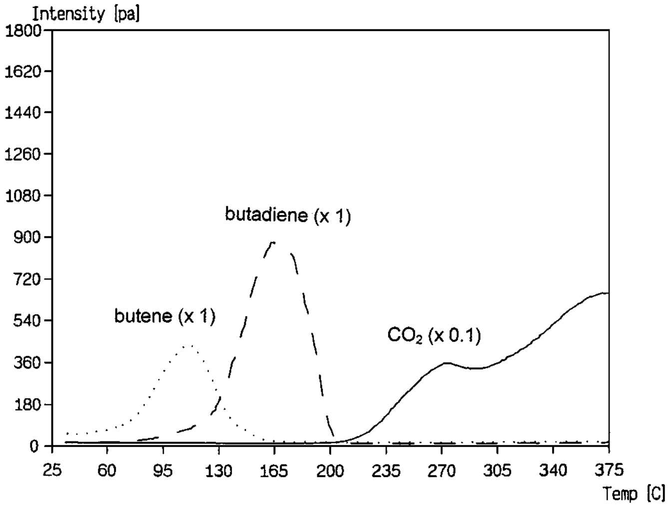


FIG. 2. Temperature-programmed desorption, after second room-temperature adsorption of butene on Pd–Fe–O.

We rationalise these results by noting that initially, both selective and nonselective oxygen species are present on the catalyst. The nonselective species are chemisorbed O atoms and oxygen associated with the palladium, which is present as Pd^{2+} in the fresh catalyst. During the first TPD run, the majority of the nonselective oxygen species are removed, via combustion of the butene to generate CO$_2$ and H$_2$O. Therefore, following the first TPD run, the concentration of the nonselective oxygen species has been reduced significantly, which means that during the second TPD run, the selective oxygen species prevails, and significant quantities of butadiene are generated.

Figure 3 shows the TPD traces obtained following the room-temperature adsorption of butene onto oxidised α-Fe$_2$O$_3$. In contrast to the Pd–Fe–O case, significant levels of both butene and butadiene are desorbed during the

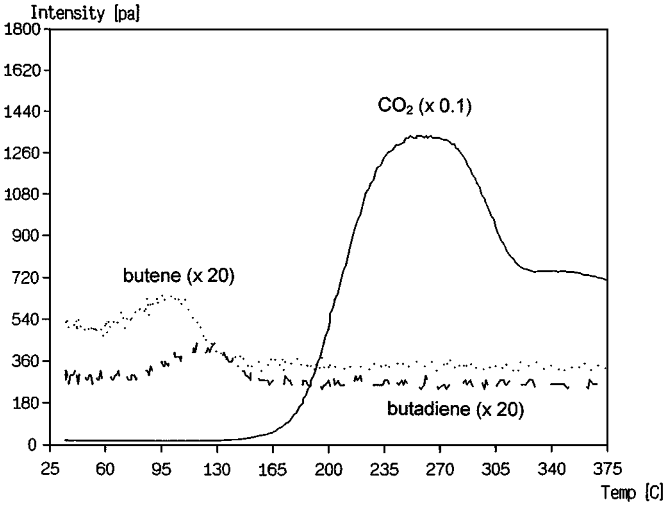


FIG. 1. Temperature-programmed desorption, after first room-temperature adsorption of butene on Pd–Fe–O.

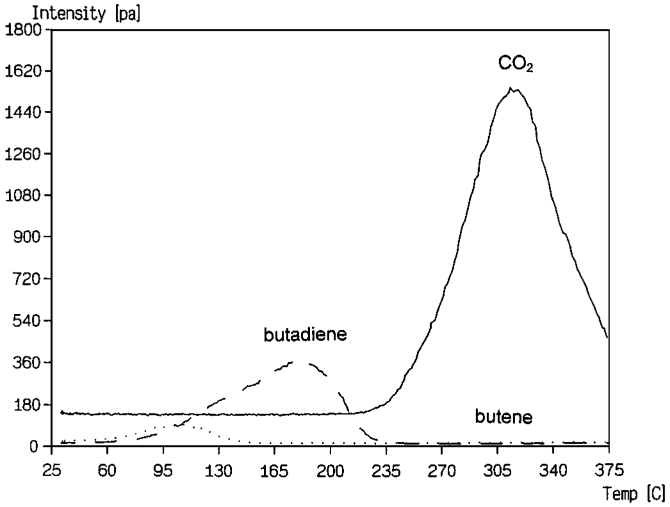


FIG. 3. Temperature-programmed desorption, after first room-temperature adsorption of butene on Fe$_2$O$_3$.

first TPD run over the oxidised Fe_2O_3 catalyst. Butene desorbs at ~110°C, while the butadiene is released in a broad peak whose maximum is observed at ~180°C. It is clear, however, that the generation and release of butadiene can occur at low temperatures over the α-Fe_2O_3 catalyst, revealing that butene has access to a selective oxygen species within Fe_2O_3 at low temperatures. One might, therefore, expect that this material would exhibit at least transient low-temperature activity for this reaction. This point is explored further below. Substantial deep oxidation of the adsorbed hydrocarbon species to CO_2 occurs along with the selective oxidation during this first TPD run.

