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Research Note

# Active site structure sensitivity in $N_2O$ conversion over FeMFI zeolites

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## Abstract

Preparation of steam-activated Fe-silicalite containing mainly isolated iron species in extraframework positions was essential for deriving structure-activity relationships in various $N_2O$ conversion reactions over iron zeolite catalysts. Characterization by UV–Vis/DRS revealed that any significant clustering of iron did not occur in this sample. Other steam-activated FeMFI zeolites, with different framework compositions or treated at higher temperatures, showed various degrees of clustering. The activity of the cluster-free Fe-silicalite was significantly higher in $N_2O$ reduction with $C_3H_8$ and CO. However, some level of association of iron species leads to higher activities in direct $N_2O$ decomposition. Due to the intrinsic reaction mechanism, this result demonstrates the sensitivity of reactions for the form of the iron species in Fe-zeolites, rather than the existence of a *unique* active site.

*Keywords:* $N_2O$ decomposition; $N_2O$ reduction; FeMFI; Steam treatment; Iron species; Active site; Isolated ions; Oligonuclear species; Iron oxide; Reaction mechanism

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## 1. Introduction

The origin of the catalytic activity in the various reactions catalyzed by Fe-zeolites has been intensively debated over the last decade. Despite considerable effort to characterize these materials, available data are not yet sufficient to conclude exclusively on the structure of the active iron. Binuclear iron species in FeZSM-5 have been designated as the active site in various reactions, including selective oxidation of benzene to phenol with $N_2O$, direct $N_2O$ decomposition, and selective catalytic reduction (SCR) of $NO_x$ with hydrocarbons [1–3]. However, in the last reaction, small oligonuclear species of composition $Fe_4O_4$ [4] and isolated iron ions [5,6] have also been proposed as active sites.

The unification of the various interpretations with respect to "the active sites" is extremely complicated due to the intrinsic heterogeneous nature of iron species in the catalyst. Application of widely different preparation approaches and amounts of iron in the catalyst, which strongly affects the variety and relative amount of iron species, makes it more intricate. Particularly challenging in practice is suppressing clustering of iron species into large inactive iron oxide particles. A further complicating aspect for a rational unification is the application of Fe-zeolites in a wide range of catalytic reactions with a different intrinsic mechanism.

In this paper, steam-activated FeMFI zeolites with a different distribution of iron species have been synthesized and characterized by UV–Vis/DRS and HRTEM. Syntheses were aimed at suppressing clustering or association of iron species in the final catalyst. The catalysts were tested in $N_2O$-related reactions with a markedly different mechanism, viz. $N_2O$ decomposition and $N_2O$ reduction using $C_3H_8$ (in excess oxygen) or CO. From the characterizations and testing, relevant structure-activity relationships have been derived. Isolated iron species are essential in $N_2O$ conversions involving reducing agents, while some degree of iron clustering appears favorable in direct $N_2O$ decomposition. The intrinsic reaction mechanism determines the required structure of the active sites in FeMFI zeolites.

## 2. Methods

Details on the hydrothermal synthesis of FeMFI zeolites (with Fe–Al–Si, Fe–Ga–Si, and Fe–Si frameworks), as

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well as the calcination and ion-exchange treatments previous to steam activation, have been described in recent publications [7,8]. The isomorphously substituted zeolites were activated in steam (30 vol% $H_2O$ in 30 ml (STP) $min^{-1}$ of $N_2$ flow) at two different temperatures (873 and 1173 K) for 5 h. Hereafter, the catalysts are denoted followed by the steam temperature, e.g., FeAlZSM-5 (873 K). UV–Vis/DRS measurements were carried out in a Cary 400 spectrometer (Varian) equipped with a diffuse reflectance accessory (Harrick). To reduce light absorption, samples were diluted with $\alpha$-$Al_2O_3$ (calcined at 1473 K for 4 h) in a ratio of 1:5. HRTEM was carried out on a Philips CM 30 T electron microscope.

