

Description**TITLE OF INVENTION: TUNGSTEN-MODIFIED HZSM-5 CATALYSTS
AND METHODS FOR THEIR PREPARATION****5 Field of the Invention**

The present invention relates to aluminosilicate zeolite catalysts, particularly to HZSM-5 catalysts modified with tungsten-containing compounds. More specifically, the present invention relates to the
10 preparation of HZSM-5 catalysts, modified with phosphotungstic acid, that can be used to catalyze the process of producing ethylene from ethanol.

Background of the Invention

15 Ether compounds and unsaturated hydrocarbons are important organic compounds in the industrial field. One of the essential compounds in the unsaturated hydrocarbon group is ethylene, which has an important role in the chemical and manufacturing industries. Ethylene is used as
20 the main raw material in the production of various chemicals and polymers, such as polyethylene, polyvinyl chloride, polystyrene, and ethylene oxide. The currently most common method for producing ethylene is through hydrocarbon thermal cracking processes, i.e. by heating raw
25 materials, such as natural gas or petroleum feedstocks, at high temperatures and thereby resulting in a chemical reaction that produces ethylene. However, the production of ethylene by hydrocarbon thermal cracking method is highly dependent on non-renewable natural resources.
30 Furthermore, this method of ethylene production generates greenhouse gas emissions, contributing to global warming.

The production of ethylene can be achieved through a recently developed method involving ethanol dehydration. This new method has the potential to reduce the negative
35 impact of ethylene production on the environment by using

ethanol raw materials from biomass feedstocks. This method uses a catalyst to break down ethanol molecules into ethylene and water. The catalytic dehydration of ethanol involves the use of a catalyst to catalyze the dehydration reaction of ethanol into ethylene and water. One of the commonly used catalysts is HZSM-5. HZSM-5 catalyst is effective in producing ethylene with high selectivity at relatively high reaction temperatures, i.e. above 300°C. At high temperatures, however, the catalytic reaction using this catalyst is susceptible to catalyst deactivation due to the formation of coke, which shortens the catalyst's lifespan. On the other hand, at lower reaction temperatures, the performance of the catalyst in producing ethylene will decrease.

Prior art discloses various attempts to improve the performance of the HZSM-5 catalyst in the dehydration process of ethanol to ethylene. One of these attempts is disclosed in Chinese Patent CN101274286A. Disclosed in the Chinese Patent document CN101274286A is the modification of the HZSM-5 catalyst by impregnating active metals into the HZSM-5 catalyst with a ratio range of 0.5-7% wt/wt. The active metals used for the impregnation include Ca, Fe, Zn, Mn, Zr, and La. Within operating conditions at atmospheric pressure and at a temperature range of 250-290°C, it is mentioned that the modified HZSM-5 catalyst was capable of achieving 96-99% ethanol conversion with 98-99% ethylene selectivity.

Although the modification of the HZSM-5 catalyst according to the Chinese Patent CN101274286A is mentioned to be able to increase the conversion of ethanol into ethylene and the selectivity of ethylene, the reaction temperature is still relatively high, which is around 250-290°C. The high reaction temperature indicates that the dehydration reaction of ethanol to ethylene using the modified HZSM-5 as disclosed in the Chinese Patent

CN101274286A required a relatively high energy consumption. For that reason, alternative modifications to the HZSM-5 catalyst are still needed to make a modified HZSM-5 catalyst able to catalyze the dehydration reaction of ethanol to ethylene at lower reaction temperatures while maintaining a high level of ethanol conversion and ethylene selectivity.

The main objective of the present invention is to solve the technical problems related to the performance of HZSM-5 catalyst in its use to catalyze the dehydration reaction of ethanol to ethylene. Another objective of the present invention is to offer an alternative modification of HZSM-5 catalyst, especially for catalyzing the dehydration reaction of ethanol to ethylene.

