CLAIMS

What is claimed is:

1. ~~A zeolitic imidazolate framework composition with an SOD framework type,~~ wherein the zeolitic imidazolate framework structure is capable of sorbing, at a temperature of ~28°C: (i) at least 0.60 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~75 Torr; (ii) at least 0.75 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~100 Torr; (iii) at least 1.15 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~200 Torr; and/or (iv) at least 0.35 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~39 Torr.

2. A zeolitic imidazolate framework composition having an empirical formula, Zn(5-azabenzimidazolate)$_2$, wherein the zeolitic imidazolate framework structure is capable of sorbing, at a temperature of ~28°C: (i) at least 0.60 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~75 Torr; (ii) at least 0.75 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~100 Torr; (iii) at least 1.15 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~200 Torr; and/or (iv) at least 0.35 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~39 Torr.

3. A porous crystalline material having an empirical formula Zn(5-aza-benzimidazolate)$_2$, exhibiting an SOD framework type, and exhibiting an x-ray diffraction pattern with peaks defined by the d-spacing ranges and relative intensity ranges described in any one of Table 1b, Table 1d, Table 7b, Table 8b, and Table 9b.

4. A method of adsorbing a gas comprising contacting the gas (*e.g.*, comprising hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon, or an amine) with ~~the porous crystalline material of claim 3.~~

5. A method of separating a gas from a fluid stream containing the gas (*e.g.*, comprising hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon, or an amine) comprising contacting the fluid stream with the porous crystalline material of claim 3.

6. A method for forming a zeolitic imidazolate framework composition, said method comprising the steps of: (a) mixing together a reaction medium, a source of a imidazolate or a substituted imidazolate reactant, IM, and a reactant source of metals M^1 and M^2 to form a synthesis mixture, wherein M^1 and M^2 comprise the same or different metal cations, at least one of which reactants is relatively insoluble in the reaction medium itself and in the synthesis mixture; (b) maintaining the synthesis mixture having at least one relatively insoluble reactant under conditions sufficient to form a zeolitic imidazolate framework composition having a tetrahedral framework comprising a general structure, M^1-IM-M^2; and (c) treating the zeolitic imidazolate framework composition under conditions sufficient to stably reduce its unit cell volume.

7. The method according to claim 6, wherein the zeolitic imidazolate framework composition product has a framework type that is different from the framework type obtained when a zeolitic imidazolate framework composition is prepared by crystallizing substantially soluble sources of M^1, M^2 and IM in the same reaction medium.

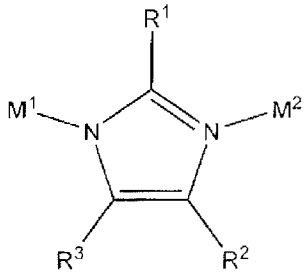
8. The method according to claim 6 or claim 7, wherein the zeolitic imidazolate framework composition product exhibits a framework type selected from the group consisting of ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAG, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CRB, CZP, DAC, DDR, DFO, DFT, DIA, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, FRL, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, ISV, ITE, ITH, ITW, IWR, IWV, IWW, JBW, KFI, LAU, LCS, LEV, LIO, LIT, LOS, LOV, LTA, LTL,

~~LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MSE,~~ MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, PAR, PAU, PHI, PON, POZ, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SGT, SIV, SOD, SOS, SSY, STF, STI, STT, SZR, TER, THO, TON, TSC, TUN, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZNI, ZON, and combinations thereof, such as selected from the group consisting of CRB, DFT, CAG, SOD, MER, RHO, ANA, LTA, DIA, ZNI, GME, LCS, FRL, GIS, POZ, MOZ, and combinations thereof, *e.g.*, SOD.

