

## Steam-activated FeMFI zeolites as highly efficient catalysts for propane and N<sub>2</sub>O valorisation *via* oxidative conversions

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**The reaction between C<sub>3</sub>H<sub>8</sub> and N<sub>2</sub>O over steam-activated FeMFI zeolites leads to high yields towards propene (24%) and propionaldehyde (6%) at 773–798 K.**

A challenging approach in oxidation catalysis is the functionalisation of lower alkanes towards olefins and oxygenates. Due to increasing demand for propene, the catalytic oxidative dehydrogenation of propane (ODP) has attracted attention as an alternative route for propene production compared to the conventional cracking and dehydrogenation processes. Promising catalysts are based on molybdenum and vanadium oxides, with propene yields in the range of 10–20%.<sup>1</sup> Exceptionally, higher propene yields have been reported over V–Mg–O catalysts (24%),<sup>2</sup> K/Mo catalyst supported on Si–Ti mixed oxides (30%),<sup>3</sup> and Ba-promoted Ni–Mo–O catalysts (30%), using O<sub>2</sub> as the oxidant.<sup>4</sup>

The application of Fe-zeolites in oxidative transformations with N<sub>2</sub>O was triggered by the accomplishments in hydroxylation of paraffins to alcohols and of aromatic hydrocarbons to phenols.<sup>5</sup> Our strategy is to utilize the specificity of N<sub>2</sub>O as a monooxygen donor and the capability of determined Fe species in the zeolite for coordinating  $\alpha$ -oxygen to develop efficient catalysts for valorisation of propane and N<sub>2</sub>O *via* oxidative conversions. Previous studies have reported high selectivities of MFI frameworks with iron towards oxidative dehydrogenation of light alkanes with N<sub>2</sub>O and O<sub>2</sub> at a low degree of hydrocarbon conversions (2–10%), thus achieving a low yield of the olefin (<10%).<sup>6,7</sup> As in many other related studies, diluted mixtures of the alkane and oxidizing agent were used, which restricts any realistic conclusion on the potential application of these catalytic materials.

We report for the first time the superior performance of steam-activated FeMFI zeolites in ODP with N<sub>2</sub>O. Initial propene yields up to 24% are comparable with the highest values reported over V and Mo oxides with O<sub>2</sub>. In addition, remarkable yields towards propionaldehyde (up to 6%) have been obtained.

Details on the preparation of steam-activated FeMFI zeolites have been described elsewhere.<sup>8,9</sup> The isomorphously substituted zeolites, with Fe–Al–Si and Fe–Si frameworks, were

calcined and activated in steam (30 vol.% H<sub>2</sub>O in 30 ml (STP) min<sup>-1</sup> of N<sub>2</sub> flow) at 873 K during 5 h, yielding FeZSM-5 (Si/Al = 31 and 0.67 wt.% Fe) and Fe-silicalite (Si/Al ~  $\infty$  and 0.68 wt.% Fe). Commercial NH<sub>4</sub>-ZSM-5 (CBV 8020, Si/Al = 37.5 and 220 ppm Fe) was calcined and steamed according to the procedure described above. Catalytic activity was measured at 723–798 K in a fixed-bed quartz reactor (6 mm id) under near isothermal conditions, using 50 mg of catalyst diluted with 150 mg of SiO<sub>2</sub> (both 125–200  $\mu$ m), and contact times in the range of  $\tau = 0.043$ – $0.097$  s g<sub>cat</sub> ml<sup>-1</sup> at atmospheric pressure. The feed consisted of 10 vol.% C<sub>3</sub>H<sub>8</sub> and 10 vol.% N<sub>2</sub>O in Ne. The product gases were analysed by GC (HP 5890) using Poraplot Q and Molsieve 5 columns.