It is interesting to note that the temperature at which CO_2 is released is significantly lower over the Pd–Fe–O catalyst, which is presumably a consequence of facile Pd-mediated total oxidation over this material. This high reactivity of the Pd–Fe–O catalyst to hydrocarbon species was also demonstrated during butadiene TPD experiments. Over the Pd–Fe–O material, no butadiene was observed to desorb during the TPD run—all of the butadiene was combusted to CO_2 and H_2O. The CO_2 peak occurred at the same temperature as was observed during the butene TPD experiments on the Pd–Fe–O catalyst (Figs. 1 and 2). This lack of butadiene desorption may be contrasted with the performance of α-Fe_2O_3 during similar butadiene TPD experiments, where butadiene was observed to desorb in a broad feature between about 75 and 235°C. CO_2 was again the major product during the run, but the fact that butadiene desorption was observed again indicates that the Fe_2O_3 surface is less reactive towards the total combustion of hydrocarbons than is the Pd–Fe–O surface. For each of the catalysts, the CO_2 peak was observed at the same temperature, regardless of whether the hydrocarbon was butene or butadiene. Note that the CO_2 release is a reaction-rate-limited process over both the Pd–Fe–O and α-Fe_2O_3 catalysts, since control experiments revealed that CO_2 desorption following room temperature CO_2 dosing occurred at much lower temperatures (<200°C).

B. Activity Measurements: 4% Pd–Fe–O and Fe_2O_3

Previous activity tests (2) have revealed that the 4% Pd–Fe–O catalyst can exhibit 70% selectivity to butadiene at 50% butene conversion when the catalyst temperature is only 120°C. Under the same conditions, α-Fe_2O_3 is not active at all. One interesting feature of the 4% Pd–Fe–O catalyst is that an induction period is always observed after introduction of the butene/air feed before significant levels of butadiene are generated. During this period, an exotherm was observed and CO_2 was evolved. Activity tests, using a 1 : 1 mixture of butene/oxygen, have also been carried out in the TAP reactor.

Figure 4 shows the relevant traces obtained when 4% Pd–Fe–O is exposed to a 1 : 1 mixture of butene/oxygen at 150°C. It is clear that there is an induction period during which CO_2 is evolved, in agreement with the activity tests. We suspect that, during this time, surface Pd^{2+} ions are being reduced to Pd^0. Following this period, butadiene generation commences and the butadiene yield rises rapidly to a steady level. Under these conditions, the butadiene generation level was stable for at least 5 h (the longest activity run carried out over the catalyst in the TAP reactor). It is important to note that the oxygen level remains constant throughout the experiment (i.e., oxygen is constantly being activated by the catalyst). (If oxygen were not being consumed from the gas phase by the catalyst, the oxygen signal in the mass spectrometer trace would have risen to ~9,500–10,000 pA.)

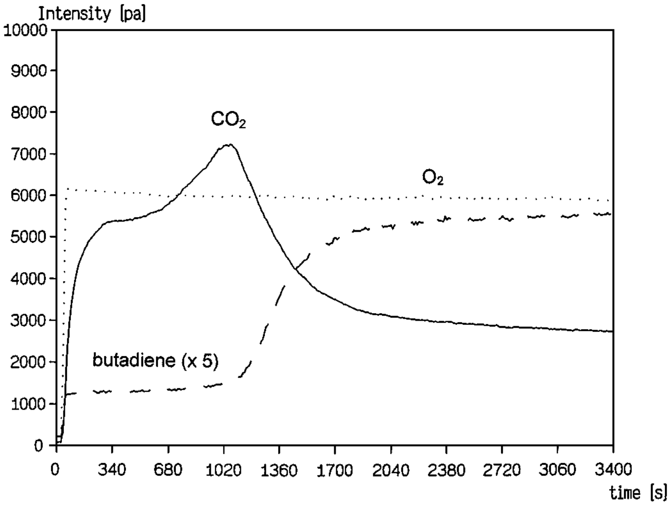


FIG. 4. Profile of butene + O_2 reaction over Pd–Fe–O at 150°C, as function of elapsed time from start of experiment.

Figure 5 shows the result of an identical experiment carried out over the α-Fe_2O_3 sample. This time the butadiene

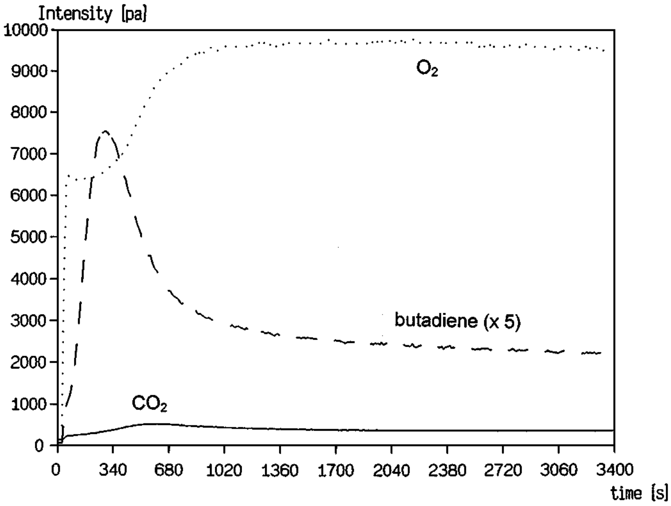


FIG. 5. Profile of butene + O_2 reaction over Fe_2O_3 at 150°C, as function of elapsed time from start of experiment.