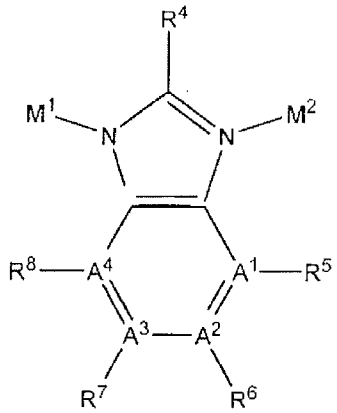
9. The method according to any one of claims 6-8, wherein the reaction medium comprises N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N,N-dimethylacetamide (DMAc), 1,3-dimethylpropyleneurea (DMPU), a sulfoxide, a phosphoramide, acetonitrile (MeCN), triethylamine (TEA), water, ammonia, ethanol, or a combination thereof.

10. The method according to any one of claims 6-9, wherein the metals are selected from the group consisting of Be, Mg, Ca, Sr, Ba, Ra, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Lr, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Uub, and combinations thereof, *e.g.*, Zn.

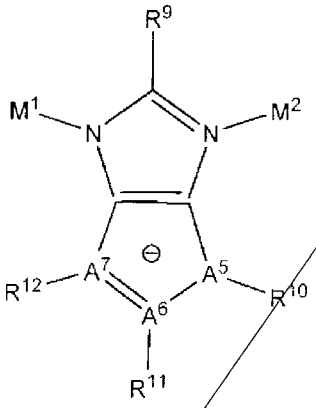
11. The method according to any one of claims 6-10, wherein the imidazolate or substituted imidazolate, IM, is selected from the group consisting of IV, V, VI, or any combination thereof:



(IV)



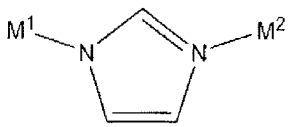
(V)



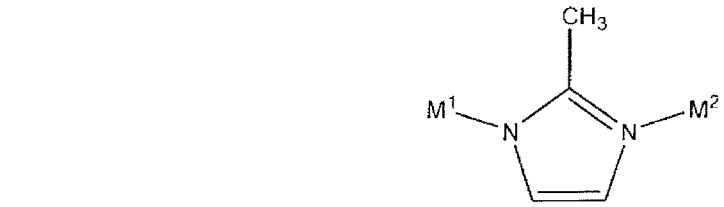
(VI)

wherein A^1, A^2, A^3 and A^4 are selected from a group of elements consisting of C, N, P, and B, wherein A^5, A^6, and A^7 can be either C or N, wherein R^5-R^8 are present when A^1 to A^4 comprise C, wherein R^1, R^4 or R^9 comprise a non-sterically hindering group that does not interfere with the adjacent M^1 or M^2, wherein R^2, R^3, R^5, R^6, R^7, and R^8 are each individually hydrogen, alkyl, halo, cyano, or nitro, wherein M^1 and M^2 comprise the same or different metal cation, and wherein R^{10}, R^{11}, and R^{12} are each individually electron withdrawing groups.

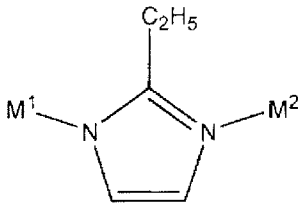
12. The method according to claim 11, wherein the imidazolate or substituted imidazolate, IM, is selected from the group consisting of VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII, and/or XVIII:



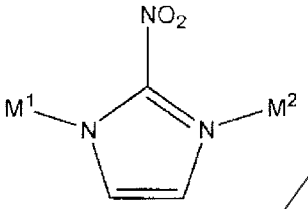
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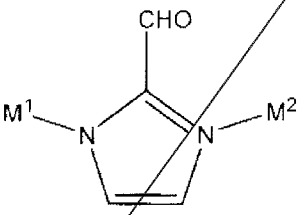
(VIII)



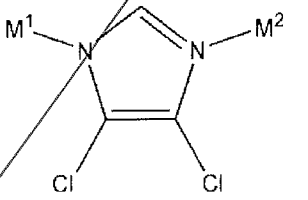
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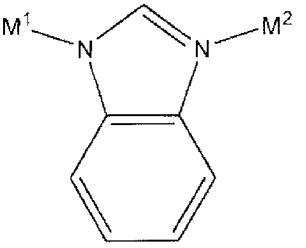
(X)



