Oxidative dehydrogenation of propane with nitrous oxide over Fe-ZSM-5 prepared by grafting: Characterization and performance

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A B S T R A C T

Iron-zeolites with well-defined extra-framework iron species were prepared via organometallic chemistry grafting route, i.e. the surface reaction between ferrocene and Brønsted acid sites in zeolites, and the calcined iron-zeolites were studied as catalysts for \( \text{N}_2\text{O} \)-mediated oxidative dehydrogenation of propane to propylene. The framework structures of zeolite hosts and the calcination temperatures showed great impact on the catalytic performances. Fe-ZSM-5 calcined at 1073 K exhibited the highest activity for \( \text{N}_2\text{O} \)-mediated propane oxidative dehydrogenation and a maximal initial propylene yield of ca. 30% can be obtained at a reaction temperature of 748 K (after time-on-stream of 15 min). A transformation of iron sites in Fe-ZSM-5 upon high-temperature calcination was well established based on the spectroscopic characterization results from UV–vis, \( \text{H}_2 \)-TPR, EPR and FTIR of NO adsorption. According to the correlation between catalytic activity and iron sites, extra-framework Fe–O–Al species are proposed to be the preferred active sites for \( \text{N}_2\text{O} \)-mediated oxidative dehydrogenation of propane.

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1. Introduction

Iron-zeolites with extra-framework iron species have attracted special attention due to their remarkable activity in \( \text{N}_2\text{O} \)-involved reactions, e.g. the catalytic decomposition and reduction of \( \text{N}_2\text{O} \) [1–8], the \( \text{N}_2\text{O} \)-mediated benzene hydroxylation [9–14] and \( \text{N}_2\text{O} \)-mediated oxidative dehydrogenation of propane (ODHP) [15–23]. To our knowledge, iron-zeolites have been successfully commercialized in the process of \( \text{N}_2\text{O} \) abatement from nitric acid plants by Uhde GmbH [24] and the process of \( \text{N}_2\text{O} \)-mediated benzene hydroxylation to phenol by SOLUTIA [25]. The \( \text{N}_2\text{O} \)-mediated ODHP has been proposed as an alternative promising route for the production of propylene.

As for the \( \text{N}_2\text{O} \)-involved reactions catalyzed by iron-zeolites, the most important thing to know is what the active iron sites are and how to produce them on purpose. However, great contradictions still exist in the identification of active iron sites for \( \text{N}_2\text{O} \)-involved reactions, which may keep away from the reliable structure-activity relationship for these reactions. Taking the \( \text{N}_2\text{O} \)-mediated ODHP for example, Bulánek et al. [15] claimed that the catalytic activity of Fe-ZSM-5 complexes could be ascribed to the presence of extra-framework Fe–oxo complexes, similar to that reported by Panov et al. [26] in \( \text{N}_2\text{O} \)-mediated benzene hydroxylation. While Kondratenko and Pérez-Ramírez [16] proposed that oligonuclear iron species in Fe-ZSM-5 was more active than isolated iron species for \( \text{N}_2\text{O} \)-mediated ODHP, probably due to the higher mobility of atomic oxygen species attached to oligonuclear iron species formed upon nitrous oxide chemisorption. Pérez-Ramírez and Gallardo-Llamas [18] suggested that traces of well-isolated iron species in Fe-ZSM-5 is extremely active in \( \text{N}_2\text{O} \)-mediated ODHP, while large iron clusters enhance the deep oxidation of important reaction intermediates to \( \text{CO}_2 \).

The controversies on active iron sites in \( \text{N}_2\text{O} \)-involved reactions, to a large extent, depend on the complicated constitution of iron sites in iron-zeolites and the resulting difficulty in the characterization of specific iron sites. Generally, extra-framework iron species in iron-zeolites may be present as isolated and oligonuclear cationic species, as well as neutral iron oxides with varying degrees of aggregation. Numerous techniques, including but not limited to Mössbauer spectroscopy [27], UV–vis spectroscopy [7,28], EPR spectroscopy [29,30] and X-ray absorption spectroscopy [31,32], have been applied to the characterization of iron sites in iron-zeolites. Due to the limitation of each single characterization technique, multiple characterization techniques should be used simultaneously with cross-reference to provide more accurate information on the specific iron sites.

The preparation of iron-zeolites is the initial step in the study of iron-zeolites, and a simple and reproducible preparation route is highly desired. Moreover, the proper preparation of iron-zeolites
with relatively simple constitution of iron species can greatly reduce the difficulty in the characterization of iron sites. Various methods, e.g. ion-exchange and isomorphous substitution followed by extraction, have been proposed for the preparation of iron-zeolites with extra-framework iron species. Isomorphous substitution is an efficient method to introduce low concentration Fe species into the zeolite framework and extra-framework iron species can be obtained after subsequent extraction. In this case, the constitution of iron sites is greatly dependent on the extraction procedure [33]. Liquid phase ion exchange is a simple and feasible means to prepare iron-zeolite, as it involves fewer steps and the preparation parameters are easily controlled. However, due to the complicated solution behavior of ferric and ferrous ions as well as the diffusion problem during ion exchange, a lack of reproducibility may be a problem for the iron-zeolites prepared by solution ion exchange [34]. To solve the problem, solid-state ion exchange [35] and vapor phase ion exchange (also known as chemical vapor deposition) [36] have been adopted to prepare fully or over-exchanged iron-zeolites. Recently, a surface organometallic chemistry grafting route, i.e. the reaction between ferrocene and Bransted acid sites in zeolites, has been proposed for the preparation of iron-zeolites [37]. This grafting route can be regarded as an improved solid-state ion exchange route using ferrocene instead of FeCl3 as reactant. Interestingly, the iron sites in iron-zeolites, i.e. Fe-HY, prepared via grafting route exhibit low nuclearity and good activity in phenol hydroxylation reaction [38].

