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N_2O-mediated propane oxidative dehydrogenation over steam-activated iron zeolites

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Abstract

Steam-activated Fe-zeolites (MFI and BEA) are efficient catalysts for the N_2O-mediated oxidative dehydrogenation of propane, with initial propylene yields up to 25% at 723 K, but deactivate as a result of coke formation. A tapered element oscillating microbalance (TEOM) coupled to GC analysis has been applied to correlate activity and deactivation by simultaneous measurements of reaction and coking. The presence of extraframework iron species, generated during steam treatment, is essential for producing active catalysts. The nature and distribution of extraframework iron species, the zeolite host, and the catalyst acidity have no significant effect on the initial propene yield, but strongly influence the deactivation behavior. FeZSM-5 shows a remarkable resistance against deactivation, while a very rapid and complete deactivation occurred in FeBEA. The initial propene yield over FeZSM-5 and FeBEA was remarkably higher than over commercial H-ZSM-5 and H-BEA (with 30–40 times lower iron content), although the residual activities after 400 min on stream were very similar.

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1. Introduction

Fe-zeolites have gained great interest in view of their excellent catalytic performance in various environmental applications and in selective oxidation for chemical production [1–5]. The most representative example within the last group of conversions is the one-step selective oxidation of benzene to phenol (BTOP) with N_2O. The unique catalytic properties of iron zeolites in this reaction have been related to the specificity of N_2O as a monooxygen donor and the capability of determined Fe species in the zeolite for coordinating reactive atomic species (referred to as α-oxygen), which is inserted in the benzene molecule yielding phenol with selectivities close to 100% [5]. Research on BTOP with N_2O has focused on the FeMFI system [6,7], in view of the higher activity as compared to other zeolite matrices, although FeZSM-11 and FeBEA were found to be active too [8].

Previous studies also noted high selectivities of MFI frameworks with iron toward oxidative dehydrogenation of light alkanes (ethane and propane) with N_2O and O_2 at a low degree of hydrocarbon conversion (2–10%), thus achieving a low yield of the olefin ($< 10\%$) [9,10]. Liquid-ion exchanged M-ZSM-5 zeolites (M = Fe, Co, Mn) have been recently applied in the oxidative dehydrogenation of propane (ODHP) with N_2O, and propene yields close to 20% were reported over Fe-ZSM-5 [11]. Steam-activated FeMFI zeolites have shown superior performances for the N_2O-mediated ODHP, with initial propene yields up to 24% at 773–798 K [12]. In addition, remarkable yields toward propionaldehyde (up to 6%) have been obtained. A major drawback of FeMFI zeolites in ODHP with N_2O is the deactivation by coke, causing a rapid decrease of the propene yield.

Following the previous study in [12], this manuscript aims at a more detailed investigation of various Fe-zeolites in ODHP with N_2O, with emphasis on the effect of the catalyst constitution with respect to iron, acidity, and zeolite host on the initial performance and deactivation behavior. To this end, a tapered element oscillating microbalance (TEOM) coupled to on-line analysis of products has been applied for simultaneous measurements of activity and coke formation.

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2. Experimental

2.1. Catalysts

The various zeolites studied are shown in Table 1. High-purity chemicals were used during preparations (>99.995%) to avoid any contamination of the samples. Details on the hydrothermal synthesis of FeZSM-5 and Fe-silicalite have been described elsewhere [13,14]. FeBEA was synthesized hydrothermally using tetraethylammonium (TEA^+) as the template and fluoride anions as the mineralizer agent. The as-synthesized samples, containing the different metals in the zeolite framework, were calcined in air at 823 K for 10 h and activated in flowing steam at ambient pressure (water partial pressure of 300 mbar and 30 ml STP min^{-1} of N_2 flow) at 873 K for 5 h. In this paper, the calcined and steamed zeolites are denoted by the prefixes *c*- and *ex*-, respectively. The catalytic performance of commercial NH_4-ZSM-5 (CBV8020, P&Q) and NH_4-BEA (CP814E, Zeolyst) was also evaluated. Previous to the testing, the as-received samples were calcined and steamed according to the procedures described above, yielding *ex*-H-ZSM-5 and *ex*-H-BEA.

