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(54) Title: METHOD OF ACTIVATING A HETEROGENEOUS OXIDE CATALYST FOR USE IN OLEFIN METATHESIS REACTION

(57) Abstract: A method of activating a heterogeneous molybdenum oxide catalyst for use in the olefin metathesis reaction, in which the catalyst is heated in a closed reactor, with a constant flow of argon, to a temperature of 550-700°C, heated for 30 minutes at this temperature, after which an activation gas is introduced into argon for an activation time, and following the activation the catalyst is heated in argon flow and cooled to 50°C, the flow rate of argon during the process being constant at 45 cm^3/min, the activation gas being ethane or propane with a flow rate of 5 cm^3/min, the activation lasting for 1-120 minutes, the heating after activation lasting for 15 minutes, and the heating and cooling of the system being carried out with a temperature change at a rate of 15°C/min.

Method of activating a heterogeneous oxide catalyst for use in olefin metathesis reaction

The invention relates to a method of activating a heterogeneous oxide catalyst for use in olefin metathesis reaction.

Heterogeneous oxide catalysts, obtained by impregnating supports with high surface area with soluble precursor salts, are universal catalytic systems for use in olefin metathesis. Metathesis catalysts activate the C=C double bonds of olefins, converting them into carbene centres (M=CHR, where M is a metal atom and R is an alkyl group or hydrogen) that are considered active centres according to the Chauvin and Herrisson mechanism. On further contact with olefin, these centres are transformed into metallacyclobutane complexes, which in turn decompose into products or substrates. The number of carbene centres formed in the reaction medium usually does not exceed 1.5-2% (J. Handzlik, J. Ogonowski, Dynamic chemical counting of active centers of molybdena-alumina metathesis catalysts, Catalysis Letters 88, 119-122 (2003); K. Amakawa, S. Wrabetz, J. Kröhnert, G. Tzolova-Müller, R. Schlögl, A. Trunschke, In situ generation of active sites in olefin metathesis, Journal of American Chemistry Society 134, 11462 (2012)). The number of these active centres can be increased at the catalyst synthesis stage or by its activation prior to the metathesis reaction.

Molybdenum oxide-containing catalysts have found widespread industrial application in the metathesis reaction due to their durability over the moderate temperature range (25-250°C). The following are examples of activation of catalysts obtained by impregnating supports with high surface area, known from the state of the art.

Patent application US20160075617A1 Supported metal oxides for olefin metathesis and related methods discloses a method for the activation of

heterogeneous molybdenum (MoO_3/SiO_2) and tungsten (WO_3/SiO_2) catalyst, deposited on silica support with a high specific surface area of the support of 1200 m^2/g, in the flow of unsaturated hydrocarbons. In a known method, 100 mg of the catalyst was calcined under air flow with a flow rate of 50 cm^3/min at 550°C for 30 min, after which the air was replaced by nitrogen with a flow rate of N_2 = 100 cm^3/min for 30 min.

After calcination, the MoO_3/SiO_2 catalyst was activated in a flow of C_3H_6:N_2 with a flow rate of 4:96 cm^3/min, respectively, at 550°C for 30 min, after which the system was purged with nitrogen (100 cm^3/min) for another 10 min, and then cooled to room temperature under nitrogen at continued flow rate. The catalyst thus activated was used in a metathesis reaction in which the C_3H_6:N_2 reactant flow rate was 40:5 cm^3/min.

Following calcination, the WO_3/SiO_2 catalyst was activated under C_3H_6:N_2 with a flow rate of 4:96 cm^3/min, respectively, at 550°C for 30 min, after which the temperature was raised to 700°C at a rate of 10°C/min, and the catalyst was maintained at this temperature for another 30 min. The system was then purged with nitrogen (100 cm^3/min) for another 10 min, and cooled to room temperature under nitrogen at continued flow rate. The catalyst thus activated was used in a propylene metathesis reaction in which the C_3H_6:N_2 reactant flow rate was 80:10 cm^3/min.

The description also discloses a catalyst regeneration procedure, in which the catalyst is heated under air flow and then reactivated as described above. The second regeneration method was heating the catalyst to 550°C (MoO_3/SiO_2) or 700°C (WO_3/SiO_2) under nitrogen flow.

The publication "Simple and Efficient Way of Molybdenum Oxide-Based Catalyst Activation for Olefins Metathesis by Methane Pretreatment" (P. Michorczyk, A. Węgrzyniak, A. Węgrzynowicz, J. Handzlik, ACS Catalysis, 9, 11461-11467 (2019)) describes a method for activation of MoO_3 catalyst deposited on

the surface of SBA-1 mesoporous silica (specific surface area of the support 1100 m^2/g). 200 mg of 20%MoO_3/SBA-1 catalyst was heated to activation temperatures of 550-700°C under argon flow of 20 cm^3/min. Once the temperature was reached, the catalyst was heated for 30 min, and then argon was replaced with methane at a methane flow rate of 20 cm^3/min for activation times of 5, 15, 30 or 60 min, respectively, and then cooled to 50°C in Ar flow. The metathesis reaction was carried out at 50°C, the flow rate of C_3H_6:Ar reaction mixture was 28:2 cm^3/min.