yield rises rapidly to a maximum, before falling away to zero. (The baseline level of the butadiene (54 amu) peak is well above zero because the gas-phase butene (56 amu) cracks in the mass spectrometer to give a peak at 54 amu.) Very little CO_2 is released during this experiment, in contrast to the observations made using the Pd–Fe–O catalyst; the H_2O trace (not shown for clarity) looks very similar to the CO_2 trace. There is good correlation between the oxygen trace and the butadiene trace, in that during the time in which butadiene is being produced, oxygen is being consumed from the gas phase. However, with time, the amount of oxygen activated and consumed by the catalyst drops rapidly—as does the yield of butadiene.

We believe that these results unambiguously reveal that α-Fe_2O_3 will convert butene into butadiene at low temperatures (150°C), as was suggested by the TPD experiments reported above. The activity, however, is only short-lived. It is clear that butadiene generation and oxygen consumption are linked—as the oxygen consumption of the catalyst decreases, so does the butadiene yield. Figure 4 clearly shows that over the Pd–Fe–O catalyst, oxygen is being activated and consumed continuously. This means that the steady state generation of butadiene can be sustained at this low temperature, over the Pd–Fe–O catalyst.

C. The Nature of the Selective Oxygen Species in the Pd–Fe–O Catalyst

Conventional, high-temperature partial oxidation catalysts are believed to operate selectively by using easily accessible oxygen species near the surface of the catalyst. Highly mobile lattice oxygen species can then replenish the selective oxygen, and the process of selective oxidation can be sustained. It is believed that the presence of chemisorbed, highly reactive oxygen leads instead to deep oxidation, producing CO_2 and H_2O. Most partial-oxidation processes operate at temperatures at which the mobility of lattice oxygen species is high (350–550°C). It seems extremely unlikely that such a mechanism for the replenishment of selective oxygen species is operative for the Pd–Fe–O catalyst, since selective partial oxidation can proceed at temperatures as low as 100°C over this catalyst. The mobility of oxygen through iron oxide at this temperature is expected to be extremely low. However, it is perhaps conceivable that the incorporation of highly dispersed Pd species into the Fe–O matrix might dramatically alter the mobility of oxygen species within the catalyst. Therefore, we do need to consider this as a possible source of the selective oxygen. Alternatively, the selective oxygen species could be a short-lived (molecular) oxygen species. It could also be an oxygen species in the surface layer of the catalyst, which can be replenished from the gas phase at low temperatures, or finally it could be a subsurface (lattice) oxygen species which can be replenished from the gas phase at low temperature. We have investigated each of these possibilities in turn.

Gas-phase (molecular) oxygen. Pump/probe TAP experiments have been used to demonstrate that the active oxygen is unlikely to be a short-lived molecular oxygen species. Figure 6 shows the butadiene yield obtained over the Pd–Fe–O catalyst at 200°C during experiments in which oxygen was pulsed at time 0 s, and butene was pulsed *dt* seconds later. It is clear that as the value of *dt* is increased from 0.01 s, through 1 s to 10 s, the butadiene yield does not decline but rises. The half-life of molecular oxygen species on the surface of the catalyst at 200°C will be a fraction of a second, so if such species were indeed selective, then the butadiene yield obtained within the butene pulse would decrease rapidly as *dt* was increased.

Oxygen in the surface layer of the catalyst. Figure 7 shows the butadiene, CO_2, and H_2O traces obtained when butene is flowed over the (preoxidised) Pd–Fe–O catalyst

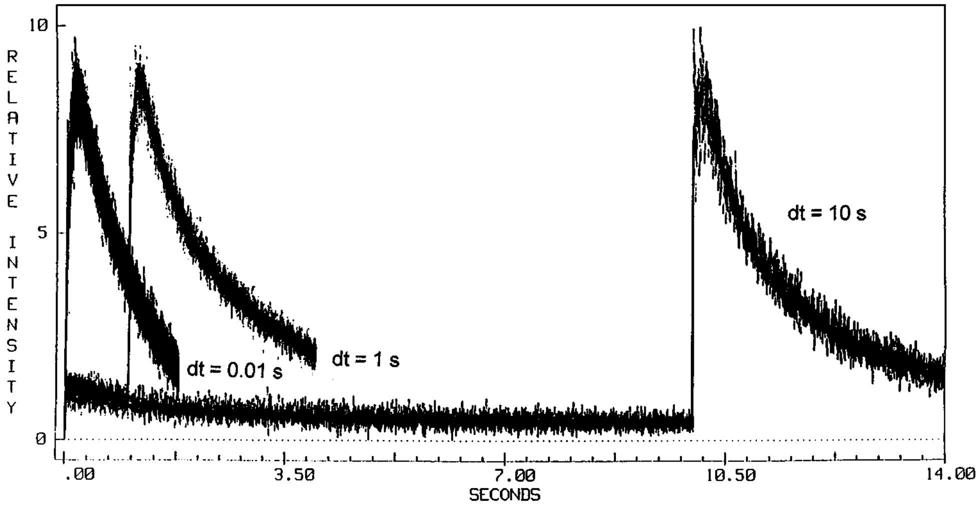


FIG. 6. Butadiene formation over Pd–Fe–O at 200°C, as function of time lapse (*dt*) between O_2 and butene pulses.