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Summary of the Invention

The present invention aims to overcome the problems relating to the performance of HZSM-5 catalyst, especially HZSM-5 catalyst used in the dehydration reaction of ethanol to ethylene. This objective can be achieved through a method of preparing HZSM-5 catalyst impregnated by a tungsten-containing compound according to the present invention. The method of preparing HZSM-5 catalyst impregnated by a tungsten-containing compound according to the present invention includes the following steps:

- a. heating a HZSM-5 material at a temperature of 50-60°C in a vacuum with a pressure of -0.5 bar,
- b. dripping a solution of a tungsten-containing compound into the HZSM-5 material at a temperature of 50°C to impregnate the tungsten metal from the tungsten-containing compound into the HZSM-5 material with a metal content ratio of 0.1 to 2% weight/weight,
- c. keeping the impregnated catalyst for 24 hours at room temperature and atmospheric pressure,
- d. drying the impregnated catalyst in an oven for

24 hours at a temperature of 60-70°C, and

- e. calcining the impregnated catalyst by heating at a heating rate of 2°C/minute until it reaches a temperature of 350°C and then keeping the catalyst for a certain time
5 at a temperature of 350°C.

In one embodiment of the present invention, the method of preparing the HZSM-5 catalyst impregnated by a tungsten-containing compound also includes mixing the tungsten-containing compound with distilled water.

- 10 In other embodiment of the present invention, the drying temperature in the method of preparing HZSM-5 catalyst containing a tungsten-containing compound is preferably 60°C.

- In further embodiment of the present invention, the
15 tungsten-containing compound used in the preparing the impregnated HZSM-5 catalyst said above is selected from phosphotungstic acid, silicotungstic acid, tungstic acid and salt forms of these acids. The tungsten-containing compound is preferably phosphotungstic acid, in particular
20 phosphotungstic acid with the chemical formula $H_3PW_{12}O_{40}$.

In other embodiment of the method of preparing HZSM-5 catalyst impregnated by a tungsten-containing compound, the ratio of the metal content mentioned in step b is 0.9 to 1.1% wt/wt.

- 25 In other embodiment of the method of preparing HZSM-5 catalyst impregnated by a tungsten-containing compound, the HZSM-5 material has a Si/Al ratio of 30-62, preferably 32-38.

- Other embodiments of the present invention also
30 include HZSM-5 catalysts impregnated with tungsten-containing compound prepared by the above mentioned methods.

Brief Description of the Drawings

- 35 In order to elucidate the present invention and to

assist in understanding its advantages, this description is accompanied by the following drawings:

Figure 1 is a flow chart showing a method for preparing a HZSM-5 catalyst impregnated by tungsten compound according to the present invention.

Figure 2A is a SEM (Scanning Electron Microscopy) image showing the morphology of the HZSM-5 catalyst before being modified with phosphotungstic acid.

Figure 2B shows the results of quantitative analysis using the ZAF Method Standardless Quantitative Analyses on the HZSM-5 catalyst before being modified with phosphotungstic acid.

Figure 3A is a SEM image showing the morphology of the HZSM-5 catalyst after modification with phosphotungstic acid.

Figure 3B shows the results of quantitative analysis using the ZAF method on the HZSM-5 catalyst before and after modification with phosphotungstic acid.

Figure 4 is a product gas analysis profile curve of the catalytic dehydration reaction of ethanol using HZSM-5 catalyst impregnated by phosphotungstic acid according to the present invention at four different temperatures, namely 220°C, 260°C, 280°C, and 300°C.

25 Detailed Description of the Invention

The present invention relates to a method of preparing a modified catalyst, namely an HZSM-5 catalyst modified with a tungsten-containing compound through wet impregnation of the tungsten-containing compound into the HZSM-5 catalyst material. The present invention uses ZSM-5 (Zeolite Socony Mobile-5) that has been activated into HZSM-5 and tungsten metal (wolfram) obtained from the tungsten compound. This modified catalyst can be used, among others, for the catalytic dehydration reaction of

alcohol compounds into ethylene, ether compounds and/or unsaturated hydrocarbons.

