



US011851335B2

(12) **United States Patent**
Hodgkins et al.(10) **Patent No.:** **US 11,851,335 B2**(45) **Date of Patent:** ***Dec. 26, 2023**(54) **NICKEL-CONTAINING ORGANOMETALLIC
FUNCTIONALIZED FIBROUS
HIERARCHICAL ZEOLITE AND METHOD
OF MAKING THE SAME**10,196,465 B2 2/2019 Han et al.
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U.S. Appl. No. 17/230,485, filed Apr. 14, 2021.
U.S. Appl. No. 17/230,500, filed Apr. 14, 2021.
U.S. Appl. No. 17/230,491, filed Apr. 14, 2021.
U.S. Appl. No. 17/230,505, filed Apr. 14, 2021.
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patent is extended or adjusted under 35
U.S.C. 154(b) by 18 days.This patent is subject to a terminal dis-
claimer(21) Appl. No.: **17/412,733**(22) Filed: **Aug. 26, 2021**(65) **Prior Publication Data**

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(51) **Int. Cl.**
C07F 17/02 (2006.01)
C01B 39/02 (2006.01)
C01B 39/40 (2006.01)(52) **U.S. Cl.**
CPC **C01B 39/026** (2013.01); **C01B 39/40**
(2013.01); **C07F 17/02** (2013.01); **C01P**
2002/82 (2013.01); **C01P 2002/85** (2013.01);
C01P 2002/86 (2013.01); **C01P 2004/03**
(2013.01); **C01P 2004/04** (2013.01)(58) **Field of Classification Search**
None
See application file for complete search history.(56) **References Cited**

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502/79

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LLP(57) **ABSTRACT**A functionalized fibrous hierarchical zeolite includes a
framework comprising aluminum atoms, silicon atoms, and
oxygen atoms, the framework further comprising a plurality
of micropores and a plurality of mesopores. The function-
alized fibrous hierarchical zeolite is functionalized with at
least one terminal hydroxyl. Terminal organometallic func-
tionalities are bonded to silicon atoms of the microporous
framework, the terminal organometallic functionalities com-
prising a nickel atom.13 Claims, 7 Drawing Sheets
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US011565942B2

(12) **United States Patent**
Hodgkins et al.

(10) Patent No.: US 11,565,942 B2**(45) Date of Patent: Jan. 31, 2023**

(54) **MODIFIED ZEOLITES THAT INCLUDE PLATINUM-CONTAINING ORGANOMETALLIC MOIETIES AND METHODS FOR MAKING SUCH**

(71) Applicants: **Saudi Arabian Oil Company**, Dhahran (SA); **King Abdullah University of Science and Technology**, Thuwal (SA)

(72) Inventors: **Robert Peter Hodgkins**, Dhahran (SA); **Omer Refa Koseoglu**, Dhahran (SA); **Jean-Marie Maurice Basset**, Thuwal (SA); **Kuo-Wei Huang**, Thuwal (SA); **Anissa Bendjeriou Sedjerari**, Thuwal (SA); **Manoj K. Gangwar**, Thuwal (SA); **Sathiyamoorthy Murugesan**, Thuwal (SA)

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 3 days.

(21) Appl. No.: 17/230,476

(22) Filed: Apr. 14, 2021

(65) **Prior Publication Data**
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(51) **Int. Cl.**
C01B 33/26 (2006.01)
C01B 39/40 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC **C01B 39/40** (2013.01); **B01J 29/40** (2013.01); **B01J 35/023** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC C01B 33/26; C01B 33/28; C01B 33/2807; C01B 33/2869; C01B 39/04; C01B 39/38; C01B 39/40
See application file for complete search history.