Catalytic activity was measured in a parallel reactor system, similar to that described in [9], using 50 mg of catalyst (125–200 µm) and a space time of $8.65 \times 10^5$ g s $mol^{-1}$. The space time is defined as the ratio $W/F(N_2O)_o$, where $W$ is the catalyst mass and $F(N_2O)_o$ the molar flow of $N_2O$ at the reactor inlet. Three reactions were investigated: (1) direct $N_2O$ decomposition (1.5 mbar $N_2O$ in He), (2) reduction of $N_2O$ by CO (1.5 mbar $N_2O$ + 1.0 mbar CO in He), and (3) selective catalytic reduction of $N_2O$ with $C_3H_8$ in the presence of excess oxygen (1.5 mbar $N_2O$ + 1.5 mbar $C_3H_8$ + 50 mbar $O_2$ in He). Before reaction, the catalysts were pretreated in the corresponding feed mixture at 723 K for 1 h. A gas chromatograph equipped with TCD and FID detectors was used to analyze reactant and product gases.

## 3. Results and discussion

### 3.1. Nature of iron species in the catalysts

A detailed characterization of the as-synthesized zeolites upon calcination and steam treatment has been reported elsewhere [7,8]. The iron content in FeAlZSM-5 (Si/Al = 31.3 and 0.67 wt%), FeGaZSM-5 (Si/Ga = 32.6 and 0.58 wt%), and Fe-silicalite (Si/Al $\sim \infty$ and 0.68 wt% Fe) catalysts was very similar. The zeolites also have similar and relatively uniform crystal sizes ($\sim$ 2.5 µm), as determined by SEM. The visual appearance of steamed FeAlZSM-5 and FeGaZSM-5 compared to that of Fe-silicalite (activated at 873 K in 30 vol% $H_2O$) already suggested a different catalyst constitution with respect to iron. Fe-zeolites with Al and Ga are light brownish, which is evidence of a certain accumulation of iron oxide/hydroxide in the zeolite. Fe-silicalite was nearly white, suggesting the more isolated nature of the iron species in the catalyst.

The UV–Vis/DRS spectra of the samples were essential for conclusions on the nature of the iron species, especially supporting and complementing previous characterizations over the same materials [7,8,10,11]. Fig. 1 shows the UV–Vis/DRS spectra of FeAlZSM-5 (873 K) and Fe-silicalite (873 K). Spectra of FeGaZSM-5 (873 K) and Fe-silicalite (1173 K), very similar to FeAlZSM-5 (873 K), are not shown here for conciseness. Two intense $Fe^{3+} \leftarrow O$ charge-transfer bands are observed in FeAlZSM-5, while Fe-silicalite only shows a single band at low wavelengths. Bands between 200 and 300 nm are typically assigned to isolated $Fe^{3+}$ species, either tetrahedrally coordinated in the zeolite framework or with higher coordination [12,13], while bands between 300 and 450 nm are attributed to small oligonuclear iron species, $(FeO)_n$. Generally $d$–$d$ transitions of $Fe^{3+}$ are expected in the range 350–550 nm, but they are symmetry and spin forbidden and, therefore, extremely weak [13]. In addition, they partly overlap with the tail of the low-energy charge-transfer bands.

Extraction of tetrahedral iron to extraframework positions in FeAlZSM-5 (873 K) and FeGaZSM-5 (873 K) was virtually complete, as shown by $^{57}$Fe Mössbauer spectroscopy and voltammetric response techniques [7,8]. Smaller extraframework iron species, including isolated iron ions and oligonuclear species in the zeolite channels, have been identified in the UV–Vis spectra and support previous charac-

