Claims

1. A catalyst for oxidative coupling of methane consisting of three active components of manganese sesquioxide, sodium tungstate, manganese titanate, and a carrier of silica,

wherein the catalyst has a composition represented by the following formula: xMn_2O_3-yNa_2WO_4-$zMnTiO_3$-(100-x-y-z)SiO_2,

wherein x, y and z respectively representing the weight fraction occupied by manganese sesquioxide, sodium tungstate, manganese titanate in the catalyst, and wherein $0<x\leq 20$, $1\leq y\leq 20$, $1\leq z\leq 40$.

2. The catalyst of claim 1, wherein $1.5 \leq x \leq 18$, $4 \leq y \leq 18$, and $2 \leq z \leq 35$.

3. A preparation method of a catalyst for oxidative coupling of methane, comprising:

a) grinding $MnTiO_3$ and SiO_2 thoroughly to form a uniform powder admixture;

b) at room temperature, dropwise adding the aqueous solution of Na_2WO_4 to the admixture of $MnTiO_3$ and SiO_2 obtained in step a); and then ultrasonically dispersing for 0.5-1 hour and subsequently mechanically stirring for 1-3 hours to obtain a slurry thick paste;

c) dropwise adding the aqueous solution of $Mn(NO_3)_2$ to the slurry thick paste obtained in step b) under stirring at room temperature; stirring was continued for 1-3 hours; and then dried at 80-100 ^oC;

d) grinding the dried product obtained in step c) into a powder; calcining the ground powder in an air atmosphere at 500-900 ^oC for 1-2 hours.

4. A preparation method of a catalyst for oxidative coupling of methane, comprising:

A) at room temperature, dropwise adding the aqueous solution of Na_2WO_4 to SiO_2; ultrasonically dispersing for 0.5-1 hour and subsequently mechanically stirring for 1-3 hours to obtain a slurry thick paste;

B) dropwise adding the aqueous solution of $Mn(NO_3)_2$ to the slurry thick paste obtained in step A) under stirring at room temperature; stirring was continued the

admixture for 1-3 hours; and then dried at 80 ^{o}C -100 ^{o}C;

C) grinding the dried product obtained in step B) with $MnTiO_3$ into a homogeneous powder; calcining the ground homogeneous powder in an air atmosphere at 500-900 ^{o}C for 1-2 hours.

5. A catalyst, comprising a manganese sesquioxide, a tungstate, a manganese composite oxide having a perovskite structure and/or a spinel structure, and a carrier,

wherein the manganese sesquioxide, the tungstate, the manganese composite oxide having a perovskite structure and/or a spinel structure are supported on the carrier,

or

the manganese sesquioxide and the tungstate are supported on the admixture of the said manganese composite oxide having a perovskite structure and/or a spinel structure and the said carrier,

wherein, based on 100 parts by weight of the catalyst, the content of the manganese sesquioxide is a parts by weight, the content of the tungstate is b parts by weight, the content of the manganese composite oxide having the perovskite structure and/or the spinel structure is c parts by weight, and the content of the carrier is d parts by weight, and wherein $0<a\leq 20$, $1\leq b\leq 20$, $1\leq c\leq 40$, $20\leq d<98$.

6. The catalyst of claim 5, wherein the catalyst is consisted of a manganese sesquioxide, a tungstate, a manganese composite oxide having a perovskite structure and/or a spinel structure, and a carrier,

wherein based on 100 parts by weight of the catalyst, the content of the manganese sesquioxide is ranged from >0 parts by weight to ≤ 20 parts by weight, or ranged from 1.5 parts by weight to 18 parts by weight;

the content of the tungstate is range from 1.0 parts by weight to 20 parts by weight, or ranged from 4 parts by weight to 18 parts by weight;

the content of the manganese composite oxide having a perovskite structure and/or a spinel structure is range from 1 parts by weight to 40 parts by weight, or ranged from 2 parts by weight to 35 parts by weight;

the balance is the carrier;

optionally, the manganese composite oxide having the perovskite structure and/or the spinel structure comprises at least one element selected from Ti, Fe, Co, Ni, Li, Pb, Cd, Sn, In, Ge, Ga, Sb, Bi, Te, Se, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Ba, Mg, Ce, La, Pr, Nd, Sm, Ca, Sr, Ba, K or combinations thereof, or

