

Description

Microsphere Catalyst for Conversion of Oxygen-Containing Compounds to Olefins and Preparation Method thereof

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Technical Field

This invention relates to the catalyst technical field and is a microsphere catalyst for the conversion of oxygen-containing compounds to olefins and the preparation method thereof, as well as the catalytic application of the catalyst
10 in the conversion reaction of oxygen-containing compounds to lower olefins.

Background Art

Ethylene and propylene are two basic organic chemical raw materials with the largest demand and the widest application in the petrochemical industry
15 and are referred to as “the mother of the modern organic synthesis industry”. The methods for preparing the lower olefins such as ethylene, propylene and the like are generally divided into two types: one type is a petroleum route, wherein ethylene is produced by employing a light oil cracking method mainly in China, and an ethane high temperature conversion method in USA and some
20 countries with abundant ethane resource. The other type is a non-petroleum route which produces lower olefins with the C₁ resources such as coal, natural gas and the like. With the increasing demand for lower olefins such as ethylene, propylene and the like and the continuous enlargement the application field thereof, as well as the petroleum resource shortage and the price advancing, it
25 is emergent increasingly to develop a technique for preparing lower olefins via the non-petroleum route. In the recent ten plus years, the research and development of preparing ethylene and propylene using coal, natural gas have become a hotspot of the technical devotions of the research organizations in China and abroad as well as each large international company. Because the
30 single series, large-scale industrialized technique of preparing methanol from

natural gas (or coal) is very mature, the research of preparing olefins from methanol has become a key technique for preparing lower olefins via a non-petroleum route.

In 1977, Mobil Co. of USA used ZSM-5 zeolite molecular sieve as a Methanol to Olefin (MTO) catalyst for the first time and made a breakthrough in this process (USP5367100). ZSM-5 zeolite is a mesopore zeolite with a pore structure of straight pipe line shape, and although a relatively high yield of light olefins can be obtained due to its superior shape selection effect, its acidic property is too strong and the selectivity for ethylene is still needed to be improved. In 1984, Union Carbide Corporation (UCC) developed new silicoaluminophosphate series molecular sieves (SAPO-n) (USP 4440871). The SAPO molecular sieves are a type of crystalline silicon aluminum phosphate and have a three-dimensional skeleton structure constituted of the tetrahedrons of PO_4^+ 、 AlO_4^- and SiO_4 . With the appearance of the silicoaluminophosphate series molecular sieves, the people began to apply these molecular sieves with small pores and moderate acidic property such as SAPO-17, SAPO-18, SAPO-34, SAPO-44 or the like (US4499327) to MTO reaction. They have a pore diameter of about 0.43 nm and are a type of preferable shape-selective catalysts. Wherein, SAPO-34 molecular sieve shows excellent catalytic performance in MTO reaction due to its adequate acidic property and pore structure and has become a hotspot of the present research. Furthermore, MeAPSO molecular sieve formed by introducing transition metals into the skeleton of the above molecular sieve also shows relatively high selectivity for lower olefins to MTO reaction (J. Mol. Catal. A **160** (2000) 437, CN1108867, CN1108868, CN1111091, CN1108869, CN1132698, CN1108870).

Although the above molecular sieves have preferable MTO catalytic performance, they can not be applied to industrial production directly. An industrial catalyst is generally needed to have a predetermined strength, an adequate morphology and an appropriate particle size under a precondition of maintaining a relatively high catalytic performance. It must also fit the above