(56) **References Cited**

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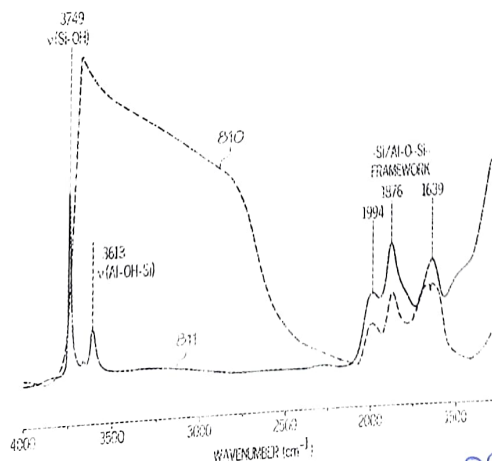
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(74) *Attorney, Agent, or Firm* — Dinsmore & Shohl LLP

(57) **ABSTRACT**

Disclosed herein are modified zeolites and methods for making modified zeolites. In one or more embodiments disclosed herein, a modified zeolite may include a microporous framework including a plurality of micropores having diameters of less than or equal to 2 nm. The microporous framework may include at least silicon atoms and oxygen atoms. The modified zeolite may further include organometallic moieties each bonded to bridging oxygen atoms. The organometallic moieties may include a platinum atom. The platinum atom may be bonded to a bridging oxygen atom, and the bridging oxygen atom may bridge the platinum atom of the organometallic moiety and a silicon atom of the microporous framework.

19 Claims, 9 Drawing Sheets



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(12) **United States Patent**
Hodgkins et al.

(10) Patent No.: US 11,591,230 B2**(45) Date of Patent: Feb. 28, 2023**

(54) **MODIFIED ZEOLITES THAT INCLUDE
HAFNIUM-CONTAINING
ORGANOMETALLIC MOIETIES AND
METHODS FOR MAKING SUCH**

(71) Applicants: **Saudi Arabian Oil Company**, Dhahran
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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
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(21) Appl. No.: 17/231,191

(22) Filed: Apr. 15, 2021

(65) **Prior Publication Data**
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(51) **Int. Cl.**
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B01J 29/40 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC **C01B 39/40** (2013.01); **B01J 29/405**
(2013.01); **B01J 35/023** (2013.01);
(Continued)

(58) **Field of Classification Search**

CPC C01B 33/26; C01B 33/28; C01B 33/2807;
C01B 33/2869; C01B 39/04; C01B 39/38;
C01B 39/40

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,523,506 A 6/1996 Benazzi et al.
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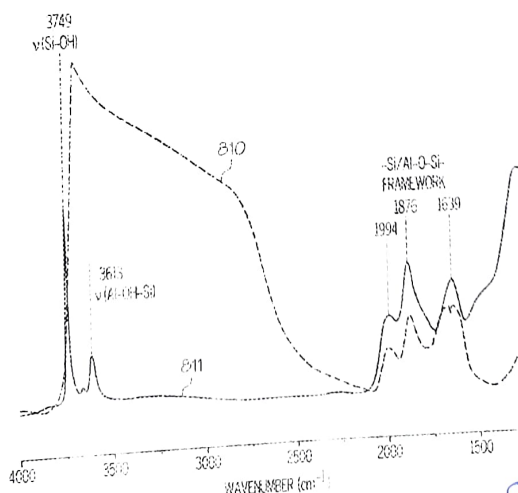
Primary Examiner — Hoa (Holly) Le

(74) Attorney, Agent, or Firm — Dinsmore & Shohl LLP

(57) **ABSTRACT**

Disclosed herein are modified zeolites and methods for
making modified zeolites. In one or more embodiments
disclosed herein, a modified zeolite may include a micropo-
rous framework including a plurality of micropores having
diameters of less than or equal to 2 nm. The microporous
framework includes at least silicon atoms and oxygen atoms.
The modified zeolite may further include organometallic
moieties each bonded to bridging oxygen atoms. The orga-
nometallic moieties include a hafnium atom. The hafnium
atom is bonded to a bridging oxygen atom, and bridging
oxygen atom bridges the hafnium atom of the organometal-
lic moiety and a silicon atom of the microporous framework.

20 Claims, 9 Drawing Sheets



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(12) **United States Patent**
Hodgkins et al.

(10) Patent No.: US 11,591,229 B2**(45) Date of Patent: Feb. 28, 2023**

(54) **MODIFIED ZEOLITES THAT INCLUDE
TITANIUM-CONTAINING
ORGANOMETALLIC MOIETIES AND
METHODS FOR MAKING SUCH**

(58) **Field of Classification Search**
CPC C01B 33/26; C01B 33/28; C01B 33/2807;
C01B 33/2869; C01B 39/04; C01B 39/38;
C01B 39/40
See application file for complete search history.