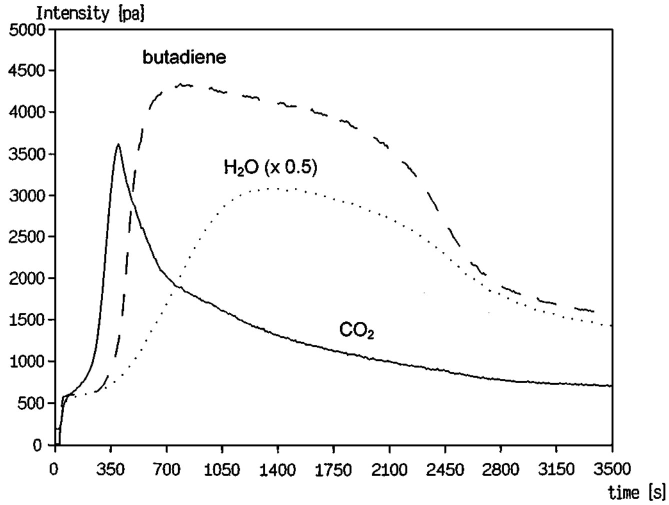


FIG. 7. Product formation as function of time, during first exposure of Pd–Fe–O to butene at 150°C.

at 150°C. From such experiments, the amount of butadiene formed can be established, and hence the quantity of selective oxygen (within the catalyst) involved in its formation can be determined. First, Fig. 7 reveals that the oxidised Pd–Fe–O catalyst can generate butadiene from a flow of butene in the absence of gas phase oxygen, reinforcing the conclusion reached in the paragraph above, that the selective oxygen species is not a short-lived molecular oxygen entity. Second, the data shown in Fig. 7, in conjunction with the BET surface area of the catalyst, indicate that between two and three monolayers of oxygen can be accessed by butene at 150°C to generate butadiene. This is in remarkably good agreement with a study performed by Misono *et al.* (12), whose butadiene yields within their butene pulsing study demonstrated that butene has access to two to three monolayers of selective oxygen within an Fe_2O_3 catalyst at 210°C. This was interpreted as indicating that subsurface oxygen participates in the formation of butadiene over Fe_2O_3. Therefore, we can see that a *lattice* oxygen species is strongly implicated in the reaction mechanism over the Pd–Fe–O catalyst.

Lattice oxygen replenished from the bulk. With notable exceptions, such as cerium and uranium oxides, the mobility of lattice oxygen species within the bulk of an oxide-based catalyst is expected to be extremely low at temperatures around 150°C. Therefore, it is unlikely that the selective oxygen species is replenished from the bulk in the case of the Pd–Fe–O catalyst, unless the incorporation of the Pd leads to a dramatic modification of the oxygen mobility characteristics of the Fe–O phase. Nevertheless, this hypothesis was tested using an extension of the experiment depicted in Fig. 7. The preoxidised Pd–Fe–O catalyst was exposed to a flow of butene at 150°C. The resulting butadiene, CO_2, and H_2O traces were virtually identical to those shown in Fig. 7, so they are not reproduced here. When butadiene generation and release had stopped, the butene flow was also stopped, and the catalyst was left at 150°C for 1 h under vacuum. No oxygen desorption was observed during this period. If the bulk lattice oxygen species within the catalyst were highly mobile at this temperature, one would expect that the accessible near-surface oxygen species would have been replenished by such a treatment. After 1 h, the butene flow was restarted. No butadiene was generated during this second experiment, indicating that the selective oxygen species have not been replenished by this treatment, and thereby implying that the lattice oxygen species are not highly mobile at 150°C. Similar experiments in which CO was used to titrate near-surface oxygen species also revealed that this was the case. The temperature at which the onset of significant lattice oxygen mobility occurs in the Pd–Fe–O and Fe_2O_3 catalysts was investigated in additional experiments described in Section D below.

Lattice oxygen replenished from the gas phase. By a process of elimination we seem to have come to the conclusion that the active oxygen species within the Pd–Fe–O catalyst is a lattice oxygen species which can be replenished from the gas phase at low temperatures. This hypothesis was tested by investigating whether the catalyst could indeed replenish its selective oxygen species at 150°C. Following the butene flow experiment shown in Fig. 7, the butene flow was stopped and the gas-phase species were purged out of the system. A flow of oxygen was then introduced at 150°C. Following this reoxidation, a second butene flow experiment was conducted, again at 150°C. The relevant traces from this experiment are shown in Fig. 8, which reveals that all of the selective oxygen removed at 150°C can indeed be replenished from the gas phase at 150°C.