several conditions to develop a catalyst for the conversion of methanol to olefins and the catalyst can be applied to the industrial devices only when each aspect has satisfied the demand. Generally, the reaction for the conversion of methanol to olefins utilizes a circulating fluid bed operation mode and the catalyst is of microsphere shape having adequate particle size distribution. From the literature reports, microsphere catalysts are all consisted of an active component such as molecular sieve and an adhesive, wherein the adhesive performs a function of dispersing the active component and enhancing the catalyst strength. Furthermore, the presence of the inactive component in the catalyst can also perform a function of diluting the molecular sieve and therefore reducing the reaction heat effect. For example, USP5126298 reported a preparation for a high strength cracking catalyst including spray drying a sizing material of $\text{pH} < 3$ made of two kinds of different clays, a zeolite molecular sieve and a phosphorus-containing compound; USP5248647 reported a method of spray drying a sizing material made of SAPO-molecular sieve, kaolin and silica sol; USP6153552 reported a preparation method for a microsphere catalyst containing SAPO molecular sieve including mixing SAPO molecular sieve, an inorganic oxide sol and a phosphorus-containing compound, and spray drying; USP6787501 reported a catalyst for methanol conversion by spray drying SAPO-34 molecular sieve, an adhesive and a substrate material; CN01132533A reported a preparation for a wearing resistance index catalyst for methanol conversion which performed a effect of reducing the wearing index of a catalyst by reducing the mass content of the molecular sieve in the catalyst.

All of the literature reports on the preparation of microsphere catalysts are from the point of view of the used raw materials and exploring the adequate preparation conditions. If the preparation of a catalyst is performed directly from the point of view of the element composition, the research work will be put on a new altitude and the design and preparation of a catalyst will be carried out from a more essential aspect. Up till now, there are no literature

reports on the research of this aspect.

Disclosure of the Invention

5 An object of this invention is to provide a microsphere catalyst for the conversion of oxygen-containing compounds to olefins and the preparation method thereof.

The invention is characterized in that the catalyst system is consisted of silicon oxide, phosphorus oxide and alumina, and simultaneously, can contain an alkaline earth metal oxide and a transition metal oxide. The mass content of
10 each component is that: 2-60% of silicon oxide, 8-50% of phosphorus oxide, 20-70% of alumina, 0-10% of alkaline earth metal oxide, 0-20% of transition metal oxide, and it is satisfied that the sum of the mass contents of all the components is 100%.

The invention is characterized in that the silicon source, aluminum source
15 and phosphorus source used in the catalyst are derived from SAPO molecular sieve or MeAPSO molecular sieve. The silicon source can also be derived from one of silica sol and kaolin or a mixture thereof. The aluminum source can also be derived from one of alumina sol, pseudoboehmite, pseudoboehmite and kaolin, or a mixture thereof. The phosphorus source can also be derived from
20 one of phosphoric acid, ammonium monohydric phosphate and ammonium hydrogen phosphate, or a mixture thereof. The source of alkaline earth metal is derived from one of an oxide, inorganic salt or organic salt of calcium, strontium or barium, or a mixture thereof. The source of transition metal is derived from one of MeAPSO molecular sieve, an oxide, inorganic salt or
25 organic salt of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium and the like, or a mixture thereof.

The invention is characterized in that as the active components in the catalyst, the oxide mass content of SAPO and MeAPSO molecular sieves in the catalyst is 15-50%. The molecular sieve is one of SAPO-17, MeAPSO-17,
30 SAPO-18, MeAPSO-18, SAPO-34, MeAPSO-34, SAPO-35, MeAPSO-35,

SAPO-44, MeAPSO-44, SAPO-56 and MeAPSO-56, or a mixture thereof. The metal contained in MeAPSO molecular sieve is one of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium and the like, or a mixture thereof. The synthesis of some SAPO molecular sieves and MeAPSO molecular sieves can be found in authorized patents: CN1037334, CN1038125, CN1131845, CN1108867, CN1108868, CN1111091, CN1108869, CN1132698 and CN1108870.

The invention is characterized in that the attrition index of the microsphere catalyst is less than 2. The diameter of the microspheres is in the range of 2-220 μm .