In the present study, a series of iron-zeolites are prepared by the grafting route and studied as possible catalysts for N2O-mediated ODHP. The iron sites in Fe-MFI are characterized by multiple techniques with cross-reference, and the transformation of iron sites upon high-temperature calcination is revealed. Based on the characterization and catalytic results, the active iron sites for N2O-mediated ODHP are discussed and the structure-activity relationship is identified, which are of great significance for the rational design of highly-active iron-zeolites.

2. Materials and methods

2.1. Catalyst preparation

A series of alumino-silicate zeolites in their H-form with different framework structure (MFI: H-ZSM-5, MOR: H-modenite, FAU: H-USY, FER: H-ZSM-35, BEA: H-Beta) were provided by Sinopec and employed as hosts for iron species. Prior to being used as hosts, the zeolite samples were calcined in flowing air at 873 K for 6h. Fe-zeolite samples were prepared by the so-called grafting method. During the grafting process, the organometallic Fe precursor ferrocene sublimated at elevated temperature and then reacted with the Bransted acid sites in zeolites [37,38]. In a typical experiment, a zeolite sample of ca. 3 g was placed in a quartz reaction chamber connected to a vacuum line and treated under vacuum of 5 × 10^{-2} Pa at 573 K for 4h. After cooling to 323 K, 0.5 g ferrocene was added into the reaction chamber and the chamber was then heated to 423 K. The chamber was kept at 423 K under vacuum for 24h to insure the complete surface reaction between ferrocene and the Bransted acid sites in zeolites. The resulting solid was then subjected to calcination in flowing air at different temperatures for 6h. The final product was labeled as Fe-zeolite-xG-y, where x indicated the Si/Al ratio of zeolite, G indicated the grafting preparation method and y indicated the calcination temperature.

For reference, Fe-MFI samples were also prepared by reductive liquid-phase ion exchange, solid-state ion exchange and isomorphous substitution followed by extraction. In a typical experiment of reductive liquid-phase ion exchange, 0.5 g zeolite MFI sample was placed in the three-necked flask and exchanged with 200 ml 0.1 M FeCl3 aqueous solution for two days under the protection of nitrogen (pH = 3). The resulting solid was thoroughly washed with deionized water, dried at 353 K overnight and calcined in flowing air at 1073 K for 6h. The final product was labeled as Fe-MFI-24LE-1073, where 24 indicated the Si/Al ratio of MFI zeolite, LE indicated the liquid-phase ion exchange preparation method and 1073 indicated the calcination temperature. In a typical experiment of solid-state ion exchange, 0.5 g zeolite MFI sample was mechanically mixed with 0.5 g FeCl3 in the glove box and the mixture was placed in a sealed reactor. The reactor was heated to 573 K at 10 K/min and kept at this temperature for 2h. The resulting solid was thoroughly washed with deionized water, dried at 353 K overnight and calcined in flowing air at 1073 K for 6h. The final product was labeled as Fe-MFI-24SE-1073, where 24 indicated the Si/Al ratio of MFI zeolite, SE indicated the solid-state ion exchange preparation method and 1073 indicated the calcination temperature. In a typical experiment of isomorphous substitution, a solution of tetraethylorthosilicate (Alfa Aesar), tetrapropylammonium hydroxide (TPAOH, 20% solution in water, Alfa Aesar), aluminum nitrate (Alfa Aesar) and ferrous nitrate (Alfa Aesar) was prepared with the proportion of SiO2:6Al2O3:Fe2O3:90 TPAOH:12.000 H2O. After vigorous stirring for 2h, the mixture was transferred to a Teflon-lined stainless steel autoclave for static crystallization at 448 K for 120h. The resulting solid was filtrated, thoroughly washed with deionized water, dried at 353 K overnight, calcined in flowing air at 873 K for 6h, and activated in 10% H2O/air at 873 K for 4h. The final product was labeled as Fe-MFI-24IS-873, where 24 indicated the Si/Al ratio of MFI zeolite, IS indicated the isomorphous substitution followed by extraction preparation method and 873 indicated the extraction temperature.

2.2. Catalyst characterization

The Si, Al and Fe contents in samples were analyzed by a Perkin Elmer Optima 2000 inductively coupled plasma optical emission spectrometer (ICP-OES).

The specific surface areas of samples were determined through low temperature N2 adsorption/desorption isotherms collected on a Quantachrome iQ-1MP gas adsorption analyzer.

The X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 ADVANCE powder diffractometer using Cu-Kα radiation (λ = 0.1542 nm) at a scanning rate of 4°/min in the region of 20 = 5°–40°.

Transmission electron microscopy (TEM) images were taken on a Philips Tecnai G2 20 S-TWIN electron microscope at an acceleration voltage of 200 K V. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of samples were measured on a Bruker Tensor 27 spectrometer with 128 scans at a resolution of 2 cm^{-1}. A self-supporting pellet made of sample was placed in the reaction chamber and pretreated in flowing dry air at 473 K for 1h. The spectra were recorded in dry air against KBr as background.

Diffuse reflectance ultraviolet–visible (UV–vis) spectra of samples were recorded in air against BaSO4 in the region of 200–800 nm on a Varian Cary 300 UV–vis spectrophotometer.

The temperature-programmed reduction (TPR) experiments were carried out on a Quantachrome ChemBET 3000 chemisorption analyzer. A sample of ca. 0.1 g was pretreated in flowing 5%O2/Ar at 873 K for 1 h, cooled to 323 K in the same atmosphere and purged with 5%H2/Ar for 30 min. H2–TPR was then carried out in flowing 5%H2/Ar in the temperature range of 323–873 K at a heating rate of 10 K/min.

