

# Cyclic Process for Propylene Production via Oxidative Dehydrogenation of Propane with N<sub>2</sub>O over FeZSM-5

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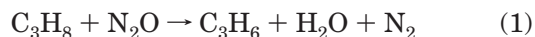
Steam-activated FeZSM-5 (Si/Al = 31.3 and 0.67 wt % Fe) is a highly efficient catalyst for the N<sub>2</sub>O-mediated oxidative dehydrogenation of propane (ODHP), with propene yields up to 25% at 723 K, but strongly deactivates due to coke formation. Because the initial ODHP performance was recovered upon air-regeneration of the spent catalyst, a process for continuous propylene production via alternation of reaction and regeneration cycles has been evaluated. A tapered element oscillating microbalance (TEOM) coupled to on-line analysis of products has been applied to correlate activity, deactivation, and regeneration of FeZSM-5 by simultaneous measurement of reaction and mass changes. This information was used to optimally design the cyclic process. In a system with five fixed-bed reactors in parallel, stable propene yields >20% were demonstrated during continuous operation for 1500 min (12 cycles), using reaction and regeneration periods of 25 and 90 min, respectively, at the same temperature (723 K). This novel process is attractive for on-site C<sub>3</sub>H<sub>6</sub> production using a low-cost source of N<sub>2</sub>O.

## 1. Introduction

Propylene, a key building block in the modern petrochemical industry, is mainly produced as a coproduct in ethylene steam crackers and gasoline-making fluidized catalytic crackers. However, as demand for propylene is growing faster than demand for ethylene or gasoline, there is a widening gap between conventional propylene supply and demand. This gap can be bridged by the development of on-purpose propylene technologies, such as propane dehydrogenation and metathesis of ethylene and butylene, which currently account for 2–3% of the global production.<sup>1</sup> Many recent studies have explored the catalytic oxidative dehydrogenation of propane (ODHP) as a potential route to propylene to overcome typical drawbacks on the nonoxidative process, that is, thermodynamic limitations and catalyst deactivation by coke. Promising formulations for ODHP are based on modified V and Mo oxides, with propene yields in the range of 10–30% using O<sub>2</sub> as the oxidant.<sup>2–5</sup>

Recent studies have reported the remarkable performance of iron zeolites for the N<sub>2</sub>O-mediated propane oxidative dehydrogenation according to eq 1.<sup>6–9</sup> This reaction leads to the simultaneous functionalization of propane, a relatively cheap and abundant feedstock, and utilization of N<sub>2</sub>O, an environmentally harmful gas. The most promising zeolitic system reported so far is steam-activated FeZSM-5, displaying initial propene yields up to 25%.<sup>6,7</sup> These results are comparable with the highest values reported over V- and Mo-based catalysts with O<sub>2</sub>. The remarkable ODHP performance of iron zeolites has been related to the specificity of N<sub>2</sub>O as a monooxygen donor and the capability of determined iron forms in the zeolite for coordinating reactive atomic oxygen species able to efficiently dehydrogenate propane.<sup>7</sup> This

unique form of oxygen, referred to as  $\alpha$ -oxygen, is also responsible for the outstanding catalytic performance of FeZSM-5 in hydroxylation of paraffins to alcohols and of aromatic hydrocarbons to phenols with N<sub>2</sub>O.<sup>10,11</sup>



A major drawback of iron zeolites in ODHP with N<sub>2</sub>O is the deactivation by coke, leading to a rapid decrease of the propene yield.<sup>7</sup> Preliminary tests showed that the original catalytic activity of FeZSM-5 was completely recovered after regeneration in pure oxygen at 773 K for 30 min.<sup>6</sup> On this basis, the present work was undertaken to evaluate the feasibility of a cyclically operated process for continuous C<sub>3</sub>H<sub>6</sub> production via ODHP with N<sub>2</sub>O using FeZSM-5. This was achieved in a configuration of fixed-bed reactors in parallel with alternation of reaction and regeneration steps, according to the concept in Figure 1. The TEOM technique was applied to evaluate catalytic performance, deactivation, and regeneration, to rationally engineer the cyclic process.

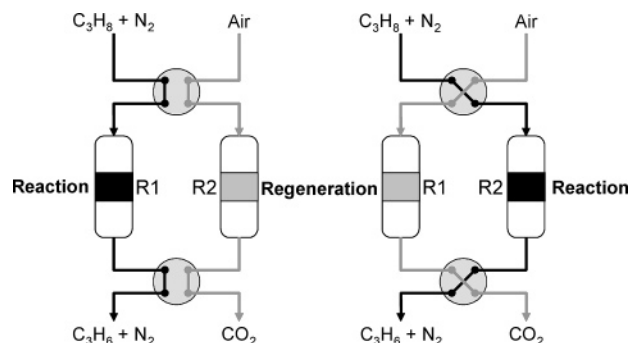
## 2. Experimental Methods

**2.1. Catalyst.** Details on the hydrothermal synthesis of FeZSM-5 have been described elsewhere.<sup>12</sup> The as-synthesized sample was calcined in air and activated in flowing steam (30 vol % H<sub>2</sub>O and 30 mL STP min<sup>-1</sup> of N<sub>2</sub>) at ambient pressure and 873 K during 5 h. Extensive characterization of this catalyst, with a molar Si/Al ratio of 31.3 and 0.67 wt % Fe, can be found in recent publications.<sup>12–15</sup> Briefly, steam treatment leads to the extraction of framework iron in isomorphously substituted FeZSM-5 and originates active extraframework iron species. The nature and distribution of iron species in the final catalyst depend on the steam activation conditions (temperature and steam partial pressure) as well as on the composition of the zeolite framework.<sup>13,15</sup> The particular catalyst

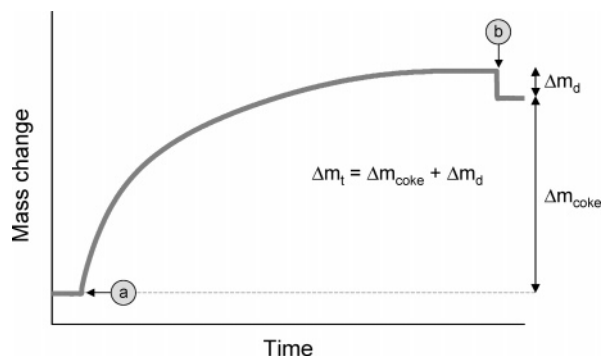
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**Figure 1.** Sketch of two reactors in parallel with alternation of reaction and regeneration steps for continuous propene production via ODHP with  $\text{N}_2\text{O}$ .

