Characterization of Fe-Loaded Zeolites Using Spectroscopic Techniques

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Introduction

Iron loading into zeolite pores is important due to its ability to reduce NO_x to nitrogen, even in the presence of water [1]. Though the iron-loading concept is commonly used for catalyst preparation, the types of complexes formed inside the zeolite pores are not well known and no process yields a single type of complex within the pores. Previous studies have determined a majority complex within the zeolite [2], however, many other complexes are able to form within the zeolite pores due to the flexibility of the iron-oxygen bond and the pore width of the zeolite. By changing various aspects of the iron-loading procedure, different iron-oxygen majority complexes can form.

We are investigating iron-complexes formed within the zeolite pores and comparing the types of iron-oxygen complexes formed using different catalyst loading. This study examines the reproducibility of two common loading methods, chemical vapor deposition (CVD) and atomic layer deposition (ALD), and the formation of the various iron-oxygen complexes formed when the Si/Al and iron precursor were varied.

Materials and Methods

The proton form of the zeolites were obtained from BP and calcined in oxygen at 600 °C for 6 hours. HMFI samples with Si/Al ranging from 33-120 (noted as FeMFI(x) where x is the Si/Al) were loaded with $FeCl_3$ using CVD [1] while HMOR (50) samples were loaded with ferrocene using the ALD [3]. Samples were then washed with deionized water to replace the ligands with hydroxide ions and rinsed until no chloride was detected by standard precipitation techniques. Following loading, the samples were re-calcined at 600 °C for 6 hours in air. ICP-AES was used to confirm both Si/Al and Fe/Al. EXAFS samples were pressed into self-supporting wafers and Fe K-edge spectra were recorded in transmission mode at ambient temperature. Data were analyzed with standard procedures using the WinXAS v. 2.1 software. The Fourier transform of the k^2-weighted EXAFS function was carried out over the range 2.5-11.5 Å^{-1}.

Results and Discussion

By producing a Fe/Al of unity, various aluminum amounts within the zeolite should allow for the formation of different iron-oxygen complexes: mononuclear formations with low aluminum content and more complex formations with higher aluminum content. EXAFS results show variation in Fe-O bond lengths and cluster sizes in FeMFI(x). Iron-oxygen bonds appear at 1.1 Å where higher shells appear at longer distances, between 2.2-4 Å with less-defined peaks. Figure 1a depicts variations in the cluster size of two samples with different

Si/Al. These samples have a comparable Fe-O region showing similar peak intensity and coordination numbers with good agreement in the imaginary portion (dashed lines). Comparison of the Fe-O first shell region and the higher shell region to that of the bulk references allows for a percentual assignment of the clusters. For both samples in Figure 1a, the Fe-O shell is assigned to approximately 50% $Fe(NO_3)_3 \cdot 9H_2O$ and 50% Fe_2O_3. Higher shells for FeMFI(90) are assigned 50% Fe_2O_3 with large clusters. Higher shells for FeMFI(33) are only assigned an approximate fraction of 25% Fe_2O_3 with medium clusters.

Even though ICP results show similar Fe/Al for samples with the same Si/Al, it is clear that they do not contain the same type of Fe-O clusters. Figure 1b shows variations of Fe-O clusters between samples with the same Si/Al. The Fe-O shell for FeMFI(90) Trial 1(T1) is assigned to approximately 50% $Fe(NO_3)_3 \cdot 9H_2O$ and 50% Fe_2O_3. FeMFI(90) Trial 2 (T2) Fe-O shell is assigned to 15% $Fe(NO_3)_3 \cdot 9H_2O$ and 85% Fe_2O_3. Higher shells also vary between Trial 1 and Trial 2, with Trial 1 containing 50% Fe_2O_3 with large clusters and Trial 2 containing 20% Fe_2O_3 with small-medium clusters. These spectra show that the CVD loads Fe/Al reproducibly, but there is not a uniform cluster-type control with this loading technique.
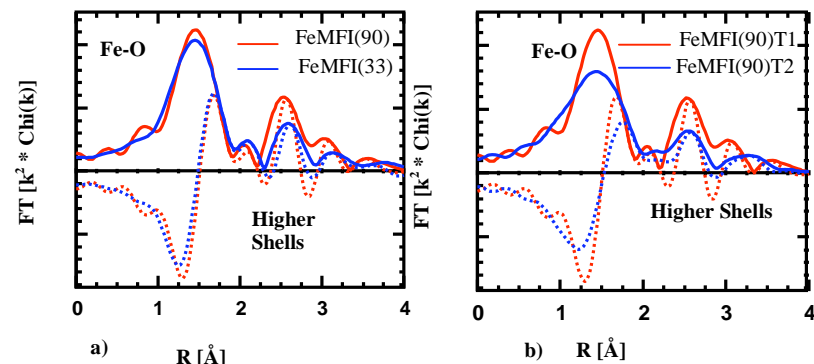
Figure 1: EXAFS spectra showing: **a)** comparison between FeMFI(90) and FeMFI(33); and b) comparison between two trials of FeMFI(90)

Significance

After determination of the types of iron-oxygen complexes within the zeolite pores, we hope to gain control over complex formation so that a single iron-oxygen entity is formed. With this, the catalytic properties can be determined to find what types of iron complexes are the most active in NO_x reduction.

References

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