The temperature-programmed desorption (TPD) experiments were carried out with a Quantachrome ChemBET 3000
chemisorption analyzer. A sample of ca. 0.1 g was pretreated in flowing He at 873 K for 1 h, cooled to 373 K in He and saturated with 5% NH₃/He. After that, the sample was purged with He for 30 min to eliminate the physisorbed ammonia. NH₃-TPD was then carried out in flowing He in the temperature range of 373–873 K at a heating rate of 10 K/min.

Solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) experiments of fully hydrated samples were performed on a Bruker Avance III spectrometer at resonance frequencies of 104.3 and 79.5 MHz for ²⁷Al and ²⁹Si, respectively. The ²⁷Al MAS-NMR spectra were recorded with a sample spinning of 8 kHz, while the ²⁹Si MAS-NMR spectra were obtained with 4 kHz. The decomposition and simulation of NMR spectra were carried out using the Bruker software WINNMR and WINFIT.

Electron paramagnetic resonance (EPR) spectra in the X-band region were recorded with a Bruker EMX-6/1 spectrometer at 120 K with a microwave power of 5.0 mW and a modulation frequency of 100 kHz. 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) was used as an internal standard for the measurement of the magnetic field.

FTIR spectra with N₂ as probe were collected on a Bruker Tensor 27 spectrometer with 128 scans at a resolution of 2 cm⁻¹. A self-supporting pellet made of the catalyst sample was placed in the reaction chamber and pretreated in flowing He at 773 K for 1 h. After cooling to room temperature in flowing He, the He stream was switched to 1% NO/He and a series of time-dependent FTIR spectra were sequentially recorded.

2.3. Catalytic evaluation

The catalytic evaluation was performed in a fixed-bed flow reactor at atmospheric pressure. Typically, 0.2 g catalyst sample (sieve fraction of 0.17–0.25 mm) was placed in a quartz reactor (4 mm i.d.) and pretreated in 15% N₂/O/He at 823 K for 1 h. After cooling to the designated temperature, the reactant gas mixture (7.5% C₃H₈, 15% N₂O, balance He) was fed to the reactor at a total flow rate of 50 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 15 000 mL h⁻¹ g⁻¹. The catalytic reactions were conducted isothermally at designated temperatures and the gas products were analyzed after 15 min reaction (quasi steady-state reaction with C balance > 90%) by using two on-line gas chromatographs. One of them was equipped with a Plot Q capillary column and an FID detector for the analysis of organic products, the other with two packed columns (Porapak Q and Carbon Molecular Sieve TDX) and TCD detector for the analysis of N₂O, N₂, O₂ and CO₂. The water was removed from the gas products before the chromatograph inlet and possible small change of the reaction volume was neglected in the formulas used for conversion, selectivity and yield calculations. The conversion, selectivity and yield are defined as follows:

\[ \text{N}_2\text{O conversion (\%)} = \frac{[\text{N}_2\text{O}]_{\text{inlet}} - [\text{N}_2\text{O}]_{\text{outlet}}}{[\text{N}_2\text{O}]_{\text{inlet}}} \times 100\% \]

\[ \text{C}_3\text{H}_8 \text{ conversion (\%)} = \frac{[\text{C}_3\text{H}_8]_{\text{inlet}} - [\text{C}_3\text{H}_8]_{\text{outlet}}}{[\text{C}_3\text{H}_8]_{\text{inlet}}} \times 100\% \]

\[ \text{C}_3\text{H}_6 \text{ selectivity (\%)} = \frac{[\text{C}_3\text{H}_6]_{\text{outlet}}}{[\text{C}_3\text{H}_8]_{\text{inlet}} - [\text{C}_3\text{H}_8]_{\text{outlet}}} \times 100\% \]

\[ \text{C}_3\text{H}_6 \text{ yield (\%)} = \frac{[\text{C}_3\text{H}_6]_{\text{outlet}}}{[\text{C}_3\text{H}_8]_{\text{inlet}}} \times 100\% \]

### Table 1

<table>
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<th>Fe-zeolite</th>
<th>Zeolite host</th>
<th>Si/Al</th>
<th>Fe (%</th>
<th>Fe/Al</th>
<th>SSA (m²/g)</th>
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<tr>
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<tr>
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<tr>
<td>Fe-FER-12G</td>
<td>ZSM-35</td>
<td>13.2</td>
<td>1.26</td>
<td>0.19</td>
<td>372</td>
</tr>
</tbody>
</table>

a Molar ratio.

b Uncalcined sample.

3. Results

3.1. Physico-chemical properties of Fe-MFI prepared via grafting

The results of surface organometallic chemistry reaction between ferroene and zeolites, and some physicochemical properties of the as-prepared Fe-zeolites under study are summarized in Table 1. Iron species can be introduced to the zeolite host through the reaction between ferrocene (kinetic diameter: 0.46 nm × 0.32 nm) and H-ZSM-5 (Si/Al = 23.7, pore dimension: [1 0 0] 0.51 nm × 0.55 nm ↔ [0 1 0] 0.53 nm × 0.56 nm); and an iron loading of 1.82% is obtained in Fe-MFI-24G. The Fe/Al ratio of 0.48 indicates that each iron atom is approximately bound to two Bronsted acid sites, in consistence with the EXAFS results on Fe-HY prepared via a similar grafting route [38]. After calcination, the iron loading in Fe-MFI-24G decreases distinctly due to the loss of iron species during the calcination process, and higher calcination temperature results in more severe loss of iron species. The distinct loss of iron species does not happen with Fe-MFI prepared by other methods, i.e., reductive solution ion exchange with FeCl₃ and conventional solid-state ion exchange with FeCl₃. Presently, we are not very sure about the exact reasons and more detailed investigations are required. When H-ZSM-5 zeolites with different Si/Al ratios (12, 24 and 48) are employed as hosts for the preparation of iron-zeolites via grafting, Fe/Al ratios of 0.15–0.18 can be obtained in the final products. When zeolites with different framework structures are employed as hosts for the preparation of iron-zeolites via grafting, Fe/Al ratios of 0.16–0.23 are obtained, indicating that the grafting method may be general route to iron-zeolites.