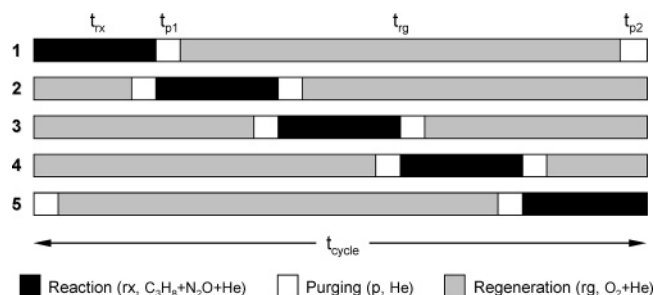


**Figure 2.** Typical continuous coking experiment in the TEOM microbalance.

used here possesses a rather heterogeneous constitution with respect to iron, where extraframework isolated iron ions and oligonuclear iron oxo-clusters in the zeolite pores coexist with iron oxide nanoparticles of 1–2 nm.

**2.2. TEOM Studies.** Reaction, coke deactivation, and regeneration studies were carried out in a Rupprecht & Patashnick TEOM 1500 pulse mass analyser. The TEOM (tapered element oscillating microbalance) consists of a microreactor with a high-resolution microbalance that generates real-time measurements of mass changes during gas–solid reactions.<sup>16,17</sup> The TEOM measures mass changes based on inertial forces, presenting various key advantages over conventional gravimetric microbalances: (i) a well-defined flow profile, eliminating possible (heat and mass) diffusion and buoyancy phenomena, (ii) a very fast response time resolution (0.1 s), and (iii) a high mass resolution across the entire range of pressure and temperature.

Figure 2 shows the experimental procedure applied for the coking experiments. The TEOM reactor was carefully loaded with 30 mg of catalyst (sieve fraction 125–200  $\mu\text{m}$ ), firmly packed between two plugs of quartz wool. The catalyst was then pretreated in flowing He at the reaction temperature for 2 h. When stable baseline was attained, He was replaced by the reaction mixture (a in Figure 2), and mass changes and product gases were continuously monitored. Equal flows of purge gas (He) and reaction gas of 200  $\text{mL min}^{-1}$  were used, and the feed gases were preheated at 423 K. The ODHP with  $\text{N}_2\text{O}$  was carried out using a mixture of 100 mbar  $\text{C}_3\text{H}_8$  and 100 mbar  $\text{N}_2\text{O}$  in He at 673–773 K at a total pressure of  $P = 2$  bar and a weight-hourly space velocity (WHSV) of 400 000  $\text{mL h}^{-1} \text{g}_{\text{cat}}^{-1}$ . The influence of  $\text{O}_2$  on the ODHP reaction was studied by adding 5 mbar  $\text{O}_2$  to the above  $\text{C}_3\text{H}_8 + \text{N}_2\text{O}$  mixture. The coking reaction



**Figure 3.** Typical sequence in the cyclic experiments with five fixed-bed reactors in parallel.

was carried out for 400 min, and subsequently the conditions were changed to be identical to those prior to introduction of the reactant (b in Figure 2). The amount of coke ( $C_{\text{coke}}$ ) was determined as:

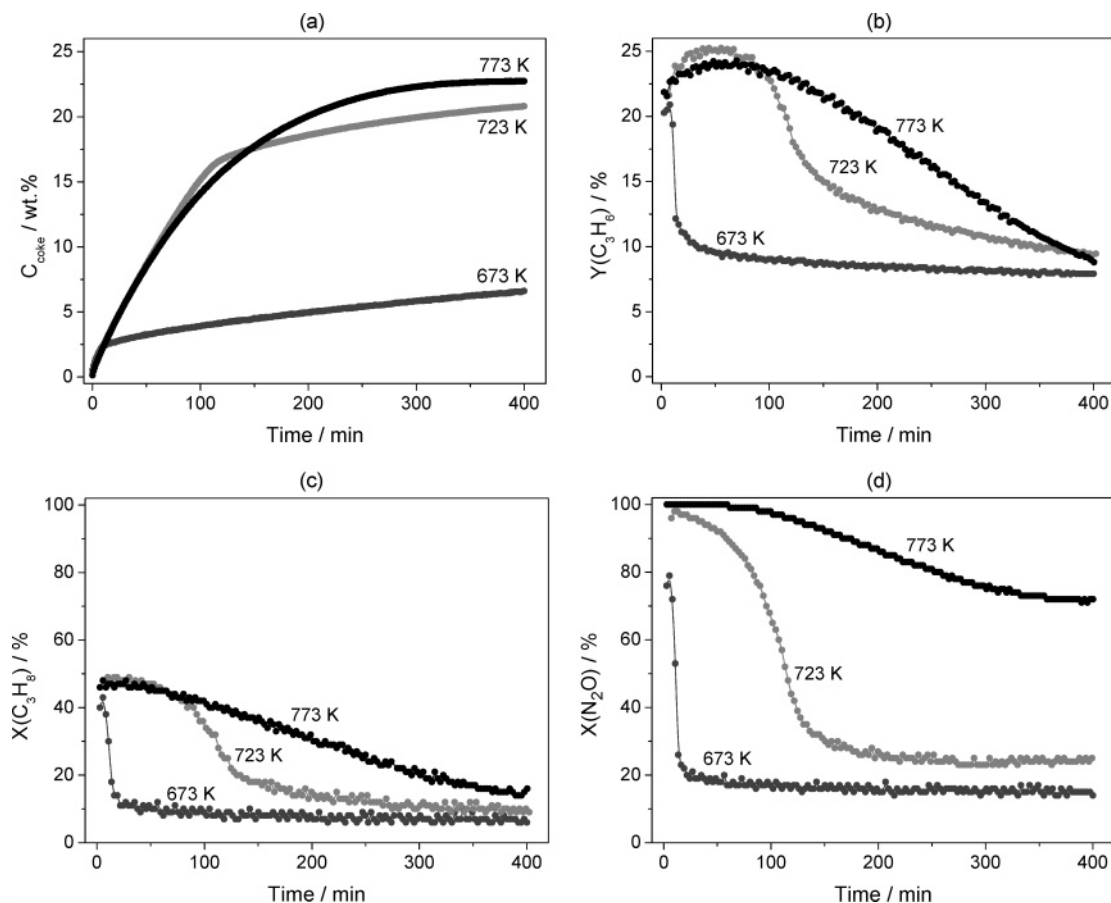
$$C_{\text{coke}} = \Delta m_{\text{coke}}/m_0 = (\Delta m_t - \Delta m_d)/m_0 \quad (2)$$