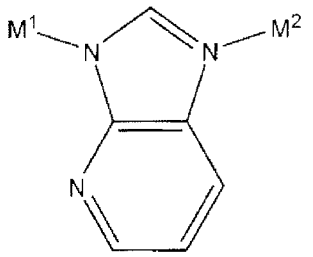
(XI)



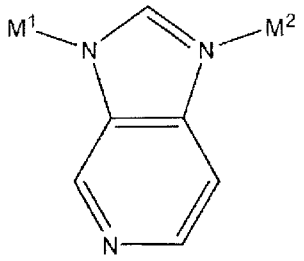
(XII)



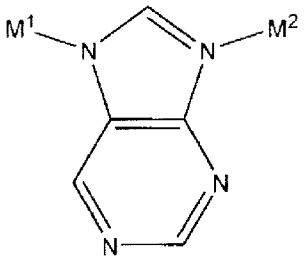
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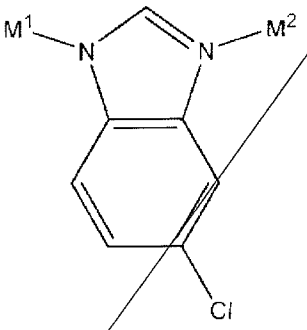
(XIV)



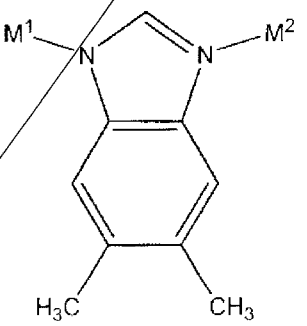
(XV)



(XVI)



(XVII)



(XVIII)

e.g., wherein the imidazolate or substituted imidazolate, IM, comprises the structure of formula XV.

13. The method according to any one of claims 6-12, wherein the sufficient conditions comprise a contact/crystallization time from 1 hour to 10 days (*e.g.*, from 12 hours to 7 days), a temperature from about -78°C to the boiling point of the reaction medium (*e.g.*, from about 15°C to about 150°C), and a reaction pressure from about 1 kPaa to about 10 MPaa (*e.g.*, from about 100 kPaa to about 10 MPaa).

~~14. The method according to any one of claims 6-13, wherein the imidazolate or~~ substituted imidazolate, IM, is 5-azabenzimidazolate, and wherein the zeolitic imidazolate framework composition has an SOD framework type.

15. The method according to any one of claims 6-14, wherein the conditions sufficient for the treatment step comprise removing the reaction medium and introducing an inert gas for a continuous period of at least 1 day, *e.g.*, at least 2 days, at least 3 days, at least 5 days, at least 7 days, at least 10 days, at least 14 days, at least 17 days, at least 20 days, at least 23 days, at least 26 days, or at least 30 days, and ~~optionally up to 365 days.~~

CLAIMS

What is claimed is:

1. A zeolitic imidazolate framework composition with an SOD framework type, wherein the zeolitic imidazolate framework structure is capable of sorbing, at a temperature of ~28°C: (i) at least 0.60 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~75 Torr; (ii) at least 0.75 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~100 Torr; (iii) at least 1.15 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~200 Torr; and/or (iv) at least 0.35 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~39 Torr.

2. A zeolitic imidazolate framework composition having an empirical formula, Zn(5-azabenzimidazolate)$_2$, wherein the zeolitic imidazolate framework structure is capable of sorbing, at a temperature of ~28°C: (i) at least 0.60 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~75 Torr; (ii) at least 0.75 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~100 Torr; (iii) at least 1.15 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~200 Torr; and/or (iv) at least 0.35 mmol of CO_2 per gram of zeolitic imidazole framework composition at a CO_2 partial pressure of ~39 Torr.

3. A porous crystalline material having an empirical formula Zn(5-aza-benzimidazolate)$_2$, exhibiting an SOD framework type, and exhibiting an x-ray diffraction pattern with peaks defined by the d-spacing ranges and relative intensity ranges described in Table 1b.