Fig. S1 displays the XRD patterns of Fe-zeolites employed in this study. For Fe-zeolite-xG-1073 (left figure), diffraction lines corresponding to zeolite hosts are observed exclusively [39]. For Fe-MFI-24G-x (right figure), high temperature calcinations at 873–1173 K do not result in visible changes in the diffraction lines of MFI host. It is evident that the framework structure of zeolite hosts can be well preserved after the introduction of iron species by grafting and subsequent calcination in air. The absence of diffraction lines corresponding to iron oxides excludes the formation of bulk iron oxides.

The TEM images of Fe-MFI-24G samples calcined at different temperatures are shown in Fig. 1. For Fe-MFI-24G-873, small clusters with sizes of less than 2 nm are observed to disperse on the surface of MFI zeolite or inside the channels. For Fe-MFI-24G calcined at higher temperatures of 973–1073 K, the clusters become smaller and almost invisible. Meanwhile, the lattice structure of MFI zeolite can be clearly observed, confirming that the framework structure of MFI is well preserved upon high temperature calcination.

The hydroxyl stretching region of DRIFT spectra of H-MFI and Fe-MFI samples are shown in Fig. S2. A strong band at 3610 cm⁻¹ corresponding to Brønsted acid hydroxyl groups and a weak band
at 3740 cm\(^{-1}\) corresponding to silanol groups are observed for the H-MFI sample [40,41]. After the introduction of iron species by grafting and subsequent calcination at 873 K, the IR band corresponding to Brønsted acid hydroxyl groups shifts to lower wave number of 3590 cm\(^{-1}\) due to the framework distortion induced by iron species, and the intensity of the band decreases dramatically. Meanwhile, a new IR band at 3660 cm\(^{-1}\) corresponding to hydroxyls attached to extra-framework aluminum species and iron species [42,43] appears. Increasing the calcination temperatures from 873 to 1173 K leads to the partial elimination of Brønsted acid hydroxyl groups and hydroxyls attached to extra-framework aluminum species and iron species, as reflected by the decreases in the intensities of the corresponding IR bands at 3660 and 3590 cm\(^{-1}\).

The acidic properties of H-MFI and Fe-MFI were evaluated by NH\(_3\)-TPD and the results are shown in Fig. S3. Two major types of ammonia desorption peaks can be observed on H-MFI: a low-temperature peak at 400–600 K corresponding to weak acid sites and a high-temperature peak at 600–800 K corresponding to strong acid sites. The high-temperature peak originates from the desorption of NH\(_3\) strongly interacting with the Brønsted acid sites in MFI and the intensity of this peak can be used for the qualitative analysis of Brønsted acid sites in the specific case of MFI [44]. During the preparation of Fe–MFI by grafting, the ferrocene precursor reacts with the protons in Brønsted acid hydroxyls and therefore leads to significant decrease in the concentration of Brønsted acid hydroxyl groups. It is also observed that intensities of the ammonia desorption peaks, both high-temperature peak and low-temperature peak, gradually decrease with increasing calcination temperatures from 873 to 1173 K, probably due to the re-arrangement and elimination of various hydroxyl groups upon thermal treatments.

Fig. S4 displays the \(^{27}\)Al and \(^{29}\)SiMAS NMR spectra of Fe-MFI-24G samples calcined at different temperatures. In the \(^{27}\)Al MAS NMR spectra, strong signals centered at 55 ppm are observed for Fe-MFI-24G-873 and these signals should be attributed to tetrahedrally coordinated aluminum at non-equivalent framework positions [45]. Besides, weak signals centered at ca. 0 ppm are observed, indicating the presence of octahedrally coordinated extra-framework aluminum species [46]. With increasing calcination temperatures, the \(^{27}\)Al MAS NMR signals become much broader, probably due to the perturbation from paramagnetic iron species with unpaired electrons [47]. Nevertheless, it can be observed that the percentage of extra-framework aluminum species increases distinctly with increasing calcination temperatures from 973 to 1173 K, indicating the framework dealumination upon high temperature calcinations. In \(^{29}\)Si MAS NMR spectra, two strong signals at –113 and –116 ppm corresponding to Si\(^{\text{III}}\)(OSi)\(_3\) sites and one weak signal at –106 ppm corresponding to AlO\(\text{Si}^{\text{III}}\)(OSi)\(_3\) sites [48,49] are observed for Fe-MFI-24G-873. High-temperature calcinations lead to the decrease in the intensity of \(^{29}\)Si NMR signal at –106 ppm corresponding to AlO\(\text{Si}^{\text{III}}\)(OSi)\(_3\) sites, due to the framework dealumination upon thermal treatment as confirmed by the \(^{27}\)Al MAS NMR results.

