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(54) Title: PRODUCTION OF LOWER OLEFINS FROM HYDROGENATION OF CO_2

(57) Abstract: Disclosed is a process for the production of lower olefins by the conversion of a feed stream comprising carbon dioxide and hydrogen, and catalysts as used therein. By virtue of the invention, lower olefins can be produced from hydrogenation of CO_2, with high selectivity (the selectivity of lower olefins is up to 80%), and low production of methane (only below 3%). The catalysts used herein were composed with two parts, including multi-metal oxide and zeolite. The two parts can be mixed by mechanical mixing and other methods. The multi-metal oxides mainly constitute the Zn and Zr oxide. The zeolites (eg. SAPO-34) exhibited the suitable acid properties. The composite catalysts not only show a high selectivity of lower olefins, but also a high catalyst activity and chemical and mechanical stability.

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Production of lower olefins from hydrogenation of CO_2

Field of the invention

The present invention pertains to the catalysts that can produce lower olefins from hydrogenation of CO_2, and the synthesis method of lower olefins over such catalysts.

Background of the invention

Developing sustainable energy resources and strategies to solve the key problems associated with the use of fossil fuels, which include global warming due to the increased concentration of greenhouse gases (eg. CO_2), has attracted more attention in modern society. Lower olefins (C_2 to C_4) as key building-block chemicals have been widely used in current chemical industry. Ethylene production is used to evaluate the petrochemical industry development level of country. Therefore, the using of CO_2 to produce lower olefins is one of important route for high-value utilization of CO_2, also has strategic and practical significance. On the one hand, the hydrogenation of CO_2 to lower olefins can not only resolve the global warming problem associated with CO_2 but also establish new carbon cycle with CO_2 for improving the environment; on the other hand, hydrogenation of CO_2 to lower olefins will open a new avenue for the production of lower olefins, and can alleviate the energy crisis associated with short of oil resource.

Recently, the production of lower olefins can be realized through two-step method. CO_2 is firstly hydrogenated to methanol, and then the methanol can be converted to lower olefins through methanol-to-olefins (MTO) process. Many company, such as Dalian Institute of Chemical Physics in china, UOP, Mobil, developed their own MTO process. Lower olefins can be produced from the hydrogenation of CO_2 by using iron and cobalt catalysts, which derived from the Fisher-Tropsch (F-T) of syngas. China patent 【CN 104437504】 show that the selectivity of lower olefins can reach to 60% on iron catalyst in hydrogenation of CO_2, however, the selectivity of the methane is also high and the selectivity of lower olefins is still low for practical application, simultaneously, the long chain paraffin can be produced. Besides the two-step method, scientists also attempt to directly produce lower olefins through one-step method, the composite catalysts always contain Cu-based catalyst (CuMOx) and zeolite【Applied Catalysis A: General, 1995, 130,105; Applied Catalysis A: General, 1995, 121, 113; Catalysis Today, 1998, 44, 165; Reaction Kinetics, Mechanisms and Catalysis, 2014, 112, 489】. Although the CuMOx/Zeolite composite catalyst can realize the conversion of CO_2 and efficiently limitation of the carbon chain growth, the Cu-based catalyst show high hydrogenation performance, only the paraffin is obtained. Overall, the reports that associated with the hydrogenation of CO_2 to lower olefins show the low selectivity of lower olefins. Therefore, the exploitation of efficient catalysts is crucial for conversion of CO_2 to lower olefins with high selectivity.

Summary of the invention

The first of technical objective of the present invention is to develop the

efficient catalyst, which can hydrogenate CO_2 to lower olefins with high conversion of CO_2 and high selectivity of lower olefins.

The second technical objective of the present invention is to efficiently prepare the catalysts that mentioned in the first part of primary technical objective.

The third technical objective of the present invention is to realize the hydrogenation of CO_2 to lower olefins with high selectivity by using the catalysts.

Brief Description of the Drawings

In order to resolve the first technical problem, technical proposal of the present invention is following:

The composite catalysts were composed by two parts (MxZy), the one part is the metal oxide catalyst (nominated as M), and another part is the zeolite (nominated as Z). The content of M is 20~70 wt%, and the content of Z is 30~80 wt%. The zeolite can be one type or several types among SAPO-34, H-ZSM-5 and HY.

M was composed by metal oxide and support, presentation as $A_aB_bC_c$. The C presents the support, the A, B and C present ZnO, ZrO_2 and support. The content of A, B and C that can be represented by a, b and c in 0~100 wt%, 0~100 wt% and 0~50 wt% respectively.