where  $m_0$  is the initial sample amount,  $\Delta m_t$  is the total mass uptake measured by the TEOM, and  $\Delta m_d$  includes the mass change of the gas density in the tapered element when He was replaced by the reaction mixture and also a small contribution by desorption of volatile components when switching from the reaction mixture back to He.

The product gases were analyzed by an on-line micro-GC (Chrompack CP-2002) equipped with a TCD, using Poraplot Q and Molsieve 5A columns.  $\text{N}_2\text{O}$  and  $\text{C}_3\text{H}_8$  conversions were calculated from the amount of  $\text{N}_2$  formed and  $\text{C}_3\text{H}_8$  reacted, respectively. Propene yield and selectivity have been determined as  $Y(\text{C}_3\text{H}_6) = C(\text{C}_3\text{H}_6)/C^0(\text{C}_3\text{H}_8)$  and  $S(\text{C}_3\text{H}_6) = Y(\text{C}_3\text{H}_6)/X(\text{C}_3\text{H}_8)$ , respectively, where  $C(\text{C}_3\text{H}_6)$  is the outlet concentration of propene at a certain time,  $C^0(\text{C}_3\text{H}_8)$  is the inlet concentration of propane, and  $X(\text{C}_3\text{H}_8)$  is the conversion of propane.

Regeneration of the coked FeZSM-5 in air (200  $\text{mL min}^{-1}$ ) was investigated by following mass changes in two ways: (a) temperature-programmed oxidation (TPO) in air, ramping the temperature from 298 to 973 K at 10  $\text{K min}^{-1}$ , and (b) isothermal oxidation, switching from He (when stable baseline was reached) to air in the temperature range of 773–823 K. TPO experiments require subtraction of a reference run with the uncoked zeolite under the same conditions to correct for the mass change caused by the variation of gas density with temperature. In isothermal regeneration, the mass change was corrected by the change in density upon replacing the inert gas by air.

**2.3. Cyclically Operated Reactor.** Cyclic experiments for continuous propene production were carried out in a reactor system consisting of three feed sections: purge (He), reaction ( $\text{N}_2\text{O} + \text{C}_3\text{H}_8 + \text{He}$ ), and regeneration ( $\text{O}_2 + \text{He}$ ), and a battery of five fixed-bed quartz reactors in parallel (4 mm i.d.) with independent feed, pressure, and temperature control. The feed section to each reactor can be selected by means of an arrangement of multi-port valves, and the sequence of cycles can be fully programmed. Cyclic experiments were conducted according to the pattern in Figure 3 and involve reaction (rx) and regeneration (rg) steps, which are mediated by purging steps (p1 and p2). Each of these steps is defined by its temperature and duration. These parameters were determined from the TEOM studies. The duration of one cycle in Figure 3 is defined as



**Figure 4.** Influence of the reaction temperature on the performance of steam-activated FeZSM-5 during ODHP with N<sub>2</sub>O: (a) coke content, (b) C<sub>3</sub>H<sub>6</sub> yield, (c) C<sub>3</sub>H<sub>8</sub> conversion, and (d) N<sub>2</sub>O conversion. Conditions: 100 mbar C<sub>3</sub>H<sub>8</sub> and 100 mbar N<sub>2</sub>O in He, WHSV = 400 000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, and  $P = 2$  bar.

$t_{\text{cycle}} = t_{\text{rx}} + t_{\text{p1}} + t_{\text{rg}} + t_{\text{p2}}$ . To ensure continuous production of propene, the above steps were synchronized so that at least one of the reactors is always under reaction, while the others are under regeneration and/or purging. Micro-GC analysis monitored the gas effluent from the catalytic reactor under ODHP conditions.

### 3. Results and Discussion

**3.1. Performance of Fresh FeZSM-5.** Previous studies have shown that the initial performance of various steam-activated iron zeolites (FeZSM-5, Fe-silicalite, and Fe-beta) is rather similar, regardless of the different form(s) of extraframework iron species, the zeolite host, and the catalyst acidity.<sup>7</sup> Initial propene yields in the range of 19–22% at 723 K were achieved over these catalysts, with a similar degree of propane conversion (ca. 45%) and propene selectivity (ca. 50%). Among the catalysts tested, FeZSM-5 exhibited a slightly higher initial activity and, most importantly, a higher resistance toward deactivation.<sup>7</sup> The influence of the reaction temperature on the performance and dynamics of deactivation of FeZSM-5 has been further investigated in this study. Figure 4 shows the coke content, propene yield, and conversions of propane and nitrous oxide versus time on stream during ODHP with N<sub>2</sub>O at different temperatures, as derived from the TEOM and coupled gas chromatographic analysis. Reaction data at 2 and 400 min on stream, representing the first and the last analysis in our experiments, are hereafter denoted as initial and final (or residual) performance, respectively.

Apart from C<sub>3</sub>H<sub>6</sub>, other quantified carbon-containing products were CO<sub>x</sub> (from total oxidation), as well as minor amounts C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub> (from cracking processes). Previous studies over FeZSM-5 also identified oxygenates, including propionaldehyde and small amounts of acrolein and acetone,<sup>6</sup> and traces of alcohols and aromatics were also reported by Bulánek et al.,<sup>9</sup> using conventional gas chromatography. The duration of each analysis in these studies was of at least 15 min and up to 100 min. The micro-GC used in this study enabled separation of the reactant (propane) and the desired product (propylene) in ca. 2 min. Fast analysis is essential to precisely follow rapid deactivation processes (vide infra), at the expenses of not having a complete determination of (minor or less important) reaction products.

