

Steam-activated FeMFI zeolites as highly efficient catalysts for propane and N₂O valorisation *via* oxidative conversions

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The reaction between C₃H₈ and N₂O 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%.¹ Exceptionally, higher propene yields have been reported over V–Mg–O catalysts (24%),² K/Mo catalyst supported on Si–Ti mixed oxides (30%),³ and Ba-promoted Ni–Mo–O catalysts (30%), using O₂ as the oxidant.⁴

The application of Fe-zeolites in oxidative transformations with N₂O was triggered by the accomplishments in hydroxylation of paraffins to alcohols and of aromatic hydrocarbons to phenols.⁵ Our strategy is to utilize the specificity of N₂O as a monooxygen donor and the capability of determined Fe species in the zeolite for coordinating α -oxygen to develop efficient catalysts for valorisation of propane and N₂O *via* oxidative conversions. Previous studies have reported high selectivities of MFI frameworks with iron towards oxidative dehydrogenation of light alkanes with N₂O and O₂ at a low degree of hydrocarbon conversions (2–10%), thus achieving a low yield of the olefin (<10%).^{6,7} 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 N₂O. Initial propene yields up to 24% are comparable with the highest values reported over V and Mo oxides with O₂. 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.^{8,9} The isomorphously substituted zeolites, with Fe–Al–Si and Fe–Si frameworks, were

calcined and activated in steam (30 vol.% H₂O in 30 ml (STP) min⁻¹ of N₂ flow) at 873 K during 5 h, yielding FeZSM-5 (Si/Al = 31 and 0.67 wt.% Fe) and Fe-silicalite (Si/Al $\sim \infty$ and 0.68 wt.% Fe). Commercial NH₄-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 SiO₂ (both 125–200 μ m), and contact times in the range of $\tau = 0.043$ – 0.097 s g_{cat} ml⁻¹ at atmospheric pressure. The feed consisted of 10 vol.% C₃H₈ and 10 vol.% N₂O 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. N₂O 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 C₃H₈ conversion. The increase in propane conversion was accompanied by a decrease in propene selectivity, from *ca.* 59 to 44%. Propionaldehyde (CH₃CH₂CHO) 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 α -oxygen (from N₂O) in Fe-zeolites has been typically found to be active for dehydrogenation or insertion into a C–H bond, forming the corresponding alcohol.^{5–7} In our experiments, very low concentrations of alcohols were found. Methane, ethylene, acetone, and acrolein, as well as CO and CO₂ 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 C₃H₈/N₂O/Ne = 10/10/80

| Catalyst | τ /s g _{cat} ml ⁻¹ | C balance (%) | T/K | Conversion (%) | | Selectivity ^a (%) | | Yield ^a (%) | |
|---------------|---|---------------|-----|-------------------------------|------------------|-------------------------------|-------------------------------------|-------------------------------|-------------------------------------|
| | | | | C ₃ H ₈ | N ₂ O | C ₃ H ₆ | CH ₃ CH ₂ CHO | C ₃ H ₆ | CH ₃ CH ₂ 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 |
| | 0.049 | 99.0 | 723 | 9.4 | 16.0 | 62.7 | 2.0 | 6.2 | 0.2 |
| H-ZSM-5 | 0.049 | 94.4 | 773 | 18.5 | 33.5 | 49.7 | 2.3 | 9.5 | 0.4 |

^a 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 N₂O conversions over Fe-zeolites, e.g. direct decomposition or selective oxidation of benzene to phenol.^{5,9,10}

Fig. 1 shows the yield of the iron zeolites vs. time-on-stream at different temperatures. The conversion of C₃H₈ and N₂O 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 O₂-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.¹¹ 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.^{8,9} 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 N₂O conversions, including direct decomposition and SCR with

CO and C₃H₈ in diluted feed mixtures.¹¹ The observed behaviour could be attributed to the different intrinsic mechanism of these processes: in direct N₂O decomposition or SCR of N₂O, removal of atomic oxygen from the catalyst surface is rate determining,¹² 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 N₂O. In contrast, Uddin *et al.*⁶ claimed that only framework iron of silicalite is selective towards the olefin in the ODP with O₂. 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 N₂O-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.^{8,9} 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 C₃H₈ with N₂O 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 O₂. Over vanadia-based catalysts, N₂O is a less effective oxidant than O₂ to obtain high propene yields,¹³ corroborating the superior performance of FeMFI with N₂O. 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 N₂O, an environmentally harmful gas. This concept can be economically applied in tail-gases of specific chemical processes, e.g. those using HNO₃ as oxidizing agent, where N₂O is produced in high concentration (typically 25–40 vol.%). This approach has been proposed for the selective oxidation of benzene to phenol with N₂O in tail-gases from adipic acid plants.⁵ 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.

Notes and references

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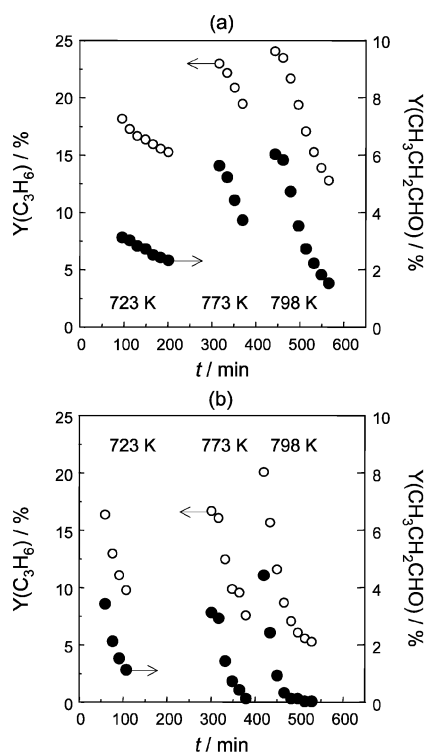


Fig. 1 Yield of (○) propene and (●) propionaldehyde vs. time-on-stream over steam-activated (a) FeZSM-5 and (b) Fe-silicalite at different temperatures. Conditions: feed mixture of C₃H₈/N₂O/Ne = 10/10/80 and τ = 0.043 s g_{cat} ml⁻¹.