Preferential Siting of Iron Atoms in an MFI-type Ferrisilicate Zeolite Framework: An Attempt to Explain Experimental Data with TPA-Silicate Solution Chemistry

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In this paper an attempt is made to explain the experimentally observed iron siting in ferrisilicate MFI-type zeolites based on TPA-silicate solution chemistry. A critical molecular step in the formation of Silicalite-1 zeolite is the formation of the precursor, counting 36 T-atoms, by condensation of three pentacyclic dodecamers around a TPA molecule. Incorporation of a tetracyclic undecamer instead of a pentacyclic dodecamer results in a precursor with a missing Si atom at a position that becomes a T_9 or T_{10} site of the orthorhombic unit cell of the MFI-type zeolite. The incorporation of iron at these empty positions of the precursor explains the experimentally observed preferred iron positions. Close examination of the precursor formation mechanism reveals that the iron is incorporated at the same T-atom positions, viz. T_9 and T_{10}, when the precursor is formed from an iron-containing pentacyclic dodecamer.

Introduction

In the field of heterogeneous catalysis, zeolites with the MFI framework topology are important materials.[1] Incorporation of heteroatoms, and particularly of aluminum, iron or titanium in the MFI-type silicate framework, leads to unique acid-base and redox catalytic properties. MFI-type zeolites have been given particular names according to their chemical composition or assignment of the inventors, such as Silicalite-1 for the purely siliceous version,[2] ZSM-5 for the aluminosilicate,[3] TS-1 for the titanosilicalite composition,[4] and Fe-ZSM-5, or Fe-MFI for the iron-containing analogue.[5,6] The ferrisilicate composition has received much attention in the recent literature as it is an effective catalyst for a variety of reactions.[7−11]

MFI zeolites have orthorhombic or monoclinic symmetry, and possess 12 or 24 crystallographically different T-atom sites, respectively. The distribution of the heteroatoms over the framework positions has already been the subject of numerous experimental[12−15] and computational studies.[16−18] The evidence for the occurrence of isomorphous substitution is convincing, and although there is general agreement that the distribution of the heteroatoms over the different T-sites is non-random, the precise location remains uncertain. The kinetic rather than thermodynamic control over the formation of siliceous zeolite phases and over the incorporation of heteroatoms[19,20] complicates the theoretical studies.[16−18]

Recently, structural evidence for preferential iron siting at the T_9 and T_{10} sites of Fe-MFI could be obtained using synchrotron radiation single-crystal X-ray diffraction.[21] Identification of the iron positions was done based on the localization of the sodium counterions in the channels of the MFI structure and comparison of T−O distances in Silicalite-1 and Fe-MFI. In parallel with this development, the initial molecular steps involved in the formation of Silicalite-1 were recently revealed.[22,23] In this paper, we explain how the oligomerization chemistry responsible for the formation of the Silicalite-1 framework can offer an explanation for the experimentally determined iron atom siting.

Discussion

The tetrapropylammonium hydroxide (TPA) directed silica oligomerization sequence, identified by ^{29}Si NMR spectroscopy, involves a bicyclic pentamer (**1**), a pentacyclic octamer (**2**), a tetracyclic undecamer (**3**), and a pentacyclic dodecamer (**4**; Figure 1).[22,23] These polyanions have curved surfaces and are hydrophobic on the inside and hydrophilic on the outside. The propyl arms of the TPA molecule interact favorably with the hydrophobic internal surface. The assembly of three dodecamers around the TPA molecule leads to the formation of the precursor (**5**; Figure 1). The precursor has the same connectivity as in the MFI framework. The T-sites of the MFI framework are

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mapped onto a model of the precursor in Figure 2. Aggregation of the precursor in the three directions leads to an MFI framework without missing T-atoms. The pentacyclic dodecamer (**4**) was detected as an intermediate in a polymerization experiment at 0 °C. At room temperature, it is a short-lived species and is quickly transformed into the precursor. The assembly of three pentacyclic dodecamers leads to precursors (**5**) containing 36 T-atoms. When a tetracyclic undecamer (**3**) is incorporated into precursor (**5**) instead of pentacyclic dodecamers (**4**), a T-atom is missing.

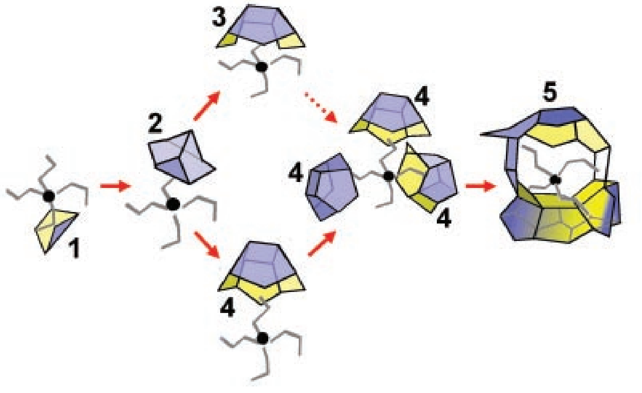

Figure 1. TPA-directed molecular steps involved in the formation of the 36-mer precursor:[22,23] (**1**) pentamer, (**2**) pentacyclic octamer, (**3**) tetracyclic undecamer, (**4**) pentacyclic dodecamer, and (**5**) precursor

