

## Overcoming the Engineering Constraints for Scaling-Up the State-of-the-Art Catalyst for Tail-Gas N<sub>2</sub>O Decomposition

Melián-Cabrera, Ignacio; Espinosa, Silvia; Mentruit, Cristina; Murray, Blaine; Falco, Lorena; Socci, Joseph; Kapteijn, Freek; Moulijn, Jacob A.

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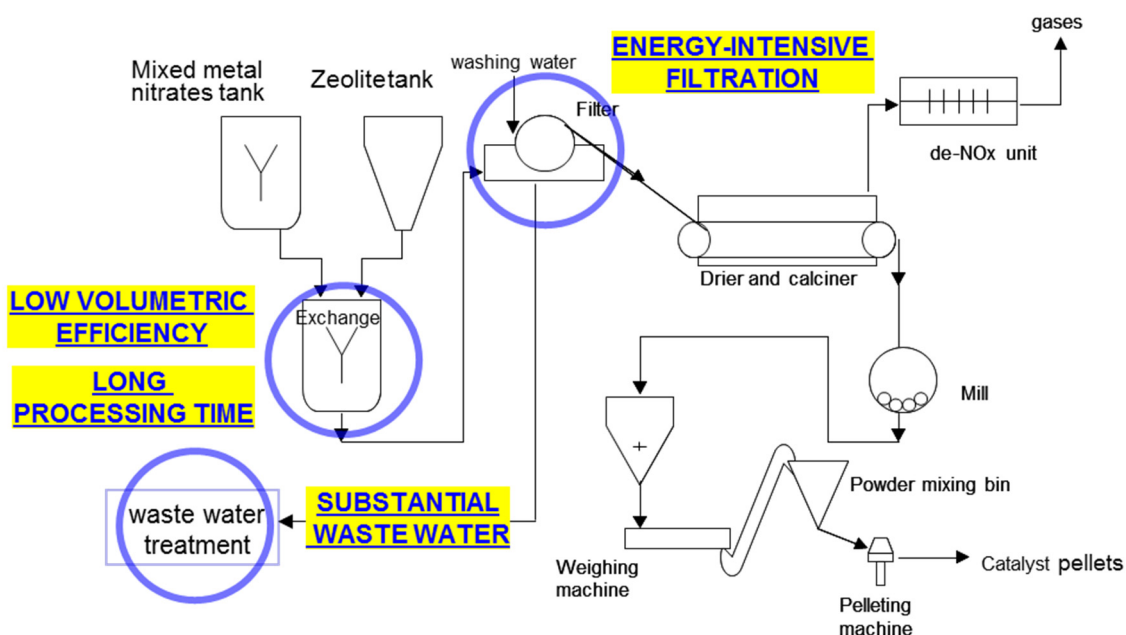
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GRAPHICAL ABSTRACT



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# Overcoming the engineering constraints for scaling- up the state-of-the-art catalyst for tail-gas N<sub>2</sub>O decomposition

Ignacio Melián-Cabrera,<sup>†\*</sup> Silvia Espinosa,<sup>§</sup> Cristina Mentrut,<sup>§</sup> Lorena Falco,<sup>†</sup> Freek Kapteijn<sup>§</sup> and  
Jacob A. Moulijn<sup>§</sup>

<sup>†</sup> European Bioenergy Research Institute (EBRI), School of Engineering and Applied Science, Aston  
University, Aston Triangle, Birmingham, B4 7ET, United Kingdom.

<sup>§</sup> Catalysis Engineering, Chemical Engineering Department, Delft University of Technology, Van der  
Maasweg 9, 2629 HZ Delft, The Netherlands.

KEYWORDS: environmental catalysis, scale-up, zeolites, N<sub>2</sub>O emissions, greenhouse gases.

**ABSTRACT**

An efficient process is reported for preparing a state-of-the-art Fe-ferrierite catalyst for N<sub>2</sub>O decomposition under industrial tail-gas conditions. In the synthesis procedure we evaluate the very demanding constraints for scale-up; *i.e.* large reactor volumes are typically needed, long processing times and considerable amounts of waste water is generated. The proposed synthesis minimizes the amount of water used, and therefore the amount produced waste water is minimal; in this approach there is no liquid residual water stream that would need intensive processing. This has remarkable benefits in terms of process design, since the volume of equipment is reduced and the energy-intensive filtration is eliminated. This route exemplifies the concept of process intensification, with the ambition to re-engineer an existing process to make the industrial catalyst manufacture more sustainable. The so-obtained catalyst is active, selective and very stable under tail gas conditions containing H<sub>2</sub>O, NO and O<sub>2</sub>, together with N<sub>2</sub>O; keeping a high conversion during 70 h time on stream at 700 K, with a decay of 0.01%/h, while the standard reference catalyst decays at 0.06%/h; hence it deactivates six times slower, with ~5% absolute points of higher conversion. The excellent catalytic performance is ascribed to the differential speciation.

