Ion exchanged Fe-FER through H2O2-assisted decomplexation of organic salts

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Published in:
Chemical Communications

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Decomposition of organic ligands through redox titration has been applied to catalyst synthesis, developing an improved preparation method for Fe-ferrierite (Fe-FER), the catalyst showing excellent performance and durability for N₂O decomposition under realistic conditions for nitric acid plants.

N₂O is nowadays mainly emitted by the nitric acid industry as an unwanted by-product. Direct end-of-pipe decomposition of the tail gas is a cost-effective technology. The estimated costs of this reduction technology is much lower than most CO₂ reduction technologies. For the Netherlands the abatement of the nitric acid plant N₂O emissions can already meet 30% of the Kyoto targets. Legislation will come soon and the market of N₂O-decomposition catalysts is developing. Since the pioneering work of Feng and Hall on over-exchanged FeZSM-5 catalysts, Fe-MFI catalysts have been widely studied and optimised for N₂O decomposition and selective catalytic reduction of NO. Different preparation methods have been developed, including wet ion exchange (WIE), sublimation of FeCl₃ (CVD), solid-state ion exchange (SSIE), and isomorphous substitution of Fe into the MFI framework and extraction by steaming. The discussion in the literature has been mainly focused on the reproducibility of the preparation method and the structure of the iron sites. The study on new zeolite matrices has received much less attention. Iron exchanged ferrierite (Fe-FER) has been claimed to be very active for N₂O decomposition by ion exchange. WIE appears to be the easiest preparation method to apply commercially. It can be controlled by accessible experimental parameters, resulting in very reproducible preparations.

According to WO 99/34901 catalysts are prepared via ion-exchange using ferric nitrate and NH₄-ferricrete, yielding the most active state-of-the-art Fe-catalyst for N₂O decomposition known. However, one important issue that remains unresolved is the waste generated during manufacturing (nitrates and NOx). Nitrates in waste water lead to eutrophication (massive growing of algae) in the emitted water. Denitrification is expensive since facultative heterotrophic bacteria are conventionally used for that. Sulphates are also employed. They also present similar problems as nitrates.

Alternatively, the use of organic Fe precursors which yield CO₂ (instead of NOx) and water during calcination will minimise the waste generated. Preliminary studies using iron citrate, acetate and oxalate revealed that the performance of these catalysts was inferior to the conventionally exchanged ferric nitrate ones. Organic salts form stable complexes with Fe cations, which hinder the exchange process. Such problem has already been reported and studied by Marturano et al. on Fe(II)-oxalate over ZSM-5. Uncharged species [Fe(C₂O₄)₂(H₂O)₃] accounted for ca. 30% of the total iron in solution. Additionally, the remaining [Fe(H₂O)⁶]²⁺ was not able to be fully exchanged on the zeolite since the oxalate complex was also blocking the zeolite pore mouths.

The concept presented here is to break down complexation equilibria by titrating the chelates with H₂O₂. The removal of ligands liberates Fe³⁺ cations and/or partially charged Fe(III) hydroxocomplexes. The exchange is expected to be improve.

A set of catalysts was prepared using iron citrate (FeC₆H₅O₇, SIGMA) as a precursor with 0.5 wt % iron loading. The choice of this salt was based on the solubility in water and cost. The complexation of citrates to Fe(III) is very strong, log KML/M₄₋ = 11.5, against 3.05 for Fe(II)-oxalate, which makes the citrate removal most challenging as being one of the worst cases. Additionally, citrate groups are bigger than oxalate ones (Fig. 1), which make its use for ion-exchange more difficult as they can block the entrance of the zeolite channels.

The Fe solution containing the desired amount of Fe (0.5 wt % in the final catalyst) was prepared and added to the zeolite (NH₄-FER, TOSOH Si/Al = 9), forming a kind of slurry containing the Fe precursor. Then, the appropriate amount of diluted H₂O₂ (Merck) was added to the slurry (molar ratio H₂O₂/citrate = 40). The total volume of the liquid added corresponded with ca. 150% of the pore volume of the zeolite. This approach is already known for impregnation (incipient wetness) but it is not normally applied in ion-exchange, where usually a large excess is used. The reaction time could be reduced to ca. 1 h including drying of the sample. Typically, ion-exchange is carried out for a much longer time (12–24 h). The N₂O-decomposition performance did not improve for longer times (not shown). After titration, the sample was dried at 373 K in the synthesis vessel for 2 h, and no washing was carried out. The sample was calcined at 823 K for 6 h.