Tungsten compounds that can be used to modify the HZSM-5 catalyst according to the present invention include
5 phosphotungstic acid (phosphorus-tungsten heteropolyacid) (such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}$, and $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$), tungstic acid H_2WO_4 , silicotungstic acid (silica-tungsten heteropolyacid), such as $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, and the salt forms of these acids.

10 In one embodiment of the present invention, the compound used to modify (impregnate) the HZSM-5 catalyst is phosphotungstic acid. The selection of phosphotungstic acid as a modifying agent for the HZSM-5 catalyst is based on its excellent ability as a proton donor. Additionally,
15 phosphotungstic acid has good thermal stability that makes it suitable for use at high temperatures. In the reaction of ethanol to ethylene, for example, tungsten metal (W) from the tungsten compound acts as a co-catalyst, enhancing the catalytic activity of the aluminum sites already
20 present in HZSM-5. The two metals exhibit analogous functions as Brønsted acid sites, which serve as the active centers for the catalytic reaction. However, W metal may exhibit greater activity than Al metal at low temperatures. The addition of W as an acid site enables
25 the catalytic reaction to occur at a lower temperature compared to that utilizing HZSM-5 alone.

In one embodiment of the present invention, a tungsten-containing HZSM-5 catalyst (W/HZSM-5) is provided, prepared by impregnating phosphotungstic acid
30 onto an HZSM-5 support material. Preferably, the catalyst is used for the catalytic dehydration reaction of ethanol into ethylene. The preparation of the HZSM-5 impregnated with tungsten catalyst (W/HZSM-5) is carried out through a wet impregnation process of phosphotungstic acid solution
35 ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) on HZSM-5 particles. The results of the

impregnation process are then calcined at a temperature of 350°C to remove the solvent used and activate the catalytic sites.

The present invention provides a W/HZSM-5 catalyst having a tungsten loading ranging from 0.1% to 2% by weight, preferably 1% by weight. This catalyst exhibits high activity at temperatures between 220°C and 300°C, achieving an ethylene conversion exceeding 95% and a selectivity greater than 94%.

In this description, the modified catalyst prepared according to the method of the present invention will hereinafter be called phosphotungstic acid-impregnated HZSM-5 catalyst or abbreviated as W/HZSM-5. The method of preparing W/HZSM-5 according to the present invention will be described in full detail with reference to the flow chart as shown in Figure 1.

As shown in Figure 1, the method of preparing W/HZSM-5 catalyst begins with a pre-treatment step (2) of the HZSM-5 catalyst raw material used as a support for the material to be impregnated (i.e. tungsten from tungsten compounds). The HZSM-5 material used in this invention has a Si/Al ratio ranging from 30-62, preferably 32-38. At this step, the HZSM-5 material, initially in pellet form, is subjected to a size reduction process until uniform pellets with a length of approximately 5-10 mm are obtained. Afterwards, the HZSM-5 material that has been cut into pieces is heated at a temperature of 50-60°C and a vacuum pressure of -0.5 bar. This heat and pressure treatment is taking place for about 15 minutes. Meanwhile, the preparation step of the impregnating material (4) is also carried out. In this preparation step (4), the tungsten compound is dissolved in distilled water with a predetermined composition so that the ratio of tungsten metal contained in the HZSM-5 material is 0.1% to 2% weight/weight, 0.9 to 1.1% weight/weight, preferably 1%

weight/weight. In the example embodiment of the invention shown in Figure 1, the tungsten compound used is phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$).

The impregnation step (6) is carried out after the pre-treatment step of HZSM-5 material (2) and the preparation step of impregnating material (4) being completed. The impregnation is conducted by dripping phosphotungstic acid solution into the HZSM-5 material at a temperature of 50°C and atmospheric pressure. Subsequently, the HZSM-5 material that has been completely wetted is held at a temperature of 50°C . The impregnated material is then kept at room temperature and atmospheric pressure for 24 hours.