## 1. Introduction

The decomposition of  $\text{N}_2\text{O}$  into  $\text{N}_2$  and  $\text{O}_2$  is a reaction with proven environmental benefits.<sup>1,2</sup>

The greenhouse warming potential (GHWP) of  $\text{N}_2\text{O}$  is 250-300 higher than that of  $\text{CO}_2$ ,<sup>3</sup> which means that eliminating relatively small  $\text{N}_2\text{O}$  gas emissions will have a large impact in terms of  $\text{CO}_2$  equivalent reduction, as compared to  $\text{CH}_4$  (GHWP of 28-36). Moreover,  $\text{N}_2\text{O}$  plays a role in ozone depletion.  $\text{N}_2\text{O}$  gas is principally emitted from anthropogenic sources; agriculture and chemical industry being the major sources. The chemical industry contributes in two major areas, viz., as by-products of adipic and nitric acid production. An attractive approach to synthesize  $\text{N}_2\text{O}$ -free adipic acid has been proposed by a photochemistry based approach using ozone and UV light,<sup>4</sup> but currently the major adipic acid producers still apply cost-effective  $\text{N}_2\text{O}$  abatement technologies or  $\text{NO}_x/\text{N}_2\text{O}$  retrofitting into the nitric acid process.<sup>5</sup> Also in the case of nitric acid production plants, it is expected that these abatement routes will play a major role in the future, since retrofitting in existing plants will be needed for at least several decades. Several options have been claimed to deal with this. Metal oxide-based catalysts have been proposed for high temperature operation conditions, for instance below the Pt-Rh gauzes in the ammonia oxidation reactors.<sup>6,7</sup> End-of-pipe catalysed direct  $\text{N}_2\text{O}$  decomposition has been recognized as an economically feasible option, in existing plants and it does not modify the nitric acid production.<sup>8</sup>

This work deals with the constraints to scale-up a state-of-the-art catalyst, leading to a new catalyst synthesis concept for the  $\text{N}_2\text{O}$  decomposition reaction under industrial tail-gas conditions. Ferrierite has been recognized as the most active zeolite support in combination

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3 with Fe species for this reaction under end-of-pipe conditions. The catalyst is prepared in such a  
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5 way that the methodology can be considered optimal for scale-up, and can be embedded in the  
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7 green chemistry<sup>9</sup> and process intensification principles.<sup>10</sup> Due to the carefully-selected synthesis  
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9 conditions, the overall process is simplified significantly in terms of less steps required, and  
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11 reduced size of equipment.  
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17 The N<sub>2</sub>O decomposition reaction can be catalysed by Fe-based zeolites, such as ZSM-5,<sup>11-15</sup>  
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19 Ferrierite,<sup>16-19</sup> beta<sup>11,19-23</sup> and TNU/IM-type zeolites.<sup>24</sup> Various methods have been proposed for  
20  
21 Fe incorporation, including wet-ion exchange, solid-state ion exchange, isomorphous  
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23 substitution, steaming, chemical vapour deposition, among others. Wet-ion exchange is a  
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25 simple methodology where a Fe-salt, dissolved in water, is contacted with the zeolite and  
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27 Fe(II)/Fe(III) cations are exchanged on the Brønsted sites resulting in a Fe-exchanged zeolite.  
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33 Wet-ion exchange appears to be the simplest procedure commercially, resulting in a  
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35 reproducible methodology. Various disadvantages, however, appear when the process would  
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37 be scaled-up. Figure 1 shows a simplified process flow diagram for a metal-exchanged zeolite  
38  
39 production facility based on wet ion exchange. The major drawbacks are highlighted as follows:  
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41 1) large volumetric reactors are needed; typically liquid/solid ratios higher than 5 kg<sub>liquid</sub>/kg<sub>solid</sub>  
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43 are used, implying the need of large-volume reactors or, in other words, the conventional  
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45 reactors work at a low volumetric efficiency; 2) the ion-exchange involves long processing times  
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47 of around 10 to 24 h, which makes the process discontinuous; 3) a large amount of waste water  
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49 is formed during the exchange, washing and filtering of the exchanged zeolite. As an example,  
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51 for producing 10 t/day of catalyst, the generated waste water is around 50 m<sup>3</sup>/day for the  
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3 exchange only.<sup>25</sup> Such amount of produced waste water requires extra equipment for storage,  
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6 and most importantly, the water has to be treated before disposal to the surface water or  
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9 municipal sewer system; usually nitrates are extensively present and denitrification based on  
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11 bacterial degradation is commonly applied that makes the process costly.<sup>26</sup> Finally, 4) filtration  
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13 is energy intensive, with high processing costs due to the small size of the zeolite grains. Based  
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15 on the above reasoning, new catalyst synthesis strategies for addressing these bottlenecks are  
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18 to be developed, which is the basis of this work.  
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## 21 22 **2. Experimental**

### 23 24 25 **2.1 Chemicals**

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28 The used chemicals are HNO<sub>3</sub>, Merk 65.0 wt.%; Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Acros 99.0 % metal basis;  
29  
30 NH<sub>4</sub>NO<sub>3</sub>, Merk extra pure; hydrofluoric acid, Merk 40%. Ferrierite Ferrierite was kindly  
31  
32 supplied by Tosoh, with material reference 720 KOA.  
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### 36 37 **2.2 Zeolite pre-treatment**

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39 The as-received commercial zeolite having an FER structure (Figure 2A) is in the sodium-  
40  
41 potassium form, and is formed by agglomerates of platelets and cylinders of different sizes and  
42  
43 shapes. The average particle size ranges from 0.5 to 2 μm as determined by SEM, Figure 2B. The  
44  
45 sample was exchanged twice with a NH<sub>4</sub>NO<sub>3</sub> solution to get the ammonium form: once using a  
46  
47 saturated solution (2.0 M at 353 K for 24 h) and then a milder exchange was applied (1.0 M  
48  
49 same temperature and time). Between the ammonium treatments, the sample was filtered and  
50  
51 washed repeatedly with distilled water to remove residual Na<sup>+</sup> and K<sup>+</sup>. The effectiveness of this  
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53 exchange procedure was verified by ICP elemental analysis, as reported in Table 1. Cation  
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3 exchange efficiencies of >99.9% for Na<sup>+</sup> and 99.8% for K<sup>+</sup> were obtained. We should note that  
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5 this step is unavoidable. If the Fe(III) exchange is carried out on the Na/K form zeolite, the Fe  
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7 cations would precipitate due to the high pH, resulting in a poor catalyst performance.  
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11 This step also produces quite some residual water, which could be optimized using the same  
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13 concept as described here for the Fe-zeolite preparation. However, at this stage we found the  
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15 NH<sub>4</sub>NO<sub>3</sub> washing step less attractive academically, compared with the Fe-exchange itself. Thus,  
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17 the overall process is not yet fully optimized.  
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## 24 **2.3 Catalyst preparation**