4. A porous crystalline material having an empirical formula Zn(5-aza-benzimidazolate)$_2$, exhibiting an SOD framework type, and exhibiting an x-ray diffraction pattern with peaks defined by the d-spacing ranges and relative intensity ranges described in Table 1d.

5. A porous crystalline material having an empirical formula Zn(5-aza-benzimidazolate)$_2$, exhibiting an SOD framework type, and exhibiting an x-ray diffraction pattern with peaks defined by the d-spacing ranges and relative intensity ranges described in Table 7b.

6. A porous crystalline material having an empirical formula Zn(5-aza-benzimidazolate)$_2$, exhibiting an SOD framework type, and exhibiting an x-ray diffraction pattern with peaks defined by the d-spacing ranges and relative intensity ranges described in Table 8b.

7. A porous crystalline material having an empirical formula Zn(5-aza-benzimidazolate)$_2$, exhibiting an SOD framework type, and exhibiting an x-ray diffraction pattern with peaks defined by the d-spacing ranges and relative intensity ranges described in Table 9b.

8. A method of adsorbing a gas comprising contacting the gas with the porous crystalline material of claim 3.

9. The method of claim 8, wherein the gas is hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon or an amine.

10. A method of separating a gas from a fluid stream containing the gas comprising contacting the fluid stream with the porous crystalline material of claim 3.

11. The method of claim 10, wherein the gas is hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon or an amine.

12. A method of adsorbing a gas comprising contacting the gas with the porous crystalline material of claim 4.

13. The method of claim 12, wherein the gas is hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon or an amine.

14. A method of separating a gas from a fluid stream containing the gas comprising contacting the fluid stream with the porous crystalline material of claim 4.

15. The method of claim 14, wherein the gas is hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon or an amine.

16. A method of adsorbing a gas comprising contacting the gas with the porous crystalline material of claim 5.

17. The method of claim 16, wherein the gas is hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon or an amine.

18. A method of separating a gas from a fluid stream containing the gas comprising contacting the fluid stream with the porous crystalline material of claim 5.

19. The method of claim 18, wherein the gas is hydrogen, nitrogen, oxygen, a noble gas, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, hydrogen sulfide, ammonia, a hydrocarbon or an amine.

20. A method for forming a zeolitic imidazolate framework composition, said method comprising the steps of: (a) mixing together a reaction medium, a source of a imidazolate or a substituted imidazolate reactant, IM, and a reactant source of metals M^1 and M^2 to form a synthesis mixture, wherein M^1 and M^2 comprise the same or different metal cations, at least one of which reactants is relatively insoluble in the reaction medium itself and in the synthesis mixture; (b) maintaining the synthesis mixture having at least one relatively insoluble reactant under conditions sufficient to

form a zeolitic imidazolate framework composition having a tetrahedral framework comprising a general structure, M^1-IM-M^2; and (c) treating the zeolitic imidazolate framework composition under conditions sufficient to stably reduce its unit cell volume.

21. The method according to claim 20, wherein the zeolitic imidazolate framework composition product has a framework type that is different from the framework type obtained when a zeolitic imidazolate framework composition is prepared by crystallizing substantially soluble sources of M^1, M^2 and IM in the same reaction medium.

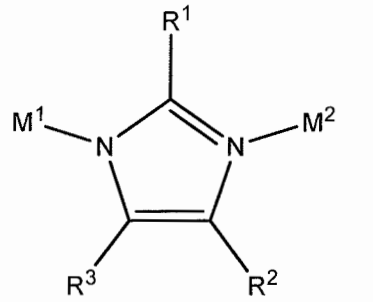
22. The method according to claim 20, wherein the zeolitic imidazolate framework composition product exhibits a framework type selected from the group consisting of ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAG, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CRB, CZP, DAC, DDR, DFO, DFT, DIA, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, FRL, GIS, GIU, GME, GON, GOO, HEU, IFR, IHW, ISV, ITE, ITH, ITW, IWR, IWV, IWW, JBW, KFI, LAU, LCS, LEV, LIO, LIT, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, PAR, PAU, PHI, PON, POZ, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SGT, SIV, SOD, SOS, SSY, STF, STI, STT, SZR, TER, THO, TON, TSC, TUN, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZNI, ZON, and combinations thereof.