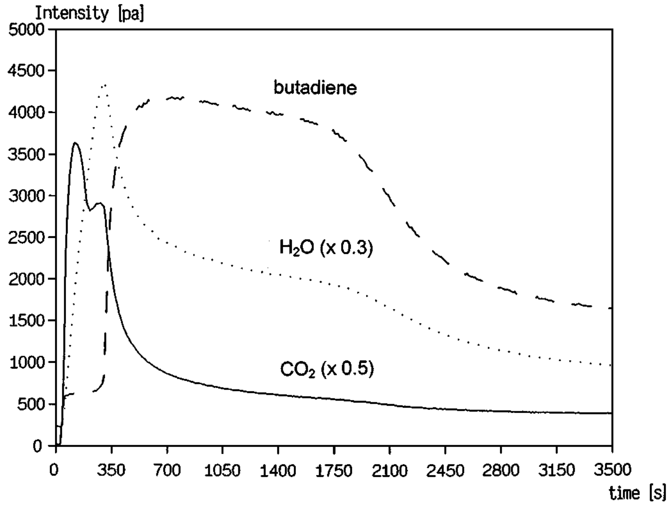


FIG. 8. Product formation as function of time, during exposure of reoxidised Pd–Fe–O to butene at 150°C.

Therefore, it appears that the highly active and selective oxygen species responsible for the low-temperature oxidative dehydrogenation of butene to butadiene over the Pd–Fe–O catalyst is a near-surface lattice oxygen species, which can be replenished from the gas phase at low temperatures. It is now necessary to isolate the role of the Pd in the Pd–Fe–O catalyst. In parallel with this, we need to investigate why the Fe_2O_3 catalyst is not capable of sustaining its low-temperature (150°C) butene-to-butadiene activity (Fig. 5).

D. The Role of Pd in the Pd–Fe–O Catalysts

So what is the role of the Pd in the low-temperature Pd–Fe–O catalysts? It is clear that the Pd helps in the activation of gas-phase oxygen. Within this framework, there are two possible roles for the Pd. (i) Pure Fe_2O_3 may not be able to activate gas-phase oxygen in selective oxygen sites at low temperatures owing to a kinetic barrier. It may be that the Pd enables the catalyst to overcome this kinetic barrier. (ii) Pure Fe_2O_3 may deactivate rapidly via site blocking at low temperatures. (Recall that CO_2 and H_2O are not released in significant quantities from the Fe_2O_3 surface during operation at 150°C (Fig. 5).) It is possible that the Pd activates the gas-phase oxygen and uses it to maintain the Fe_2O_3 surface in a clean state over which the butene-to-butadiene reaction can be sustained at low temperatures (150°C).

These two hypotheses were tested in the experiments below.

Butene flow over oxidised α-Fe_2O_3 at 150°C. Figure 9 shows the traces obtained when butene is passed over oxidised Fe_2O_3 at 150°C. Butadiene is formed, and released as a clear peak, but there are no associated peaks for CO_2 or H_2O. Quantification of the butadiene peak revealed that the amount of oxygen consumed would correspond to two to three monolayers within the Fe_2O_3 catalyst—in excellent agreement with the work of Misono *et al.* (12) and with the Pd–Fe–O experiments reported above (Fig. 7).

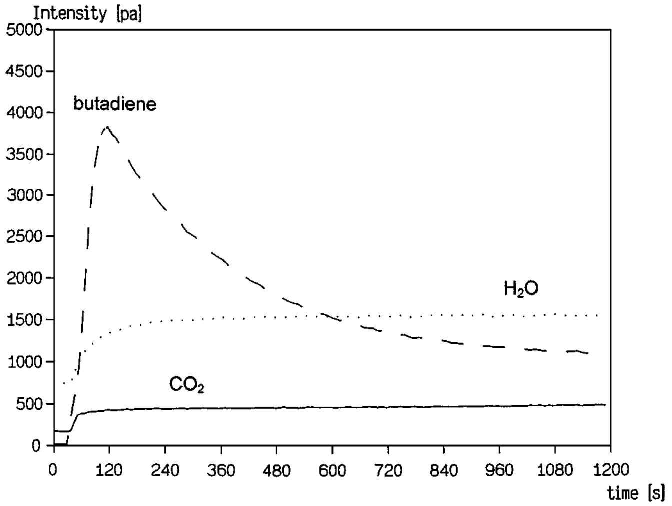


FIG. 9. Product formation as function of time, during first exposure of Fe_2O_3 to butene at 150°C.

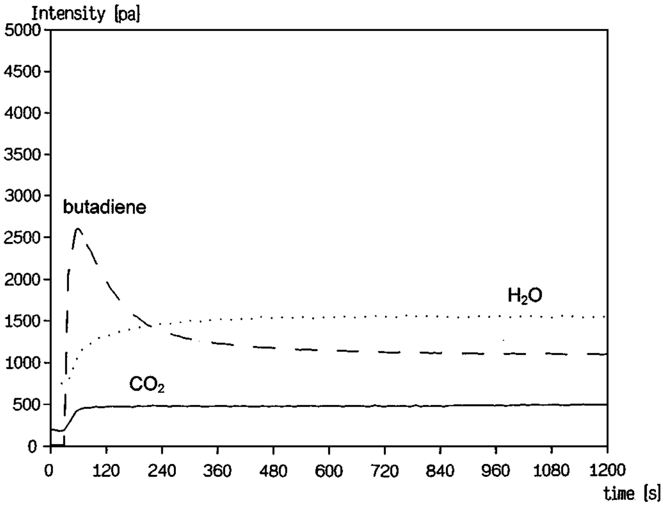


FIG. 10. Product formation as function of time, during exposure of reoxidised Fe_2O_3 to butene at 150°C.