### 25 **2.3.1 Static mode**

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27 The Fe(NO<sub>3</sub>)<sub>3</sub> solution was prepared considering the total pore volume of the zeolite  
28  
29 with a slight excess; the concept of the 'total liquid pore volume' is illustrated in Figure  
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31 3. In total, a ratio of 2.5 ml solution/g zeolite was employed. The pH was adjusted in the  
32  
33 following way. Milli-Q water was adjusted to pH = 2 using diluted HNO<sub>3</sub>. The Fe-  
34  
35 precursor was added to this solution, and the resulting solution was added to the NH<sub>4</sub>-  
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37 zeolite (described in 2.2). The exchange was performed at three increasing ageing times:  
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39 1, 6 and 24 h, resulting in three different samples. The preparation was carried out at  
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41 room temperature and after the Fe-exchange, water was removed by heating the  
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43 sample at 363 K in a stove furnace overnight.  
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### 51 **2.3.2 Dynamic mode**

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53 The procedure is very similar to the previous one. The solution was prepared in the  
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55 same way, but after adding the zeolite, the sample was continuously stirred by means of  
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3 a 2D shaker, as shown in Figure 3B. The ageing time was varied for 1, 6 and 24 h,  
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6 resulting in three different samples. After the exchange, all the water was evaporated  
7  
8  
9 using a rota-evaporator set-up at 353 K.

## 10 11 **2.4. Calcination**

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14 All the catalysts were calcined at 723 K for 4 h, prior to the activity tests.  
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## 17 **2.5 Catalyst characterization**

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20 The elemental content of Na, K, Fe, Si and Al was determined by ICP, of the previously dissolved  
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23 zeolites in a 6 wt.% HF solution, using a Perkin-Elmer Optima 3000DV.  
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27 SEM pictures were recorded with a Philips Scanning Electron Microscope (XL 20) at 10 kV. The  
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30 sample was *sputtered* with gold three times using a standard gas plate metallizing chamber.

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33 Temperature-programmed reduction with H<sub>2</sub> was performed in a Micromeritics TPD/TPR 2900  
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36 apparatus, using a high purity mixture of 10 vol.% H<sub>2</sub> in Ar as reducing mixture. A cold trap was  
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39 used to remove the water stemming from the reduction before the gas of the reactor outlet  
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42 was sent to the TCD. The experimental conditions were carefully chosen via the characteristic  
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45 parameter  $P (P = \beta \cdot S_0) / (\phi_v \cdot C_0)$ , where:  $S_0$  is the initial amount of reducible oxide (mol),  $\phi_v$  the  
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47  
48 total flow rate (cm<sup>3</sup>/min),  $\beta$  the heating rate (K/min) and  $C_0$  the initial H<sub>2</sub> concentration  
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51 (mol/cm<sup>3</sup>). The  $P$  parameter was smaller than 1 K, which is very conservative as compared to  
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53  
54 the recommended  $P \leq 20$  K by Malet and Caballero.<sup>29</sup>

## 55 **2.6 Catalytic activity tests**

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58 The activity tests were carried out in a parallel six-flow reactor set-up using approximately 50  
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61 mg of 125-250 μm catalyst particles. The applied conditions are as follows: 4.5 mbar N<sub>2</sub>O of a

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3 N<sub>2</sub>O/He mixture at a total pressure of 3 bar absolute, a space time of ~900 kg·s/mol  
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5 (W/F<sup>0</sup>(N<sub>2</sub>O) where W is the catalyst mass and F<sup>0</sup>(N<sub>2</sub>O) the molar flow of N<sub>2</sub>O in the feed). The  
6  
7 reactor outlet stream was analyzed on-line by gas chromatography; Chrompack CP 9001  
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9 equipped with a Poraplot Q column (for N<sub>2</sub>O and N<sub>2</sub>/O<sub>2</sub> separation) and a Molsieve 5A column  
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11 (for N<sub>2</sub> and O<sub>2</sub>). Helium is used as carrier gas in the GC analysis instead of nitrogen in order to  
12  
13 detect the nitrogen produced in the reaction. The catalysts were pretreated in a flow of He at  
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15 673 K for 1 h prior the reaction, and cooled down in the same gas to the starting reaction  
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17 temperature. Steady state was achieved after 1 h on-stream, since the composition of the  
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19 product flows were constant.  
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27 The catalyst was also tested under nitric acid-based tail gas conditions with the following  
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29 composition: 4.5 mbar N<sub>2</sub>O, 0.6 mbar NO, 15 mbar H<sub>2</sub>O and 75 mbar O<sub>2</sub>, maintaining the same  
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31 space time W/F<sup>0</sup>(N<sub>2</sub>O) of ~900 kg·s/mol at 3 bar(a) of total pressure. The feed is simulated by  
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33 adding these components from more concentrated mixtures in helium. Stability tests were  
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35 carried out under these conditions at 700 K for 70 h time on stream.  
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### 40 **3. Results and discussion**

