invention, i.e., the Sn-Ti-MEL molecular sieve.

The specific reaction conditions for the synthesis of the tin-titanium-silicon molecular sieve are listed in Table 1. The physicochemical characterization and the activity evaluation result of the tin-titanium-silicon molecular sieve are shown in Table 2.

Examples 23-24

The Sn-Ti-MEL molecular sieve was prepared according to the method of Example 22. Its ratio, synthesis condition and material ratio are shown in Table 1; the physicochemical characterization and the activity evaluation result of the tin-titanium-silicon molecular sieve are shown in Table 2, and refer to Example 22 for synthesis conditions if not involved in Table 1.

Comparative Example 1

The Sn-Ti-MFI molecular sieve was prepared by hydrothermal method in this comparative example.

Stannic tetrachloride pentahydrate ($SnCl_4.5H_2O$) was dissolved in water. The aqueous solution was added with tetraethyl orthosilicate (TEOS) and stirred, followed by addition of tetrabutyl titanate (TBOT), addition of tetrapropyl ammonium hydroxide (TPAOH, 20% aqueous solution) and water under stirring, stirred continuously for 30 min to obtain a clear liquid with a chemical composition of 0.015 TiO_2: 0.03 SnO_2: SiO_2: 0.45 TPA: 35 H_2O, aged at 70 °C for 6 hours, and then crystallized at 433 K for 2 days. After that, the obtained solid was filtered, washed with distilled water, dried at 393 K for 5 hours, and then calcined at 823 K for 10 hours to obtain a molecular sieve sample. Therein the amount of TEOS ewas 15.31 g, the amount of TPAOH was 33.67 g, the amount of $SnCl_4.5H_2O$ was 0.38 g, the amount of TBOT was 0.38 g, and the amount of water was 39.64 g. The XPS diagram of the prepared Sn-Ti-MFI molecular sieve is shown in Figure 2.

Comparative Example 2

The Sn-Ti-MEL molecular sieve was prepared by a hydrothermal

method in this comparative example.

Stannic tetrachloride pentahydrate ($SnCl_4.5H_2O$) was dissolved in water. The aqueous solution was added with tetraethyl orthosilicate (TEOS) and stirred, followed by addition of tetrabutyl titanate (TBOT), addition of tetrapropyl ammonium hydroxide (TPAOH, 20% aqueous solution) and water under stirring, stirred continuously for 30 min to obtain a clear liquid with a chemical composition of 0.015 TiO_2: 0.03 SnO_2: SiO_2: 0.45 TPA: 35 H_2O, aged at 70 °C for 6 hours, and then crystallized at 433 K for 2 days. After that, the obtained solid was filtered, washed with distilled water, dried at 393 K for 5 hours, and then calcined at 733 K for 10 hours to obtain a molecular sieve sample. Therein the amount of TEOS was 15.31 g, the amount of TPAOH was 42.96 g, the amount of $SnCl_4.5H_2O$ was 0.38 g, the amount of TBOT was 0.38 g, and the amount of water was 39.64 g.

Comparative Examples 3-10

The Sn-Ti-MFI molecular sieve was prepared according to the method of Comparative Example 1. Its ratio, synthesis condition and material ratio are shown in Table 1; the physicochemical characterization and activity evaluation result of the tin-titanium-silicon molecular sieve are shown in Table 2, and refer to Comparative Example 1 for synthesis conditions if not involved in Table 1.

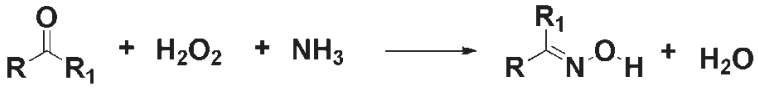
Test Examples

(1) Preparation of methyl lactate from catalysis of dihydroxyacetone

The samples obtained in the examples and the comparative examples were used as catalysts for the catalysis reaction of dihydroxyacetone to prepare methyl lactate. The specific reaction conditions were as follows: in the slurry bed reactor, the reactant of dihydroxyacetone and the solvent of methanol were reacted at 60 °C and the self-generated pressure at a molar ratio of 1: 200, the amount of the catalyst being 3.0% by weight of the total reaction solution, and samples were taken every hour of reaction to determine the composition of the product. The calculation results are shown in Table 2.