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(56) **References Cited**

U.S. PATENT DOCUMENTS

5,523,506 A 6/1996 Benazzi et al.
7,994,085 B2 8/2011 Chaumonnot et al.
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FOREIGN PATENT DOCUMENTS

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heterogeneous molecular catalysts, *Coordination Chemistry Reviews*
178-180 (1998) 1679-1702 (Year: 1998) *

(Continued)

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) Appl. No.: 17/230,500

(22) Filed: Apr. 14, 2021

(65) **Prior Publication Data**
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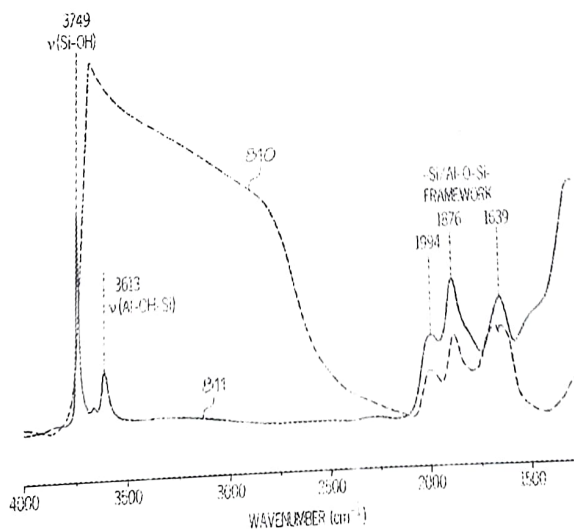
(51) **Int. Cl.**
C01B 39/40 (2006.01)
B01J 29/40 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC **C01B 39/40** (2013.01); **B01J 29/405**
(2013.01); **B01J 35/023** (2013.01);
(Continued)

(57) **ABSTRACT**

Disclosed herein are modified zeolites and methods for
making modified zeolites. In one or more embodiments
disclosed herein, a modified zeolite may include a micropo-
rous framework comprising a plurality of micropores having
diameters of less than or equal to 2 nm. The microporous
framework may include at least silicon atoms and oxygen
atoms. The modified zeolite may further include organome-
tallic moieties each bonded to bridging oxygen atoms. The
organometallic moieties may include a titanium atom. The
titanium atom may be bonded to a bridging oxygen atom,
and the bridging oxygen atom may bridge the titanium atom
of the organometallic moiety and a silicon atom of the
microporous framework.

20 Claims, 10 Drawing Sheets



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Mar. 2, 2023

(54) PLATINUM NANOPARTICLE
FUNCTIONALIZED FIBROUS
HIERARCHICAL ZEOLITE AND METHOD
OF MAKING THE SAME

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Publication Classification

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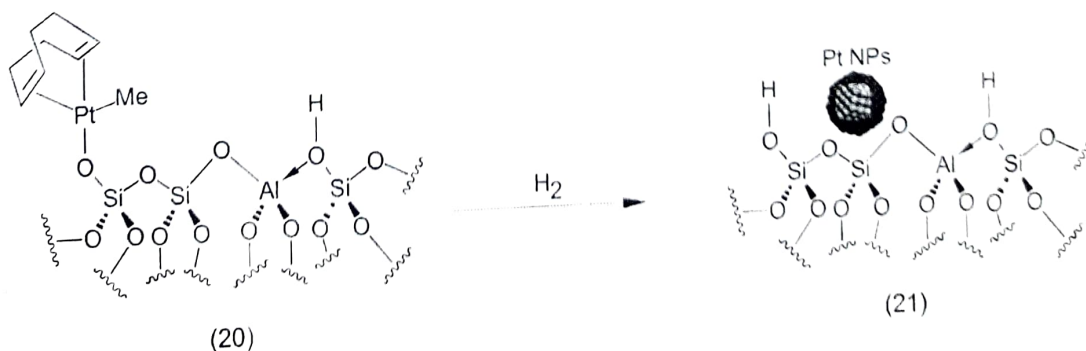
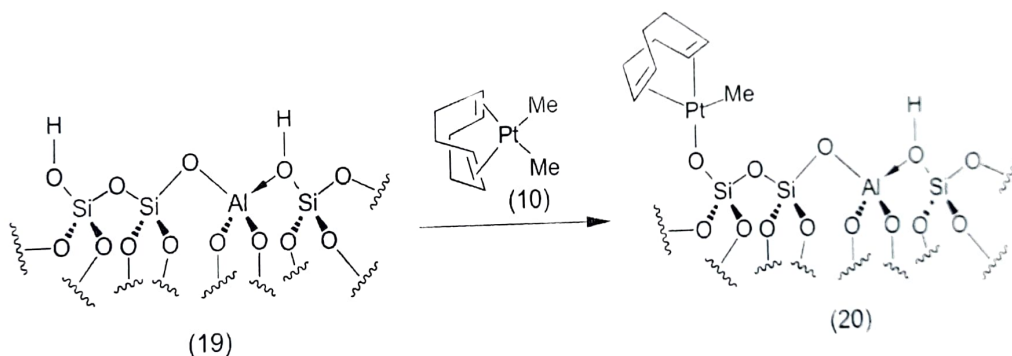
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(52) U.S. Cl.
CPC C01B 39/48 (2013.01);
C01P 2004/64 (2013.01)