2.2. Reaction and coking studies

Reaction and coke deactivation studies were carried out in a Rupprecht & Patashnick TEOM 1500 pulse mass analyser. The TEOM consists of a microreactor with a high-resolution microbalance that generates real-time measurements of mass changes during gas-solid reactions. Its operation principle has been described elsewhere [15,16]. Briefly, the active element of the TEOM consists of a tapered tube that maintains oscillation at its natural frequency. The natural frequency changes in terms of the mass change in the tapered tube. The mass uptake is then determined by the change of the oscillating frequency. The TEOM reactor was loaded with 30 mg of catalyst (sieve fraction 125–200 µm), firmly packed between two plugs of quartz wool. Prior to experiments the catalysts were pretreated in flowing He at 723 K for 2 h. The He flow was replaced by the reaction mixture, and mass changes and evolved product gases were continuously monitored. The oxidative dehydrogenation of propane with N_2O was carried out at 723 K in a mixture of 100 mbar C_3H_8 and 100 mbar N_2O in He at a total pressure of 2 bar and a weight-hourly space velocity (WHSV) of 400,000 ml $h^{-1}\,g_{cat}^{-1}$. 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. The conversions of N_2O and C_3H_8 were determined from the amounts of N_2 formed and C_3H_8 disappeared, respectively. Propene yield and selectivity were calculated as $Y(C_3H_6) = C(C_3H_6)/C^o(C_3H_8)$ and $S(C_3H_6) = Y(C_3H_6)/X(C_3H_8)$, respectively, where $C(C_3H_6)$ is the outlet propene concentration at a certain time, $C^o(C_3H_8)$ is the inlet concentration of propane, and $X(C_3H_8)$ is the conversion of propane.

3. Results

Table 1 shows the chemical composition of the catalysts investigated. The synthesized Fe-zeolites have a very similar iron content, and the molar Si/Al ratio in *ex*-FeZSM-5 and *ex*-FeBEA is nearly identical. The amount of iron in the steamed commercial *ex*-H-ZSM-5 and *ex*-H-BEA zeolites was 30–40 times lower. Fig. 1 shows the coke content and propene yield with time on stream during ODHP with N_2O over the different catalysts investigated, as derived from the TEOM experiments and coupled gas chromatographic analysis. The coke content (C_{coke}) was determined from the mass change measured during reaction, accounting for the change in gas density when the helium flow was replaced by the reaction mixture ($C_3H_8 + N_2O$ in He). Fig. 2 shows the corresponding conversions of C_3H_8 and N_2O. A summary of reaction data after 2 min on stream (denoted as initial, t_o) and after 400 min on stream (denoted as residual or final, t_f) is given in Table 1.

Steam-activated FeZSM-5, Fe-silicalite, and FeBEA zeolites showed initial propene yields in the range of 19–22% at 723 K, with a similar degree of propane conversion (ca. 45%) and propene selectivity (ca. 50%), and complete

Table 1
Catalysts investigated in this study and reaction parameters during ODHP with N_2O

Catalyst	Si/Al[a]	Fe[a] (wt%)	$X(N_2O)$ (–)		$X(C_3H_8)$ (–)		$Y(C_3H_6)$ (–)		$S(C_3H_6)$ (–)	C_{coke} (wt%)
			t_o[b]	t_f[c]	t_o	t_f	t_o	t_f	t_o	t_f
c-Fe-silicalite	∞	0.68	0.25	0.04	0.14	0	0.05	0	0.48	3.7
ex-Fe-silicalite	∞	0.68	0.98	0.12	0.42	0.03	0.22	0.02	0.51	7.6
ex-FeZSM-5	31.3	0.67	0.96	0.25	0.48	0.10	0.22	0.09	0.45	20
ex-FeBEA	31.8	0.61	0.99	0.07	0.45	0	0.19	0	0.43	9.2
ex-H-ZSM-5	37.5	0.017[d]	0.33	0.17	0.19	0.07	0.16	0.08	0.95	4.5
ex-H-BEA	15.1	0.021[d]	0.34	0.06	0.18	0	0.13	0	0.72	5.0

Prefixes *c*- and *ex*- refer to calcined and steamed zeolites, respectively.
[a] Chemical composition as determined from ICP-OES.
[b] t_o: initial activity (after 2 min on stream).
[c] t_f: reaction parameters after 400 min on stream.
[d] Traces of iron in commercial zeolites as determined by instrumental neutron activation analysis [14].