The catalytic performance of the steam-activated zeolites in the ODP reaction is shown in Table 1 and Fig. 1. The values in Table 1 correspond to the analysis of reaction products after 15 min on stream, denoted hereafter as initial activity. At all the temperatures investigated propene was the main olefin, with yields as high as 24% at 798 K. At similar degrees of propane conversion, the propene selectivity over FeZSM-5 was higher than over Fe-silicalite. N<sub>2</sub>O conversion ranged from *ca.* 45 to 95%, increasing with temperature and contact time. A similar but less pronounced increase from *ca.* 30 to 52% was observed for C<sub>3</sub>H<sub>8</sub> conversion. The increase in propane conversion was accompanied by a decrease in propene selectivity, from *ca.* 59 to 44%. Propionaldehyde (CH<sub>3</sub>CH<sub>2</sub>CHO) was the main oxygenate formed, with yields up to 6%. No significant dependence was found between the selectivity to propionaldehyde and the degree of propane conversion, suggesting that this oxygenate is a primary (stable) product of the ODP reaction. This result is notable, since  $\alpha$ -oxygen (from N<sub>2</sub>O) in Fe-zeolites has been typically found to be active for dehydrogenation or insertion into a C–H bond, forming the corresponding alcohol.<sup>5–7</sup> In our experiments, very low concentrations of alcohols were found. Methane, ethylene, acetone, and acrolein, as well as CO and CO<sub>2</sub> were reaction products too. The carbon balance in Table 1 indicates that other (non-identified) products in concentrations <0.1 vol.% were also formed, including coke deposits on the catalyst. Steam-activated commercial H-ZSM-5, containing 220 ppm Fe, showed a rather low but measurable activity at 723

**Table 1** Performance of steam-activated zeolites in ODP at different temperatures and contact times in a mixture of C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub>O/Ne = 10/10/80

Catalyst	$\tau$ /s g <sub>cat</sub> ml <sup>-1</sup>	C balance (%)	T/K	Conversion (%)		Selectivity <sup>a</sup> (%)		Yield <sup>a</sup> (%)	
				C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub> O	C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>2</sub> CHO	C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>2</sub> CHO
FeZSM-5	0.043	94.2	723	30.6	45.4	58.9	10.2	18.1	3.1
	0.043	90.3	773	49.8	92.6	49.2	12.0	22.9	5.6
	0.043	89.4	798	51.6	94.7	46.3	11.7	24.0	6.0
Fe-silicalite	0.049	92.2	723	31.2	52.1	51.8	10.6	16.3	3.4
	0.097	96.3	723	40.9	83.3	45.5	10.4	18.7	4.3
	0.049	91.1	773	31.4	51.1	49.9	8.9	16.0	2.9
	0.097	92.6	773	45.7	93.7	43.6	9.9	20.1	4.6
	0.049	89.4	798	44.0	92.0	44.8	8.2	19.8	3.6
H-ZSM-5	0.049	99.0	723	9.4	16.0	62.7	2.0	6.2	0.2
	0.049	94.4	773	18.5	33.5	49.7	2.3	9.5	0.4

<sup>a</sup> Selectivity and yield were calculated as  $S(i) = Y(i)/X(C_3H_8)$  and  $Y(i) = C(i)/C^0(C_3H_8)$ , respectively, where  $X(C_3H_8)$  is the conversion of propane and  $C^0(C_3H_8)$  is the inlet concentration of propane.

and 773 K, with propene yields <10% and traces of propionaldehyde. The relatively low yield of these products over steamed H-ZSM-5 strongly supports that iron is predominantly responsible for the observed performance, as concluded in other N<sub>2</sub>O conversions over Fe-zeolites, e.g. direct decomposition or selective oxidation of benzene to phenol.<sup>5,9,10</sup>

Fig. 1 shows the yield of the iron zeolites vs. time-on-stream at different temperatures. The conversion of C<sub>3</sub>H<sub>8</sub> and N<sub>2</sub>O continuously declines in a period of 100 min, due to coke formation. As a consequence, the high initial yield towards propene and propionaldehyde progressively decreases. The rate of deactivation over FeZSM-5 is significantly lower at 723 K than at higher temperatures, in agreement with the decreased carbon balance upon increasing temperature in Table 1. Fe-silicalite is very sensitive to deactivation, even at 723 K. Both catalysts completely recovered the initial activity at all the temperatures after pretreatment in pure oxygen at 773 K for 30 min. This was checked upon by repetition of five successive ODP-reaction and O<sub>2</sub>-regeneration cycles.

From the results above, it can be concluded FeZSM-5 is more active and selective than Fe-silicalite. However, the difference in performance between both catalysts is marginal if their constitution with respect to iron is taken into account. Steam-activated Fe-silicalite does not show any sign of iron association, and the majority of extraframework iron species are uniform and well isolated, with a small fraction of iron in framework positions.<sup>11</sup> In contrast, significant iron clustering was observed in steam-activated FeZSM-5, where extraframework isolated iron ions and oligonuclear species in the zeolite channels coexist with iron oxide nanoparticles of 1–2 nm.<sup>8,9</sup> Our results suggest that the markedly different nature and distribution of extraframework iron species in the steam-activated catalysts does not have a strong influence on the initial ODP performance. This observation contrasts with the active site structure sensitivity exhibited by these catalysts in other N<sub>2</sub>O conversions, including direct decomposition and SCR with