The aim of the present invention is to develop a method of activating a heterogeneous molybdenum oxide catalyst, increasing the catalyst efficiency in the olefin metathesis reaction.

According to the invention, the method of activating a heterogeneous molybdenum oxide catalyst for use in an olefin metathesis reaction, in which the catalyst is heated in a closed reactor, with a constant flow of argon, to a temperature of 550-700°C, heated for 30 minutes at this temperature, after which an activation gas is introduced into argon for an activation time, and following the activation the catalyst is heated in argon flow and cooled to 50°C, characterized by that the flow rate of argon during the process is constant at 45 cm^3/min, the activation gas is ethane or propane with a flow rate of 5 cm^3/min, the activation lasts for 1-120 minutes, the heating after activation lasts for 15 minutes, and the heating and cooling of the system is carried out with a temperature change at a rate of 15°C/min.

The catalyst activated by the method of the invention is used in olefin metathesis reaction, immediately after the catalyst is cooled to 50°C.

The efficiency of the catalyst activated by the method of the invention was studied in propylene metathesis reaction under the following conditions:

The flow rate of argon was 5 cm^3/min with a simultaneous 47 cm^3/min flow of propylene. The propylene (99.5% purity) metathesis reaction occurred on the

catalyst at 50°C. After 60 minutes, the catalyst ceases to work with a satisfactory efficiency, undergoing deactivation.

The catalyst activated by the method of the invention, after its use in the metathesis reaction, can be regenerated 4 times by heating under argon flow of 45 cm^3/min to a temperature in the range of 550-700°C and heating for 30 minutes at this temperature. After 4-time regeneration and use of the catalyst in the metathesis reaction, the catalyst can undergo reactivation.

The subject of the invention is explained in detail in the following examples, in which the methods for obtaining an exemplary catalyst are presented, together with their application in the propylene metathesis reaction.

Preparation of the catalyst for activation

The catalyst containing 5 wt. % of MoO_3 used in the examples was obtained by a method known from the art. For this purpose, 1 g of silica with a specific surface area of 480 g/m^2 was impregnated with 1 cm^3 of an aqueous solution of ammonium molybdate containing 0.0646 g of ammonium heptamolybdate (POCH Gliwice). Following impregnation, the material was dried at room temperature for 8 h, and then at 120°C for 4 h. The dried material was heated to 550°C, in air, raising the temperature at a rate of 2°C/min, and heated under isothermal conditions for 10 h. The catalyst was grounded to a fraction of 0.2-0.3 mm grain size.

Example 1

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 700°C at a rate of 15°C/min, and then heated at 700°C for 30 minutes. After this time, ethane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 30 minutes with no

change in temperature. Then the flow of ethane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 1 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The activity of the catalyst activated according to Example 1 is shown in Table 1.

Table 1

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
12.74	88.0	76.89

Example 2

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 600°C at a rate of 15°C/min, and then heated at 600°C for 30 minutes. After this time, ethane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 15 minutes with no change in temperature. Then the flow of ethane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 2 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5

cm^3/min of argon. The activity of the catalyst activated according to Example 2 is shown in Table 2.

Table 2

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
4.06	28.23	24.498

Example 3

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 600°C at a rate of 15°C/min, and then heated at 600°C for 30 minutes. After this time, propane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 30 minutes with no change in temperature. Then the flow of propane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 3 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The activity of the catalyst activated according to Example 3 is shown in Table 3.

Table 3

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]

34.92	242.58	698.342

Example 4

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 550°C at a rate of 15°C/min, and then heated at 550°C for 30 minutes. After this time, propane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 60 minutes with no change in temperature. Then the flow of propane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 4 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The activity of the catalyst activated according to Example 4 is shown in Table 4.

Table 4

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
26.66	185.99	535.42

Example 5

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 700°C at a rate of 15°C/min, and then heated at 700°C for 30 minutes.

After this time, ethane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 1 minute with no change in temperature. Then the flow of ethane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 5 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The activity of the catalyst activated according to Example 5 is shown in Table 5.

Table 5

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
30.05	208.55	181.31

Example 6

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 650°C at a rate of 15°C/min, and then heated at 650°C for 30 minutes. After this time, propane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 2 minutes with no change in temperature. Then the flow of propane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 6 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5

cm^3/min of argon. The activity of the catalyst activated according to Exam ple 6 is shown in Table 6.