### 3.2. Characterization of iron sites in Fe-MFI

Fig. 2 displays the UV–vis spectra of Fe-MFI-24G samples calcined at different temperatures. All Fe-MFI samples exhibit strong absorbance in 200–600 nm region, corresponding to O → Fe ligand to metal charge transfer transitions in various ferric ions. Typically, the absorbance occurring at 215 and 245 nm is attributed to isolated ferric ions in tetrahedral coordination, while the absorbance at 275 nm is attributed to isolated ferric ions in octahedral
coordination [14,28]. Generally, the absorbance between 300 and 400 nm is attributed to octahedral ferric ions in oligonuclear Fe₆O₇ clusters, while the absorbance at above 400 nm is attributed to large Fe₂O₃ nanoparticles [50]. It has been argued that dinuclear ferric ions in hydrated Fe-MFI sample also showed UV absorption below 300 nm [50] and it should be more careful when dealing with UV–vis spectra. Nevertheless, it can be concluded from UV–vis spectra that isolated ferric ions and oligonuclear Fe₆O₇ clusters are the dominant iron species in Fe-MFI. High temperature calculations at 1073 and 1173 K result in the distinct decreases in the percentage of Fe₂O₃ nanoparticles. The H₂–TPR profiles of Fe-MFI-24G samples calcined at different temperatures are shown in Fig. 3. A mechanical mixture of 2 wt.% γ-Fe₂O₃ with H-ZSM-5 (Si/Al = 24) was prepared and its H₂-TPR profile is also shown for reference. A broad H₂ consumption peak in the temperature range of 600–950 K is observed for sample 2% Fe₂O₃/H-MFI and the total H/Fe ratio of 2.9 reveals that almost all the ferric ions can be reduced to metallic iron below 950 K. For the Fe-MFI-24G samples, broad H₂ consumption peaks in the temperature range of 600–950 K are observed as well. The total H/Fe ratios are calculated to be 1.1–1.3, depending on the calcination temperature. The H/Fe ratio of 1 corresponds to the reduction of ferric ions to ferrous ions. It has been reported that the reduction of ferrous ions in isolated state or oligonuclear clusters to metallic iron is accompanied by the collapse of zeolite framework and the peaks of H₂ consumption should appear well over 1000 K [7,44]. Therefore, the H/Fe ratios of close to 1 reveal that the iron species in Fe-MFI-24G mainly exist in the form of isolated ferric ions and oligonuclear ferric clusters. It should be noted that the H₂ consumption peak in H₂-TPR profiles of Fe-MFI-24G slightly shifts to higher temperatures with increasing calcination temperature.

Fig. 4 displays the EPR spectra of Fe-MFI-24G samples calcined at different temperatures. For Fe-MFI-24G-873, strong EPR signals at g' = 2.0 and weak g' = 4.3 can be observed. The g' = 4.3 signal should originate from the ferric ions in tetrahedral coordination while signals at g' = 2.0 may originate from highly symmetric isolated ferric ions and/or small oligomers with weak dipolar coupling. [31,51]. The latter would cause the considerable line width observed in the spectra. With increasing calcination temperature, the intensity of g' = 2.0 EPR signal decreases, while the intensity of g' = 4.3 EPR signal increases. Obviously, the iron sites in Fe-MFI undergo transformation upon high temperature calcination.

FTIR spectroscopy with NO probe is informative and sensitive technique for the characterization of iron sites in zeolite [52–54]. The characteristic of this technique lies in that only exposed iron sites can be explored, while iron sites in sub-surface position or buried inside cannot be detected. Thus, it can provide us with necessary information on the available or so-called working iron sites in catalytic reactions. It should also be mentioned that the adsorption of NO on oxidized ferric ions is negligible at room temperature, and the nitrosyls are formed exclusively with the participation of
ferrous ions [52]. Therefore, the Fe-MFI samples calcined in air are further treated in flowing He at 773 K for 1 h to induce the auto-reduction of ferric ions to ferrous ions [44,55]. Through this process, easy reducible iron species can be auto-reduced and these iron species should be most active for the activation of nitrous oxide [29].

Fig. 5 displays the FTIR spectra of NO adsorption on Fe-MFI samples at room temperature. NO adsorption on Fe-MFI without calcination, i.e., Fe-MFI-24G, results in a broad band centered at 1850 cm⁻¹, which should be assigned to mono-nitrosyl on ferrous ions in the straight channels of ZSM-5 [56,57]. According to the grafting preparation method, the ferrous ions could be in the form of exchanged isolated ions or in oligonuclear clusters formed during the removal of cyclopentadiene ligands. For Fe-MFI-24G-873, NO adsorption results in the appearance of two strong bands at 1875 and 1890 cm⁻¹, and one weak band at 1855 cm⁻¹. The band at 1855 cm⁻¹ should be shifted from the band at 1850 cm⁻¹, due to the change in the environment and nuclearity through calcination. The band at 1875 cm⁻¹ is assigned to mono-nitrosyl on extra-framework Fe²⁺–O–Al species [54,58], while the band at 1890 cm⁻¹ is assigned to mono-nitrosyl on isolated ferrous ions located at the γ sites of ZSM-5 structure [6,36]. It is evident that calcination in air results in the transformation of iron sites Fe-MFI, i.e., from isolated ions or oligonuclear clusters in the straight channels of ZSM-5 to isolated ions in the sinusoidal channels and extra-framework Fe–O–Al species. With increasing calcination temperatures from 873 to 1073 K, all the detectable ferrous iron species transform to extra-framework Fe–O–Al species. While for Fe-MFI-24G-1173, NO saturated adsorption results in the appearance of a broad IR band centered at around 1810 cm⁻¹, corresponding to poly-nitrosyl on isolated ferrous ions (Fe²⁺(NO)ₙ, n ≥ 2) [52–55]. Since the initial adsorption of NO on Fe-MFI-24G-1173 results in the appearance of IR band at 1875 cm⁻¹, the IR bands at 1810 and 1875 cm⁻¹ should be originated from the same ferrous species, i.e., isolated extra-framework Fe²⁺–O–Al species. The formation of poly-nitrosyl species requires sufficient space, and therefore the Fe–O–Al species in Fe-MFI-24G-1173 should be located at more accessible position than that in Fe-MFI-24G-1073.