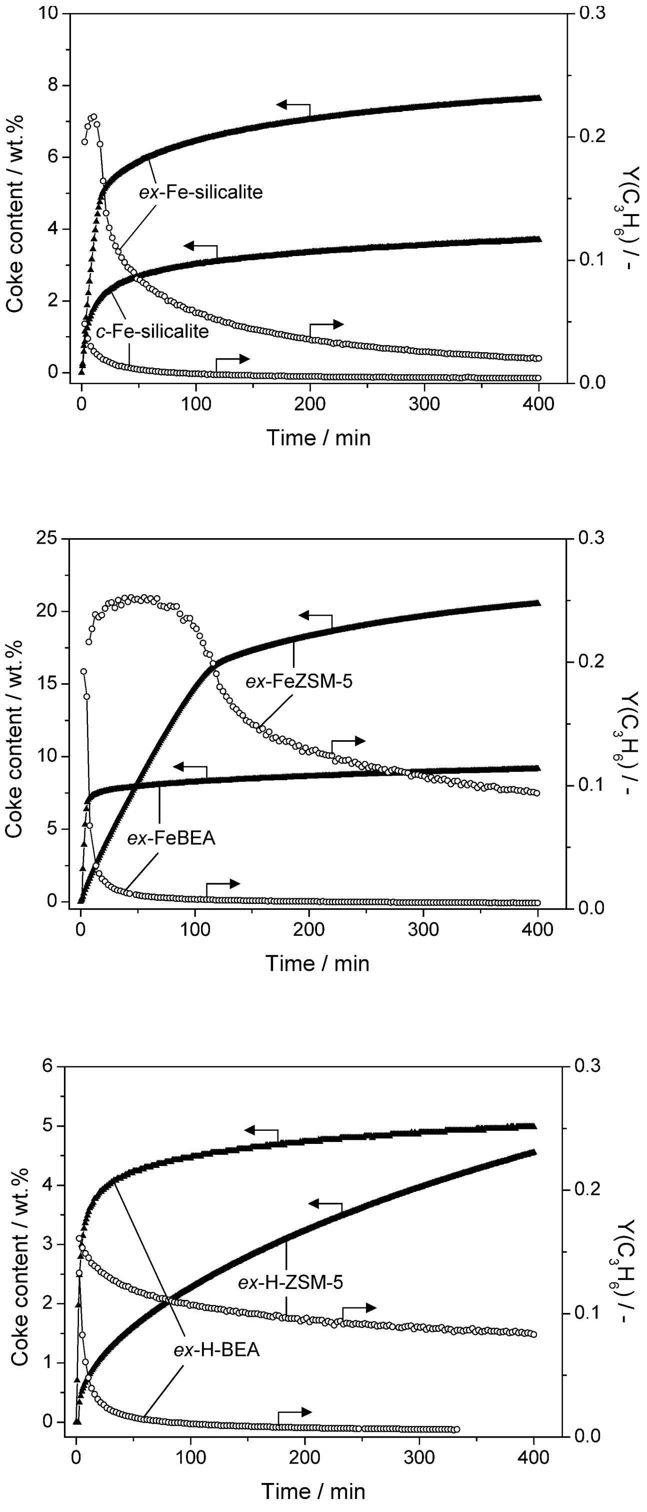

Fig. 1. Coke content (▲) and C_3H_6 yield (○) vs time over iron zeolites. Conditions: 100 mbar C_3H_8 and 100 mbar N_2O in He, $T = 723$ K, WSHV = 400,000 ml h^{-1} g_{cat}^{-1}, and $P = 2$ bar.

N_2O conversion. The propene yields achieved are similar to state-of-the-art catalysts based on V and Mo-oxides with O_2 as the oxidant [17,18]. The space velocity in our experiments is one order of magnitude higher than typically applied in the literature, which is a clear indication of the remarkable performance of steamed iron zeolites in ODHP with N_2O. The interaction of C_3H_8 with the iron zeolites in the absence of N_2O did not lead to propene production, indicating the essential role of the oxidant for propane dehydrogenation.

Steam activation is essential to achieve superior catalytic performances. The initial conversions of propane and N_2O over the calcined zeolites were very low in comparison with the steamed zeolites. This is exemplified in Fig. 2 and Table 1 for the Fe-silicalite system. Accordingly, the initial propene yields over *c*-Fe-silicalite and *ex*-Fe-silicalite largely differ (5 and 22%, respectively).