Following the experiment shown in Fig. 9, the catalyst was reoxidised at 150°C. During this reoxidation step, neither CO_2 nor H_2O was evolved from the catalyst. The sample was then subjected to the butene flow once more. The results clearly reveal that not all the accessible, selective oxygen can be replenished by oxidation at 150°C (Fig. 10). This result may be contrasted with that obtained over Pd–Fe–O, where it is clear (Fig. 8) that all the selective oxygen can be replenished from the gas phase at 150°C.

Reoxidising the Fe_2O_3 catalyst at successively higher temperatures (200 and 250°C) resulted in some additional replenishment of the selective oxygen species, but a treatment at 300°C in oxygen was required to return the catalyst to its original state. To investigate this phenomenon more closely, an α-Fe_2O_3 catalyst which had been subjected to a butene flow at 150°C was initially purged of gas phase and weakly adsorbed species by holding it under vacuum at 150°C until the relevant gas-phase signals returned to their baseline levels. Next, a flow of oxygen was introduced to the catalyst at 150°C, and the catalyst temperature was ramped at 10°C/min to 300°C. The relevant traces recorded during this experiment are shown in Fig. 11. It is clear that CO_2 and H_2O are only evolved at high temperatures. Neither butene nor butadiene was observed to desorb during this experiment.

These results again reveal that the “used” (i.e., butene-reduced) Fe_2O_3 catalyst has difficulty in activating oxygen at low temperatures, but they do not reveal why this is the case. Returning to the role of Pd, it is possible that the high-temperature oxidation treatment overcomes the proposed kinetic barrier to oxygen activation. It could also be

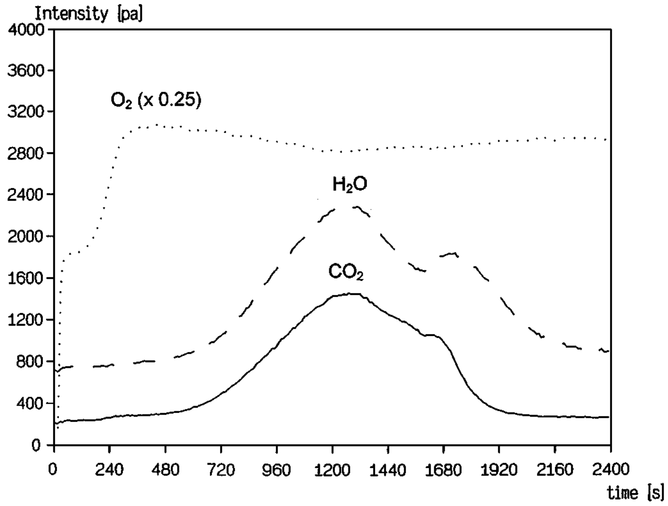


FIG. 11. Temperature-programmed oxidation of Fe_2O_3 (starting temperature, 150°C, at $t = 0$ s; final temperature, 300°C, at $t = 900$ s) after exposure to butene.

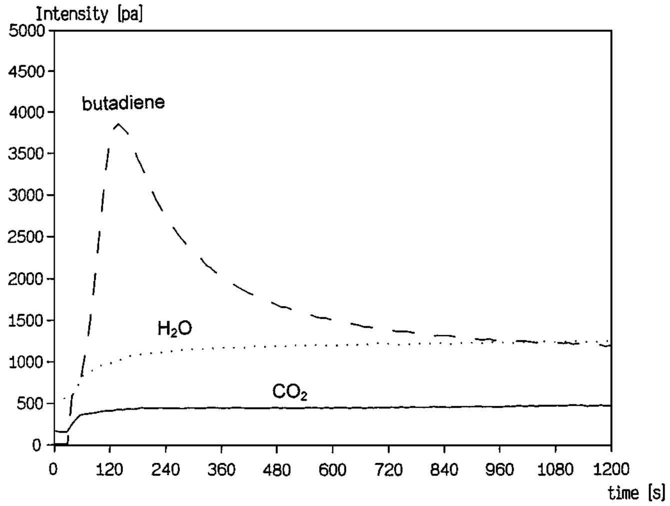


FIG. 13. Product formation as function of time at 150°C, during exposure of Fe_2O_3 to butene, after temperature-programmed desorption and reoxidation.

the case that the high-temperature oxidation treatment is merely removing blocking species from the surface of the catalyst (recall that CO_2 and H_2O are evolved during the high-temperature reoxidation).

