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Preparation of Ferrisilicate ZSM-5 Molecular Sieves

The ferrisilicate molecular sieve analog of the zeolite ZSM-5 can be prepared from ferrisilicate gels containing low-molecular-weight silica species. Precipitation of rust-red iron hydroxide at the high pH necessary for crystallization and complex formation of the iron with amine impurities present in the crystal directing agent are avoided by titrating the basic silica solution into an acidic iron containing solution followed by introduction of the template. Pure white crystalline materials have been prepared in this manner over a SiO_2/Fe_2O_3 ratio of 15 to 200.

The incorporation of ferric ion into tetrahedral sites of the molecular sieve generally occupied by aluminum in the zeolite has been shown for several natural and synthetic zeolites (*1–8*). To date, no discussion has been put forth toward understanding the preparation of pure single-phase ferrisilicate molecular sieves. We have determined three factors to be critical in the successful preparation of these materials, they include the avoidance of iron hydroxide precipitation, the necessity of using low-molecular-weight silica sources, and the need to suppress the formation of iron complexes with the amine templating or crystal directing agents.

Iron is well known to form complexes with silica in solution. The ability of iron to precipitate silica was reported in early studies concerning silicate and soil chemistry (*9–11*). Complexes form between the two species at pH values between 3 and 4. The initial formation of a ferrisilicate gel at low pH is found to be one way of avoiding precipitation of iron hydroxide. After formation of the ferrisilicate gel the pH can be adjusted to the alkaline environment necessary for crystallization of a molecular sieve structure without observing the formation of the rust-red iron hydroxide phase. The amount of silica that will react with iron is dependent on the extent of polymerization of the primary silica source therefore short-chain silica species are the preferred starting materials.

Modification of the standard method of zeolite synthesis has been devised to consistently prepare these ferrisilicate molecular sieves in pure form. The ferrisilicates crystallized in this study are the analogs of the zeolite ZSM-5 (*12, 13*). All materials prepared by this method are white and highly crystalline based on X-ray diffraction and *n*-hexane adsorption studies using the aluminosilicate ZSM-5 zeolite and silicalite, the high silica end member of this family of zeolites, as standards for comparison. SEM images and EDX analysis of these materials show no detectable amorphous iron containing phase. Crystal morphology in all samples prepared is comparable to the corresponding zeolites.

Shown in Example 1 is a typical preparation of the ferrisilicate analog of zeolite ZSM-5. Example 2 is a typical synthesis recipe for the aluminosilicate with the comparable aluminum content. This method of preparation is based on the reported preparation of zeolite ZSM-5. The silica source in both examples is N-brand silicate (PQ Corp.), which contains low-molecular-weight fragments of silica. To avoid the problems described previously, the silica source is titrated into the acidic iron(III) containing solution. In this manner the iron is kept from any severe alkaline environment until after it has been reacted with the silica. We have found the reaction between iron and silica facile. The reverse addition, where the acidic iron (III) solution is slowly

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TABLE 1

Comparison of Properties of Silicalite, Aluminosilicate, and Ferrisilicate Molecular Sieves with the ZSM-5 Structure

	Silicalite	Alumino-silicate	Ferri-silicate
SiO_2/M_2O_3 (M = Al, Fe)	1800[a]	55	51
IR symmetric stretch (CM(−1)) ν(Si—O—Si); ν(Si—O—Fe)	800;—	798;—	798;656[c]
Unit cell volume (Å^3)	5337.4	—[b]	5382.5
g/100 g H_2O adsorbed (18 Torr, 150°C)	0.8	3.5	3.2
Ion exchange ability K^+/Fe mol ratio	Negligible	0.91	0.40
K(A) (*15*) cm^3(STP)/g–min	Approx. 1.5	80–90	9.0

[a] M = Al impurity for silicalite.

[b] Not determined in this study.

[c] Very weak vibration, observed only in materials containing high concentration of iron (SiO_2/Fe_2O_3 = 15–50).

added to the base, will also produce ferrisilicate gels but difficulties can be encountered in preparing the more iron-rich containing gels where precipitation of iron hydroxide can be readily observed. In the zeolite ZSM-5 preparation, a crystal directing organic cation, TPA^+ (the tetrapropylammonium cation) is required to obtain this structure. In order to avoid any possible complex formation between the iron and any free amine impurity present, the TPA^+, added as the bromide salt, is introduced after the ferrisilicate gel is formed.