The initial conversion and selectivity were quite similar in the steam-activated iron zeolites, regardless of the host (MFI vs BEA), the acidic properties of the zeolite (ZSM-5 vs silicalite), and the catalyst constitution with respect to iron. However, the dynamics of the reaction (deactivation behavior and coke formation) are considerably different. As shown in Fig. 1, an excellent correlation is obtained between the increase of coke content and the decrease of propene yield with time from the TEOM experiments. This strongly suggests that coke formation is responsible for catalyst deactivation. Coke deposits likely originate by condensation of propene, the main olefin formed over all the catalysts investigated. Traces of ethylene were also detected (ca. 15 times lower concentration than propene).

As shown in Fig. 1, deactivation of *ex*-FeBEA is very rapid. The yield of propene rapidly decreases during the first 5 min on stream, and the catalyst is completely deactivated after 50 min. The sudden activity drop nicely coincides with the sharp increase of the coke content, and the coking profile reaches a well-defined plateau when the conversion of C_3H_8 approaches zero and thus propene production vanishes. A residual N_2O conversion of 7% was obtained (Fig. 2). The rate of deactivation over *ex*-Fe-silicalite was significantly lower than over *ex*-FeBEA; the continuous decline of the C_3H_6 yield over *ex*-Fe-silicalite is clearly connected with the more gradual increase of the coke content, in contrast to *ex*-FeBEA. *Ex*-Fe-silicalite preserves a very low residual propene yield after 400 min on stream with a N_2O conversion of 12%. The remarkable behavior of *ex*-FeZSM-5 against deactivation deviates from the former iron zeolites. First of all, *ex*-FeZSM-5 *activates* during the first 20 min on stream, with an increase in propene yield from 22 to 25%. A similar behavior, although much less pronounced and durable, was observed over *ex*-Fe-silicalite too (Fig. 1). This high propene yield over *ex*-FeZSM-5 was maintained during 75 min, and the coke content at this particular time is ca. 15 wt%. Oppositely, *ex*-Fe-silicalite and *ex*-FeBEA were severely or completely deactivated after 75 min on stream. After this stable period, the propene yield over *ex*-FeZSM-5 progressively decreases, but a residual propene yield of 8% is preserved after a reaction period of 400 min, with conversions of C_3H_8 and N_2O of 10 and 25%, respectively.

Considering that propene is the major coke precursor in the process investigated, the amount of coke formed should