The present invention also provide a preparation method of a microsphere catalyst for the conversion of oxygen-containing compounds to olefins, the preparation process is as follows:

a) A SAPO or MeAPSO molecular sieve, a pore-forming agent and other raw materials containing silicon, phosphorus, aluminum, alkaline earth metal and transition metal are mixed with deionized water, and the ratios of components (by oxide mass ratio) are:

	$\text{SiO}_2/\text{SAPO} = 0 \sim 2.5$	SiO_2 is derived from silica sol
20	$\text{Al}_2\text{O}_3/\text{SAPO} = 0 \sim 4.5$	Al_2O_3 is derived from one of alumina sol, pseudoboehmite, pseudoboehmite, or a mixture thereof
	$\text{P}_2\text{O}_5/\text{SAPO} = 0 \sim 3.0$	
	$\text{T}/\text{SAPO} = 0 \sim 5.0$	T is kaolin
25	$\text{AO}/\text{SAPO} = 0 \sim 0.7$	AO is a alkaline earth metal oxide
	$\text{MeO}/\text{SAPO} = 0 \sim 1.3$	MeO is a transition metal oxide
	$\text{H}_2\text{O}/\text{SAPO} = 1.0 \sim 37.0$	

b) The slurry obtained in step a) is stirred and colloid-milled with a colloid mill to reduce the diameter of the contained particles, wherein, the diameter of the particles contained in the slurry after the colloid-milling is less

than 20 μm , the diameter of 90% of the particles is less than 10 μm , and the diameter of 70% of the particles is less than 5 μm ;

c) The slurry obtained in step b) is dried using a spray drying method to prepare microsphere shaped particles;

5 d) The microsphere particles are calcined at 500-800 $^{\circ}\text{C}$ and therefore a catalyst for the conversion of oxygen-containing compounds to olefins is obtained.

The pore-forming agent added in said step a) is natural sesbania powder or starch, and the addition amount thereof is 0.01-3% of the total mass of all
10 the inorganic oxides. The spray drying device used in said step c) is of pressure type or centrifugal type.

The microsphere catalyst prepared in the invention can be applied to the conversion of oxygen-containing compounds to olefins directly.

15 **Preferred embodiments of the invention**

This invention will be described in detail below by way of examples.

Example 1 (a catalyst of silicon-phosphorus-aluminum system)

2.0 kg of silica sol (SiO_2 content is 30 wt %), 0.94 kg of kaolin (water
20 content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %) and 0.72 kg of as-synthesized SAPO-34 molecular sieve were added in turn into 3 kg of deionized water, and 10 g of sesbania powders (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so
25 as to make 70% of the particle diameter in the slurry less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The slurry was spray dried using a pressure type spray drying device. The obtained spray dried product was calcined at 650 $^{\circ}\text{C}$ in air for 4 h,
30 therefore a microsphere catalyst for the conversion of oxygen-containing

compounds to olefins was obtained.

Example 2 (a catalyst of silicon-phosphorus-aluminum system)

3.0 kg of alumina sol (Al_2O_3 content is 20 wt %), 0.94 kg of kaolin (water
5 content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %) and 0.72 kg of as-synthesized SAPO-34 molecular sieve were added in turn into 2 kg of deionized water, and 15 g of sesbania powders (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so
10 as to make 70% of the particle diameter in the slurry less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The slurry was spray dried using a pressure type spray drying device. The obtained spray dried product was baked at 650°C in air for 4 h,
15 therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 3 (a catalyst of silicon-phosphorus-aluminum system)

1.69 kg of phosphoric acid (H_3PO_4 content is 85 wt %), 9 kg of deionized
20 water and 2.95 kg of pseudoboehmite (Al_2O_3 content is 70 wt %) were mixed and stirred for 30 min to prepare an aluminum phosphate gel. 1.56 kg of as-synthesized SAPO-34 molecular sieve, 0.83 kg of silica sol (30% content) and 10 kg of deionized water were mixed and stirred for 20 min, and then the mixture was added into the above gel. The solid content for oxides in the slurry
25 was 20 wt %, and 20 g of sesbania powders (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the slurry less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured
30 by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was

spray dried using a centrifugal type spray drying device and the spray dried product was calcined at 650°C in air for 4 h, therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

5 Example 4 (a catalyst of silicon-phosphorus-aluminum system)

1.33 kg of silica sol (SiO_2 content is 30 wt %), 0.94 kg of kaolin (water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %), 0.72 kg of as-synthesized SAPO-34 molecular sieve and 1.0 kg of alumina sol (Al_2O_3 content is 20 wt %) were added in turn into
10 1.72 kg of deionized water, and 5 g of sesbania powders (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution
15 instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a centrifugal type spray drying device. The obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