The support is one type or several types among SiO_2, Al_2O_3, TiO_2 and CeO_2, but it is not only limited to these supports.

In order to resolve the second technical problem, technical proposal of the present invention is following:

The preparing method of catalysts that described the every proposal in first technical problem contains following steps:

a: the Zn and Zr metal salt were dissolved into doionized water with certain concentration, and then this solution can be mixed with support, finally the metal salt was precipitated on the support (the impregnation method, co-precipitation method, deposition-precipitation method and mechanical mixing method can be used in this process)

b: aging;

c: drying;

d: calcinations.

In above-mentioned prepared method: the metal salt can be precipitated by using precipitant with uniform distribution. The metal salt can also be distributed on the support through direct deposition by using c step.

In above-mentioned prepared method: the metal salt can be direct precipitated by using precipitant without using support.

In above-mentioned prepared method: the different metal salts can be precipitated one after another by using precipitant respectively. It can be precipitated by using co-precipitation.

In above-mentioned prepared method: the pH value of the system can be controlled about at 6~10 in the process of precipitation.

Method one: the Zn metal salt can be precipitated on the ZrO_2;

Method two: the Zr metal salt can be precipitated firstly, and then the Zn salt can be precipitated (the Zn can be precipitated firstly, and then the Zr salt can be

precipitated). The obtained catalyst was dried and then calcinated.

Method three: the Zn and Zr salt can be co-precipitated and then dried. Finally, it was calcinated.

Method four: the Zn and Zr salt can be co-precipitated on the support and then dried. Finally, it was calcinated.

In above-mentioned prepared method, part A and Part B can be direct mixed though mechanical mixing or ball-milling.

In above-mentioned prepared method, the Zn and Zr salts can prefer to select nitrate salts.

The example of method one: the ZrO_2 (commercial) was firstly distributed into deionized water, and then the certain amount of $Zn(NO_3)_2$ and ammonium carbonate solution were added into above solution dropwise, and the pH value of system can be controlled about 6~10, after adding, the mixture was standing for 1~24 h at 20~100 ^oC. It then can be dried at 70~120 ^oC for 10~24 h. Finally, the sample can be calcinated at 300~800 ^oC for 3~10 h.

The example of method two: the certain amount of $Zr(NO_3)_4$ and ammonium carbonate solution were added into flask dropwise respectively, and then the certain amount of $Zn(NO_3)_2$ and ammonium carbonate solution were added into above solution. The pH value of system can be controlled about 6~10. After adding, the mixture was standing for 1~24 h at 20~100 ^oC. It then can be dried at 70~120 ^oC for 10~24 h. Finally, the sample can be calcinated at 300~800 ^oC for 3~10 h.

The example of method three: the certain amount of mixture of $Zn(NO_3)_2$ and $Zr(NO_3)_4$ with ammonium carbonate solution were added into flask dropwise, and the pH value of system can be controlled about 6~10, after adding, the mixture was standing for 1~24 h at 20~100 ^oC. It then can be dried at 70~120 ^oC for 10~24 h. Finally, the sample can be calcinated at 300~800 ^oC for 3~10 h.

The example of method four: the support was firstly distributed into deionized water, and then the certain amount of mixture of $Zn(NO_3)_2$ and $Zr(NO_3)_4$ with ammonium carbonate solution were added into above solution, and the pH value of system can be controlled about 6~10, after adding, the mixture was standing for 1~24 h at 20~100 ^oC. It then can be dried at 70~120 ^oC for 10~24 h. Finally, the sample can be calcinated at 300~800 ^oC for 3~10 h.

In above-mentioned prepared method, the optimizing aging temperature is 40~100 oC, and the optimized time is 6~24 h. The optimized drying temperature is 80~110 oC, and the optimized time is 10~20 h. The optimized calcination temperature is 400~600 oC, and the optimized time is 3~5 h.

In order to dissolve the second technical problem, the Z part in technical proposal of the present invention is zeolite (one type or several types of SAPO-34, H-ZSM-5 and HY).

In order to dissolve the second technical problem, the mixing of M and Z can be realized through mechanical mixing, but is not only mechanical mixing.

In order to dissolve the third technical problem, technical proposal of the present invention following:

The synthesis of lower olefins can be realized by using CO_2 and hydrogen, and

the reaction can use the catalyst that described the every technical proposal in the above technical problem.