Figure 12 shows the traces obtained during a TPD experiment following an experiment identical to that presented in Fig. 9. As with the TPO experiment (Fig. 11), CO_2 and H_2O are evolved at elevated temperatures. Following this TPD run, the catalyst was cooled to 150°C under vacuum. It was then reoxidised at 150°C. Figure 13 shows that following this sequence of treatments, the selective oxygen has been completely replenished. The reoxidation step was essential to the recovery of the butadiene activity, indicating that the replenishment of selective oxygen was not being caused by the transport of oxide ions from the bulk to the surface during TPD. This result strongly implies that there is not a kinetic barrier to oxygen activation on the Fe_2O_3 surface at 150°C; rather, it indicates that once the blocking species on the catalyst surface are removed, the catalyst can activate oxygen into a selective state. The blocking species are likely to be carbon-containing, and not hydroxyl groups, because desorption of water alone is not enough to restore butadiene activity.

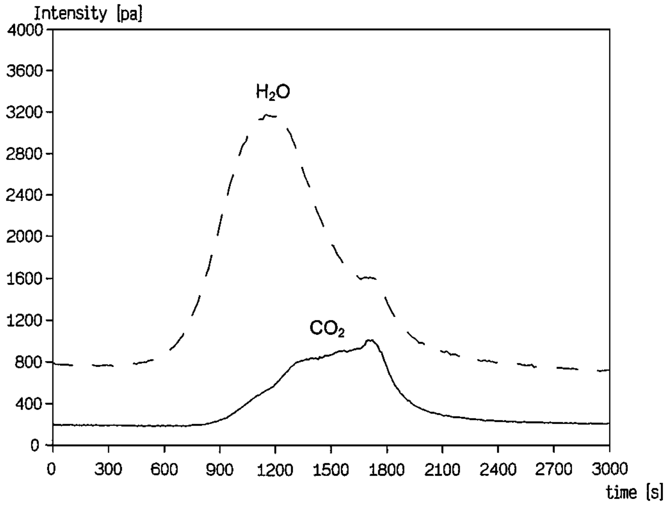


FIG. 12. Temperature-programmed desorption (starting temperature, 150°C, at $t = 0$ s; final temperature, 300°C, at $t = 900$ s) after exposure of Fe_2O_3 to butene at 150°C.

Replenishment of selective oxygen from the bulk of Fe_2O_3. As it is often assumed that selective oxygen species are replenished from the bulk of the catalyst at the high operating temperatures typical of most partial oxidation reactions ($T \geq 350$°C), the mobility of oxygen within the α-Fe_2O_3 and Pd–Fe–O catalysts was examined using the following procedure: (i) prepare an oxidised catalyst surface, (ii) reduce it using butene at 150°C (see, e.g., Fig. 9), (iii) evacuate the system, (iv) apply TPD to the catalyst to an elevated temperature (300, 350, or 400°C) under vacuum and leave at the chosen temperature for 15 min, (v) cool under vacuum to 150°C, and (vi) retest using butene at 150°C (i.e., repeat step (ii)). Clearly, the only way that the catalyst can replenish selective oxygen species within such an experiment is from its own bulk, since it is never exposed to gas-phase oxygen following the initial reduction treatment (step (ii)). The results of a number of such experiments on the α-Fe_2O_3 catalyst are summarised in Fig. 14. As expected, the results reveal that the mobility of lattice oxygen increases significantly as a function of temperature. At 300°C, virtually none of the selective oxygen can be replenished from the bulk of Fe_2O_3. At 350 and 400°C, however, significant quantities of selective oxygen can be moved from the bulk of the sample to selective sites near the catalyst surface.

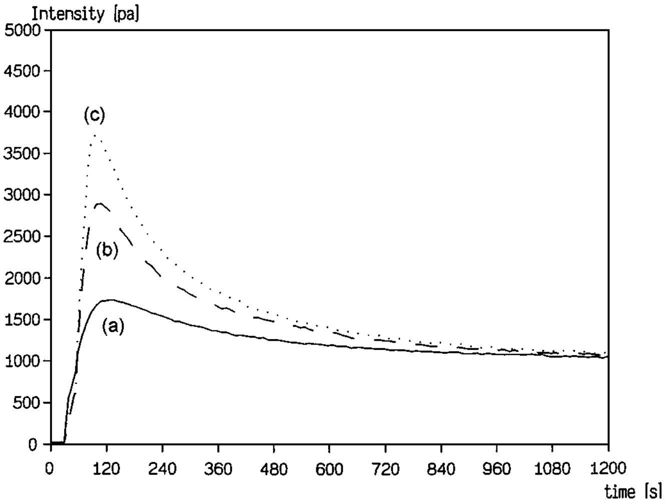


FIG. 14. Replenishment of selective oxygen from bulk of Fe_2O_3 at (a) 300°C, (b) 350°C, and (c) 400°C, as monitored by butadiene formation at 150°C.

The same trend was apparent over the Pd–Fe–O catalyst, where there was certainly no transport of bulk lattice oxygen toward the surface at temperatures $\leq$250°C. These results demonstrate once again that the Pd–Fe–O catalysts operate using oxygen replenished from the gas phase. They also show that the mobility of bulk lattice oxygen within the Fe–O phase is not significantly enhanced by the incorporation of Pd.