Table 6

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
1.42	9.85	28.35

Example 7

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 600°C at a rate of 15°C/min, and then heated at 600°C for 30 minutes. After this time, ethane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 120 minutes with no change in temperature. Then the flow of ethane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 7 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The activity of the catalyst activated according to Example 7 is shown in Table 7.

Table 7

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
30.0	208.36	181.03

Example 8

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 550°C at a rate of 15°C/min, and then heated at 550°C for 30 minutes. After this time, propane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 120 minutes with no change in temperature. Then the flow of propane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst activated according to Example 8 was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The activity of the catalyst activated according to Example 8 is shown in Table 8.

Table 8

Catalytic activity of the activated catalyst in propylene metathesis reaction		
Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
23.37	161.41	464.68

Example 9 - operation in cycles

200 mg of 5% MoO_3/SiO_2 catalyst obtained as above was placed in a pressure flow reactor under argon flow rate of 45 cm^3/min. The catalyst was heated to 600°C at a rate of 15°C/min, and then heated at 600°C for 30 minutes. After this time, propane was additionally introduced into the reactor at a flow rate

of 5 cm^3/min and the catalyst activation was carried out for 30 minutes with no change in temperature. Then the flow of propane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst thus activated was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon. The metathesis was carried out until the activity of the catalyst decreased.

The catalyst was then subjected to regeneration. For this purpose, it was heated under argon flow rate of 45 cm^3/min to 600°C at a rate of 15°C/min, heated at 600°C for 30 minutes, and then the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The regenerated catalyst was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon until the catalyst activity decreased.

The catalyst regeneration and the propylene metathesis reaction were repeated 4 times.

Then the catalyst was reactivated again. For this purpose, the catalyst was heated under argon flow rate of 45 cm^3/min to 600°C at a rate of 15°C/min, and then heated under air flow rate of 50 cm^3/min for 30 min, after which the air was replaced with argon at a flow rate of 45 cm^3/min and left for 30 min with no change in temperature. After this time, propane was additionally introduced into the reactor at a flow rate of 5 cm^3/min and the catalyst activation was carried out for 30 minutes with no change in temperature. Then the flow of propane was cut off and the catalyst was heated for 15 min without changing the other parameters, after which the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The re-activated catalyst was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon until its activity decreased.

The catalyst was then subjected to regeneration, for which purpose it was heated under argon flow rate of 45 cm^3/min to 600°C at a rate of 15°C/min, heated at 600°C for 30 minutes, and then the temperature of the system was lowered to 50°C at a rate of 15°C/min.

The catalyst regenerated as above was used in the propylene metathesis reaction at a volumetric flow rate of 47 cm^3/min of propylene and 5 cm^3/min of argon until its activity decreased.

Following re-activation, the regeneration of the catalyst and the propylene metathesis reaction were repeated 4 times.

The activities of the catalyst activated and then regenerated and re-activated according to Example 9 are shown in Table 9.

Table 9

Catalytic activity of the catalyst in propylene metathesis reaction			
Step	Propylene conversion rate [%]	Specific activity [$mmol_{propylene} h^{-1} g_{cat}^{-1}$]	TOF [h^{-1}]
Activation	37.28	258.44	744.00
1st Regeneration	35.85	248.49	715.35
2nd Regeneration	34.43	238.69	687.13
3rd Regeneration	27.39	189.91	546.70
4th Regeneration	7.01	48.62	139.97
Re-activation	36.91	255.85	736.54
1st Regeneration	30.42	210.88	607.08

2nd Regeneration	22.89	158.68	456.83
3rd Regeneration	5.22	36.15	104.08
4th Regeneration	6.81	47.19	135.86

Claim

A method of activating a heterogeneous molybdenum oxide catalyst for use in an olefin metathesis reaction, in which the catalyst is heated in a closed reactor, with a constant flow of argon, to a temperature of 550-700°C, heated for 30 minutes at this temperature, after which an activation gas is introduced into argon for an activation time, and following the activation the catalyst is heated in argon flow and cooled to 50°C, characterized by that the flow rate of argon during the process is constant at 45 cm^3/min, the activation gas is ethane or propane with a flow rate of 5 cm^3/min, the activation lasts for 1-120 minutes, the heating after activation lasts for 15 minutes, and the heating and cooling of the system is carried out with a temperature change at a rate of 15°C/min.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J21/08 B01J23/28 B01J23/92 B01J35/00 B01J37/02
B01J38/02 B01J38/04 B01J38/12 B01J38/14 B01J38/30
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 9 815 753 B2 (UNIV NORTHWESTERN [US]) 14 November 2017 (2017-11-14) 23, 26, 41,43, 62-65 -----	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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US 9815753 B2	14-11-2017	NONE	