For the synthesis of lower olefins, the key of this invention is the selective of catalyst. The other technological condition, such as reaction temperature, reaction pressure and space velocity can be tuned by technicists in such field. For example, the reaction temperature is 300~450 °C; reaction pressure is 0.5~3 MPa; the volume ratio of H_2 to CO_2 is 2~4; the space velocity is 1000~30000 mL/(g_{cat} • h). For easily controlling the reaction, the inertness gas can be introduced into feed gas, such as N_2 but it is not only limited to N_2.

The catalysts in this invention can realize the conversion of CO_2 with 10 % (mol), and the selectivity of CO was limited below 40 %, the selectivity of lower olefins can reach to 80 % (CO-free). The space time yield of lower olefins is 72.5 mg/(g_{cat} • h) with the space velocity of feed gas of 3600 mL/(g_{cat} • h).

The stability of catalyst in example 5 is shown in Figure 1. Sel.(CO, CH_4, C_2-$C_4^=$, C_2-C_4^0) % present the selectivity of CO, CH_4, C_2-$C_4^=$ and C_2-C_4^0; Conv.(CO_2)% present the conversion of CO_2.

The invention will be illustrated hereinafter with reference to the following, non-limiting examples.

Example 1

Catalyst preparation

The 49.2 g of ZrO_2 (commercial, 80~120 mesh) was distributed into deionized water (400 g). The solution of zinc nitrate (200 g, the content of zinc is 6.5 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the above solution, the pH value of system was controlled about 8~9, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 330 °C for 3 h, after cooling to room temperture, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.5) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 360 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 2

Catalyst preparation

The 49.2 g of ZrO_2 (commercial, 80~120 mesh) was distributed into deionized water (400 g). The solution of zinc nitrate (200 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the above solution, the pH value of system was controlled about 9~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 400 °C for 5 h, after cooling to room temperture, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 360 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 3

Catalyst preparation

The solution of zirconium nitrate (400 g, the content of zirconium is 36.5 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~7. The solution of zinc nitrate (400 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the above solution, the pH value of system was controlled about 7~8, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 °C for 8 h, after cooling to room temperture, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 360 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 4

Catalyst preparation

The solution of zinc nitrate (400 g, the content of zirconium is 26.25 g) and the solution of ammonium carbonate (0.5 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~7. The solution of zirconium nitrate (400 g, the content of zinc is 36.5 g) and the solution of ammonium carbonate (0.5 mmol/mL) were added dropwisely into the above solution, the pH value of system was controlled about 6~7, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 ^{o}C for 6 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 360 ^{o}C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 5

Catalyst preparation

The solution of zirconium nitrate and zinc nitrate (400 g, the content of zirconium is 36.5 g and the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 9~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 400 ^{o}C for 10 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.5) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor.

The reaction condition: the reaction temperature is 360 ^{o}C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in

table 1. Based on the results of figure 1, this catalyst show the high conversion of CO_2 (10%) and high selectivity of lower olefins (80%). Although the selectivity of the lower olefins decreased slightly as the reaction progress (the major reason was the formation of macrocycle molecular).

Example 6

Catalyst preparation

The solution of zirconium nitrate and zinc nitrate (600 g, the content of zirconium is 36.5 g and the content of zinc is 52.4 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 9~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 400 ^{o}C for 10 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.4) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 360 ^{o}C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 7

Catalyst preparation

The 50 g of ZrO_2 (commercial, 80~120 mesh) was distributed into deionized water (200 g). The solution of zirconium nitrate and zinc nitrate (600 g, the content of zirconium is 36.5 g and the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~7, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 400 ^{o}C for 10 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.5) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction

condition: the reaction temperature is 360 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 8

Catalyst preparation

The solution of zirconium nitrate (400 g, the content of zirconium is 36.5 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~10. The solution of zinc nitrate (400 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the above solution, the pH value of system was controlled about 8~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 °C for 6 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.1) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 9

Catalyst preparation

The solution of zirconium nitrate and zinc nitrate (400 g, the content of zirconium is 36.5 g and the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 8~9, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 400 °C for 10 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (H-ZSM-5, Si/Al=25) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 360 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Example 10

Catalyst preparation

The solution of zirconium nitrate and zinc nitrate (400 g, the content of zirconium is 36.5 g and the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~7, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 400 °C for 10 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (HY) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 2 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 11

Catalyst preparation

The solution of copper nitrate, zinc nitrate and aluminium nitrate (400 g, the content of copper is 51.2 g, the content of zinc is 26.2 g and the content of aluminium is 3.5 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 9~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 350 °C for 10 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 12

Catalyst preparation

The solution of chromic nitrate and zinc nitrate (400 g, the content of chromic is 10.4 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~7, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 500 °C for 6 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 13

Catalyst preparation

The solution of palladium nitrate and zinc nitrate (400 g, the content of palladium is 1.06 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.3 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 8~9, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 °C for 5 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction

condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 14

Catalyst preparation

The solution of palladium nitrate, zinc nitrate and zirconium nitrate (400 g, the content of palladium is 2.13 g, the content of zirconium is 36.5 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 9~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 °C for 6 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.