3.3. Catalytic performance of iron-zeolites

The catalytic performance of iron-zeolite samples calcined at 1073 K (quasi steady-state after time-on-stream of 15 min) in N₂O-mediated ODHP at 748 K is shown in Fig. 5S. Fe-zeolites with different framework structures and similar Si/Al ratios exhibit quite different catalytic behavior. Fe-FER-12G exhibits quite low dehydrogenation activity and CO₂ (CO and CO₂) are detected as exclusive products from propane-N₂O reaction. In contrast, Fe-MOR-12G, Fe-BEA-12G, Fe-FAU-12G and Fe-MFI-12G exhibit certain dehydrogenation activity, and the desired product propylene can be detected together with the undesired product CO₂. Amongst, Fe-MFI-12G exhibits the highest propane conversion of ca. 38% and propylene selectivity of ca. 64%, leading to the propylene yield of ca. 24%. Besides the major by-product CO₂, trace acrolein and some other oxygenates (<2%) can be detected in the products. The Si/Al ratios of MFI zeolite hosts slightly influence the catalytic performance of Fe-MFI-xG samples in N₂O-mediated ODHP. Typically, the highest propylene yield of ca. 30%, with propane conversion of 46% and propylene selectivity of ca. 65%, is obtained with the Fe-MFI-24G catalyst.

Fe-MFI-24G calcined at different temperatures were studied as catalysts for N₂O-mediated ODHP, and the results are shown in Fig. 6. For all Fe-MFI-G catalysts, the propane and N₂O conversions gradually increase with increasing reaction temperature, while the propylene selectivity decreases with increasing reaction temperatures. The calcination temperatures show strong impact on the catalytic performance of Fe-MFI-G. Typically, the propane and N₂O conversions decrease with increasing calcination temperature from 873 to 1173 K, while the propylene selectivity increases with increasing calcination temperature. The highest propylene yield of ca. 30% can be obtained over Fe-MFI-1073 at the reaction temperature of 748 K.

Fig. S6 displays the results of N₂O decomposition over Fe-MFI-24G calcined at different temperatures. Significant N₂O decomposition to N₂ and O₂ starts at ca. 648 K over all Fe-MFI-G catalysts, and the N₂O conversion increases with increasing reaction temperatures. The calcination temperatures of Fe-MFI-24G samples show distinct influence on the N₂O decomposition activity. Typically, N₂O decomposition activity over Fe-MFI-24G decreases with increasing calcination temperatures from 673 to 1173 K, similar to the changing trend of N₂O conversion in N₂O-mediated ODHP (Fig. 6).

The result of propane oxidation with O₂ catalyzed by Fe-MFI-24G-1073 is shown in Fig. S7. Propane conversion starts at ca. 573 K and then gradually increases to ca. 90% with increasing reaction temperature from 573 to 773 K. The main oxidation products are CO and CO₂, while only very low percentage of propylene (<10%) can be detected at 698–773 K. Based on the results presented in Figs. 6 and S7, the use of N₂O as an oxidant predominantly leads to the dehydrogenation of propane to propylene, while the use of O₂ as an oxidant leads to the deep oxidation of propane to CO₂. It is thus confirmed that N₂O can be used as mono-oxygen donor and the active oxygen species from N₂O chemisorption on specific iron sites facilitate the dehydrogenation of alkanes [59].

The iron-zeolites suffer serious deactivation by coke in N₂O-mediated ODHP and rapid decreases in propylene yield are reported [18–20]. Therefore, the deactivation and regeneration of selected catalyst Fe-MFI-24G-1073 in N₂O-mediated ODHP are further investigated. As shown in Fig. 7, a steady decrease in propane conversion and propylene yield is observed. Typically, the propylene yield decreases from ca. 30% to 12% in time-on-stream of 960 min. After regeneration in 15% N₂O/He at 748 K for 120 min, the catalytic activity of Fe-MFI-24G-1073 in N₂O-mediated ODHP can recover to the initial level. The regenerated catalyst exhibits similar deactivation behavior to the fresh catalyst. This suggests that
the Fe-MFI-24G-1073 catalyst can be continuously regenerated for \( \text{N}_2\text{O} \)-mediated ODHP, which is quite important for industrial application.

4. Discussion

4.1. Advantages of grafting preparation method to Fe-MFI

The preparation of Fe-zeolites is a very important issue and a simple route to active Fe-zeolites is highly desired. However, a lack of reproducibility has been claimed for the preparation of Fe-zeolite due to the intrinsic complexity of iron species as well as their interaction with zeolite host [33,60]. The formation of different iron species in Fe-zeolite is very sensitive to the preparation parameters and a slight modification on the preparation process may lead to quite different iron site constitutions and different catalytic activities. The grafting method employed in this study is a kind of solid-state ion exchange using organometallic ferrocene as iron precursor. The chemical reaction between ferrocene and the Brønsted acid sites in zeolite ensures the strong bonding of iron species to the zeolite host and the existence of cyclopentadiene ligands in ferrocene effectively prevents the aggregation of iron species. In a repeated preparation of Fe-MFI-24G-1073 via grafting, the obtained iron loading was quite similar to that obtained in the original experiment (Table 2). Furthermore, the catalytic performance in \( \text{N}_2\text{O} \)-mediated ODHP, including the maximal propylene yield, propane conversion and propylene selectivity, of both preparations of Fe-MFI-24G-1073 are almost identical (Table 2). These results clearly confirm that the grafting preparation method is feasible route to Fe-MFI with excellent reproducibility.