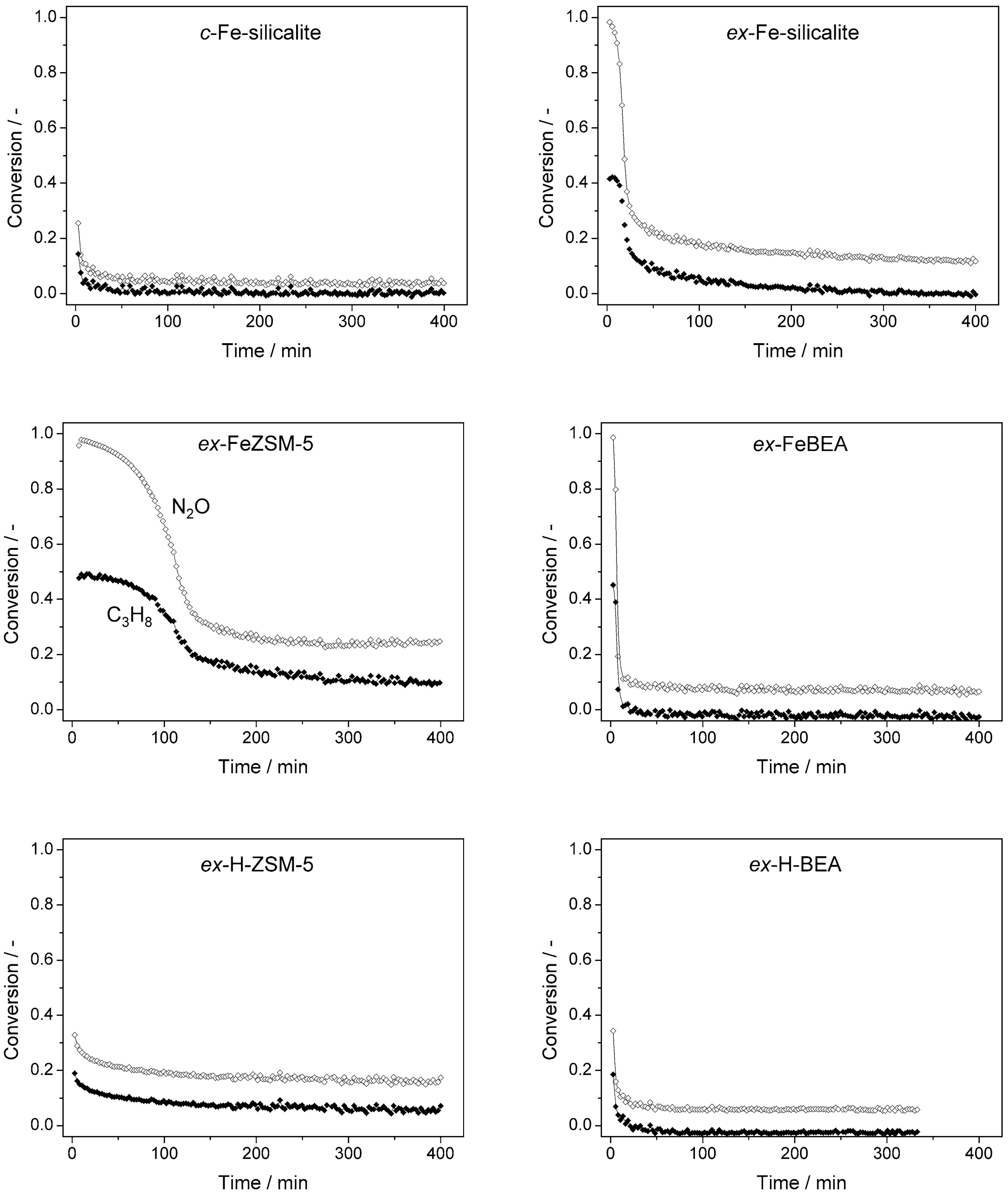

Fig. 2. Conversion of N_2O (◇) and C_3H_8 (◆) vs time over iron zeolites. Conditions: 100 mbar C_3H_8 and 100 mbar N_2O in He, $T = 723$ K, WSHV $= 400{,}000\ \mathrm{ml\,h^{-1}\,g_{cat}^{-1}}$, and $P = 2$ bar.

give a rough indication of the catalyst activity in ODHP. Accordingly, the final coke content over *ex*-FeZSM-5, the most active catalyst in our study is 20 wt%, i.e., ca. 3 times higher than over *ex*-Fe-silicalite (7.6 wt%) and *ex*-FeBEA (9.2 wt%). The coke content over calcined *c*-Fe-silicalite amounts to 4 wt% after 400 min, i.e., half than the amount measured in the corresponding steamed sample. However, other factors also affect the amount of coke formed, especially the presence of Brønsted acidic sites in the Al-containing samples or in the calcined zeolites (with iron in framework positions), which may participate in coking via acid-catalyzed carbenium ion reactions.

Tests with steamed commercial zeolites, containing impurities of iron, are important for understanding the role of iron on the catalytic performance. The higher activity and lower rate of deactivation of *ex*-H-ZSM-5 (170 ppm Fe) compared to *ex*-H-BEA (210 ppm Fe) draw parallels with the results obtained over *ex*-FeZSM-5 (0.67 wt% Fe) and *ex*-FeBEA (0.61 wt% Fe). Steamed commercial zeolites induced much lower C_3H_8 and N_2O conversions than the synthesized Fe-zeolites (Fig. 2), hence resulting in a lower propene yield and coke content (see Figs. 1 and 2 and Table 1). This implies a beneficial effect of the amount of iron on the catalytic performance, as it was also concluded in other N_2O conversions over Fe-zeolites, e.g., direct decomposition [19] or selective oxidation of benzene to phenol [5]. Strikingly, the residual yield of propene over *ex*-FeZSM-5 and *ex*-H-ZSM-5 after 400 min on stream was very similar (8%, see Figs. 1 and 2).