For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 15

Catalyst preparation

The solution of iron (III) nitrate and zinc nitrate (400 g, the content of iron is 22.4 g, the content of zirconium is 26.2 g) and the solution of ammonium carbonate (0.1 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 6~10, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 °C for 3 h, after cooling to room temperature, the catalyst was obtained and was represented as M.

The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.

The synthesis of lower olefins

The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume

ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.
For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 16

Catalyst preparation

The solution of iron (III) nitrate and zinc nitrate (400 g, the content of iron is 22.4 g, the content of zirconium is 36.5 g) and the solution of ammonium carbonate (0.2 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 8~9, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 500 °C for 6 h, after cooling to room temperature, the catalyst was obtained and was represented as M.
The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.
The synthesis of lower olefins
The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.
For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 17

Catalyst preparation

The solution of iron (III) nitrate, zinc nitrate and zirconium nitrate (400 g, the content of iron is 22.4 g, the content of zirconium is 36.5 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.3 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 8~9, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 600 °C for 3 h, after cooling to room temperature, the catalyst was obtained and was represented as M.
The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.
The synthesis of lower olefins
The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst

was reduced for 1 h in hydrogen before reaction.
For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Comparative Example 18

Catalyst preparation

The solution of copper (Ⅱ) nitrate, zinc nitrate and zirconium nitrate (400 g, the content of copper is 51.2 g, the content of zirconium is 36.5 g, the content of zinc is 26.2 g) and the solution of ammonium carbonate (0.5 mmol/mL) were added dropwisely into the deionized water (200 g), the the pH value of system was controlled about 7~8, and then aging for 12 h, filtration, washing with deionized water and drying. Finally, the catalyst was calcinated at 500 °C for 8 h, after cooling to room temperature, the catalyst was obtained and was represented as M.
The M and zeolite (SAPO-34, Si/Al=0.2) were mixed by mechanical mixing with the same quality. The composite catalyst was pressed to piece, and fragmentation and sieving to 40~60 mesh.
The synthesis of lower olefins
The synthesis of lower olefins was performed by using fixed bed reactor. The reaction condition: the reaction temperature is 400 °C, reaction pressure is 1 MPa, the volume ratio of $H_2/CO_2/N_2$ is 24/72/4, the space velocity is 3600 mL/(g_{cat} • h). The catalyst was reduced for 1 h in hydrogen before reaction.
For easily comparing with other catalyst system, the reaction results were exhibited in table 1.

Table 1. The composition of catalysts and the reaction results.

Example	Composition of catalysts	Preparation method of catalysts	Conv. CO_2 %	Sel. CO %	Hydrocarbon distribution, %				STY
					CH_4	C_2-$C_4^=$	C_2-C_4^0	C_5	C_2-$C_4^=$
1	ZnO/4ZrO_2-SAPO-34	Method 1	7.4	39	2	81	14	3	56.8
2	ZnO/ZrO_2-SAPO-34	Method 1	9.3	42	2	80	15	3	65.1
3	ZnO/ZrO_2-SAPO-34	Method 2	9.6	36	2	81	14	3	72.5
4	ZrO_2/ZnO-SAPO-34	Method 2	8.1	50	2	82	13	3	46.3
5	$ZnZrO_3$-SAPO	Method 3	9.3	41	2	81	14	3	65.5