the manganese composite oxide having a perovskite structure and/or a spinel structure is at least one selected from manganese titanate, manganese ferrite, manganese cobaltate, manganese nickelate, lithium manganite, lithium nickel cobalt manganese oxide, manganese plumbite, cadmium acid manganese, manganese stannate, manganese germanate, manganese metagallate, manganese antimonate, manganese bismuthate, manganese tellurate, manganese selenate, manganese zirconate, manganese hafnate, manganese vanadate, manganese niobate, manganese tantalite, manganese chromate, manganese molybdate, manganese tungstate, batium manganate, magnesium manganate, cerium manganate, $LnAFeMnO_6$(Ln=La, Pr, Nd, Sm, Ce; A=Ca, Sr, Ba), $La_{0.5}Sr_{0.5}Mn_{1-m}Fe_mO_3$, $Ca_\alpha La_\beta K_{1-\alpha-\beta}Mn_{0.5}Fe_{0.5}O_3$, $Ca_pLa_qK_{1-p-q}Mn_{0.78}Fe_{0.22}O_3$, $Bi_{0.5}Ca_{0.5-n}La_nFe_{0.3}Mn_{0.7}O_3$ or combinations thereof; $0<m\leq0.25$, $0<\alpha\leq0.25$, $0<\beta\leq0.25$, $0<p\leq0.25$, $0<q\leq0.25$, $0<n\leq0.25$;

or the manganese composite oxide having a perovskite structure and/or a spinel structure comprises particles having a size varied from 100 to 2000 mash, or from 100 to 1000 mesh.

7. The catalyst of any of claims 5 or 6, wherein the carrier is selected from SiC, Fe_2O_3, Fe_3O_4, TiO_2, ZrO_2, Al_2O_3, La_2O_3, CaO, SrO, MgO, SiO_2 or combinations thereof;

optionally, the carrier having a particle size varied from 100 to 2000 mash, or from 100 to 1000 mesh;

wherein the carrier having a specific surface varied from 10 to 1000 m^2/g, or from 50 to 250 m^2/g;

wherein the carrier having a pore volume varied from 0.1 to 1.2 mL/g, or from 0.5 to 0.9 mL/g;

wherein the carrier having a most probable pore size varied from 2.0 to 20.0 nm, or from 2.0 to 10.0 nm.

8. A preparation method of a catalyst, comprising:

1) admixing the manganese composite oxide having the perovskite structure and/or the spinel structure with the carrier in solid-phase to obtain a solid phase admixture A;

2) admixing a precursor of tungstate salt and a precursor of manganese sesquioxide with the solid phase admixture A obtained in step 1) to obtain a admixture B;

3) subsequently drying and calcining the admixture B obtained in step 2)；

or

i) admixing a precursor of tungstate salt and a precursor of manganese sesquioxide with the carrier in the presence of a solvent to obtain a mixed product X;

ii) drying the mixed product X obtained in step i) to obtain a dried product Y;

iii) admixing the manganese composite oxide having the perovskite structure and/or the spinel structure with the dried product Y obtained in step ii) in solid-phase and then calcining the obtained mixed product.

9. The preparation method of claim 8, wherein the solid phase admixing is carried out under grinding conditions, which makes the ground admixture have a particle size varied from 200 to 2000 mesh, or from 200 to 1000 mesh.

10. The preparation method of claim 8, wherein the admixing in the presence of a solvent is a stepwise impregnation or ultrasonic agitation mixing.

11. The preparation method of claim 8, wherein the solvent is water, the precursors of tungstate salts and the precursors of the manganese sesquioxide are water-soluble.

12. The preparation method of claim 8, wherein the drying process is performed at temperature varied from 80 to 100 ^{o}C for time period varied from 1 hour to 2 hours; the calcining treatment is performed under oxygen-containing atmosphere at temperature varied from 500 to 900 ^{o}C for time period from 1 hour to 2 hours.

13. The preparation method of any one of claims 8 to 12, wherein based on 100 parts by weight of the total amount of the precursor of the manganese sesquioxide (calculated by manganese sesquioxide), the precursor of the tungstate, the manganese

composite oxide having a perovskite structure and/or a spinel structure, and the carrier, the content of the precursor of the manganese sesquioxide (calculated by manganese sesquioxide) is from over 0 to less than 20 parts by weight, or from 1.5 to 18 parts by weight,

the content of the precursor of the tungstate is from 1 to 20 parts by weight ,or from 4 to 18 parts by weight,

the content of the manganese composite oxide having the perovskite structure and/or the spinel structure is from 1 to 40 parts by weight, or from 2 to 35 parts by weight,

and the content of the carrier is from 20 to 98 parts by weight ,or from 29 to 90 parts by weight.