After the impregnation step (6), the next step of the W/HZSM-5 catalyst preparation method according to the present invention is the drying step (8). In the drying step (8), the HZSM-5 material that has been impregnated with phosphotungstic acid is completely dried in a drying oven at a temperature of $60\text{--}70^\circ\text{C}$ for 24 hours. The next step is the calcination step (10). In this calcination step (10), the HZSM-5 material that has been impregnated with phosphotungstic acid and dried is heated at a heating rate of $2^\circ\text{C}/\text{min}$ until it reaches a temperature of 350°C . The material is then maintained at a temperature of 350°C .

The HZSM-5 catalyst plays a role in protonating the hydroxyl group (OH)- which then being converted into water molecules (H_2O). The conjugate base of the catalyst then releases protons (H^+) from the methyl group to form ethylene. The presence of tungsten metal (W) from phosphotungstic acid accelerates this process.

A phosphotungstic-acid-impregnated HZSM-5 catalyst (W/HZSM-5) was obtained by the preparation method as mentioned above, and surface characterization, pore structure analysis, and elemental distribution tests were conducted on the catalyst using SEM (Scanning Electron

Microscopy) and EDX (Energy-Dispersive X-ray Spectroscopy) instruments. The SEM instrument depicted the sample surface through scanning using high-energy electron beams in a raster scan pattern. Figure 2A shows the SEM image with a magnification of 10000x, and Figure 2B shows the results of the analysis using the EDX tool for the HZSM-5 material before being modified with phosphotungstic acid. Based on the results of the EDX analysis, it can be seen that HZSM-5 contains the elements C (carbon), O (oxygen), Si (silica), and Al (alumina), and the comparison of the mass percentage of the constituent elements: C = 8.38%; O = 47.63%; Si = 24.89%; and Al = 19.10%.

Figure 3A shows the SEM image with 10000x magnification and EDX analysis of W/HZSM-5 material, namely HZSM-5 impregnated with phosphotungstic acid prepared by the method according to the present invention. Based on the EDX analysis shown in Figure 3B, it can be seen that W/HZSM-5 contains the elements C (carbon), O (oxygen), Si (silica), Al (alumina), and W (tungsten). The mass percentage comparison of the constituent elements is as follows: C = 6.92%; O = 38.74%; Si = 23.94%; Al = 17.66; and W = 12.74%. Furthermore, the mole percentage of the constituent elements is as follows: C = 12.60%; O = 52.94%; Si = 18.64%; Al = 14.31; and W = 1.51%.

To assess the performance of the phosphotungstic-acid-impregnated HZSM-5 prepared by the method according to the present invention, the catalyst was tested for the catalytic dehydration reaction of ethanol to ethylene. The test was carried out using a tubular fixed bed reactor containing 2.2 g of W/HZSM-5 catalyst material. Before the catalytic reaction process began, the W/HZSM-5 catalyst material was first flushed. Flushing was carried out by flowing nitrogen gas at a flow rate of 100 mL/min through the reactor column until no O₂, CH₄, and CO₂ gases remained.

Next, the catalytic dehydration reaction was tested by flowing ethanol vapor from a bubbler at a temperature of 62°C using carrier nitrogen gas with a flow rate of 50 mL/min. Ethanol vapor underwent preheating, so that when it reached the catalyst bed the reaction temperature had reached several variations, namely 220°C, 240°C, 260°C, 280°C, and 300°C. The product gas was flowed through an impinger containing water to absorb the remaining unreacted ethanol vapor. Afterwards, the product gas was flowed through a condenser to purify ethylene gas from condensable gas that might still be contained in the product gas. Analysis of ethylene gas composition was carried out using a Shimadzu GC-8A type Gas Chromatography (TCD Detector Type), and analysis of residual ethanol from the solution in the impinger was conducted using a Shimadzu GC-14B type Gas Chromatography (FID Detector Type).