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42 The preparation method is based on the 'total liquid pore volume' concept ( $V^{T-LIQ}$ ) to reach the  
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44 caking end-point.<sup>28</sup> The amount of solution used for exchange is enough to fill the  $V^{T-LIQ}$  of the  
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46 material; for practical purposes a slight excess of liquid is used resulting in a liquid/solid = 2.5  
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48 (ml/g). The excess of water is necessary to allow the mixing of the material during the exchange  
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50 and, in practice, making easier its handling. The low liquid use implies that the filtration step in  
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52 Figure 1 can be eliminated, simplifying the overall process scheme and reducing the operational  
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3 costs. In Figure 3, the typical experimental set-up is shown, where a two-dimensional shaker  
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5 was employed in order to homogenize the so-obtained slurry. Since the method uses a minimal  
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7 amount of water, this can be easily evaporated, while the anions are left on the zeolite's  
8  
9 surface. These anions decompose during the drying and calcination, and in a deNO<sub>x</sub> unit the  
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11 produced NO<sub>x</sub> is reduced into N<sub>2</sub>. Overall, this strategy avoids a large volume of nitrates  
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13 containing waste water, which would require denitrification with bacterial broths, which is  
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15 energy intensive and costly as reported elsewhere.<sup>26</sup> The amount of water used is two times  
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17 lower compared to the amount of water used in the most effective method in patent  
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19 literature.<sup>25</sup>  
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27 The preparation rheology was the first studied parameter. Two variants were considered: a  
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29 static versus a dynamic exchanging procedure. The main difference between them is that for  
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31 the dynamic mode the slurry is shaken during the exchange, while the other variant is fully  
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33 static. The results of the catalysts prepared by these two variants are presented in Figure 4 and  
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35 5; representing the N<sub>2</sub>O conversion as a function of the reaction temperature. The graphs  
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37 include various catalyst samples prepared at increasing exchange time (*i.e.* 1, 6 and 24 h). A  
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39 benchmarked Fe-FER catalyst having similar Fe loading, which gave excellent results in terms of  
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41 activity and stability, was used as reference standard.<sup>17</sup> This reference catalyst is the most  
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43 active for this reaction under end-of-pipe conditions;<sup>16,17,25</sup> it was prepared in house by wet-ion  
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45 exchange of iron nitrate at pH of 2.5 with 0.5 wt. % nominal loading of iron.  
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53 Results of the static-based catalysts do show quite some differences in the activity profiles  
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55 (Figure 4). For long exchange time (24 h), the activity decreased considerably. For exchange  
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3 times of 1 and 6 h the catalysts show similar levels of N<sub>2</sub>O conversion, which were always below  
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5 the performance of the reference catalyst. Because of the lower N<sub>2</sub>O conversion than the  
6  
7 reference catalyst, a dynamic variant was investigated subsequently.  
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11 The results are different for the dynamic wetness impregnation (Figure 5). Similar activity levels  
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13 were achieved for all the exchange times. It should be noted that the activity of all these  
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15 catalysts was as good as that of the reference catalyst. No significant differences by increasing  
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17 the exchange time were found; it means that it is possible to achieve a highly active N<sub>2</sub>O  
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19 decomposition catalyst by using a short exchange time with small liquid volumes.  
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24 An interpretation for the differences between dynamic and static conditions could be found in  
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26 the mass transfer: under stirred conditions concentration gradients in the slurry may cancel  
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28 out, improving the concentration distribution over the particles. Whereas under the static  
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30 mode, the metal deposition could further be occurring unevenly due to agglomerate formation.  
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35 The optimal Fe-FER catalyst (dynamic, 1 h) was tested under practical conditions of the nitric  
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37 acid plant tail-gases. These conditions are more appropriate than only in N<sub>2</sub>O/He in order to  
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39 evaluate its applicability as an end-of-pipe catalytic technology. Typical gases and  
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41 concentrations found in tail gases of nitric acid plants are NO (200 ppm), O<sub>2</sub> (2.5 vol.%) and H<sub>2</sub>O  
42  
43 (0.5 vol.%) together with N<sub>2</sub>O (1500 ppm). Figure 6 presents the N<sub>2</sub>O conversion for the optimal  
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45 Fe-FER catalyst both in N<sub>2</sub>O/He and in the presence of tail gas components. The presence of  
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47 tail-gas components has no significant impact on the catalyst performance. The activity  
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49 obtained under tail gas conditions was only slightly lower than with pure N<sub>2</sub>O/He; a very  
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51 positive result. Previous investigations on the effect of every individual component revealed a  
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3 clear promoting effect of NO, counterbalanced by water inhibition, while O<sub>2</sub> has a neutral  
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5 impact.<sup>17</sup>  
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9 The stability of the catalyst was further investigated by an isothermal test under tail gas  
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11 conditions with increasing time on stream (TOS) up to 70 h. In Figure 7 the stability is compared  
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13 with the reference catalyst. The obtained results are excellent; the optimal catalyst keeps a high  
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15 conversion during the whole period of time, with a decay of only 0.01%/h, while the reference  
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17 catalyst decays at a rate of 0.06%/h; *i.e.* the optimal catalyst deactivates six times slower over  
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19 the same TOS range. A second finding is that the optimal catalyst yields ~5% absolute points of  
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21 higher conversion than the reference catalyst.  
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28 Preliminary characterization shows that the Fe content was close to the nominal value, 0.47  
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30 wt.% Fe and the Si/Al ratio was 8.7. The slightly lower Fe loading than the theoretical value 0.50  
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32 wt.% can be explained by the H<sup>+</sup>/Fe<sup>3+</sup> competition during the exchange; as discussed  
33  
34 elsewhere.<sup>30</sup> The Si/Al ratio is comparable to that of the as-received zeolite material (8.9).  
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36  
37 Temperature-programmed reduction (TPR) characterization shed some light on the type of Fe  
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39 species formed during exchange, on both the optimal and reference catalysts. The TPR profiles  
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41 for both catalysts reveal two clear reduction peaks at low temperatures, at ~600 and ~700 K  
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43 (Figure 8). This region corresponds to the reduction of the Fe<sup>3+</sup> in exchanged positions (cations  
44  
45 and oxocations) on the zeolite framework.<sup>16</sup> The optimal catalyst shows a fraction of Fe<sub>2</sub>O<sub>3</sub>  
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47 species, represented by the broad peak centred at 800 K,<sup>30</sup> that accounts for *ca.* 10% of the Fe,  
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49 based on a TPR quantification method for Fe-zeolites.<sup>31</sup> The presence of only such a small Fe<sub>2</sub>O<sub>3</sub>  
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60 fraction is unexpected thermodynamically, if we take into account that the concentration of the