Based on the literature reports, the steam-activated isomorphously-substituted Fe-ZSM-5 are the most active catalysts for the \( \text{N}_2\text{O} \)-mediated ODHP [17–19]. To make a fair comparison between various catalysts, the catalytic performance of Fe-MFI samples prepared by different methods was evaluated under identical reaction conditions in the present study. As shown
Table 2
N2O-mediated ODHP catalyzed by Fe-MFI prepared by different methods.*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Fe (%)</th>
<th>Temp. (K)</th>
<th>Propane conversion (%)</th>
<th>Propylene selectivity (%)</th>
<th>Propylene yield (%)</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-MFI-24G-1073</td>
<td>24.5</td>
<td>0.63</td>
<td>748</td>
<td>46.3</td>
<td>64.8</td>
<td>30.0</td>
<td>0.037</td>
</tr>
<tr>
<td>Fe-MFI-24G-1073</td>
<td>24.7</td>
<td>0.66</td>
<td>748</td>
<td>46.7</td>
<td>64.5</td>
<td>30.2</td>
<td>0.036</td>
</tr>
<tr>
<td>Fe-MFI-24LE-1073</td>
<td>25.9</td>
<td>1.01</td>
<td>723</td>
<td>26.7</td>
<td>69.1</td>
<td>18.4</td>
<td>0.014</td>
</tr>
<tr>
<td>Fe-MFI-24SE-1073</td>
<td>24.6</td>
<td>1.14</td>
<td>723</td>
<td>22.4</td>
<td>66.1</td>
<td>14.8</td>
<td>0.011</td>
</tr>
<tr>
<td>Fe-MFI-24SE-1073</td>
<td>23.9</td>
<td>2.61</td>
<td>748</td>
<td>48.7</td>
<td>25.6</td>
<td>11.2</td>
<td>0.003</td>
</tr>
<tr>
<td>Fe-MFI-24G-1073</td>
<td>23.5</td>
<td>2.54</td>
<td>748</td>
<td>51.6</td>
<td>23.9</td>
<td>12.3</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe-MFI-24G-1073</td>
<td>26.5</td>
<td>0.56</td>
<td>723</td>
<td>46.7</td>
<td>50.2</td>
<td>23.4</td>
<td>0.033</td>
</tr>
<tr>
<td>Fe-MFI-24G-1073</td>
<td>26.1</td>
<td>0.02</td>
<td>723</td>
<td>43.3</td>
<td>50.6</td>
<td>21.9</td>
<td>0.032</td>
</tr>
</tbody>
</table>

* Reaction conditions: 7.5% C3H8, 15% N2O and He balance; GHSV = 15,000 mL h⁻¹ g⁻¹; activity data recorded at time-on-stream of 15 min.
+ Molar ratio.
- Reaction temperature when maximal propylene yield is obtained.
d Turnover frequency for propylene production based on overall iron species.
e Repeated experiments.

In Table 2, Fe-MFI prepared by grafting method exhibits distinctly higher activity for N2O-mediated ODHP than Fe-MFI samples prepared by other methods with similar Si/Al ratios. The turnover frequency for propylene production over Fe-MFI-24IS-873 is calculated to be 0.033 s⁻¹, quite similar to the most recent result reported by Sazama et al. [61]. While a higher turnover frequency of 0.037 s⁻¹, with both higher propane conversion and propylene selectivity, can be obtained with our Fe-MFI-24G-1073. Considering the rather low turnover frequency for propylene production over Fe-MFI-24E-1073 prepared by conventional solid-state ion exchange (0.004 s⁻¹), the use of ferroce instead of FeCl₃ for solid-state ion exchange shows its great advantage in the preparation of Fe-MFI for N2O-mediated ODHP.

4.2. Transformation of iron sites in Fe-MFI upon high-temperature calcinations

Through the surface reaction between ferroce and Brønsted acid sites in MFI zeolites, mononuclear cyclopentadiene-iron complexes should be formed and bonded to the zeolite surface, similar to those reported for Fe-HY [37]. During drying and calcination in the air, the cyclopentadiene ligands are removed and ferrous ions are oxidized to ferric ions. The strong interaction between iron species and zeolite surface as well as the existence of cyclopentadiene ligands effectively prevents the aggregation of ions species and the formation of Fe₂O₃ nanoparticles is greatly avoided. As a result, isolated ferric ions and oligonuclear clusters are obtained as dominant extra-framework iron species in Fe-MFI-24G-673, as revealed by the characterization results from UV–vis (Fig. 2) and H₂-TPR (Fig. 3).

For Fe/Zeolite-5 prepared by chemical vapor deposition of FeCl₃, high temperature thermal or hydrothermal treatment would lead to the transformation of iron species and, therefore, show great impacts on the catalytic activities [62,63]. In the present study, the transformation of iron sites in Fe-MFI prepared by grafting upon high-temperature calcinations is clearly observed (also visualized by the changes of sample color from brown to light yellow, as shown in Fig. 8). The results from DRIFT spectra (Fig. S2), NH₃-TPD profiles (Fig. S3) and NMR spectra (Fig. S4) indicate the dealumination of MFI zeolites during calcination at elevated temperatures. Accompanied by the dealumination process, the transformation of iron species takes place (UV–vis spectra in Fig. 2, H-TPR profiles in Fig. 3 and ESR spectra in Fig. 4) and the transformation of iron species in Fe-MFI accordingly results in the changes of catalytic activities in N₂O-mediated ODHP (Fig. 6) and N₂O decomposition (Fig. 6).

The TEM image of Fe-MFI-24G-673 shows the presence of small clusters of <2 nm on the surface of MFI zeolite or inside the channels (Fig. 1). These clusters could be due to Fe₂O₃ nanoparticles and/or large oligonuclear FeₙOₘ species. Considering that the percentage of Fe₂O₃ nanoparticles in Fe-MFI-24G-673 is estimated to be below 5% based on the UV–vis spectra, the contribution of Fe₂O₃ nanoparticles with very low loadings (<5% × 1.39×695 ppm) to the visible clusters can be neglected. The visible clusters in the TEM images gradually disappear with increasing calcination temperatures from 673 to 1073 K (Fig. 1), due to the re-dispersion of iron species upon high-temperature calcinations similar to the re-dispersion of platinum species on different supports [64,65].