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(57) ABSTRACT

A functionalized fibrous hierarchical zeolite includes a framework comprising aluminum atoms, silicon atoms, and oxygen atoms, the framework further comprising a plurality of micropores and a plurality of mesopores. A plurality of nanoparticles comprising platinum are immobilized on the framework.



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(54) NICKEL NANOPARTICLE
FUNCTIONALIZED AMINE-MODIFIED
FIBROUS HIERARCHICAL ZEOLITE AND
METHOD OF MAKING THE SAME

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- (51) Int. Cl.
C01B 39/02 (2006.01)
C01B 39/40 (2006.01)
- (52) U.S. Cl.
CPC C01B 39/026 (2013.01); C01B 39/40
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2004/03 (2013.01); C01P 2002/85 (2013.01);
C01P 2004/04 (2013.01); C01P 2004/51
(2013.01)

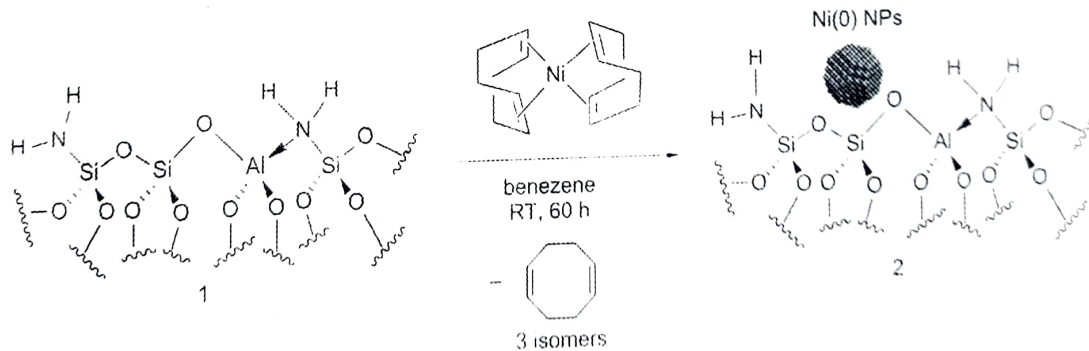
(71) Applicants: Saudi Arabian Oil Company, Dhahran
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(21) Appl. No.: 17/412,817

(22) Filed: Aug. 26, 2021

(57) ABSTRACT

A functionalized fibrous hierarchical zeolite includes a framework comprising aluminum atoms, silicon atoms, and oxygen atoms, the framework further comprising a plurality of micropores and a plurality of mesopores. The functionalized fibrous hierarchical zeolite is functionalized with at least one amine. A plurality of nanoparticles comprising nickel are immobilized on the framework.



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Hodgkins et al.(10) Pub. No.: **US 2023/0082855 A1**(43) Pub. Date: **Mar. 16, 2023**(54) **PLATINUM NANOPARTICLE
FUNCTIONALIZED AMINE-MODIFIED
FIBROUS HIERARCHICAL ZEOLITE AND
METHOD OF MAKING THE SAME****Publication Classification**

(51) Int. Cl.