Evidence for incorporation of iron into the tetrahedral framework sites is indicated in Table 1 where selected properties of the ferrisilicate are compared with those of zeolite ZSM-5 and silicalite. The presence of the symmetric $(Si—O—Fe)_n$ vibration in the framework vibration region of the infrared spectrum of the final crystalline ferrisilicate material verifies the incorporation of the iron into the framework structure. This assignment is based on previous work on framework vibration assignments in molecular sieve materials (*14*). Expansion of the unit cell further confirms iron positioned in the framework sites. Iron is approximately 1.5 times larger than the silicon or aluminum ion which may occupy that site, therefore, expansion of the unit cell is expected. EPR and Mössbauer studies confirm the presence of tetrahedrally coordinated iron. The ferrisilicate is more hydrophilic than silicalite with water adsorption proportional to the SiO_2/Fe_2O_3. It also exhibits ion exchange capacity for K^+ proportional to the framework iron content. The lower K^+/Fe ratio reported in Table 1 is attributed to thermal loss of the iron from framework positions during high-temperature treatment to remove the organic template and prepare the material for the ion exchange studies. The thermal loss of framework iron is confirmed using EPR and Mössbauer spectroscopy. A decrease in the signal at 4.3 in the ESR for tetrahedrally coordinated iron is observed and bands in both spectra corresponding to the presence of octahedral iron species appear after thermal treatment. The framework iron contributes to the acidity of the H^+ exchange form. Using butane cracking as a catalytic test for acid activity (*15*), the ferrisilicate is found to be more acidic than silicalite, where acid sites are due to trace levels of aluminum in the framework.

However, it is significantly lower in acidity than that aluminosilicate with a comparable aluminum content as shown in the table.

The incorporation of transition metals such as iron into molecular sieve structures offers another approach to preparing shape selective transition metal containing catalysts.

EXPERIMENTAL PROCEDURE

Example 1: 50 g N-brand Silica (PQ Corp., Valley Forge, Pa., $Na_2SiO_3 \cdot 5H_2O$) in 50 g H_2O is added to a solution containing 3.75 g $Fe(NO_3)_3 \cdot 9H_2O$ in 85 g H_2O. The pH is adjusted to be strongly acidic with 5.0 g H_2SO_4 (96%). To the resulting pale lemon colored gel is added 6.5 g tetrapropylammonium bromide (Aldrich Chemical) in 10 g H_2O. After vigorous agitation the mixture is placed in a stainless-steel autoclave, sealed, and heated under its own pressure at 170°C for 2 to 5 days. The resulting white solid is filtered, washed with water, and dried at 100°C. X-Ray powder diffraction confirms the formation of the ZSM-5 structure. The iron concentration in the crystals is changed by increasing or decreasing the amount of iron present in the gel phase and adjusting the hydroxide content.

Example 2: 2.92 g $Al_2(SO_4)_3 \cdot 16H_2O$ in 85 g H_2O is acidified with 5.2 g H_2SO_4 (96%) and mixed with 6.5 g tetrapropylammonium bromide. This solution is added to 50 g of N-brand Silica in 50 g H_2O. After vigorous agitation the mixture is placed in a stainless-steel autoclave, sealed, and heated under its own pressure at 170°C for 2–5 days. The resulting white solid is filtered, washed with water, and dried at 100°C. X-Ray powder diffraction confirms the formation of the zeolite ZSM-5.

Unit cell volumes reported were determined using the materials with no further treatment. These materials were examined by infrared, Mössbauer, and EPR spectroscopy. For the catalytic acidity measurements using butane cracking and the ion exchange studies, the materials were treated thermally at 550°C for 18 h in flowing dry nitrogen followed by 5 h at that temperature in flowing dry air. After cooling, they were exchanged with 1 *M* NH_4NO_3 and thermally treated for several hours in dry flowing air to produce the acid (H^+) forms which were used in the butane cracking, *n*-hexane, and water adsorption studies. The potassium-exchanged forms were prepared from the acid forms by titrating with aqueous KOH to a pH of 8 and stirring for 30 min.

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