In order to determine which T-atoms are missing, a close examination of the tetracyclic undecamer (**3**), pentacyclic dodecamer (**4**) and precursor (**5**) formation mechanism is needed. Incorporation of a tetracyclic undecamer (**3**) into the precursor (**5**) requires opening of the four-ring, which results in an intermediate with a three five-ring sequence, corresponding to the ones occurring in the precursor (**5**). Incorporation of the pentacyclic dodecamers (**4**) needs the opening of two rings, one five-ring and one four-ring. Comparison of the two opened intermediates shows that in the intermediate obtained from the tetracyclic undecamer (**3**), the Q^1-atom is missing. The latter atoms are always positioned in the precursor at positions that become T_9 or T_{10} sites of the orthorhombic MFI framework. They are marked with an asterisk in Figure 2. The T_9 and T_{10} sites represent extremities of the precursor (Figure 2). Incorporation of trivalent iron at these missing T-positions does not interfere with the hydrophobic interactions of the inner surface of the precursor with the TPA molecule. Near the T_9 and T_{10} sites of the precursor, there is ample space for the cation necessary for balancing the framework charge generated by incorporation of a trivalent iron atom as well as for possible non-framework ligands of iron when adopting a higher than fourfold coordination (Figure 2).

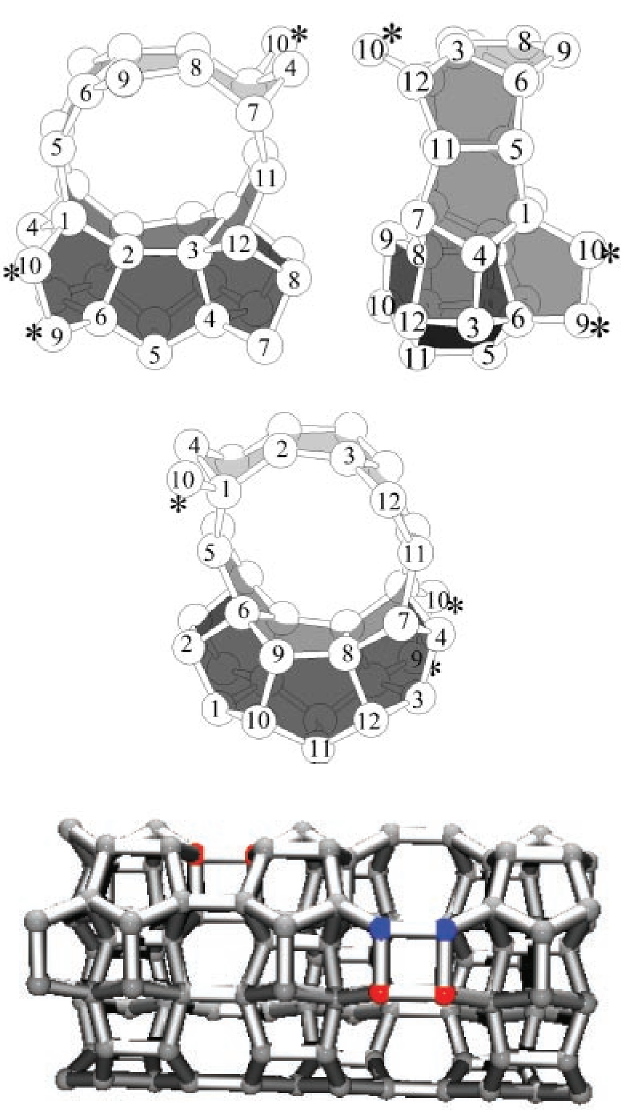

Figure 2. (top) Three views of the precursor model and T-atom numbering; at the T-atoms marked with an asterisk, the Si atom is missing when tetracyclic undecamer (**3**) is incorporated instead of pentacyclic dodecamer (**4**) and Fe^{3+} incorporated; (bottom) coupling of the precursor (**5**) into the MFI framework showing T_9 (blue) and T_{10} (red) sites forming four-rings

The T_9 and T_{10} positions constitute the four-rings in the MFI framework (Figure 2 bottom). Preferential substitution of aluminum in four-membered rings was earlier proposed based on upper substitution limits.[24] For iron incorporation into ferrisilicate MFI, the upper limit according to Szostak et al.[6] corresponds to an Si/Fe atomic ratio of 36, or 2.5 iron atoms per unit cell. When higher iron loadings are attempted, part of the iron is located at non-framework sites.[25] The experimentally observed maximum iron loading of one iron atom per 36 T-atoms suggests the incorporation of one iron atom per precursor. The achievement of higher iron loadings of the MFI zeolite would require the formation of precursors with two irons incorporated. Formation of these precursors is difficult, and coupling with other doubly substituted precursors will be impossible due to the Löwenstein's rule and/or formation of four-rings with double iron substitution. These doubly substituted four-rings are unlikely to form considering the preferred octahedral coordination of iron. This explains the maximum iron loading of one iron per 36 T-atoms.

If the exclusive pathway for iron incorporation were through occupation of missing T-sites in the precursor (**5**), to obtain this maximum ratio each precursor would have to be defective. It is therefore likely that iron atoms can already be part of pentacyclic dodecamers (**4**). In view of the large atomic radius of iron, these heteroatoms will preferably be at the Q^2-positions of the pentacyclic dodecamers (**4**). Fe^{3+}-containing rings are the least stable, and ring opening preceding the precursor formation will occur in this ring, inevitably resulting in Fe^{3+}-atoms at the T_9 or T_{10} positions of the precursor.

Conclusion

In conclusion, the early molecular steps involved in the TPA-directed formation of Silicalite-1 offer an explanation for the experimentally observed iron location at T_9 and T_{10} [21] sites in the niche of the sinusoidal channel of the MFI-type framework. Examination of the synthesis model reveals that trivalent iron can be incorporated into the pentacyclic undecamer and at T-site vacancies created by the incorporation of tetracyclic undecamers in the precursor. Both incorporation mechanisms result in the same iron siting, viz. T_9 and T_{10}.

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