23. The method according to claim 20, wherein the zeolitic imidazole framework composition product exhibits a framework type selected from the group consisting of CRB, DFT, CAG, SOD, MER, RHO, ANA, LTA, DIA, ZNI, GME, LCS, FRL, GIS, POZ, MOZ, and combinations thereof.

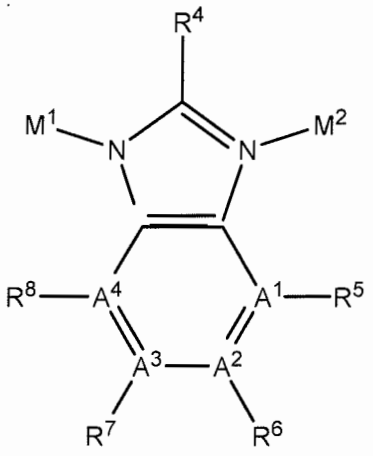
24. The method according to claim 20, wherein the reaction medium comprises N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N,N-dimethylacetamide (DMAc), 1,3-dimethylpropyleneurea (DMPU), a sulfoxide, a phosphoramide, acetonitrile (MeCN), triethylamine (TEA), or a combination thereof.

25. The method according to claim 20, wherein the metals are selected from the group consisting of Be, Mg, Ca, Sr, Ba, Ra, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Lr, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Uub, and combinations thereof.

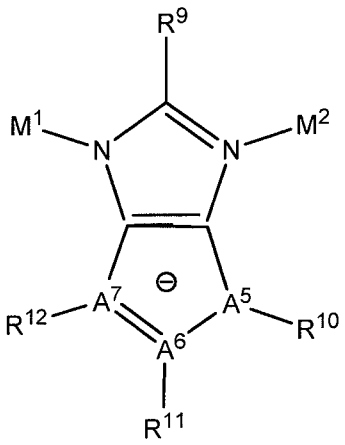
26. The method according to claim 20, wherein the imidazolate or substituted imidazolate, IM, is selected from the group consisting of IV, V, VI, or any combination thereof:



(IV)



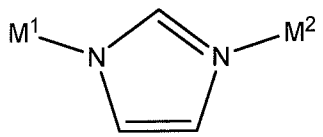
(V)



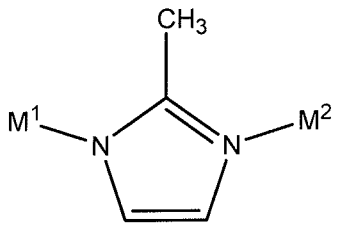
(VI)

wherein A^1, A^2, A^3 and A^4 are selected from a group of elements consisting of C, N, P, and B, wherein A^5, A^6, and A^7 can be either C or N, wherein R^5-R^8 are present when A^1 to A^4 comprise C, wherein R^1, R^4 or R^9 comprise a non-sterically hindering group that does not interfere with the adjacent M^1 or M^2, wherein R^2, R^3, R^5, R^6, R^7, and R^8 are each individually hydrogen, alkyl, halo, cyano, or nitro, wherein M^1 and M^2 comprise the same or different metal cation, and wherein R^{10}, R^{11}, and R^{12} are each individually electron withdrawing groups.