The initial N<sub>2</sub>O conversion increases from 76% at 673 K to 100% at 723 and 773 K, while the increase in C<sub>3</sub>H<sub>8</sub> conversion is less pronounced (from 40% to 50%) and does not increase further at 773 K. The propane conversion after 400 min on stream was between 10% and 20% at the temperatures investigated. The final N<sub>2</sub>O conversion amounts are 14% and 25% at 673 and 723 K, respectively, being remarkably higher at 773 K (72%). The initial (20–22%) and final (7–10%) C<sub>3</sub>H<sub>6</sub> yields showed no significant differences in the temperature range of 673–773 K. However, the rate of deactivation is progressively reduced with an increase in temperature. The catalyst typically activates during the first minutes of reaction. This process is particularly noticeable at 723 K, leading to an increase in propene yield



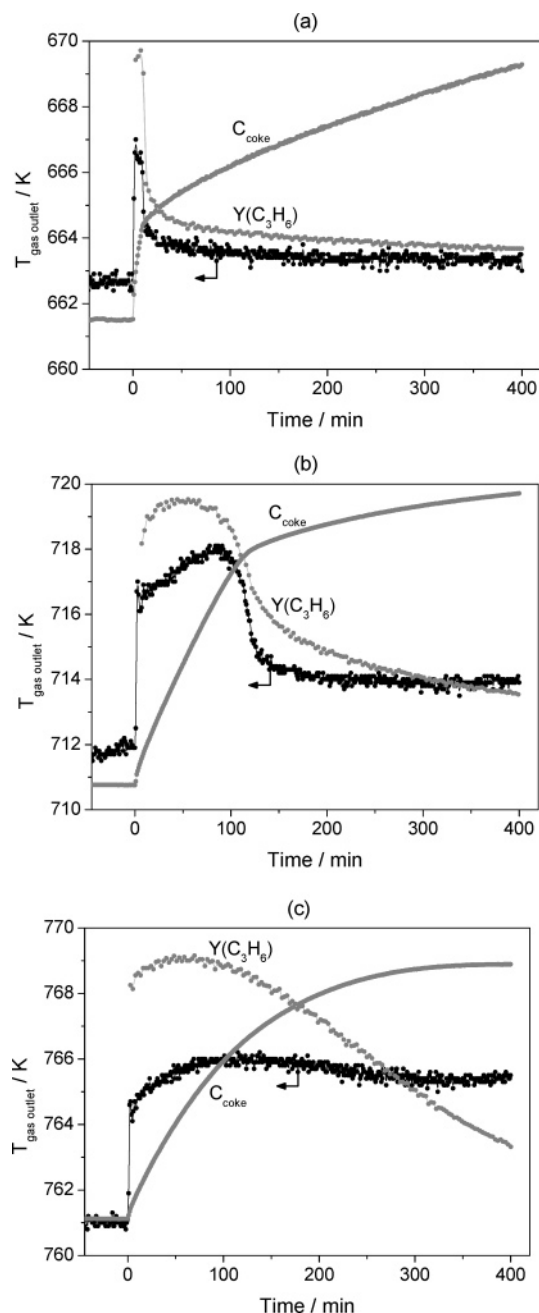
from 22% to 25% after ca. 20 min on stream. At 773 and 723 K, a propene yield >20% was preserved during 200 and 100 min, respectively, in contrast to the rapid deactivation at 673 K. In all cases, the decrease of propene yield is coupled with the decrease of  $C_3H_8$  and  $N_2O$  conversions.

A good correlation was obtained between the increase of coke content and the decrease of propene yield with time on stream. This indicates that deactivation is caused by coke formation. Coke formation likely originates from polymerization and dehydrogenation (condensation) of propene, the main olefin formed over FeZSM-5. The concentration in the product gas of the other olefin formed (ethylene) was 15 times lower than that of propylene. These reactions leave a layer of highly hydrogen-deficient carbonaceous material on the catalyst surface, making the active sites inaccessible (poisoning of iron species or causing pore blockage). If propylene is the main coke precursor, the amount of coke should give an indication of the catalyst efficiency toward ODHP. In agreement with this, the final coke content at 723 K was 3 times higher than that at 673 K (20 wt % vs 6.7 wt %), while the final coke content at 773 K was 22.7 wt %. A larger difference in the coke content after 400 min on stream could be expected between the experiments at 723 and 773 K, in view of the significantly higher overall production of  $C_3H_6$  at 773 K. It should be noted that the characteristic inflection point in the coking profiles at the time of the drop of the propene yield at 673 and 723 K, which was also noticed in other iron zeolites,<sup>7</sup> was not observed at 773 K. This distinctive behavior can be tentatively related to the slower decrease of propene yield at 773 K, which correlates with a more gradual increase of the coke content.

An additional feature of the TEOM microbalance to follow catalyst deactivation consists of simply monitoring the temperature of the outlet gas by a thermocouple situated at a distance of 3 mm after the catalyst bed. These profiles are shown in Figure 5 for three reaction temperatures. The profiles of coke formation and propene yield, which are also depicted in the same figure, evidence an excellent correlation between outlet gas temperature, mass change due to coking, and catalyst deactivation. A sharp increase of the gas outlet temperature can be observed after switching the feed gas from He to the  $C_3H_8+N_2O$  mixture at  $t = 0$  min, as a consequence of the exothermicity of the propane oxidation. The rapid deactivation of FeZSM-5 at 623 K, as concluded from the fast coking rate and the decrease of  $C_3H_6$  yield during the first 10 min on stream, nicely correlates with the decrease of the temperature of the gas at the reactor outlet. The temperature does not drop to the baseline (temperature in He) due to the residual activity after 400 min (see Figure 4).

