

preserving encapsulation. These protocols have led to the successful encapsulation of Pt and Ru clusters within ANA.

[0004] MFI (ZSM-5) is a medium-pore silica-rich zeolite that typically requires high crystallization temperatures (423-473 K) and pH (>11) for its template-free synthesis. Encapsulation in such materials remains inaccessible via procedures involving direct hydrothermal synthesis using ligand-stabilized metal precursors, as well as post-synthesis exchange, except in the case of monovalent or divalent cations.

[0005] It would be of benefit to the industry if more efficient and facile methods of metal encapsulation were available for silica-rich zeolites.

Summary of the Invention

[0006] Provided is a method of encapsulating a metal in a zeolite by the method of:

- (a) inserting a metal precursor into a lower framework density (FD) zeolite, and
- (b) converting the lower framework density (FD) zeolite to a zeolite having higher framework density values in the absence of an organic structure directing agent (SDA), wherein the conversion is conducted in a basic solution having a NaOH/SiO₂ ratio in the range of from 0.25 to 1.0 and a H₂O/SiO₂ ratio greater than 50, and at a temperature above the crystallization temperature of the parent zeolite. The conversion is generally conducted by direct hydrothermal synthesis.

[0007] In one embodiment, the metal is Pt, Rh, Ru or Cu. In another embodiment, the zeolite having higher framework density values is ZSM-5, SSZ-35, ZSM-12 or chabazite.

[0008] In one embodiment, the zeolite having higher framework density values is a silica-rich zeolite, having a Si/Al ratio of 10 or higher.

[0009] Among other factors, it has been discovered by the inventors that a general strategy for the encapsulation of metal clusters within silica-rich zeolites such as ZSM-5, SSZ-35, ZSM-12 or chabazite is possible by exploiting interzeolite transformations of low framework density parent structures, such as BEA or FAU zeolites, into zeolite daughter structures, without the need for organic structure directing agents (SDA). The catalytic consequences of the selective encapsulation

of metal clusters (Pt, Ru, Rh, Cu) within the void spaces of silica-rich frameworks such as ZSM-5 have also been discovered.

[0010] These interzeolite transformations provide a general and convenient route for the encapsulation of clusters within microporous solids in those cases for which the

successful placement of precursors can be accomplished within a large pore parent zeolite structure via post-synthesis exchange or during hydrothermal crystallization. This parent structure, containing metal clusters within its microporous voids, can then be recrystallized without loss of encapsulation into a daughter structure of higher framework density, for example MFI (ZSM-5), for which more direct methods of encapsulation are unavailable or impractical. The transformation also occurs without use of an SDA. The overall process is efficient and facile.

Brief Description of the Drawings

[0011] FIGURE 1 shows X-ray diffraction patterns of the products synthesized from (i) BEA ($\text{Si}/\text{Al} = 37.5$) and (ii) FAU ($\text{Si}/\text{Al} = 40$) parent zeolites via (a) direct, (b) template-assisted (using TPABr), and (c) seed-assisted transformations (using MFI seeds). Syntheses were carried out at 423 K, $\text{NaOH}/\text{SiO}_2 = 0.35$ (from BEA) and 0.50 (from FAU) and $\text{H}_2\text{O}/\text{SiO}_2 = 65$ (from BEA) and 95 (from FAU) (Table 1).

[0012] FIGURE 2 shows X-ray diffraction patterns of MFI products synthesized by interzeolite transformations of (a) BEA and (b) FAU containing metal clusters as parent zeolites. Syntheses were carried out at molar composition 0.35 NaOH: 1.0 SiO_2 : 0.0133 Al_2O_3 : 65.0 H_2O from BEA without seeds and 0.50 NaOH: 1.0 SiO_2 : 0.0125 Al_2O_3 : 95.0 H_2O from FAU with 10 % wt. MFI seeds at 423 K (Table 1).

[0013] FIGURE 3 shows TEM images and metal cluster size distributions of parent (a) BEA and (b) FAU zeolites containing Pt clusters, synthesized by ion exchange methods and (c) Pt clusters dispersed on SiO_2 , synthesized by incipient wetness impregnation method.

[0014] FIGURE 4 shows TEM images and metal cluster size distributions of Pt containing MFI samples synthesized by interzeolite transformations of (a) BEA and (b) FAU zeolites containing Pt clusters as parent materials.

[0015] FIGURE 5 shows TEM images of (a) Ru containing MFI synthesized by interzeolite transformation of Ru/BEA and (b) Ru and (c) Rh containing MFI synthesized by interzeolite transformations of Ru and Rh containing FAU as parent zeolites.

[0016] FIGURE 6 shows schematic representation of the synthesis factors that limit encapsulation of metal clusters within MFI over a broad range of synthesis conditions. Mi represents the synthesis method used (see Table 5).

What is claimed is:

1. Encapsulating a metal in a zeolite by the method of:
 - (a) inserting a metal or metal precursor into a parent zeolite, and
 - (b) converting the parent zeolite to a zeolite having a higher framework density than the parent zeolite, in the absence of an organic structure directing agent (SDA),wherein the conversion is conducted in a basic solution having a NaOH/SiO₂ ratio in the range of from 0.25 to 1.0 and a H₂O/SiO₂ ratio greater than 50, and at a temperature above the crystallization temperature of the parent zeolite.
2. The method of claim 1, wherein seed crystals of the higher framework density zeolite are added to the parent zeolite prior to or during the conversion.
3. The method of claim 1, wherein the conversion is achieved by hydrothermal synthesis.
4. The method of claim 1, wherein the metal precursor in aqueous solution has dimensions such that it cannot be ion-exchanged or impregnated directly into the higher framework density zeolite.
5. The method of claim 4, wherein the metal is Pt, Rh, Ru or Cu.
6. The method of claim 1, wherein the parent zeolite is BEA or FAU.
7. The method of claim 1, wherein the parent zeolite is a Y zeolite.
8. The method of claim 1, wherein the higher framework density zeolite is ZSM-5, SSZ-35, ZSM-12 or chabazite.

9. The method of claim 1, wherein the parent zeolite is BEA or FAU, the higher framework density zeolite is ZSM-5, and the metal is Pt, Rh or Ru.
10. The method of claim 1, wherein the parent zeolite comprises a Y zeolite, the higher framework zeolite is a chabazite, and the metal is Cu.
11. The method of claim 1, wherein the higher framework density zeolite has a Si/Al ratio of 10 or greater.
12. The method of claim 11, wherein the Si/Al ratio is 22 or greater.
13. The method of claim 1, wherein the metal precursor comprises an amine or ethylene diamine complex.
14. The method of claim 1, wherein the metal precursor is a ligated metal.
15. The method of claim 1, wherein the metal comprises a metal cluster.
16. The method of claim 1, wherein the insertion is achieved by exchanging cationic metal precursors and reducing the metal precursors with H₂ to form metal clusters.