4. Discussion

Steam-activated Fe-zeolites are highly active and selective catalysts for the ODH of propane with N_2O, achieving propylene yields up to 25% at 723 K and space velocities of 400,000 $\mathrm{ml\,h^{-1}\,g_{cat}^{-1}}$. This novel application of iron zeolites leads to the simultaneous valorization of propane, a relatively cheap and abundant feedstock and N_2O, an environmentally harmful gas. A major drawback of this process is the catalyst deactivation by coke, although the high initial activity was completely recovered after regeneration of the coked zeolites in oxygen at 773 K [12]. The TEOM technique presented here is a unique tool for the simultaneous measurement of reaction and coking, so that catalyst deactivation and coke formation can be precisely monitored and correlated. The TEOM presents three main advantages over conventional gravimetric microbalances: (i) a well-defined flow pattern, eliminating possible (heat and mass) diffusion and bouyancy 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.

Relevant conclusions on the effect of the amount and form(s) of iron in the catalysts as well as of the zeolite acidity and host on the initial catalytic performance and deactivation behavior can be drawn from our study. The hydrothermally synthesized iron zeolites were calcined and steam-activated using the same procedures and contain very similar iron contents, enabling a direct comparison of catalytic performances. Steam activation is essential for achieving high catalytic activities, as concluded from the low conversion of reactants and propene yield obtained over the calcined iron zeolites. The calcined samples contain the majority of iron in tetrahedral positions of the zeolite framework [13,14]. Activation of N_2O, the first step in ODHP as well as in other N_2O conversions [5,19,20], requires coordination of atomic oxygen to the active site, which is impossible for framework iron. Extraframework iron species, generated during steam treatment, are thus responsible for the oxydehydrogenation of propane with nitrous oxide. This result contrasts with former statements of Uddin et al. [9], who claimed that only framework iron in silicalite matrices was selective toward the olefin in the ODH of propane with O_2. Recent characterization of *c*-Fe-silicalite has shown that a very small fraction of iron is not isomorphously substituted in the zeolite framework [14,21], either not incorporated during the hydrothermal synthesis or most likely extracted during template removal by calcination. This result suggests that the (low) activity observed in *c*-Fe-silicalite may even originate from this fraction of iron species in extraframework active positions.

The similar initial degree of N_2O and propane conversion, as well as propene selectivity (and thus propene yield) obtained over *ex*-FeZSM-5, *ex*-FeBEA, and the non-acidic *ex*-Fe-silicalite further indicates that the origin of the catalyst activity is mainly associated to the presence of extraframework iron species. Brønsted acid sites (Si–OH–M groups with M = Al, Fe) and Lewis acid sites (mainly extraframework Al species generated upon steaming [13]) do not seem to be directly involved in the oxidative conversion of propane to propene. In agreement, Meloni et al. [22] have also concluded that the acidity was not responsible for the initial activity of FeMFI in the one-step hydroxylation of benzene to phenol with N_2O.

Application of Fe-zeolites in oxidations has mainly focused on the MFI matrix [5–12], while other zeolite types have received little attention. The geometrical parameters of the micropores are decisive in stabilizing active iron complexes, a difficult task in relatively open spaces. This explains the numerous frustrated attempts to produce active catalysts for the N_2O-mediated oxidation of benzene to phenol over iron zeolites with larger pore dimensions (Y, MOR) or mesoporous materials (MCM-41) [5]. BEA is a good candidate attending to the three-dimensional pore structure and larger internal accessibility as compared to MFI. The obtained initial activity of *ex*-FeBEA, comparable to that of *ex*-FeMFI catalysts, has clearly shown that the topology and pore architecture of BEA are suitable for generating active iron species for the N_2O-mediated conversion of propane to propene.

The difference in initial C_3H_6 yield between *ex*-FeZSM-5 and *ex*-Fe-silicalite is marginal if their constitution with respect to iron is taken into account. Previous characterization evidenced that *ex*-Fe-silicalite does not show any sign of iron association, and the majority of extraframework iron species is uniform and well isolated, with a small fraction of iron in framework positions. Contrarily, significant iron clustering was observed in *ex*-FeZSM-5, where extraframework isolated iron ions and oligonuclear species in the zeolite channels coexist with iron oxide nanoparticles of 1–2 nm [13,14,20,21]. Based on these results, it is suggested that the initial ODHP performance is not strongly affected by the forms of extraframework iron species in the steam-activated zeolites.