	-34								
6	Zn_2ZrO_4-SAPO-34	Method 3	8.9	40	2	82	13	3	52.9
7	$ZnZrO_3/SiO_2$-SAPO-34	Method 4	7.2	43	2	80	15	3	47.5
8	ZnO/ZrO_2-SAPO-34	Method 2	15	60	6	65	35	4	49.1
9	$ZnZrO_3$-H-ZSM-5	Method 3	12	46	1	56	13	40[a]	46.5
10	$ZnZrO_3$-HY	Method 3	13	52	5	69	16	10[b]	41.2
11	CuZnAl-SAPO-34	Method 3	19	85	2	11	83	4	4.5
12	Zn/CrOx-SAPO-34	Method 3	17	90	2	80	15	3	19.7
13	Pd/ZnO-SAPO-34	Method 3	15	87	3	10	84	3	2.8
14	Pd/ZnZrO-SAPO-34	Method 3	13	85	3	11	83	3	3.1
15	Fe/ZnOx-SAPO-34	Method 3	18	76	2	35	58	5	21.9
16	Fe/ZrOx-SAPO-34	Method 3	15	78	2	32	61	5	15.3
17	Fe/ZnZrOx-SAPO-34	Method 3	16	75	2	33	60	5	19.4
18	Cu/ZnZrOx-SAPO-34	Method 3	16	87	2	10	84	4	3.1

In table 1, the C_2-$C_4^=$ represent the lower olefin and C_2-C_4^0 represent the lower paraffin, STY represent the space-time yield (mg/(g_{cat}· h)); a: represent the yield of hydrocarbon (that the carbon chain is longer than 4) and, aromatic hydrocarbon; b: represent the yield of hydrocarbon that the carbon chain is longer than 4.

Based on the above reaction results, the composite catalysts show the good performance for production of lower olefins. Once the metal, such as copper, palladium and iron, were doped into metal oxide, the side product CO was generated as major products, and the paraffin was obtained but the lower olefins disappeared. These metalS showed good hydrogenation ability and the lower olefin was hydrogenated again. Although the lower olefins can be obtained over Zn-CrOx catalysts, the reverse water-gas shift reaction was increased, and the amount CO was

produced. Therefore, the composite catalysts can realize the conversion of CO_2 to lower olefins, the key problem is to increase the selectivity of lower olefins and is not to suppress the catalytic performance for producing intermidate. Zn-ZrOx can not only realize the hydrogenation of CO_2 but also suppress the reverse water-gas shift reaction.

Claims

1.The characteristic of catalysts for hydrogenation of CO_2 is:

The composite catalysts were composed by two parts (MxZy), the one part is the metal oxide catalyst (nominating as M), and another part is the zeolite (nominating as Z). The content of M is 20~70 wt%, and the content of Z is 30~80 wt%. The zeolite can be one type or several types among SAPO-34, H-ZSM-5 and HY. The optimized select of zeolite is SAPO-34.

The optimized content of M is 40~60 wt%;

M was composed by metal oxide, represented as $A_aB_bC_c$. The C presents the support, the A, B and C present ZnO, ZrO_2 and support. The content of A, B and C that can be represented by a, b and c is 0~100 wt%, 0~100 wt% and 0~50 wt% respectively. The optimized content of a, b and c are 50 wt%, 50 wt% and 0 wt% respectively.

2.According to claim 1, the support is one type or several types among SiO_2, Al_2O_3, TiO_2 and CeO_2, but it is not only limited to these supports.

3.According to claim 1 and 2, part M was prepared by using impregnation method, co-precipitation method, deposition-precipitation method and mechanical mixing method. Detailed procedure following:

a:

Impregnation method: the Zn and Zr metal salt were dissolved into doionized water with certain concentration, and then this solution can be mixed with support, finally the metal salt was precipitated on the support.

Co-precipitation method: in a step, the metal salt can be direct precipitated by using precipitant. The different metal salts (zinc nitrate or zirconium nitrate) can be precipitated one after another by using precipitant respectively.

Deposition-precipitation method: the metal salt and support can be distributed in deionized water. And then it can be precipitated by controlling the pH value of system.

Mechanical mixing method: the metal oxide of Zn and Zr can be direct mixed.

B: aging

c: drying;

d: calcinations, the calcinations temperature is 300~800 ^oC, and the optimized temperature is 400~600 ^oC.

4.According to claim 3, the pH value of system can be in 6~10, the optimized pH value is 6~8 in step a.

5.According to claim 3, the aging temperature is in 40~100 ^oC for 6~24 h; the drying temperature is 80~110 oC for 10~20 h; the calcinations time is 3~5 h.

6.According to claim 1, the metal oxide and zeolite can be direct mixed though mechanical mixing (such as ball-milling).

7.According to claim 1 and 6, the composite catalyst can be reduced for 0.5~4 h before reaction in hydrogen. The reduction temperature is the reaction temperature. The reaction temperature is 300~450 ^oC, the optimized reaction temperature is 350~450 ^oC.

8.The synthesis of lower olefins from hydrogenation of CO_2 used the catalysts

that showed in claim 1 to 7.