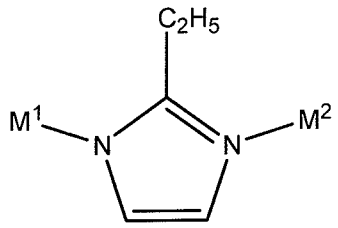
27. The method according to claim 26, wherein the imidazolate or substituted imidazolate, IM, is selected from the group consisting of VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII, and/or XVIII:



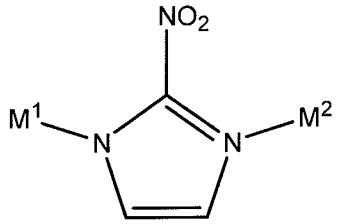
(VII)



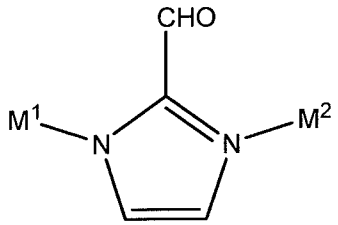
(VIII)



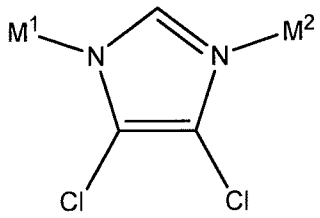
(IX)



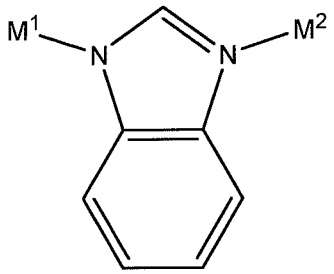
(X)



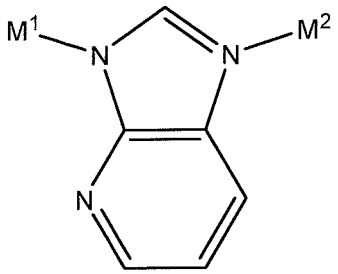
(XI)



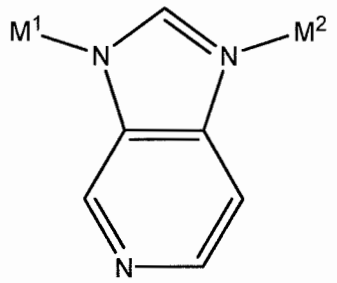
(XII)



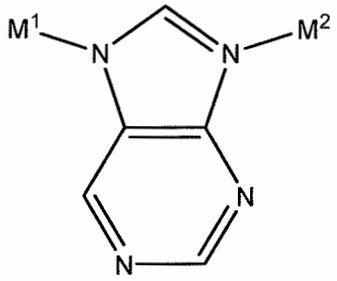
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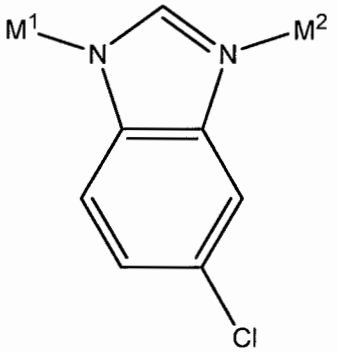
(XIV)



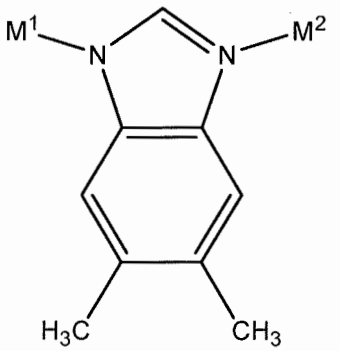
(XV)



(XVI)



(XVII)



(XVIII)

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28. The method according to claim 27, wherein the imidazolate or substituted imidazolate, IM, comprises the structure of formula XV.

29. The method according to claim 20, wherein the sufficient conditions for the maintaining step comprise a contact/crystallization time from 1 hour to 10 days, a temperature from about -78°C to the boiling point of the reaction medium, and a

reaction pressure from about 1 kPaa to about 10 MPaa.

30. The method according to claim 20, wherein the sufficient conditions comprise a contact/crystallization time from 12 hours to 7 days, a temperature from about 15°C to about 150°C, and a reaction pressure from about 100 kPaa to about 10 MPaa.

31. The method according to claim 20, wherein the imidazolate or substituted imidazolate, IM, is 5-azabenzimidazolate, and wherein the zeolitic imidazolate framework composition has an SOD framework type.

32. The method according to claim 20, wherein the conditions sufficient for the treatment step comprise removing the reaction medium and introducing an inert gas for a continuous period of at least 10 days.