14. The preparation method of any of claims 8 to 13, wherein the manganese composite oxide having a perovskite structure and/or a spinel structure comprises at least one element selected from Ti, Fe, Co, Ni, Li, Pb, Cd, Sn, In, Ge, Ga, Sb, Bi, Te, Se, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Ba, Mg, Ce, La, Pr, Nd, Sm, Ca, Sr, Ba, K or combinations thereof;

optionally, the manganese composite oxide having a perovskite structure and/or a spinel structure is at least one selected from manganese titanate, manganese ferrite, manganese cobaltate, manganese nickelate, lithium manganite, lithium nickel cobalt manganese oxide, manganese plumbite, cadmium acid manganese, manganese stannate, manganese germanate, manganese metagallate, manganese antimonate, manganese bismuthate, manganese tellurate, manganese selenate, manganese zirconate, manganese hafnate, manganese vanadate, manganese niobate, manganese tantalite, manganese chromate, manganese molybdate, manganese tungstate, batium manganate, magnesium manganate, cerium manganate, $LnAFeMnO_6$(Ln=La, Pr, Nd, Sm, Ce; A=Ca, Sr, Ba), $La_{0.5}Sr_{0.5}Mn_{1-m}Fe_mO_3$, $Ca_\alpha La_\beta K_{1-\alpha-\beta}Mn_{0.5}Fe_{0.5}O_3$, $Ca_pLa_qK_{1-p-q}Mn_{0.78}Fe_{0.22}O_3$, $Bi_{0.5}Ca_{0.5-n}La_nFe_{0.3}Mn_{0.7}O_3$ or combinations thereof; $0<m\leqslant 0.25$, $0<\alpha\leqslant 0.25$, $0<\beta\leqslant 0.25$, $0<p\leqslant 0.25$, $0<q\leqslant 0.25$, $0<n\leqslant 0.25$;

or the manganese composite oxide having a perovskite structure and/or a spinel structure comprises particles having a size varied from 100 to 2000 mash, even further

from 100 to 1000 mesh.

15. The preparation method of any one of claims 8 to 14, wherein the carrier is selected from SiC, Fe_2O_3, Fe_3O_4, TiO_2, ZrO_2, Al_2O_3, La_2O_3, CaO, SrO, MgO, SiO_2 or combinations thereof;

optionally, the carrier having a particle size varied from 100 to 2000 mash, or from 100 to 1000 mesh;

wherein the carrier having a specific surface varied from 10 to 1000 m^2/g, or from 50 to 250 m^2/g;

wherein the carrier having a pore volume varied from 0.1 to 1.2 mL/g, or from 0.5 to 0.9 mL/g;

wherein the carrier having a most probable pore size varied from 2.0 to 20.0 nm, or from 2.0 to 10.0 nm.

16. The catalyst as prepared according to any of claims 3, 4 and 8-15.

17. Use of the catalyst of any one of claims 1, 2, 5-7 and 16 in oxidative coupling of methane.

18. A method for oxidative coupling of methane, comprising: bringing a catalyst into contact with a feed gas stream containing methane and oxygen to have the methane reacting with oxygen under oxidative coupling of methane conditions, wherein the catalyst is the each one of claims 1- 2, 5-7 and 16.

19. The method of claim 18, wherein the methane to oxygen volume ratio in the feed gas stream is 3: 1~8: 1; the reaction temperature is from 620 to 900 ^oC, or from 620 to 800 ^oC; the reaction pressure is from 0.1 to 2 MPa, or from 0.1 to 1 MPa; on the basis of the total amount of methane and oxygen, the gas hourly space velocity is from 3000-50000 $mL \cdot h^{-1} \cdot g^{-1}$, or from 4000-8500 $mL \cdot h^{-1} \cdot g^{-1}$.

20. The preparation method of claim 10, wherein the admixing in the presence of a solvent is an ultrasonic agitation mixing, optionally comprising sequentially mixing under unltrasonic and agitation conditions, wherein the ultrasonic condition includes under the ultrasonic power varied from 400 to 2500W and the ultrasonic frequency varied from 20 to 60 kHz, the mixing time under ultrasonic condition is 0.5-1 hour, and the mixing time under agitation condition is 1-3 hours.