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3 used Fe solution was 100 times higher than the solution used for the reference catalyst:  
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6  $3.71 \times 10^{-2}$  M versus  $3.71 \times 10^{-4}$  M, respectively. In view of the solubility at pH = 2 of  $2.7 \times 10^{-3}$  M  
7  
8 (using  $K_{SP} = 2.7 \times 10^{-39}$ ),<sup>32</sup> precipitation of  $\text{Fe}(\text{OH})_3$  is thermodynamically expected for our catalyst  
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10 synthesis conditions. Apparently, the kinetics of the  $\text{Fe}^{3+}$  exchange is faster than the  $\text{Fe}(\text{OH})_3$   
11  
12 precipitation.  
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17 Several groups have evidenced that TPR provides relevant information on the Fe species  
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19 present. Guzmán-Vargas *et al.*<sup>16</sup> compared the performance of Fe-BEA, -ZSM-5 and -FER  
20  
21 catalysts with TPR results. They found for FER the largest amounts of “oxo-species” reducible at  
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23 low temperature. This was confirmed by Jíša *et al.*<sup>33</sup> who also reported a correlation between  
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25 the low-temperature reduction and the  $\text{N}_2\text{O}$  conversion; in both studies the dissociation of  $\text{N}_2\text{O}$   
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27 was studied under model conditions, *i.e.* not under realistic tail gas conditions.  
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33 The TPR patterns (Figure 8) evidence the presence of Fe-exchanged active species, namely  
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35 those reduced at  $\sim 600$  and  $\sim 700$  K, for the optimal catalyst as well as for the reference catalyst  
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37 (and some  $\text{Fe}_2\text{O}_3$  species for the optimal catalyst). The optimal catalyst has a different Fe  
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39 speciation than the reference catalyst, with more of the 700 K species; this is tentatively  
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41 attributed to a difference in distribution of the optimal active sites. This suggests that the  
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43 second Fe species reduction peak may represent the most optimal active sites. The sites  
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45 reduced at lower temperature are also active, otherwise the reference catalyst would not be  
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47 about equally active. Ultimately, the FeOx peak probably does not represent sites with a high  
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49 activity since it has a low intrinsic activity.<sup>11</sup>  
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#### 4. Conclusions

A synthesis strategy of Fe-Ferrierite, the state-of-the-art tail gas N<sub>2</sub>O decomposition catalyst, has been proposed circumventing constraints for scale-up. The method minimizes the amount of waste water produced and this has benefits from the process design point of view. The catalyst synthesis method utilizes only slightly more water compared to the total liquid pore volume of the zeolite. Consequently, it does not produce waste water that would require intensive processing. The catalyst shows excellent performance under end-of-pipe nitric acid conditions, which is attractive for retrofitting existing plants, with potential substantial savings in greenhouse gas emissions. In terms of process design, the proposed route simplifies the scale-up since the required equipment will be smaller (ion-exchange reactor) or can be avoided (filtration step). Further, the processing costs will be lower due to the low exchange times, and the elimination of filtration costs that are often considerable due to the small size of the zeolite grains.

#### AUTHOR INFORMATION

Corresponding Author: [i.melian-cabrera@aston.ac.uk](mailto:i.melian-cabrera@aston.ac.uk) (Ignacio V. Melián Cabrera)