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Example 5 (a catalyst of silicon-phosphorus-aluminum system)

0.29 kg of pseudoboehmite (content is 70 wt %), 0.71 kg of kaolin (water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %), 0.84 kg of as-synthesized SAPO-34 molecular sieve
25 and 2.5 kg alumina sol (Al_2O_3 content is 20 wt %) were added in turn into 1.37 kg of deionized water, and 10 g of wheat starch (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was
30 tested using a BT-9300 type laser particle size distribution instrument

manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a centrifugal type spray drying device. The obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 6 (a catalyst of silicon-phosphorus-aluminum system)

1.0 kg of silica sol (SiO_2 content is 30 wt %), 0.94 kg of kaolin (water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %) and 1.08 kg of as-synthesized SAPO-34 molecular sieve were added in turn into 2.69 kg of deionized water, and 10 g of sesbania powders (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a pressure type spray drying device. The obtained spray dried product was baked at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 7 (a catalyst of silicon-phosphorus-aluminum- alkaline earth metal system)

0.67 kg of silica sol (SiO_2 content is 30 wt %), 0.71 kg of kaolin (water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %), 0.72 kg of as-synthesized SAPO-34 molecular sieve and 2.5 kg of alumina sol (Al_2O_3 content is 20 wt %) were mixed in turn and stirred. 0.2 kg of strontium nitrate (SrO content is 49 wt %) was added into 0.2 kg of deionized water and dissolved by stirring, then the solution of strontium nitrate was added into the above mixed slurry. 10 g of sesbania powders

(wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a centrifugal type spray drying device and the obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 8 (a catalyst of silicon-phosphorus-aluminum-transition metal system)

1.25 kg of zirconium carbonate (ZrO_2 content is 40 wt %), 5 kg of deionized water and 5 kg of silica sol (SiO_2 content is 30 wt %) were mixed in turn and stirred for 20 min. 1.76 kg of kaolin (the water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %), 1.84 kg of SAPO-34 molecular sieves and 5 kg of water were mixed in turn and stirred for 20 min. The two slurries were mixed and stirred for 20 min. At last, 15 g of sesbania powders (wetted with a little ethanol) was added and stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a pressure type spray drying device. The obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 9 (a catalyst of silicon-phosphorus-aluminum-transition metal

system)

1.33 kg of silica sol (SiO_2 content is 30 wt %), 0.82 kg of kaolin (water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %), 0.84 kg of ZnSAPO-34 molecular sieves (zinc oxide content is 2 wt %) and 1.0 kg of alumina sol (Al_2O_3 content is 20 wt %) were added in turn into 2.68 kg of deionized water and stirred for 20 min. At last, 5 g of sesbania powders (wetted with a little ethanol) was added and stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a centrifugal type spray drying device. The obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 10 (a catalyst of silicon-phosphorus-aluminum- alkaline earth metal -transition metal system)

0.5 kg of zirconium carbonate (ZrO_2 content is 40 wt %), 3.19 kg of deionized water, 1.67 kg of silica sol (SiO_2 content is 30 wt %), 0.71 kg of kaolin (the water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %), 0.72 kg of SAPO-34 molecular sieves were mixed in turn and stirred for 20 min. 0.21 kg of strontium nitrate (SrO content is 49 wt %) was added into 1.0 kg of deionized water and dissolved by stirring, then the solution of strontium nitrate was added into the above mixed slurry and stirred for 20 min. At last, 5 g of sesbania powders (wetted with a little ethanol) was added and stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm

(the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a centrifugal type spray drying device and the obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Comparative example 1 (a catalyst of silicon-phosphorus-aluminum system)

3.33 kg of silica sol (SiO_2 content is 30 wt %), 0.47 kg of kaolin (water content is 15 wt %, and in the solid after ignition, SiO_2 content is 53 wt %, Al_2O_3 content is 45 wt %) and 0.72 kg of as-synthesized SAPO-34 molecular sieve were added in turn into 3 kg of deionized water, and 10 g of sesbania powders (wetted with a little ethanol) was added at last, then stirred for 30 min. A colloid-milling was performed by passing the slurry through a colloid mill so as to make 70% of the particle diameter in the sizing material less than 5 μm (the particle size distribution was tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China). The sizing material was spray dried using a pressure type spray drying device. The obtained spray dried product was calcined at 650°C in air for 4 h, and therefore a microsphere catalyst for the conversion of oxygen-containing compounds to olefins was obtained.