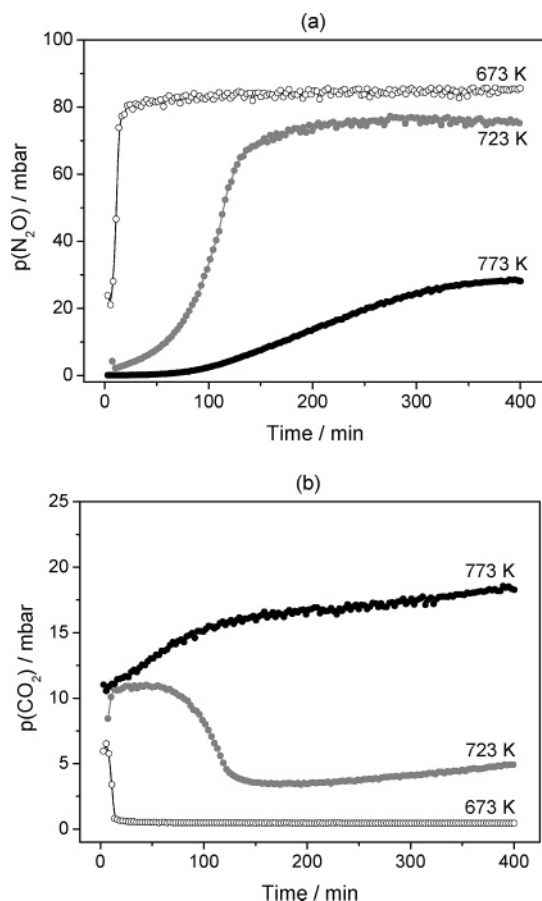
An excellent agreement is obtained at 723 K too: the outlet gas temperature drops at the inflection point of the coking profile (at ca. 100 min), due to the sudden catalyst deactivation. The experiment at 773 K deviates from the other reaction temperatures, because the decrease of propene yield and propane conversion due to coke deactivation is not accompanied by a decrease in the gas outlet temperature, which remains practically constant at ca. 765 K.

The relatively slow deactivation of FeZSM-5 at 773 K can be associated with the high  $N_2O$  conversion measured after 400 min on stream (72%, see Figure 4).



**Figure 5.** Temperature of the gas at the outlet of the catalyst bed in the TEOM during ODHP over FeZSM-5 at (a) 673 K, (b) 723 K, and (c) 773 K (black symbols). Conditions are as in the caption of Figure 4. The profiles of coke and propene yield are depicted in gray (without scale) for comparative purposes.

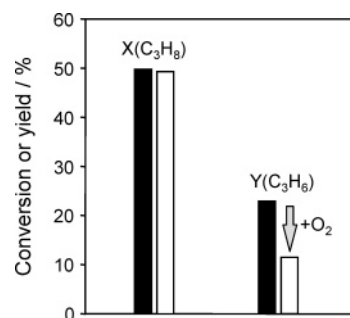
The partial  $N_2O$  and  $CO_2$  pressures versus time on stream during ODHP at various temperatures in Figure 6 support this. As expected, the amount of  $CO_2$  decreases upon deactivation of FeZSM-5 at 673 and 723 K, approaching a nearly constant (residual) value after 10 and 100 min, respectively. Contrarily, the amount of  $CO_2$  evolved progressively increases with time on stream at 773 K. This result can be interpreted as follows: upon  $N_2O$  decomposition, which is favored at high temperature, adsorbed atomic oxygen or desorbed  $O_2$  participates, to a certain extent, in the regeneration of the zeolite surface by oxidation of coke, leading to  $CO_2$  formation. This leads to a retarded catalyst deactivation. Coke oxidation and  $N_2O$  decomposition are exothermic processes, and their occurrence substantiates the



**Figure 6.** Partial pressure of (a) N<sub>2</sub>O and (b) CO<sub>2</sub> at the reactor outlet during ODHP over FeZSM-5 at different reaction temperatures. Other conditions are as in the caption of Figure 4.

observation that the gas temperature at the outlet of the catalyst bed in Figure 5 remains nearly constant, even if the conversion of propane continuously decreases due to catalyst deactivation. The participation of the oxidant in coke oxidation above a certain reaction temperature may also explain the similar final coke content obtained in FeZSM-5 at 723 and 773 K.

Previous studies have concluded that the ODH of propane with O<sub>2</sub> over FeZSM-5 leads to very low C<sub>3</sub>H<sub>6</sub> yields (<5%) as compared to N<sub>2</sub>O.<sup>8,18</sup> In an attempt to minimize coke deactivation over FeZSM-5, the effect of O<sub>2</sub> addition to the C<sub>3</sub>H<sub>8</sub>+N<sub>2</sub>O mixture on the performance has been investigated. Following the results of Chaki et al.,<sup>19</sup> addition of excess O<sub>2</sub> in the feed suppresses the formation of carbonaceous deposits in the reaction of C<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>O over FeZSM-5. Accordingly, our strategy was to combine the specificity of N<sub>2</sub>O as monooxygen donor in ODHP and the ability of molecular O<sub>2</sub> to continuously regenerate the coke deposits formed. The effect of adding small amounts of O<sub>2</sub> (molar feed N<sub>2</sub>O/O<sub>2</sub> ratio = 20) on the ODHP performance of FeZSM-5 at 723 K is shown in Figure 7. The degree of C<sub>3</sub>H<sub>8</sub> conversion (after 2 min on stream) was very similar in both cases (ca. 50%), but the C<sub>3</sub>H<sub>6</sub> selectivity decreased from 46% to 22% upon O<sub>2</sub> addition, leading to an increased amount of CO<sub>x</sub>. As a result, the initial C<sub>3</sub>H<sub>6</sub> yield in the absence of O<sub>2</sub> (22%) is reduced to 11% in the presence of O<sub>2</sub>. TEOM experiments have indeed evidenced a reduced coke amount in the presence of O<sub>2</sub> and thus a diminished catalyst deactivation (not shown), which is attributed to the total oxidation by O<sub>2</sub> of reaction intermediates leading to coke formation to CO<sub>x</sub>.