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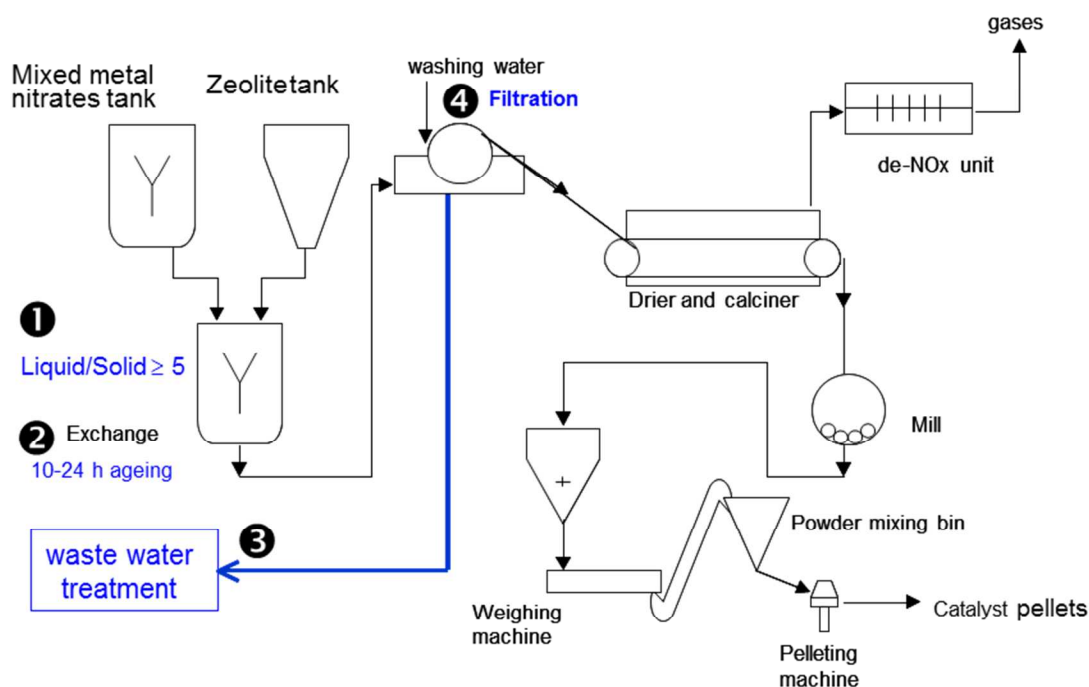
## FIGURES AND TABLES

**Table 1.** Na and K content before and after ion exchange  $\text{NH}_4$ -treatment of the parent ferrierite.

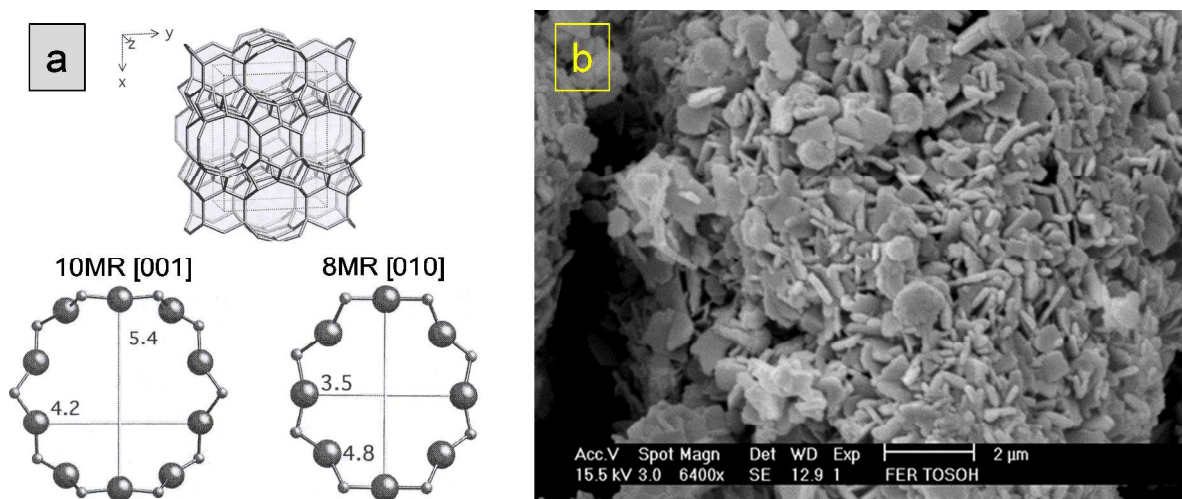
Material	Na	K
As-received <sup>a</sup>	1.2 wt. %	1.2 wt. %
After $\text{NH}_4$ -treatment	< 10 ppm (99.9) <sup>b</sup>	82 ppm (99.8) <sup>b</sup>

<sup>a</sup> Commercial specifications

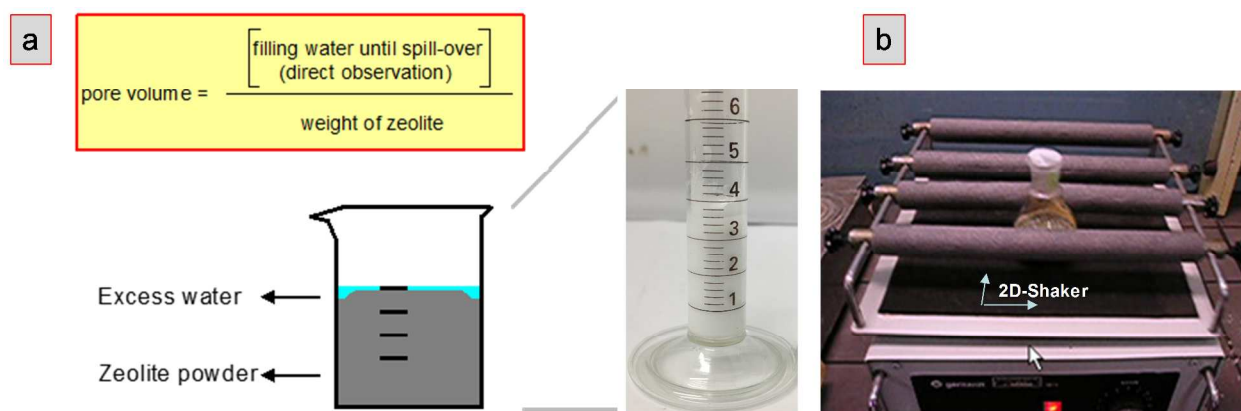
<sup>b</sup> Values between parentheses are the cation exchange efficiency (%).