9.The characteristic of synthesis method of lower olefins is: the feed gas is CO_2 and H_2 (the volume ratio of CO_2 to H_2 is 1~4). The catalyst that showed in calim 1 to 7 was used to prepare lower olefins. The reaction temperature is 300~450 ^oC, the optimized reaction temperature is 350~450 ^oC; the reaction pressure is 0.5~3 MPa, the optimized reaction pressure is 1~3 Mpa, the volume ratio of CO_2 to H_2 is 1~4, the optimized volume ratio of CO_2 to H_2 is 3, the space velocity of feed gas is 1000~30000 mL/(g_{cat} • h).

10.The characteristic of the synthesis method of lower olefin according claim 8 and 9 is to introduce the inert gas into feed gas for better controlling the reaction system. The inert gas can be nitrogen or Ar or both, the volume content of inert gas is 0~20%.

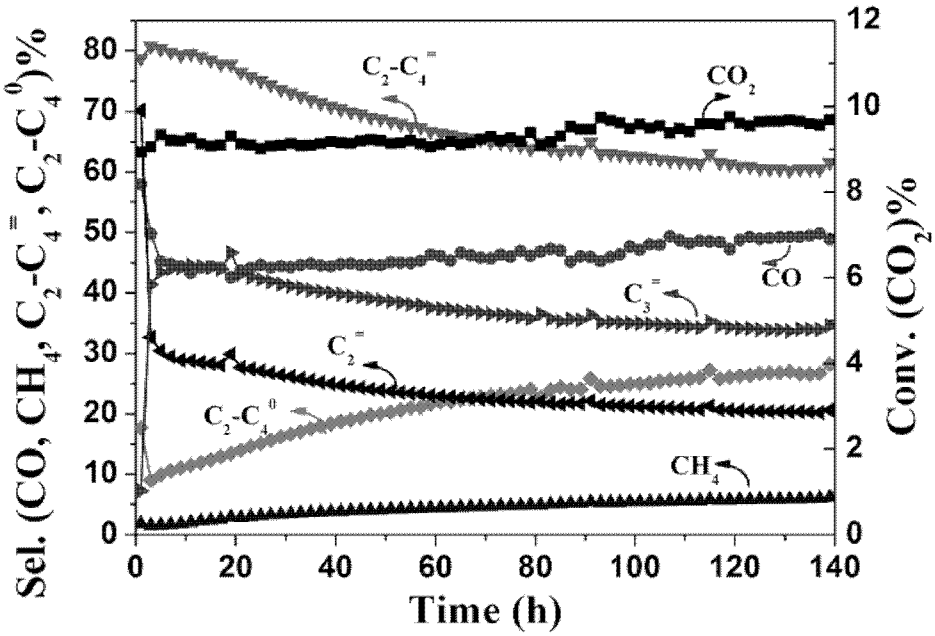
Sel. (CO, CH4, C2-C4=, C2-C4^0)%
Conv. (CO2)%
Time (h)
C2-C4=
CO2
CO
C3=
C2=
C2-C4^0
CH4
0
20
40
60
80
100
120
140
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10
12

Fig.1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2016/109125

A. CLASSIFICATION OF SUBJECT MATTER

B01J 29/85(2006.01)i; B01J 29/40(2006.01)i; B01J 29/08(2006.01)i; C07C 1/12(2006.01)i; C07C 11/04(2006.01)n; C07C 11/06(2006.01)n; C07C 11/08(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J 29; C07C 1; C07C 11

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS,VEN,CNKI,REG,CAPLUS: hydrogenation, catalyst,zeolite,metal oxide,hydrogen,lower olfin,ethylene,propylene,ZnO, ZrO2

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 106423263 A (DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES) 22 February 2017 (2017-02-22) claims 1-10	1-10
A	Young-Kwon Park et.al. "Hydrocarbon Synthesis through C02 Hydrogenation over CuZnOZrO2/Zeolite Hybrid Catalysts" *Catalysis Today*, No. 44, 31 December 1998 (1998-12-31), ISSN: 0920-5861, 165-173	1-10
A	CN 104437504 A (NINGXIA UNIVERSITY) 25 March 2015 (2015-03-25) the whole document, especially claim 1	1-10
A	CN 104909975 A (DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES) 16 September 2015 (2015-09-16) the whole document	1-10

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 June 2017	**14 June 2017**

Name and mailing address of the ISA/CN	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2016/109125

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 106423263 A	22 February 2017	None	
CN 104437504 A	25 March 2015	None	
CN 104909975 A	16 September 2015	None	