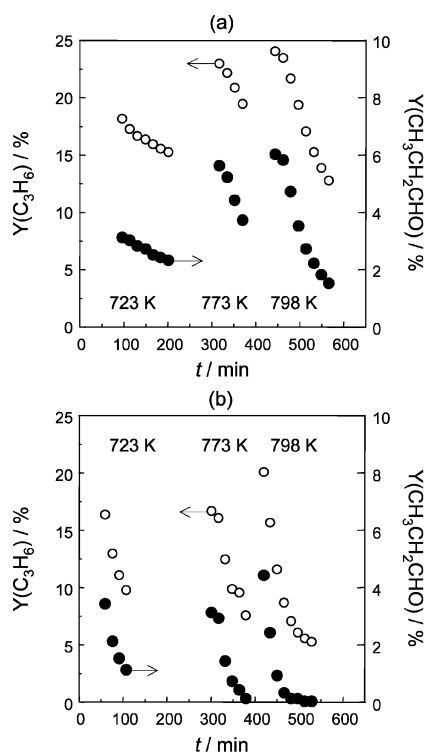
CO and C<sub>3</sub>H<sub>8</sub> in diluted feed mixtures.<sup>11</sup> The observed behaviour could be attributed to the different intrinsic mechanism of these processes: in direct N<sub>2</sub>O decomposition or SCR of N<sub>2</sub>O, removal of atomic oxygen from the catalyst surface is rate determining,<sup>12</sup> while propane activation determines the rate of the ODP reaction. What is clear from our results is that extraframework iron species in FeMFI catalysts are active and selective towards propene in ODP with N<sub>2</sub>O. In contrast, Uddin *et al.*<sup>6</sup> claimed that only framework iron of silicalite is selective towards the olefin in the ODP with O<sub>2</sub>. The similar initial performance of the Fe-zeolites also indicates that Brønsted and Lewis acidity in steam-activated FeZSM-5 plays a minor role in the N<sub>2</sub>O-mediated ODP reaction. The faster deactivation over Fe-silicalite compared to FeZSM-5 is remarkable, especially at 723 K (see Fig. 1). The acidity in FeZSM-5 should in principle accelerate the deactivation process due to coke formation, while the opposite was observed. This is tentatively attributed to the presence of mesopores in FeZSM-5, due to dealumination upon steam treatment, which are absent in Fe-silicalite.<sup>8,9</sup> The more open structure of FeZSM-5 may reduce pore blocking by coke and also improve transport of reactants and products, retarding deactivation.

Our results show that steam-activated FeMFI zeolites are highly efficient catalysts for oxidative dehydrogenation of C<sub>3</sub>H<sub>8</sub> with N<sub>2</sub>O using high partial reactant pressures. Initial propene yields of 21–24% at 773–798 K are very similar to state-of-the-art catalysts based on V and Mo oxides with O<sub>2</sub>. Over vanadia-based catalysts, N<sub>2</sub>O is a less effective oxidant than O<sub>2</sub> to obtain high propene yields,<sup>13</sup> corroborating the superior performance of FeMFI with N<sub>2</sub>O. Another feature of FeMFI relates to the high propionaldehyde yield, since this product has been never observed in ODP over typical oxide systems.

This novel application of FeMFI leads to the simultaneous functionalisation of propane, a relatively cheap and abundant feedstock, and utilisation of N<sub>2</sub>O, an environmentally harmful gas. This concept can be economically applied in tail-gases of specific chemical processes, e.g. those using HNO<sub>3</sub> as oxidizing agent, where N<sub>2</sub>O is produced in high concentration (typically 25–40 vol.%). This approach has been proposed for the selective oxidation of benzene to phenol with N<sub>2</sub>O in tail-gases from adipic acid plants.<sup>5</sup> An apparent drawback of steam-activated FeMFI catalysts in ODP is the rapid deactivation by coke. This issue can be easily overcome, since the initial performance is completely recovered after oxygen pretreatment at 773 K. The practical realisation of this process in continuous mode can be accomplished using a configuration of two reactors in parallel with alternating reaction–regeneration. Investigations in such a system are on the way.

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**Fig. 1** Yield of (○) propene and (●) propionaldehyde vs. time-on-stream over steam-activated (a) FeZSM-5 and (b) Fe-silicalite at different temperatures. Conditions: feed mixture of C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub>O/Ne = 10/10/80 and τ = 0.043 s g<sub>cat</sub> ml<sup>-1</sup>.