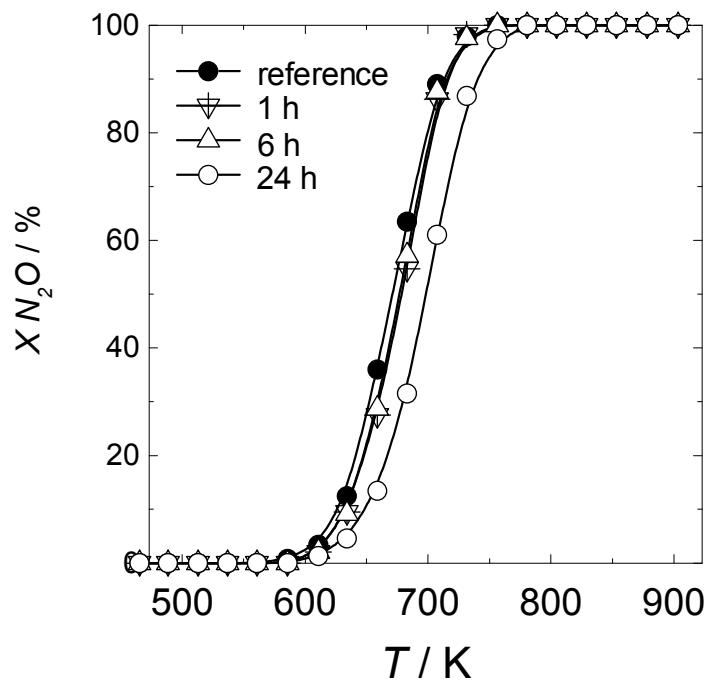
**Figure 1.** The constraints for the scale-up of a state-of-the-art Fe-Ferrierite  $\text{N}_2\text{O}$  decomposition catalyst are highlighted. The process flow diagram describes the steps of a Fe-exchange zeolite facility highlighting the major bottlenecks: **1)** high volumetric requirements; **2)** long exchange processing times (*i.e.* discontinuous process); **3)** a large volume of generated waste water that needs to be processed before emission, by denitrification based bacterial degradation and **4)** filtration is an energy-intensive and slow process, limited by the zeolite grain size.



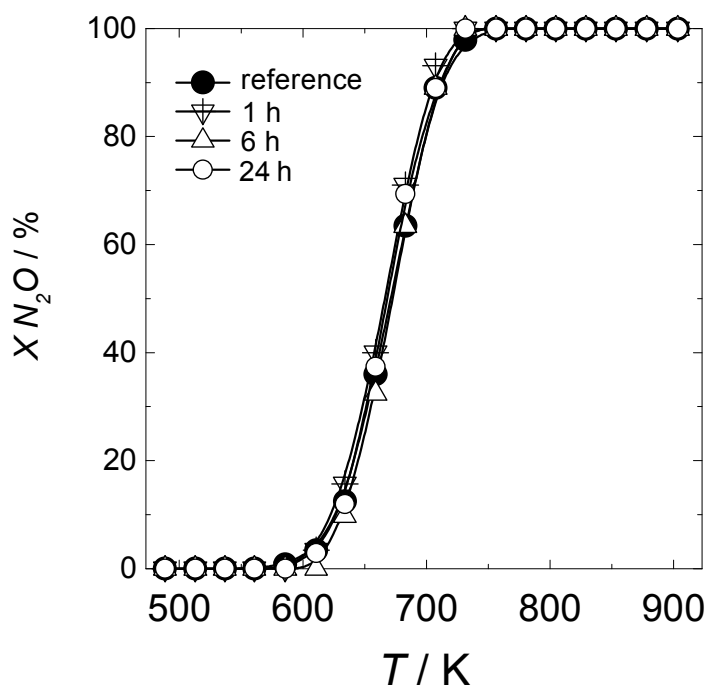
**Figure 2.** A) Top. FER framework. Bottom. 10-ring channel viewed along [001] and 8-ring through [010].<sup>27</sup> B) SEM picture of the investigated Ferrierite.



**Figure 3.** A) Definition of the 'total liquid pore volume' ( $V^{T-LIQ}$ ). This parameter is determined visually based on the method proposed by Innes.<sup>28</sup> Such values are higher than those determined from gas adsorption. B) Experimental set-up used for the dynamic  $\text{Fe}^{3+}$  exchange of this study.

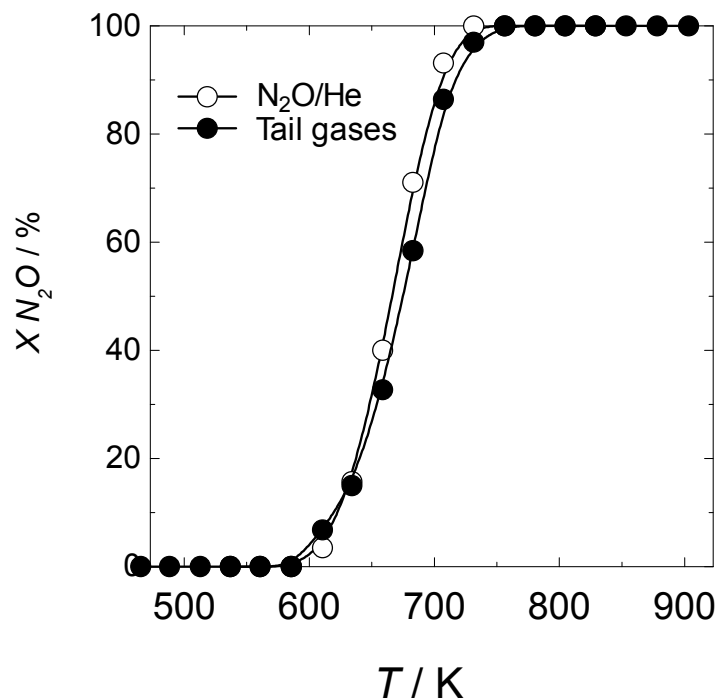


**Figure 4.** Static wetness impregnation for different exchange times.  $N_2O$  decomposition conversion as a function of the reaction temperature for 0.5 wt. Fe Fe-FER catalysts prepared under wetness conditions (liquid/solid = 2.5). Reaction conditions: 3 bar(a) total pressure and  $W/F = 8.95 \times 10^2$  kg·s/mol, He balance.