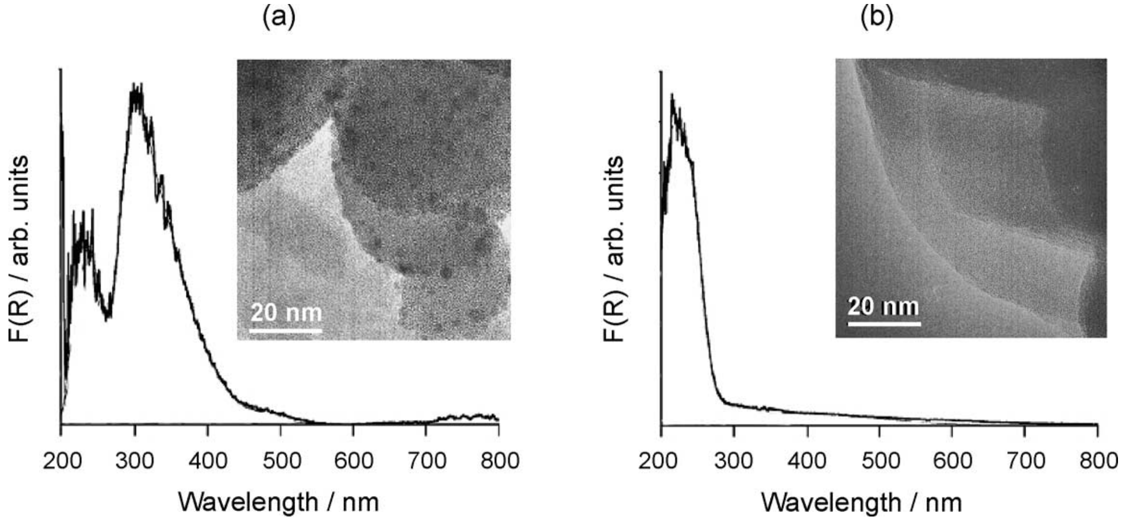

Fig. 1. UV–Vis/DRS spectra of (a) FeAlZSM-5 (873 K) and (b) Fe-silicalite (873 K). Insets: HRTEM micrographs of the samples.

terizations [8,10]. In addition, relatively small iron oxide nanoparticles of 1–2 nm were observed by HRTEM (inset in Fig. 1a), which clearly indicates the extensive degree of clustering during steam activation of these samples. The absorption around 500 nm in the UV–Vis/DRS spectrum of FeAlZSM-5 (873 K) is typical for absorption of Fe(III) ions in this aggregate form.

The complete absence of the band in the range of 300–450 nm in Fe-silicalite (873 K) indicates that the majority of $Fe^{3+}$ species in this catalyst are uniform and well isolated. Previous characterization by voltammetric response techniques showed that a fraction of iron in this sample remains in the framework, but this fraction is small compared to the extraframework species [8]. Such extraframework isolated species exhibit a high coordinative unsaturation [14]. The absence of iron clustering in Fe-silicalite (873 K) has been corroborated by voltammetry [8] and HRTEM, where no iron oxide nanoparticles were observed (inset in Fig. 1b). Increasing the steam-activation temperature of Fe-silicalite to 1173 K leads to a light brownish catalyst, indicating iron clustering. From the characterization of this material here and elsewhere [8], it was concluded that these iron species were similar to those in FeAlZSM-5 and FeGaZSM-5 (873 K).

### 3.2. Catalytic activity in $N_2O$ conversions

The different nature of iron species in the catalysts has a strong influence on the catalytic performance in various investigated $N_2O$-related reactions. $N_2O$ conversion vs temperature in different feed mixtures is shown in Fig. 2. The conversion curves of FeAlZSM-5 (873 K), FeGaZSM-5 (873 K), and Fe-silicalite (1173 K) in direct $N_2O$ decomposition are very similar. For the sake of clarity, only FeAlZSM-5 is shown in the figure. The similar light-off temperature and activation energy ($\sim 140\ \mathrm{kJ\,mol^{-1}}$) nicely correlate with the identical nature of iron species in these catalysts. The activity of these samples is higher than that of Fe-silicalite (873 K), which is shifted $\sim 40$ K to higher temperatures. In this case, a slightly higher activation energy was obtained ($155\ \mathrm{kJ\,mol^{-1}}$), suggesting the participation of different iron species in the process. Activation energies were estimated around the inflection (50% conversion) of the activity vs temperature curves by assuming a plug-flow model and first-order reaction in $N_2O$.