Example 11 (a catalyst of silicon-phosphorus-aluminum system)

The element compositions (using the X-ray fluorescence method) and the particle size distributions (using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China) of the catalysts in example 1, 2, 3, 4, 5, 6, 7, 8, 10 and the comparative example are shown in Table 1. It can be seen that, except for the sample of comparative example 1, the element compositions of other samples are all in the element composition range specified in the present invention.

The catalyst samples obtained in example 1-10 were subjected to attrition measurement and the attrition indexes of all the samples are less than 1.5. The catalyst sample obtained in comparative example was subjected to attrition measurement and the wearing index thereof was 5. The measurement method of attrition index was as follows: about 7g of catalyst sample was put into a goose neck tube with an inner diameter of about 2.5 cm, and a wet air was made to pass the tube at a flow rate of 20 L/min to provide a fluidized circumstance. The fine catalyst powders blown out of the catalyst were collected in a special filter bag and the test was performed for 4 h. The attrition index was calculated from the average lost mass percentage per hour with respect to the initial loading amount of the catalyst.

It is obvious that the relatively high attrition index of the sample in comparative example 1 relates to the inadequate element composition thereof. Therefore, by carrying out a design of the microsphere catalyst directly from the point of view of the element composition, the present invention can guide the addition amount of each raw material component at the initial stage of the catalyst preparation and avoid the blindness during the process of catalyst preparation, thereby a microsphere catalyst with a relatively low attrition index is obtained.

Table 1 The element compositions and particle size distributions of the microsphere catalysts

Example	element composition(wt%) ^a					particle size distribution ^b	
	SiO ₂	Al ₂ O ₃	P ₂ O ₅	MeO	AO		
1	54.2	30.3	4.7	0.6	0.2	<20μm: 4% 20μm-40μm: 13.7% 40-80μm: 42.5% 80-120μm: 23.2% >120μm: 16.6%	
2	30.1	55.1	13.8	0.7	0.3	<20μm: 4.5% 20μm-40μm: 17.6% 40-80μm: 50.3% 80-120μm: 16.4% >120μm: 11.2%	
3	7.5	51.6	40.0	0.6	0.3		
4	44.8	40.6	13.8	0.5	0.3	<20μm: 3.2% 20μm-40μm: 12.7% 40-80μm:	

						48.5% 80-120 μ m: 19.2% >120 μ m: 16.4%
5	20.1	63.2	16.1	0.4	0.2	
6	40.7	36.5	22.1	0.4	0.3	<20 μ m: 5.6% 20 μ m-40 μ m: 17.7% 40-80 μ m: 53.1%
						80-120 μ m: 14.6% >120 μ m: 9.0%
7	28.9	50.8	14.1	0.3	5.6	
8	48.9	26.6	15.0	8.9	0.6	
10	44.7	26.3	14.6	9.3	4.6	
Comparative	63.5	21.0	14.6	0.6	0.3	
example 1						

^aMeO=transition metal oxide AO=alkaline earth metal oxide

^bThe particle size distributions were tested using a BT-9300 type laser particle size distribution instrument manufactured by BaiTe instrument Co. Ltd., DanDong city, China).

5 Example 12

The catalysts obtained in example 1, 2, 3, 4, 8, 10 were subjected to an evaluation of the conversion reaction of methanol to lower olefins (MTO). The evaluation conditions are as follows: 10 g of sample was weighed and loaded into a fixed fluid bed reactor, and the sample was firstly heated to 550°C under a nitrogen gas at 40 ml/min and activated for half an hour, then reduced to 500°C to perform the reaction. Then the nitrogen gas was stopped and a 40 wt % aqueous methanol solution was fed with a micropump, the weight space rate is 2.0 h⁻¹. The reaction products were analyzed by an on-line gas chromatograph and the results were shown in Table 2.