The essential role of iron in the reaction can be clearly concluded from the significantly higher C_3H_8 and N_2O conversions over *ex*-FeZSM-5 and *ex*-FeBEA, as compared to *ex*-H-ZSM-5 and *ex*-H-BEA. The initial activity of the synthesized Fe-zeolites, expressed as mole C_3H_8 converted per unit of time and catalyst mass is 2–3 higher than over the commercial zeolites, while the former catalysts contain 30–40 times more iron. This indicates that the activity and selectivity per iron atom in, e.g., *ex*-H-ZSM-5, are ca. 10 times higher than in *ex*-FeZSM-5, suggesting that a significant fraction of iron in the synthesized Fe-zeolites is not utilized. In other words, the iron species present in the commercial samples as impurities are considered as highly efficient sites for the oxydehydrogenation of propane with N_2O.

As concluded above, the initial performance of the steam-activated iron zeolites in ODHP with N_2O is similar, but the deactivation behavior strongly differs. Coke formation causes physical blocking of the active reaction sites inside the zeolitic pore system, resulting in a decreased C_3H_6 yield. In general terms, the coking rate in zeolites depends on the acidic sites (number and strength), the zeolite structure, and the reaction conditions [23,24]. In the reaction investigated, the nature and location of the active extraframework iron species may play an essential role on the deactivation behavior too. The origin of coke is mainly associated to the condensation of propene, as indicated by direct relation between the propene yield and the amount of coke determined from the TEOM (see Fig. 1 and Table 1). The final amount of coke in *ex*-FeZSM-5 (with a residual propene yield of 8%) is 3 times higher than in *ex*-Fe-silicalite and in the totally deactivated *ex*-FeBEA (Table 1). The coke content in *ex*-FeZSM-5 is 4–5 times higher that in *ex*-H-ZSM-5, while similar residual propene yields were achieved. These results nicely illustrate that, as generally found, the location of coke is far more relevant than the total coke quantity in the deactivation process.

The rapid deactivation observed in *ex*-FeBEA and *ex*-H-BEA can be connected to the presence of large cavities with relatively small apertures in the BEA framework, especially at the intersection of the channels. Apparently, these trap cavities cause the entire blocking of the access to the active sites, leading to complete catalyst deactivation. The rate of deactivation over the MFI catalysts is significantly lower, and can be related to the absence of large cages in this zeolitic structure, since channels and intersections are of similar size. Accordingly, coke precursors are not trapped inside the intersections, but diffuse out unless they are too strongly adsorbed. As a consequence, deactivation is not complete over these catalysts (particularly *ex*-FeZSM-5 and *ex*-H-ZSM-5), showing a significant residual activity with a slow but continuous increase in the amount of coke. This clearly evidences a certain accessibility of the reactants to active iron sites in the zeolite pores. The amount of iron sites participating in the reaction leading to propene after 400 min on stream is presumably very low, as suggested by the similar residual performance of *ex*-FeZSM-5 and *ex*-H-ZSM-5.

One could expect the presence of acidic groups in *ex*-FeZSM-5 to accelerate the deactivation process due to coke formation during ODHP compared to *ex*-Fe-silicalite, while the opposite was observed in our experiments. Perathoner et al. [25] claimed the beneficial effect of Al in the zeolite framework to reduce the deactivation rate with respect to Fe-silicalite in the selective oxidation of benzene to phenol with N_2O. Contrarily, Meloni et al. [22] concluded that the surface acidity in FeZSM-5 leads to a faster catalyst deactivation compared to Fe-silicalite in the same reaction. The higher deactivation resistance of steam-activated *ex*-FeZSM-5 in ODHP with N_2O is unclear at this stage, but can be tentatively related to the different iron constitutions in both catalysts and/or the different porous structure associated to the presence of aluminum in the original zeolite framework. *Ex*-FeZSM-5 contains mesopores due to dealumination upon steam treatment, which are absent in *ex*-Fe-silicalite [13,14]. The more open structure of FeZSM-5 may reduce pore blocking by coke and also to improve transport of reactants and products, slowing down deactivation. In this case, development of mesopores in the zeolites investigated, e.g., by desilication in alkaline medium [14], can be advantageous to improve transport properties and active site accessibility. The activity of *ex*-FeZSM-5 in direct N_2O decomposition is significantly higher than that of *ex*-Fe-silicalite [13], which is confirmed attending to the higher conversion of N_2O over *ex*-FeZSM-5 in Fig. 2. This has been attributed to the larger fraction of iron as active oligonuclear iron species in *ex*-FeZSM-5, which favors oxygen desorption, as compared to *ex*-Fe-silicalite [14,20]. N_2O activation generates atomic oxygen over certain iron species, which is efficiently utilized for the oxidative dehydrogenation of propane. However, recombination of atomic oxygen and desorption as O_2 may lead to reaction with coke at specific locations of the zeolite at the operating temperature, resulting in CO_x. This function would partially regenerate the catalyst surface. This hypothesis would imply that highly active Fe-zeolite catalysts in direct N_2O decomposition have an increased resistance toward coke deactivation in ODHP with N_2O. Further research will be undertaken to clarify this aspect.