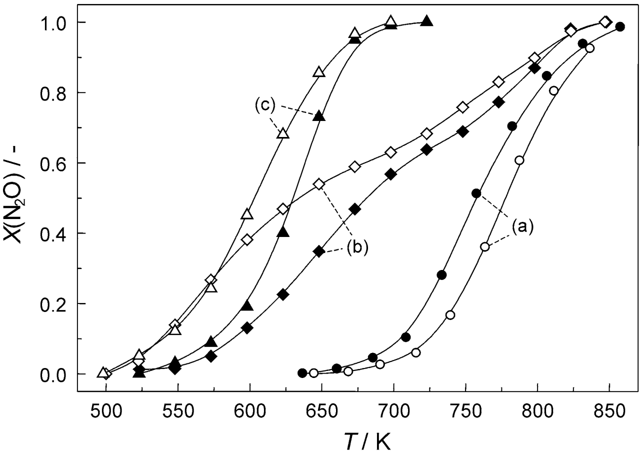

Fig. 2. $N_2O$ conversion vs temperature over Fe-silicalite (873 K) (open symbols) and FeAlZSM-5 (873 K) (solid symbols) in (a) 1.5 mbar $N_2O$ in He, (b) 1.5 mbar $N_2O$ and 1.0 mbar CO in He, and (c) 1.5 mbar $N_2O$, 1.5 mbar $C_3H_8$, and 50 mbar $O_2$ in He; $W/F(N_2O)_o = 8.65 \times 10^5\ \mathrm{g\,s\,mol^{-1}}$; $P = 1$ bar.

Addition of reducing agents ($C_3H_8$ or CO) to the feed mixture lowers the operation temperature of the catalysts by $\sim 150$ K. The $N_2O$ conversion over Fe-silicalite (873 K) in $N_2O + C_3H_8 + O_2$ and $N_2O + CO$ mixtures was significantly higher as compared to the other catalysts. The $N_2O$ conversion over this catalyst starts at the same temperature using either $C_3H_8$ or CO and separates above 575 K. The higher activity of Fe-silicalite (873 K) in the low-temperature range of these processes (500–600 K) compared to the other samples is of special significance. Above 873 K, the activity curves of the catalysts converge. Not only the $N_2O$ conversion is enhanced over Fe-silicalite (873 K) but also the conversion of $C_3H_8$ and CO to $CO_2$. This indicates that conversions of $N_2O$ and reducing agent are activated and effectively coupled. In particular, the higher activity of Fe-silicalite in SCR of $N_2O$ with $C_3H_8$ suggests that hydrocarbon activation occurs over iron species. This was previously suggested by other authors [15] using Na-ZSM-5 ion-exchanged with Fe-sulfate or nitrate for $N_2O$ reduction with $CH_4$. Acidity does not seem to play a decisive role in the process, which is hard to conclude from experiments using zeolitic supports with Brønsted acidity. In the $N_2O$ + CO mixture a transition is visible. When the limiting reactant CO becomes exhausted ($\sim 66\%$ $N_2O$ conversion), the $N_2O$ conversion curve shifts to that of the pure $N_2O$ decomposition.

It should be stressed that the activation of $N_2O$ to produce $O_\alpha$ species is an essential step in the reactions investigated here and is controlled by the presence of extraframework iron species. In an earlier work [16], we demonstrated that extraframework Al or Ga species as well as Brønsted sites in the catalysts play a minor role in $N_2O$ activation. Having this as a solid basis, the activity differences between FeAlZSM-5 (873 K) and Fe-silicalite (873 K) in Fig. 2 are strictly related to the distinct nature of the (extraframework) iron species in the catalysts. The similarity between the iron species and activities of FeAlZSM-5 (873 K), FeGaZSM-5 (873 K), and Fe-silicalite (1173 K) further supports our previous conclusion.

The preparation method of iron-zeolites has been recognized as critical in order to obtain reproducible catalysts with a desired performance [4,7,17]. A distribution of iron species is normally obtained upon activation of catalysts by available methods. Suppressing clustering of iron species into iron oxide is convenient, since these species are proven inactive at low temperatures in the various reactions catalyzed by Fe-zeolites [1,3,4,8,18,19]. We have recently reported [8] that steam activation of isomorphously substituted FeMFI zeolites (with $< 1$ wt% Fe) enables a certain control of the degree of iron clustering, and thus on the relative amount of certain species in the final catalyst, as compared to other methods. A rather unique achievement has been attained here with Fe-silicalite (873 K), in view of the remarkable uniform nature of extraframework species in isolated positions. A minor association of iron species is present in this sample. The presence of Al or Ga in such a structure destabilizes framework iron, leading to extraction and clustering of extraframework species, as also happens by steam activation at higher temperatures with Fe-silicalite (1173 K) [8,13].