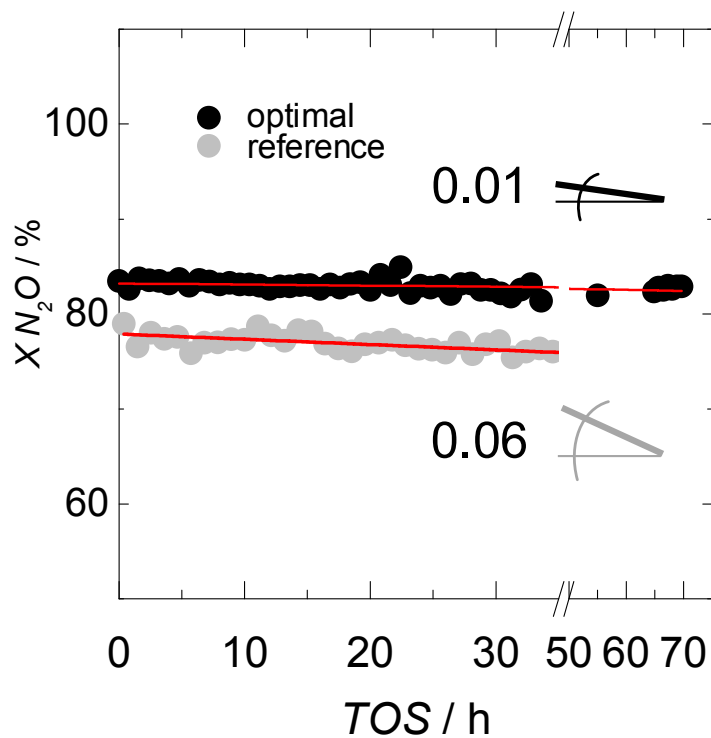


**Figure 5.** Dynamic wetness impregnation for different exchange times.  $N_2O$  decomposition conversion as a function of the reaction temperature for 0.5 wt. Fe Fe-FER catalysts prepared under wetness conditions (liquid/solid = 2.5). Reaction conditions: 3 bar(a) total pressure and  $W/F = 8.95 \times 10^2$  kg·s/mol, He balance.

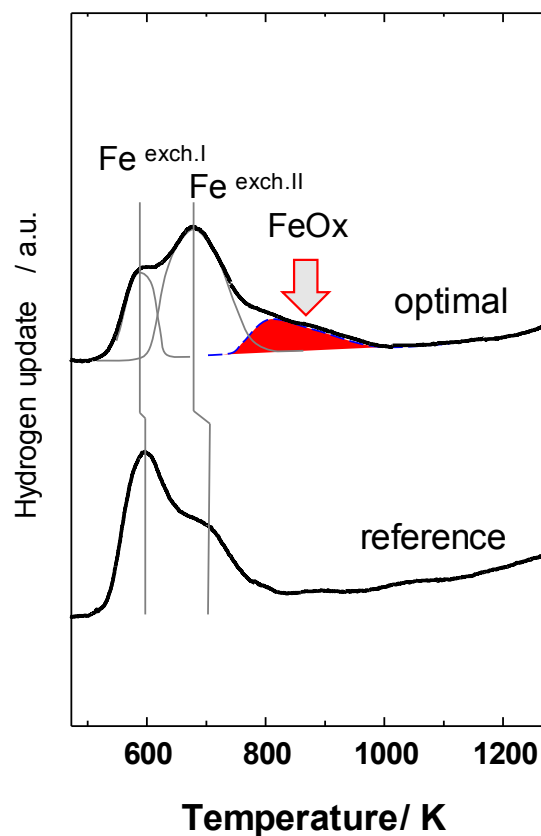




**Figure 6.** Comparison for the optimal catalyst (dynamic, 1h) under N<sub>2</sub>O/He (○, 1500 ppm N<sub>2</sub>O) and tail gas conditions (●, 1500 ppm N<sub>2</sub>O, 200 ppm NO, 2.5% O<sub>2</sub> and 0.5% H<sub>2</sub>O). Reaction conditions: 3 bar(a) total pressure and W/F = 8.95×10<sup>2</sup> kg·s/mol, He balance.



**Figure 7.** Stability test under tail gas conditions for the optimal and reference catalysts at 700 K, given as  $N_2O$  conversion as a function of the time on stream (TOS). Red lines are the linear regression correlations, and the indicated numbers are the slope as %/h. Reaction conditions: 3 bar(a) total pressure and  $W/F = 8.95 \times 10^2$  kg·s/mol, He balance.



**Figure 8.** H<sub>2</sub>-TPR profiles of the Fe-FER zeolites, optimal (dynamic, 1h) versus reference catalyst. Conditions: H<sub>2</sub>/Ar, 10%; ramp: 10 K/min. The FeO<sub>x</sub> contribution of the optimal catalyst is highlighted to indicate that it is relatively small as compared to what is expected from the thermodynamic values, as discussed in the text.