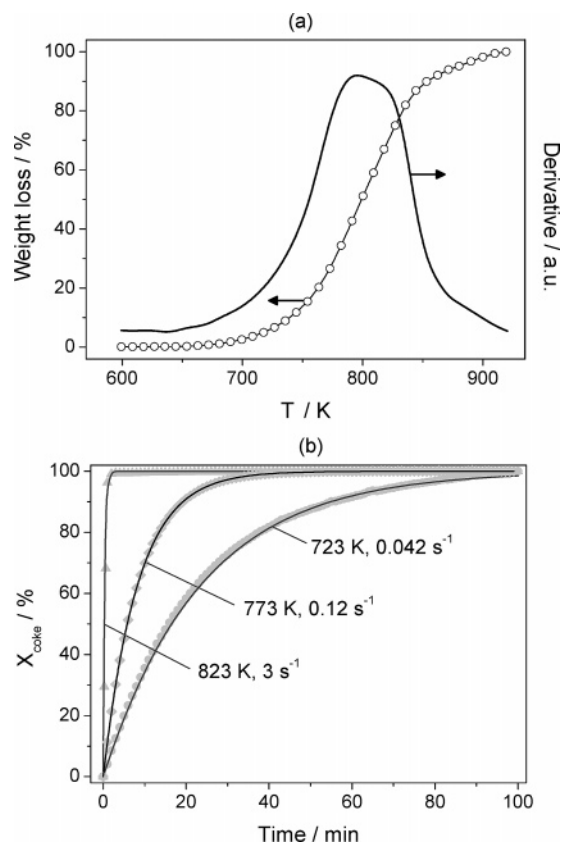


**Figure 7.** Influence of O<sub>2</sub> addition to the C<sub>3</sub>H<sub>8</sub>+N<sub>2</sub>O mixture on the propane conversion and propene yield at WHSV = 400 000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> and *P* = 2 bar. Solid bars: 100 mbar C<sub>3</sub>H<sub>8</sub> and 100 mbar N<sub>2</sub>O in He. Open bars: 100 mbar C<sub>3</sub>H<sub>8</sub>, 100 mbar N<sub>2</sub>O, and 5 mbar O<sub>2</sub> in He.

Such intermediates appear to be essential for propene production. Accordingly, the performance of FeZSM-5 in the N<sub>2</sub>O-mediated ODH of propane is severely deteriorated in the presence of small amounts of O<sub>2</sub>.

The results in Figure 7 differ from those reported by Bulánek et al.<sup>9</sup> These authors concluded that although the propene selectivity over H-ZSM-5 (30–1200 ppm Fe) was decreased in N<sub>2</sub>O+O<sub>2</sub> as compared to N<sub>2</sub>O, the propene yield was not significantly changed, due to the increased propene conversion in the presence of O<sub>2</sub>. However, it should be mentioned that the experimental conditions in both studies are not directly comparable. The amount of oxygen used in ref 9 (N<sub>2</sub>O/O<sub>2</sub> = 1.5) was ca. 15 times higher than that in our study (N<sub>2</sub>O/O<sub>2</sub> = 20), and the experiments were carried out in the excess of oxidant (C<sub>3</sub>H<sub>8</sub>/(N<sub>2</sub>O+O<sub>2</sub>) = 0.3), this ratio being 1 in our experiments. Besides, the space velocity applied (30 000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) is 1 order of magnitude lower than in our study (400 000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>).

**3.2. Regeneration of Coked FeZSM-5.** Catalyst deactivation due to coke formation poses the problem of catalytic activity restoration, which is commonly reached via oxidative treatment of the coked catalyst with air or oxygen-containing mixtures at relatively high temperatures. Temperature-programmed oxidation (TPO) as well as isothermal oxidation experiments in air were carried out to determine the optimal regeneration conditions (temperature and duration) of the coke-deactivated FeZSM-5. Figure 8a shows the weight loss during TPO experiments over FeZSM-5 after ODHP reaction at 723 K for 400 min (containing 20 wt % coke). Coke oxidation occurs in the temperature range of 650–900 K, and the derivative of the weight loss shows a maximum at 795 K. With these data, isothermal regeneration in the temperature range of 723–823 K was applied to further establish the duration of the regeneration step. The coke conversion versus time characteristics in Figure 8b were obtained over FeZSM-5, having the same initial coke amount (20 wt %, after ODHP at 723 K for 400 min, see Figure 4a). In good agreement with TPO results, regeneration at 823 K is extremely fast, with a total conversion of coke in ca. 2 min. The time needed for complete combustion of coke is significantly increased at a lower temperature, requiring ca. 40 and 90 min at 773 and 723 K, respectively. Equation 3 was used to model the experimental results in Figure 8b. It can be observed that a first-order kinetics describes well the relation between coke conversion (*X*<sub>coke</sub>) and time (*t*). The rate coefficients for coke conversion (*k*) at the different regeneration temperatures are shown in Figure 8b. The estimated constants



**Figure 8.** (a) Weight loss profile and its derivative during TPO in air of coked FeZSM-5 (after ODHP with  $\text{N}_2\text{O}$  at 723 K for 400 min) using a heating rate of  $10 \text{ K min}^{-1}$ , and (b) coke conversion during isothermal-regeneration of coked FeZSM-5 in air at different temperatures. Conditions:  $\text{WHSV} = 400\,000 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$  and  $P = 2 \text{ bar}$ . Lines in (b) represent fitted data according to eq 3.

increase 1 order of magnitude each 50 K in the temperature range of 723–823 K.

$$X_{\text{coke}} = 1 - \exp(-kt) \quad (3)$$

**3.3. Performance of Regenerated FeZSM-5.** The results presented so far have been obtained over fresh FeZSM-5 samples. Aiming at a cyclic process, it is essential to analyze the performance of FeZSM-5 after various reaction and regeneration runs in the TEOM with the same sample. The ODHP performance of the fresh and regenerated FeZSM-5 is shown in Figure 9. In agreement with previous observations,<sup>6</sup> the initial performance is completely recovered after regeneration. However, the regenerated catalyst deactivates much faster than the fresh one, with a final amount of coke 4 times lower in the regenerated catalyst. This behavior was observed at regeneration temperatures in the range of 723–823 K. Remarkably, the residual propylene yield over fresh and regenerated FeZSM-5 is very similar. As shown in Figure 9, the performance of the regenerated zeolite was very reproducible after 2 and 10 consecutive reaction and regeneration runs at 723 K. Therefore, an irreversible change on the fresh catalyst only occurs in the first run.