E. Discussion of the Role of Pd within the Pd–Fe–O Catalysts

From the data collected on the α-Fe_2O_3 and Pd–Fe–O catalysts, the following basic statements can be made:

- Butene can reduce the Pd–Fe–O catalyst to generate butadiene at 150°C. The oxygen species used within this process reside(s) close to the surface of the catalyst.
- The selective oxygen, once removed, can be rapidly replenished from the gas phase at 150°C (i.e., the selective oxygen is not replenished from the bulk of the catalyst at these low temperatures).
- Butene can also reduce the α-Fe_2O_3 catalyst to generate butadiene at 150°C. Once again, an oxygen species close to the catalyst surface is involved.
- In the case of α-Fe_2O_3 , however, the selective oxygen species cannot be rapidly replenished from the gas phase at 150°C, so the activity rapidly drops to zero at this temperature.

Therefore, it is clear that the role of the palladium within the Pd–Fe–O catalysts involves the activation of gas-phase oxygen. This oxygen then spills over onto the Fe_2O_3 phase and reoxidises it. The experiments described in this paper indicate that one of the principal roles of the spilt-over oxygen is to remove carbon-containing deposits, which would otherwise build up and block the catalyst surface completely. The oxygen-activation sites are likely to be on the metallic palladium that is formed during the induction period, which follows the exposure of the catalyst to a butene/air mixture.

The role of oxygen spillover within partial oxidation reactions at conventional temperatures has been studied in detail by Delmon, who believes that these reactions function by a “remote control” mechanism (13). He demonstrated that physical mixtures of oxides often cooperate (act synergistically) during these reactions. He proposed a general mechanism in which one phase, the donor, dissociates gas-phase oxygen to form a surface mobile species which spills over to the other phase, the acceptor. The acceptor is the potentially active phase. For example, Weng and Delmon (14) have shown that the selectivity of $Fe_2(MoO_4)_3$ for the oxydehydrogenation of butene to butadiene can be dramatically increased (from 9 to 44%) by mixing it with α-Sb_2O_4, which is itself inactive for the reaction.

Clearly, the concept of synergy can be invoked to explain the low-temperature partial oxidation performance of the Pd–Fe–O catalysts. Within such a mechanism, the Pd component acts as the donor phase, activating the gas-phase oxygen and spilling it over onto the iron oxide component, which acts as the acceptor phase; recall that we have shown that α-Fe_2O_3 is potentially active for the butene-to-butadiene reaction at 150°C (it generates butadiene initially, but its activity is rapidly lost at 150°C).

Delmon and co-workers have investigated the exact nature of the synergy using the selective oxidation of propene to acrolein as the probe reaction (15). They investigated the properties of a physical mixture of MoO_3 (acceptor) and α-Sb_2O_4 (donor) at 400°C. The experiments were all conducted in the absence of gas-phase oxygen. The baseline acrolein selectivity of the MoO_3 is around 10%; a 50 : 50 mixture of MoO_3 and α-Sb_2O_4 has an acrolein selectivity exceeding 50%. They then studied the characteristics of physical mixtures of $Mo^{16}O_3$ and ^{18}O-labelled α-Sb_2O_4 for the propene to acrolein reaction, again in the absence of gas-phase oxygen. The purpose of these experiments was to study the role of oxygen species spilt over from the α-Sb_2O_4 to the MoO_3 phase. Their main conclusion from this study was that the spilt-over oxygen serves principally to burn coke, rather than being used directly to react with propene to generate acrolein.

In a further experiment, Delmon showed that the removal of coke from precoked MoO_3 was significantly enhanced by physically mixing the MoO_3 with α-Sb_2O_4. This result demonstrates that spilt-over oxygen produced by α-Sb_2O_4 eliminates coke deposited on MoO_3 in a more efficient way than does gas-phase oxygen. A similar conclusion may also be reached in the case of the Pd–Fe–O catalysts. It appears that a principal role of the oxygen spilt over from the Pd phase is to maintain the “Fe–O” phase in an active, selective state by preventing the buildup of site-blocking, carbon-containing deposits and so allowing low-temperature activity to persist.

CONCLUSIONS

The incorporation of Pd into α-Fe_2O_3 increases the reducibility of the metal oxide, as predicted by junction effect theory (16). However, the low-temperature oxydehydrogenation activity of Pd–Fe–O cannot simply be attributed to the ease with which oxygen is removed and vacancies (alkene adsorption sites) created. Instead, the key role of Pd is in activating and supplying oxygen. In conventional catalysts, this concerted process of activation and supply of oxygen does not occur readily until much higher temperatures are reached (17).

Pd–Fe–O and α-Fe_2O_3 are capable of converting butene into butadiene at 150°C, with the accessible and selective O species comprising the top two to three monolayers of oxygen within both catalysts. However, the low-temperature activity of the Pd–Fe–O catalyst is stable and long-lived, whereas that of α-Fe_2O_3 is extremely short-lived. The Pd activates gas-phase oxygen and spills it over onto the surface of the Fe–O phase. By doing this, the Pd induces sustainable, low-temperature oxydehydrogenation activity. One of the principal functions of the spilt-over oxygen species appears to be the prevention of site-blocking, carbon-containing species accumulating on the Fe–O phase.

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