The catalyst’s performance was tested in the decomposition of N₂O. Temperature is very important during the titration reaction.
with hydrogen peroxide. Fine-tuning experiments were performed at different temperatures: 333, 353 and 373 K. Fig. 2 shows the \( \text{N}_2\text{O} \) conversion level at 673 K for different titration temperatures. The optimal temperature was around 353 K. The activity level was even higher than the reference catalyst (Fe-FER prepared by conventional ion exchange, according to WO 99/34901). An intermediate temperature (ca. 353 K) is optimal to break down the complexation equilibria efficiently, and in a controlled fashion. The obtained results are not straightforward. Many phenomena occur during the removal of the ligands, for instance the hydrolysis of metal cations. Once the ligands are being removed, the metal cation starts to hydrolyse (Fe(III) to Fe(III)(OH)\(_x\)), which in the end gives inactive hydroxide species. The complexity of the situation may refrain people from using oxidising agents to remove ligands in catalyst preparation. Currently, research is ongoing to further clarify the effect of the synthesis parameters. It can be assumed that at lower temperatures the titration is slow and therefore not all the citrate complexes have decomposed. At the highest temperature, the kinetics of the titration is that fast that the Fe-exchange with the zeolite is too slow and the excess Fe\(^{3+}\) is hydrolysed to Fe(OH)\(_3\), which yields inactive species for \( \text{N}_2\text{O} \) decomposition. So, an intermediate temperature, where a balance between these competing processes is obtained, allows an optimal synthesis. Fenton-like oxidation involving hydroxyl radicals can occur as well. Ferric salts in the presence of \( \text{H}_2\text{O}_2 \) generate OH\(^-\) radicals which are strongly oxidizing agents. The rate of oxidation depends on the initial concentration of ferric ions. According to thermodynamic predictions of ferric citrate solutions, the presence of free Fe\(^{3+}\) is not negligible at the synthesis conditions employed. Therefore, both direct \( \text{H}_2\text{O}_2 \) and hydroxyl radicals may be involved during titration.

The Fe species in the catalyst have been characterised by TPR in the optimal catalyst (Figure 3). The Fe species detected are similar to those typically encountered in the ion-exchanged catalysts using Fe-nitrates: Fe–hydr(oxo) complexes stabilised in the zeolite cavities. Although the relative intensities of the peaks are different, it is clear that exchanged species are formed. No traces of (inactive) FeO\(_x\) clusters, that reduce at higher temperatures, were detected. The structure of the active Fe-complexes for this reaction is still under lively debate. The current work does not shed new light on this aspect.

The stability of the optimized catalyst (Fe-FER, \( \text{H}_2\text{O}_2\)-citrate-353) was tested under simulated conditions of a nitric acid plant for 45 h on-stream, including the presence of NO, O\(_2\) and \( \text{H}_2\text{O} \) together with \( \text{N}_2\text{O} \). The results obtained were excellent. It shows high stability (no deactivation, activity loss <2%) under such conditions.

The innovative aspect of the presented study is the use of a mild oxidant (\( \text{H}_2\text{O}_2 \)) to remove organic ligands present in solution during catalyst preparation. Strong complexating equilibria can be overcome during ion-exchange by controlled redox titration of the ligands. Hydrogen peroxide oxidizes citrate groups effectively, releasing Fe species at a controlled rate. This opens new ways to use organic salts of the metals in catalyst synthesis, which only renders water and carbon dioxide during titration. Additionally, hydrogen peroxide is decomposed in water and oxygen, which makes the preparation environmentally very attractive. As catalysts are specialty products, the market price of \( \text{H}_2\text{O}_2 \) is less critical than is usually the case in the chemical industry.

In conclusion, we have developed a new synthesis route involving less waste water, much shorter synthesis time and less undesired gas emissions in calcination. The \( \text{H}_2\text{O}_2\)-citrate Fe-FER is a greener synthesis route and an example of process intensification. An intensified process involves for instance less energy consumption, shorter time-to-market, but it does also require less waste emissions. Both aspects of the current study, the preparation...
and application of the catalyst in N₂O abatement, contribute to an intensified technology.

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Notes and references