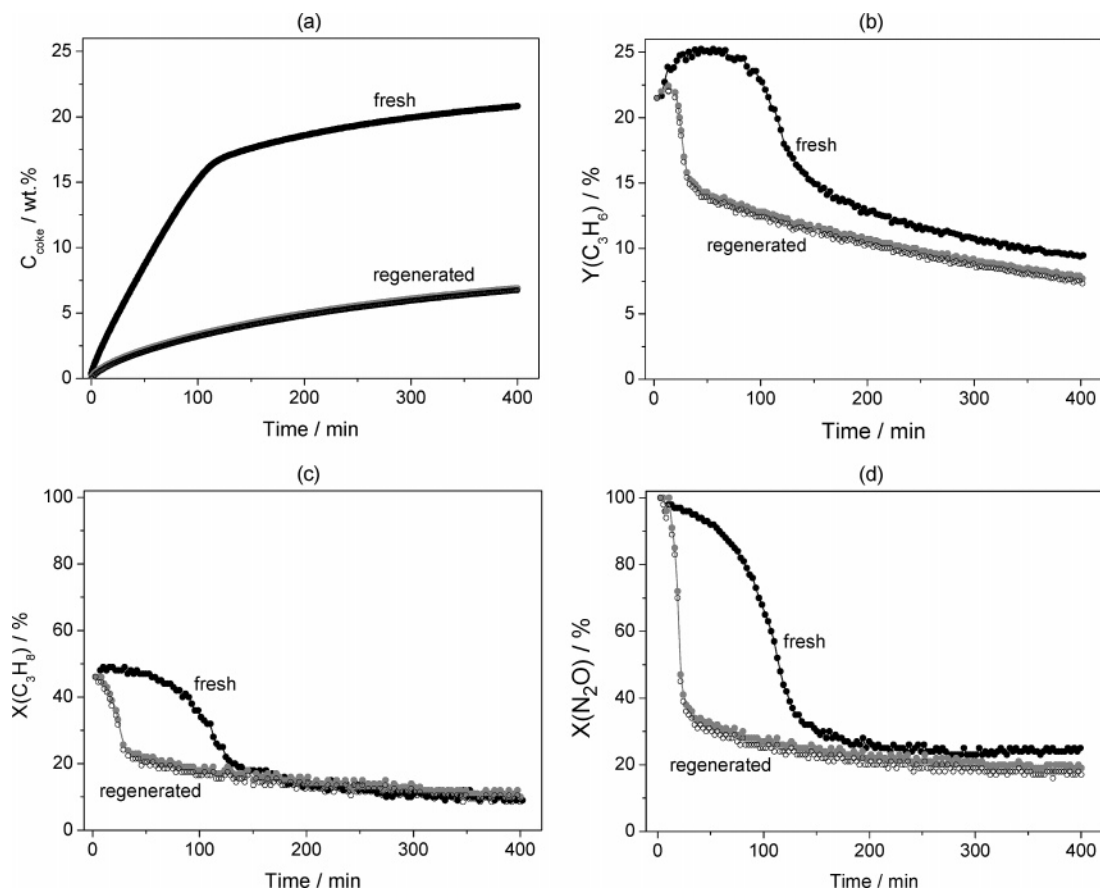
Catalyst deactivation is a complex process, which may be caused by a series of various phenomena. In the simplest case, according to Moulijn et al. (2001),<sup>20</sup> deactivation can be caused by: (i) a decrease in the number of active sites, (ii) a decrease in the quality of the active sites, or (iii) a decrease of accessibility of the

pore space. The fact that the initial and residual propylene yields over FeZSM-5 were very similar over the fresh and regenerated FeZSM-5 indicates that the number of active sites in the beginning of the reaction and in steady-state conditions is not reduced in the regenerated samples. However, the different dynamics of deactivation may be related to a fraction of the active species, which is more susceptible toward deactivation or simply not participating in the reaction due to a reduced accessibility. An eventual alteration of a fraction of active iron species in the zeolite channels during the first reaction and/or regeneration run, for example, leading to inactive or inaccessible iron forms, can be assumed. Comparative characterization studies of the iron species and zeolite support in the fresh, spent, and regenerated catalysts, as well as of the nature and location of the coke deposits, will focus our attention to unravel the interesting behavior shown in Figure 9. This understanding may eventually lead to modifications in the zeolite catalyst or operating conditions to maintain the remarkable stability of the fresh FeZSM-5 zeolite in the first period of the ODHP reaction in the regenerated samples. This aspect is of practical importance for extending the duration of the reaction step in the cyclic process presented in the next section.