4.3. Active iron sites for N₂O-mediated ODHP

Based on literature reports, N₂O decomposition over Fe-zeolite proceeds according to the following simplified mechanism (* indicates the active site) [66]:

\[ \text{N}_2\text{O} + * \rightarrow \text{N}_2 + * - \text{O} \]  
\[ 2* - \text{O} \rightarrow \text{O}_2 + 2* \]  
\[ \text{N}_2\text{O} + * - \text{O} \rightarrow \text{N}_2 + * - \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2 + * \]  

N₂O chemisorption first takes place on the active site of catalyst, followed by the liberation of dinitrogen and the deposition of oxygen on the active site (R1). The deposited oxygen may desorb as dioxygen via Langmuir–Hinshelwood mechanism (R2) or Eley–Rideal mechanism (R3), with the regeneration of active site.

As for N₂O reduction by propane, the redundant propane may react with gaseous dioxygen from the decomposition of N₂O or react with deposited oxygen on the active site. Considering that

![Fig. 7. Deactivation and regeneration of Fe–MFI catalyst for N₂O-mediated ODHP at reaction conditions: 7.5% C₃H₈, 15% N₂O and He balance; GHSV = 15,000 mL h⁻¹ g⁻¹ 748 K.](image-url)
the reaction between propane and O2 leads to the formation of COx as main products (Fig. S7), the reaction between propane and deposited oxygen is the desired pathway for the production of propylene (R4). The further oxidation of propylene and the reaction between propane and dioxygen (R5) are the side reactions to be avoided.

\[
\begin{align*}
\text{R4:} & \quad \text{C}_3\text{H}_8 + \ast - \text{O} \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \ast \\
\text{R5:} & \quad \text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}
\end{align*}
\]

Interestingly, the properties of the deposited oxygen play a key role for N2O-mediated ODHP. Two types of oxygen species have been identified for N2O activation over Fe-zeolite: highly-active so-called α-O and thermal-stable mono-oxygen [16,67]. The α-O is known to be excellent oxidant for oxygen addition reaction instead of hydrogen abstraction reaction [25]. In the present study, the reaction stoichiometry of N2O/C3H8 ≈ 1 and the high propylene selectivity of >85% below 648 K (Fig. 6) indicate that the thermal-stable mono-oxygen is highly selective for dehydrogenation reaction. The further reaction between propylene and thermal-stable mono-oxygen, even if might exist, could be ignored.

The properties of oxygen species deposited on the surface of Fe-MFI are greatly dependent on the specific iron sites. Since only exposed iron sites can be utilized during catalytic reaction, FTIR spectra of NO adsorption are employed to titrate the exposed iron sites. The results presented in Fig. 5 reveal the transformation of exposed active iron sites in Fe-MFI upon high temperature calcination, i.e., from isolated ions or oligonuclear clusters in the straight channels of ZSM-5 to extra-framework Fe–O–Al species. Meanwhile, the catalytic performances in Fig. 6 clearly indicate the enhancement in the propylene selectivity in N2O-mediated propylene dehydrogenation upon high temperature calcination. Based on the correlation between the exposed active iron sites in Fe-MFI characterized by FTIR spectra of NO adsorption (Fig. 5) and the dehydrogenation performance (Fig. 6), it is rational to say that extra-framework Fe–O–Al species are preferred active species for N2O-mediated propylene hydrogenation. Particularly for Fe-MFI-24G-1073 and Fe-MFI-24G-1173, extra-framework Fe–O–Al species is detected as exclusively active iron site for N2O-mediated propylene hydrogenation. The single constitution of iron site may greatly simplify the mechanism study not only for N2O-mediated propylene hydrogenation, but also for other N2O-involved reactions on these model catalysts.

5. Conclusion

Extra-framework iron species can be introduced to zeolites hosts via organometallic chemistry grafting route, i.e. the surface reaction between ferrocene and Brønsted acid sites in zeolites. After removing the organic ligands through calcinations, the iron-zeolites exhibit certain activities in N2O-mediated ODHP to propylene. The framework structures show decisive effects on the catalytic activity and MFI appears to most suitable zeolite host of iron species. Besides, calcination temperatures show distinct impacts on the catalytic activity of Fe-MFI in N2O-mediated ODHP.

The highest initial propylene yield of ca. 30%, with propane conversion of 46% and propylene selectivity of 65%, can be obtained on Fe-MFI-24G-1073 at a reaction temperature of 748 K (after time-on-stream of 15 min). In addition to the high activity of as-prepared Fe-MFI in N2O-mediated ODHP, the organometallic chemistry grafting route shows great advantage over other preparation routes due to its excellent reproducibility.

Isolated ferrocene and oligonuclear clusters are detected as major iron species in Fe-MFI after the surface reaction between ferrocene and Brønsted acid sites in MFI and subsequent calcinations. High-temperature calcinations result in the obvious dealumination in MFI framework and severe loss of iron species, accompanied by the transformation of iron species. More important, exposed active iron sites in Fe-MFI transform from isolated ions or oligonuclear clusters to extra-framework Fe–O–Al species upon high-temperature calcinations. Based on the correlation between exposed active iron sites in Fe-MFI and the catalytic activities, extra-framework Fe–O–Al species are established to be preferred active species for N2O-mediated ODHP and mono-oxygen from the activation of N2O on extra-framework Fe–O–Al species are proposed to be key oxygen species for oxidative dehydrogenation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.08.051.

References