(2) Ammoximation reaction of aldehydes and ketones

The samples obtained in the examples and comparative examples were used as catalysts, and reacted according to the formula of



wherein R is selected from alkyl and aryl, such as phenyl; R_1 is selected from hydrogen and alkyl; or R and R_1 are combined to form a ring.

The specific reaction conditions were as follows: in the slurry bed reactor, the reactants of aldehydes and ketones, hydrogen peroxide and the solvent (such as tert-butyl alcohol) were reacted at 80 °C and the self-generated pressure at a molar ratio of 1: 1: 200, the amount of catalyst being 5.0% by weight of the total reaction solution, and samples were taken every hour of reaction to determine the composition of the product. The results are shown in Table 3.

(3) Epoxidation reaction of olefins

The samples obtained in the examples and comparative examples were used as catalysts, and reacted according to the formula of



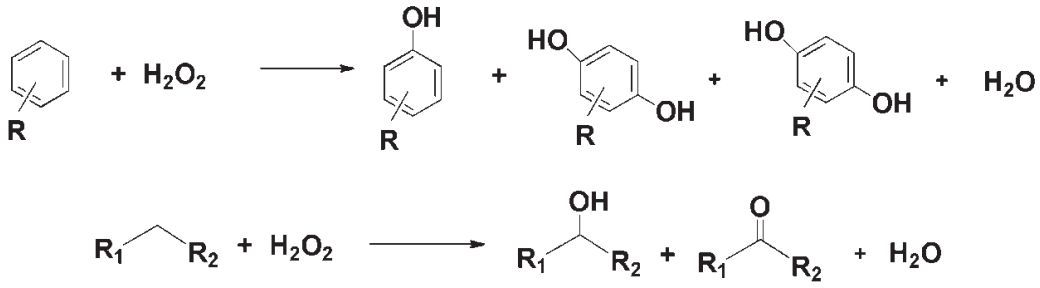
wherein R_1 and R_2 are respectively selected from hydrogen and alkyl optionally containing heteroatoms (such as oxygen), or R_1 and R_2 are combined to form a ring.

The specific reaction conditions were as follows: in the slurry bed reactor, the reactants of olefin, hydrogen peroxide and the solvent (such as tert-butyl alcohol) were reacted at 50 °C and the self-generated pressure at a molar ratio of 1: 1: 200, the amount of catalyst being 5.0% by weight of the total reaction solution, and samples were taken every hour of reaction to determine the composition of the product. The results are shown in Table 3.

(4) Oxidation reaction of aromatics/alkanes

The samples obtained in the examples and comparative examples were

used as catalysts, and reacted according to the formula of



wherein R is selected from hydrogen, alkyl and hydroxyl, and R can represent two substituents; R_1 and R_2 are respectively selected from hydrogen and alkyl, or R_1 and R_2 are combined to form an optionally alkyl-substituted ring.

The specific reaction conditions were as follows: in the slurry bed reactor, the reactants (aromatics/alkanes), hydrogen peroxide and the solvent (such as tert-butyl alcohol) were reacted at 80 °C and self-generated pressure at a molar ratio of 1: 1: 200, the amount of catalyst being 5.0% by weight of the total reaction solution, and samples were taken every hour of reaction to determine the composition of the product. The results are shown in Table 3.

Table 1

	organic silicon sources	titanium sources	inorganic tin sources	alkaline template	organic bases	organic silicon source: titanium source: organic base: solvent	organic silicon source: tin source	tin source: alkaline template	temperature and time of heating in step S2	temperature and time of hydrothermal reaction
Example1	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 2	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 3	tetraethyl orthosilicate	tetrabutyl titanate	stannous chloride	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 4	tetraethyl orthosilicate	tetrabutyl titanate	stannous chloride dihydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 5	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	ammonia	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 6	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	ethylamine	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 7	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	triethanolamine	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 8	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.1:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 9	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.4:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 10	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:15	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 11	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:30	1:0.02	1:1	70℃, 6h	160℃ , 3 days