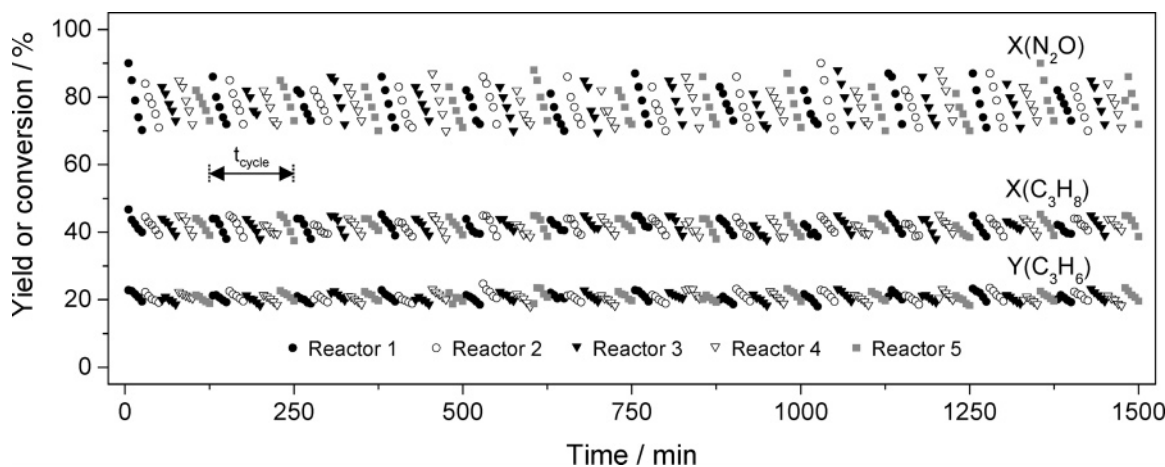
**3.4. Continuous Propylene Production in a Cyclically Operated Reactor.** The feasibility of a process for continuous propylene production has been demonstrated in a cyclically operated reactor with five fixed-bed reactors in parallel using the same reaction and regeneration temperature. Figure 10 shows that a continuous propylene yield  $> 20\%$  can be maintained over steam-activated FeZSM-5 during 1500 min by alternation of the reaction, purging, and regeneration steps. The TEOM experiments were essential to rationally adjust the parameters of the sequence in Figure 3. Particularly for the example in Figure 10, reaction was carried out at  $T_{\text{rx}} = 723 \text{ K}$  for  $t_{\text{rx}} = 25 \text{ min}$  to maintain the propylene yield over  $20\%$ , according to the result in Figure 9 with the regenerated zeolite. Regeneration was carried out at the same temperature as the reaction step ( $T_{\text{rg}} = 723 \text{ K}$ ) during a period of  $t_{\text{rg}} = 90 \text{ min}$ , to ensure complete coke combustion according to the TEOM results in Figure 8b. Before and after the regeneration steps, a purging period of  $t_{\text{p1}} = t_{\text{p2}} = 5 \text{ min}$  has been included. The cycle duration in each reactor is 125 min, and 12 consecutive cycles are shown in Figure 10. With these settings, reaction and regeneration can be effective coupled to ensure continuous propylene production at the desired yield. Cyclic experiments were also conducted using reaction and regeneration temperatures of 773 K. In this case, regeneration is significantly faster than at 723 K (ca. 40 min, see Figure 8b), thus requiring a reduced number of reactors in parallel (three) for the same duration of the reaction and purging steps as in Figure 10. The reactor configuration presented here resembles the cyclic Catofin process (Lummus) for nonoxidative dehydrogenation of alkanes into isobutylene, propylene, and amylene over a  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst, where three to eight fixed-bed reactors in parallel are alternatively on stream for reaction and off stream for regeneration by coke burnoff.<sup>20</sup>

The novel process presented in this manuscript can be applied for on-site  $\text{C}_3\text{H}_6$  production and is particularly attractive if a low-cost source of  $\text{N}_2\text{O}$  is available. An appealing process option consists of the utilization of  $\text{N}_2\text{O}$  in tail-gas of chemical production plants where





**Figure 9.** Comparison of the coke content and  $\text{C}_3\text{H}_6$  yield of the fresh FeZSM-5 (1st run, ●) and regenerated FeZSM-5 (2nd run, gray-shaded circle, and 10th run, ○). ODHP conditions are as in the caption of Figure 4 at 723 K for 400 min. Regeneration conditions are as in the caption of Figure 8b at 723 K for 90 min.



**Figure 10.** Performance of steam-activated FeZSM-5 for ODHP with  $\text{N}_2\text{O}$  in a cyclic process with five fixed-bed reactors in parallel. Sequence conditions (see Figure 3):  $T_{\text{rx}} = T_{\text{rg}} = T_{\text{p}} = 723$  K,  $t_{\text{cycle}} = 125$  min,  $t_{\text{rx}} = 25$  min,  $t_{\text{rg}} = 90$  min, and  $t_{\text{p1}} = t_{\text{p2}} = 5$  min. Experimental conditions for reaction and regeneration steps are as in the caption of Figures 4 and 8, respectively.

$\text{N}_2\text{O}$  is produced in high concentration. This waste-to-chemical concept was introduced by Solutia for the utilization of  $\text{N}_2\text{O}$  produced in adipic acid production as a selective oxidant in the one-step hydroxylation of benzene to phenol.<sup>11</sup> Other sources of concentrated  $\text{N}_2\text{O}$  (up to 50 vol %) include tail-gases of production plants of caprolactan, glyoxal, and in general organic syntheses using  $\text{HNO}_3$  as an oxidant.<sup>21</sup> The efficient utilization of  $\text{N}_2\text{O}$  in tail-gases should involve a previous purification step. As shown here, the presence of  $\text{O}_2$  (a typical component of tail-gases) has a negative impact on the  $\text{N}_2\text{O}$ -mediated propane oxidative dehydrogenation to

propylene over FeZSM-5. The presence of NO traces in the gas however leads to a negative effect on the propylene yield, as shown previously for the reduction of  $\text{N}_2\text{O}$  with  $\text{C}_3\text{H}_8$  in the presence of excess oxygen.<sup>22</sup> Such a purification/separation process upstream of the cyclic reactor would certainly add a substantial cost to the oxidant. An alternative for low-cost and reasonably pure  $\text{N}_2\text{O}$  may arise from the development of cheap and selective catalyst systems for the low-temperature  $\text{NH}_3$  oxidation to  $\text{N}_2\text{O}$ . The cost of the oxidant is an essential aspect to further establish the potential application of this technology.

#### 4. Conclusions

Steam-activated FeZSM-5 is a highly efficient catalyst for the oxidative dehydrogenation of propane using  $N_2O$ , with initial propene yields in the range of 20–25% at 723–773 K. Small amounts of  $O_2$  in the  $C_3H_8+N_2O$  mixture are detrimental for achieving a high propene selectivity, further indicating the vital role of  $N_2O$  as the oxidant in ODHP over iron zeolites. The catalyst presents a strong deactivation due to coke formation; its initial activity is recovered by air-regeneration. On this basis, a cyclic process for continuous propylene production has been demonstrated. Propene yields >20% were achieved during a period of 1500 min (12 cycles), in a configuration of five fixed-bed reactors in parallel with alternation of reaction, purging, and regeneration cycles at 723 K. Results from a tapered element oscillating microbalance (TEOM) coupled to on-line micro-GC analysis were essential to correlate activity, deactivation, and regeneration by simultaneous measurement of reaction and mass changes. This information was used to design the reaction and regeneration sequences (temperature and duration) in the cyclic process. This novel process presents an attractive alternative for the production of moderate (on-purpose) propylene volumes in localized sites having a low-cost source of  $N_2O$  with a sufficient purity, in view of the detrimental effect of gases such as  $O_2$  or  $NO$  on the  $N_2O$ -mediated propane oxidative dehydrogenation over Fe-zeolites.

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