15 It can be seen that all of the catalysts showed relatively high selectivity for lower olefins on the conversion reaction of methanol to olefins.

Table 2 The conversion reaction results of methanol to olefins^a

Product distribution	Catalyst sample					
	Example	Example	Example	Example	Example	Example

	1	2	3	4	8	10
CH ₄	3.57	2.57	2.60	2.81	3.06	2.70
C ₂ H ₄	57.90	57.18	57.23	57.10	57.91	57.03
C ₂ H ₆	0.52	0.45	0.52	0.52	0.50	0.40
C ₃ H ₆	31.25	31.75	31.98	31.98	31.69	31.95
C ₃ H ₈	0.51	0.82	0.56	0.60	0.50	0.76
C ₄ +	5.00	5.31	5.31	5.43	5.01	5.46
C ₅ +	1.21	1.65	1.80	1.56	1.33	1.70
C ₆ +	0.00	0.27	0.00	0.00	0.00	0.00
$\Sigma C_2^- - C_3^-$	89.15	88.93	89.21	89.08	89.60	88.98

a: The highest selectivity for lower olefins when methanol conversion is 100%.

Claims

1. A microsphere catalyst for the conversion of oxygen-containing compounds to olefins, characterized in that the catalyst includes silicon oxide, phosphorus oxide and alumina, or simultaneously, contains alkaline earth metal oxide and transition metal oxide, and the mass contents of respective components thereof are: 2-60% of silicon oxide, 8-50% of phosphorus oxide, 20-70% of alumina, 0-10% of alkaline earth metal oxide, 0-20% of transition metal oxide, and the sum of the mass contents for all the components is 100%, wherein the microsphere catalyst is prepared by a preparation process comprising the following steps:

a) An as-synthesized silicoaluminophosphate SAPO or metal-containing silicoaluminophosphate MeAPSO molecular sieve, a pore-forming agent and at least two of raw materials containing silicon, phosphorus, aluminum, alkaline earth metal and transition metal are mixed with deionized water, and the ratios of respective components (by the oxide mass ratio) are as follows:

$\text{SiO}_2/\text{SAPO} = 0 \sim 2.5$ SiO_2 is derived from silica sol

$\text{Al}_2\text{O}_3/\text{SAPO} = 0 \sim 4.5$ Al_2O_3 is derived from one of alumina sol, pseudoboehmite, pseudoboehmite, or a mixture thereof

$\text{P}_2\text{O}_5/\text{SAPO} = 0 \sim 3.0$

$\text{T}/\text{SAPO} = 0 \sim 5.0$ T is kaolin

$\text{AO}/\text{SAPO} = 0 \sim 0.7$ AO is a alkaline earth metal oxide

$\text{MeO}/\text{SAPO} = 0 \sim 1.3$ MeO is a transition metal oxide

$\text{H}_2\text{O}/\text{SAPO} = 1.0 \sim 37.0$

b) The slurry obtained in step a) is stirred and colloid-milled with a colloid mill to reduce the diameter of the contained particles, wherein, the particles contained in the slurry after the colloid-milling have a diameter less than 20 μm , 90% of the particles have a diameter less than 10 μm , and 70% of the particles have a diameter less than 5 μm .

2. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that the diameter of said microspheres is in a range of 2-220 μm .

3. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that the silicon source for said silicon oxide, the aluminum source for said alumina and the phosphorus source for said phosphorus oxide are derived from silicoaluminophosphate SAPO molecular sieve or metal-containing silicoaluminophosphate MeAPSO molecular sieve.

4. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that said silicon source for the silicon oxide can also be derived from one of silica sol and kaolin or a mixture thereof, and the total mass content of the silicon oxide in the microsphere catalyst is 5-55%.

5. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that said aluminum source for the alumina can also be derived from one of alumina sol, pseudoboehmite, pseudoboehmite and kaolin or a mixture thereof, and the total mass content of the alumina in the microsphere catalyst is 25-65%.

6. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that said phosphorus source for the phosphorus oxide can also be derived from one

of phosphoric acid, ammonium monohydric phosphate and ammonium hydrogen phosphate or a mixture thereof, and the total mass content of the phosphorus oxide in the microsphere catalyst is 10-45%.

7. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that the source of said alkaline earth metal oxide is derived from one of a oxide, inorganic salt or organic salt of calcium, strontium or barium, or a mixture thereof, and the total mass content of the alkaline earth metal oxides in the microsphere catalyst is 0-8%.

8. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that the source of said transition metal oxide is one of MeAPSO molecular sieve, a oxide, inorganic salt or organic salt of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc or zirconium, or a mixture thereof, and the total mass content of the transition metal oxides in the microsphere catalyst is 0-16%.

9. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that said microsphere catalyst is drying formed using a spray drying method.

10. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that the attrition index of said microsphere catalyst is less than 2.

11. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 1, characterized in that said catalyst can be directly applied to the conversion of oxygen-containing compounds to olefins.

12. The microsphere catalyst for the conversion of oxygen-containing

compounds to olefins as claimed in claim 3, characterized in that said SAPO or MeAPSO molecular sieve is an active component in the catalyst and the oxide mass content thereof in the catalyst is 15-50%.

13. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 3, characterized in that the metal contained in said MeAPSO molecular sieve is one of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, or a mixture thereof.

14. The microsphere catalyst for the conversion of oxygen-containing compounds to olefins as claimed in claim 3, characterized in that said SAPO or MeAPSO molecular sieve is one of SAPO-17, MeAPSO-17, SAPO-18, MeAPSO-18, SAPO-34, MeAPSO-34, SAPO-44, MeAPSO-44, SAPO-35, MeAPSO-35, SAPO-56 and MeAPSO-56, or a mixture thereof.

15. A preparation method of the microsphere catalyst for the conversion of oxygen-containing compounds to olefins according to claim 1, characterized in that the preparation process comprises the following steps:

a) An as-synthesized silicoaluminophosphate SAPO or metal-containing silicoaluminophosphate MeAPSO molecular sieve, a pore-forming agent and at least two of raw materials containing silicon, phosphorus, aluminum, alkaline earth metal and transition metal are mixed with deionized water, and the ratios of respective components (by the oxide mass ratio) are as follows:

$\text{SiO}_2/\text{SAPO} = 0 \sim 2.5$ SiO_2 is derived from silica sol

$\text{Al}_2\text{O}_3/\text{SAPO} = 0 \sim 4.5$ Al_2O_3 is derived from one of alumina sol, pseudoboehmite, pseudoboehmite, or

a mixture thereof

P_2O_5 / SAPO = 0 ~ 3.0

T/ SAPO = 0 ~ 5.0 T is kaolin

AO/ SAPO = 0 ~ 0.7 AO is a alkaline earth metal oxide

MeO/ SAPO = 0 ~ 1.3 MeO is a transition metal oxide

H_2O /SAPO= 1.0~37.0

b) The slurry obtained in step a) is stirred and colloid-milled with a colloid mill to reduce the diameter of the contained particles, wherein, the particles contained in the slurry after the colloid-milling have a diameter less than 20 μm , 90% of the particles have a diameter less than 10 μm , and 70% of the particles have a diameter less than 5 μm ;

c) The slurry obtained in step b) is dried using a spray drying method to prepare microsphere shaped particles;

d) The microsphere shaped particles are calcined at 500-800°C and therefore a catalyst for the conversion of oxygen-containing compounds to olefins is obtained.

16. The method as claimed in claim 15, characterized in that the pore-forming agent added in said step a) is natural sesbania powder or starch.

17. The method as claimed in claim 15, characterized in that the amount of the pore-forming agent added in said step a) is 0.01-3% of the total mass of all the inorganic oxides.

18. The method as claimed in claim 15, characterized in that the spray drying device used in said step c) is of pressure type or centrifugal type.