Example 12	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.01	1:1	70℃, 6h	160℃ , 3 days
Example 13	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.03	1:1	70℃, 6h	160℃ , 3 days
Example 14	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	50℃, 6h	160℃ , 3 days
Example 15	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	80℃, 6h	160℃ , 3 days
Example 16	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 5h	160℃ , 3 days
Example 17	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 8h	160℃ , 3 days
Example 18	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	120℃ , 3 days
Example 19	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	170℃ , 3 days
Example 20	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 2 days
Example 21	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃ , 5 days
Example 22	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrabutyl ammonium hydroxide	1:0.02:0.2:20	1:0.01	1:1	70℃, 6h	160℃ , 3 days
Example 23	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrabutyl ammonium hydroxide	1:0.02:0.2:21	1:0.03	1:1	70℃, 6h	160℃ , 3 days
Example 24	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrabutyl ammonium hydroxide	1:0.02:0.2:22	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Example 25	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrabutyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1: 9	70℃, 6h	160℃ , 3 days
Example 26	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrabutyl ammonium hydroxide	1:0.04:0.5:32	1:0.035	1:1	70℃, 6h	160℃ , 3 days
Comparative Example 1	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	-	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	-	70℃, 6h	160℃ , 3 days
Comparative Example 2	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	-	tetrabutyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	-	70℃, 6h	160℃ , 3 days
Comparative Example 3	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.01:20	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Comparative Example 4	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:5	1:0.02	1:1	70℃, 6h	160℃ , 3 days
Comparative Example 5	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.001	1:1	70℃, 6h	160℃ , 3 days
Comparative Example 6	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.06	1:1	70℃, 6h	160℃ , 3 days
Comparative Example 7	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	10℃, 6h	160℃ , 3 days
Comparative Example 8	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 1h	160℃ , 3 days
Comparative Example 9	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	100℃ , 3 days
Comparative Example 10	tetraethyl orthosilicate	tetrabutyl titanate	stannic chloride pentahydrate	tetrapropyl ammonium hydroxide	tetrapropyl ammonium hydroxide	1:0.02:0.2:20	1:0.02	1:1	70℃, 6h	160℃, 1 day

In Table 1, organic silicon source: titanium source: organic base: solvent refers to the molar ratio of the amounts of the organic silicon source, the titanium source, the organic base and the solvent; organic silicon source: tin source refers to the molar ratio of the amounts of the organic silicon source and the tin source; tin source: alkaline template

CLAIMS

1. A tin-titanium-silicon molecular sieve, wherein the electron binding energy of framework tin active centers in the tin-titanium-silicon molecular sieve is 488.5 eV or less,

wherein the tin-titanium-silicon molecular sieve is an Sn-Ti-MFI molecular sieve or an Sn-Ti-MEL molecular sieve.

2. The tin-titanium-silicon molecular sieve according to claim 1, wherein, in the tin-titanium-silicon molecular sieve, the molar ratio of titanium to silicon is 0.005-0.03, preferably 0.005-0.02, and/or the molar ratio of tin to silicon is 0.005-0.025, preferably 0.005-0.02.

3. The tin-titanium-silicon molecular sieve according to claim 1 or 2, wherein the electron binding energy of framework tin active centers is 488.0-488.4 eV.

4. The tin-titanium-silicon molecular sieve according to any of claims 1-3, wherein the electron binding energy of framework titanium active centers is 460.0-461.2 eV, preferably 460.8-461.2 eV.

5. The tin-titanium-silicon molecular sieve according to any of claims 1-4, wherein chemical shift data of phosphorus corresponding to double-quantum nuclear magnetic framework tin species adsorbed by a trimethylphosphine probe molecule are $\leq$ -23 ppm; and/or chemical shift data of phosphorus corresponding to double-quantum nuclear magnetic framework titanium species adsorbed by a trimethylphosphine probe molecule are $\geq$ -34 ppm.

6. The tin-titanium-silicon molecular sieve according to any of claims 1-5, which has an external specific surface area of 100-150 m^2/g, and a total pore volume of 0.25-0.35 cm^3/g.