The test results of the catalytic dehydration reaction of ethanol into ethylene using the W/HZSM-5 catalyst are shown in Table 1 below. From the table, it can be seen that the W/HZSM-5 catalyst prepared by the method according to the present invention produced an ethanol conversion of above 96% with an ethylene selectivity of above 94% for a reaction operating temperature of 220-300°C. The variation of HZSM-5-based catalyst modification at various reaction temperatures is also shown in Table 1.

The profile analysis curve of gas produced in the catalytic dehydration reaction of ethanol using the W/HZSM-5 catalyst at (a) reaction temperature of 220°C, (b) reaction temperature of 260°C, (c) reaction temperature of 280°C, and (d) reaction temperature of 300°C are shown in Figure 4.

As briefly mentioned before, the use of the tungsten compound-supported HZSM-5 catalyst (W/HZSM-5) according to the present invention is not limited to the catalytic dehydration reaction of ethanol into ethylene, but may also

be used to catalyze the dehydration reaction of alcohol into ether and/or unsaturated hydrocarbons.

The description above is solely for the purpose of explaining how the method according to the invention
5 prepares HZSM-5 catalysts modified with tungsten compound, in particular HZSM-5 catalysts impregnated with phosphotungstic acid (W/HZSM-5). The scope of the present invention is, therefore, not limited to the above description. The scope of the present invention is set
10 forth in the claims below.

Table 1

Material	Ethanol Conversion (%)					Ethylene Selectivity (%)				
Temperature	220°C	240°C	260°C	280°C	300°C	220°C	240°C	260°C	280°C	300°C
HZSM-5	51.26	74.33	69.57	69.60	93.82	0.00	17.53	30.86	55.76	92.24
1%-W/HZSM-5	96.20	97.77	99.93	99.95	99.93	94.20	95.55	99.84	99.90	99.88

*Overall WHSV: 1.8/hour; Ethanol WHSV: 0.3/hour

Claims

1. A method for preparing HZSM-5 catalyst impregnated with a tungsten-containing compound, wherein the method is characterized by comprising the following steps:

- 5 a. heating a HZSM-5 material at a temperature of 50-60°C in a vacuum with a pressure of -0.5 bar,
- b. dripping a solution of a tungsten-containing compound into the HZSM-5 material at a temperature of 50°C to impregnate the tungsten metal from the tungsten-
- 10 containing compound into the HZSM-5 material with a metal content ratio of 0.1 to 2% weight/weight,
- c. keeping the impregnated catalyst for 24 hours at room temperature and atmospheric pressure,
- d. drying the impregnated catalyst in an oven for 24 hours
- 15 at a temperature of 60-70°C, and
- e. calcining the impregnated catalyst by heating at a heating rate of 2°C/minute until it reaches a temperature of 350°C and then keeping the catalyst for a certain time at a temperature of 350°C.

20 2. The method according to claim 1, wherein the method is also including the mixing of said tungsten-containing compound with distilled water.

3. The method according to previous claims, wherein the drying temperature in step d) is preferably 60°C.

25 4. The method according to previous claims, wherein the tungsten-containing compound is selected from phosphotungstic acid, silicotungstic acid, tungstic acid and salt forms of these acids. The tungsten-containing compound is preferably phosphotungstic acid, in particular

30 phosphotungstic acid with the chemical formula $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

5. The method according to claim 4, wherein the tungsten-containing compound is phosphotungstic acid.

6. The method according to claim 5, wherein the tungsten-containing compound is phosphotungstic acid with

the chemical formula $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

7. The method according to previous claims, wherein the ratio of the metal content as mentioned in step b is 0.9 to 1.1% wt/wt.

5 8. The method according to previous claims, wherein the HZSM-5 material has a Si/Al ratio of 30-62.

9. The method according to claim 8, wherein the HZSM-5 material has a Si/Al ratio ranging from 32-38.

10 10. The HZSM-5 catalyst prepared by the method according to any of previous claims.