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References

[1] J. Pérez-Ramírez, F. Kapteijn, G. Mul, J.A. Moulijn, Chem. Commun. (2001) 693.

[2] J. Pérez-Ramírez, F. Kapteijn, K. Schöffel, J.A. Moulijn, Appl. Catal. B 44 (2003) 17.

[3] H.-Y. Chen, W.M.H. Sachtler, Catal. Today 42 (1998) 73.

[4] R.Q. Long, R.T. Yang, Chem. Commun. (2000) 1651.

[5] G.I. Panov, CATTECH 4 (2000) 18.

[6] L.V. Pirutko, A.K. Uriarte, V.S. Chernyavsky, A.S. Kharitonov, G.I. Panov, Micropor. Mesopor. Mater. 48 (2001) 345.

[7] L.V. Pirutko, V.S. Chernyavsky, A.K. Uriarte, G.I. Panov, Appl. Catal. A 227 (2002) 143.

[8] A.S. Kharitonov, G.I. Panov, G.A. Sheveleva, L.V. Pirutko, T.P. Voskresenskaya, V.I. Sobolev, US patent 5,672,777 (1997).

[9] Md.A. Uddin, T. Komatsu, T. Yashima, J. Catal. 150 (1994) 439.

[10] S.N. Vereshchagin, N.P. Kirik, N.N. Shishkina, A.G. Anshits, Catal. Lett. 56 (1998) 145.

[11] K. Nowińska, A. Wącław, A. Izbińska, Appl. Catal. A 243 (2003) 225.

[12] J. Pérez-Ramírez, E.V. Kondratenko, Chem. Commun. (2003) 2152.

[13] J. Pérez-Ramírez, G. Mul, F. Kapteijn, J.A. Moulijn, A.R. Overweg, A. Ribera, I.W.C.E. Arends, J. Catal. 207 (2002) 113.

[14] J. Pérez-Ramírez, F. Kapteijn, J.C. Groen, A. Doménech, G. Mul, J.A. Moulijn, J. Catal. 14 (2003) 33.

[15] D. Chen, H.P. Rebo, K. Moljord, A. Holmen, Chem. Eng. Sci. 51 (1996) 2687.

[16] W. Zhu, J.M. van de Graaf, L.J.P. van den Broeke, F. Kapteijn, J.A. Moulijn, Ind. Eng. Chem. Res. 37 (1998) 1934.

[17] O. Buyevskaya, M. Baerns, Catalysis 155 (2002) 16, and references therein.

[18] C. Pak, A.T. Bell, T. Don Tilley, J. Catal. 206 (2002) 49.

[19] J. Pérez-Ramírez, F. Kapteijn, G. Mul, J.A. Moulijn, Catal. Commun. 3 (2002) 19.

[20] J. Pérez-Ramírez, F. Kapteijn, A. Brückner, J. Catal. 218 (2003) 234.

[21] J. Pérez-Ramírez, M.S. Kumar, A. Brückner, J. Catal. 223 (2004) 13.

[22] D. Meloni, R. Monaci, V. Solinas, G. Berlier, S. Bordiga, I. Rossetti, C. Oliva, L. Forni, J. Catal. 214 (2003) 169.

[23] M. Guisnet, P. Magnoux, Stud. Surf. Sci. Catal. 88 (1994) 53.

[24] M. Guisnet, P. Magnoux, D. Martin, Stud. Surf. Sci. Catal. 111 (1997) 1.

[25] S. Perathoner, F. Pino, G. Centi, G. Giordano, A. Katovic, J.B. Nagy, Top. Catal. 23 (2003) 125.