7. The tin-titanium-silicon molecular sieve according to claim 1, wherein the Sn-Ti-MEL molecular sieve has a structure in which long-strip grains having a length of 10-50 nm and a width of 10-30 nm overlap and stack.

8. A method for preparing the tin-titanium-silicon molecular sieve

according to any of claims 1-7, said method comprising:

S1, mixing an organic silicon source, an organic base, a solvent, a tin source, a titanium source and an alkaline template to obtain a first mixture, wherein the organic base is tetrapropyl ammonium hydroxide and/or tetrabutyl ammonium hydroxide; the molar ratio of the amounts of the organic silicon source, the organic base, the solvent, the tin source and the titanium source is 1: (0.05-0.6): (10-30): (0.005-0.04): (0.005-0.04), wherein the organic silicon source is calculated based on SiO_2, the tin source is calculated based on SnO_2, and the titanium source is calculated based on TiO_2; the molar ratio of the amounts of the tin source and the alkaline template is 1: (1-10), wherein the tin source is calculated based on anion;

S2, heating the first mixture at 30-80 °C for 2-10 hours to obtain a second mixture;

S3, subjecting the second mixture to a hydrothermal reaction at 120-200 °C for 2-7 days to obtain a third mixture;

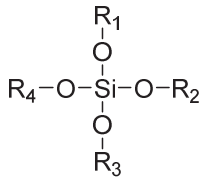
S4, taking out a solid in the third mixture and subjecting it to drying and calcination,

wherein step S1 comprises: mixing the organic silicon source, the organic base, the solvent and the titanium source to obtain a fourth mixture, mixing the resulting fourth mixture with the tin source and stirring for 0.5-2 hours, and then adding the alkaline template to obtain the first mixture.

9. The method according to claim 8, wherein the molar ratio of the amounts of the tin source and the alkaline template is 1: (4-8).

10. The method according to claim 8 or 9, wherein the molar ratio of the amounts of the organic silicon source, the organic base, the solvent, the tin source and the titanium source is 1: (0.1-0.4): (15-30): (0.01-0.03): (0.01-0.03).

11. The method according to any of claims 8-10, wherein the organic silicon source has a structure shown in formula (I) below,



Formula (I)

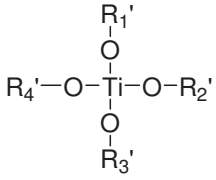
wherein, R_1, R_2, R_3 and R_4 are each independently selected from C1-C4 alkyl, such as C1-C4 linear alkyl and C3-C4 branched alkyl, preferably one or more of tetramethyl orthosilicate, tetraethyl orthosilicate, tetra-n-propyl orthosilicate and tetra-n-butyl orthosilicate, more preferably tetraethyl orthosilicate and/or tetramethyl orthosilicate;

the solvent is selected from deionized water and/or distilled water;

the alkaline template is selected from one or more of ammonia, aliphatic amine, aliphatic alcohol amine and quaternary ammonium base, preferably one or more of ammonia, ethylamine, tetrapropyl ammonium hydroxide and triethanolamine;

the tin source is selected from one or more of stannic chloride, stannic chloride pentahydrate, stannous chloride, stannous chloride dihydrate, calcium stannate, potassium stannate, sodium stannate, lithium stannate, stannous sulfate and stannous pyrophosphate, preferably stannic chloride pentahydrate; and/or

the titanium source has a structure shown in formula (II) below,



Formula (II)

wherein, R_1', R_2', R_3' and R_4' are each independently selected from C1-C6 alkyl, such as C1-C6 linear alkyl and C3-C6 branched alkyl; the titanium source is preferably one or more of tetramethyl titanate, tetraethyl titanate, tetraisopropyl titanate and tetrabutyl titanate.

12. The method according to any of claims 8-11, wherein the hydrothermal reaction conditions in S3 include: a temperature of 120-170

°C and time of 2-5 days.

13. Application of the tin-titanium-silicon molecular sieve according to any of claims 1-7 in the preparation of lactate from dihydroxyacetone, an ammoximation reaction of aldehydes and ketones, an epoxidation reaction of olefins or an oxidation reaction of aromatics/alkanes.

14. A catalyst comprising the tin-titanium-silicon molecular sieve according to any of claims 1-7.