The activity order of the different catalysts in Fig. 2 strongly depends on the reaction investigated. Isolated extraframework iron sites, present in the largest relative proportion in Fe-silicalite (873 K), appear essential in $N_2O$ processes involving reducing agents, showing higher $N_2O$ and $C_3H_8$ (or CO) conversions (or the same conversion at lower temperatures) than catalysts with a more extensive degree of iron clustering. The small remaining fraction of framework iron in Fe-silicalite (873 K) is inactive for $N_2O$ activation [16], so their controlled extraction as isolated sites could even lead to a higher activity differences. On the contrary, samples with a larger clustering of iron, either by a different framework composition or higher steam activation temperature, are more active in direct $N_2O$ decomposition. This activation is not caused by the presence of iron oxide nanoparticles observed in TEM (1–2 nm), but oligonuclear species in extraframework positions [8]. The difference in activities between Fe-silicalite catalysts steam-activated at 873 or 1173 K was in principle assigned to the suboptimal extraction of inactive framework iron in the first sample. But a very pronounced extraction of iron was observed in this sample, so it is rather due to a different constitution of extraframework species. The apparent activation energy of both samples differs, indicating that different species are involved in the process.

Elaborating further on what is understood by "active iron species" is required at this stage. In $N_2O$-related conversions, an iron site can be considered as being active when it easily desorbs molecular oxygen (in $N_2O$ decomposition) or transfers atomic oxygen (in reduction and/or oxidation reactions), starting from Fe–O. This ability should in principle not be exclusive of a certain structure of the site. The operation temperature is often used for labeling a species as "active." Following the previous definition, one can say that in $N_2O$ conversions involving reducing agents, isolated iron sites are the active sites, in view of the higher activity of Fe-silicalite (873 K). It is, however, more appropriate to reformulate this concept and state that isolated iron ions are more reactive toward atomic oxygen transfer to CO or $C_3H_8$ at a lower temperature. At a somewhat higher temperature, other iron species, e.g., oligonuclear iron species, may become operative too. Analogously, in direct $N_2O$ decomposition, oligonuclear iron species appear to facilitate molecular oxygen desorption at the lowest temperature, not excluding other species to contribute at higher temperature, like the isolated iron.

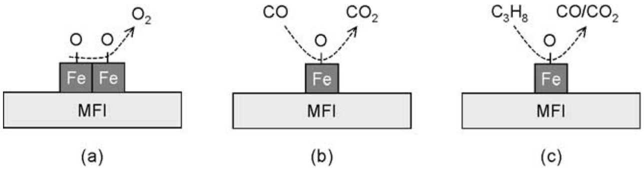

Fig. 3. Schematic mechanisms of the reactions investigated: (a) direct $N_2O$ decomposition, (b) $N_2O$ reduction with CO, and (c) $N_2O$ reduction with $C_3H_8$ under excess oxygen. Atomic "O" results from the activation of $N_2O$ over the extraframework iron site ($N_2O + ^* \rightarrow N_2 + O^*$).

Here, not only oligonuclear iron species could act as a temporary storage for the first oxygen atom but even the zeolite matrix can act as such, important in the case of isolated iron species. Evidence for this can be deduced from experiments with $^{18}O$-labeled $N_2O$ [20,21]. In these experiments much more $^{18}O$ could be accommodated in the sample than Fe present ($\sim 7$ times more). Fe was proposed as a "porthole" through which the $^{18}O$ was transferred to its direct vicinity of the zeolite matrix. Most of the oxygen will not be present as excess, but is probably exchanged, but this indicates the dynamics of the oxygen in the Fe catalyst.

The results presented here are evidence of the possibilities of tailoring uniform iron sites in FeMFI zeolites, under specific synthesis and activation conditions. This is of relevance from both a fundamental and a practical perspective, since every reaction determines its optimal active species. This is schematically shown in Fig. 3. In direct $N_2O$ decomposition, oligonuclear species are preferred over isolated ions in view of the easier oxygen recombination (rate-determining step in the process) of two iron centers that are close together. In $N_2O$ conversions involving reducing agents, atomic oxygen deposited on an isolated iron site can be cleaned off. This implies that the hydrocarbon "activation" is in fact done by the $O^*$ deposited by the $N_2O$.

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