C01B 39/02 (2006.01)*C01B 39/40* (2006.01)*C07F 15/00* (2006.01)*C07F 17/02* (2006.01)

(52) U.S. Cl.

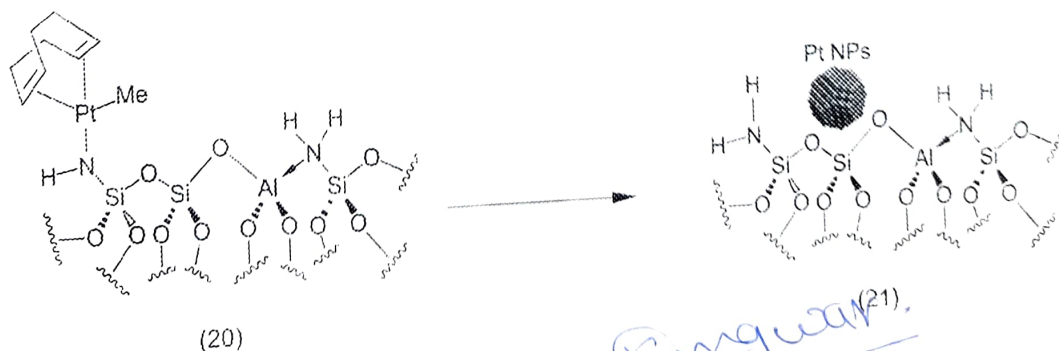
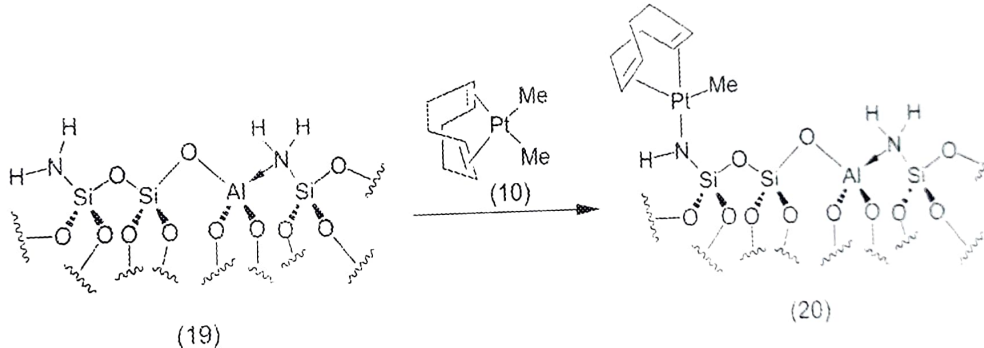
CPC *C01B 39/026* (2013.01); *C01B 39/40*(2013.01); *C07F 15/0086* (2013.01); *C07F**17/02* (2013.01); *C01P 2002/86* (2013.01);*C01P 2002/85* (2013.01); *C01P 2004/03*(2013.01); *C01P 2004/04* (2013.01)(71) Applicants: Saudi Arabian Oil Company, Dhahran
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(21) Appl. No.: 17/412,697

(22) Filed: Aug. 26, 2021

(57) **ABSTRACT**

A functionalized fibrous hierarchical zeolite includes a framework comprising aluminum atoms, silicon atoms, and oxygen atoms, the framework further comprising a plurality of micropores and a plurality of mesopores. The functionalized fibrous hierarchical zeolite is functionalized with at least one amine. A plurality of nanoparticles comprising platinum are immobilized on the framework.



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Hodgkins et al.(10) **Pub. No.: US 2023/0085197 A1**(43) **Pub. Date: Mar. 16, 2023**(54) **PLATINUM ORGANOMETALLIC COMPLEX
FUNCTIONALIZED AMINE-MODIFIED
FIBROUS HIERARCHICAL ZEOLITE AND
METHOD OF MAKING THE SAME**(71) Applicants: **Saudi Arabian Oil Company**, Dhahran
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(21) Appl. No.: 17/412,732

(22) Filed: Aug. 26, 2021

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C01B 39/02 (2006.01)
C01B 39/40 (2006.01)
C07F 15/00 (2006.01)
(52) **U.S. Cl.**
CPC **C01B 39/026** (2013.01); **C01B 39/40**
(2013.01); **C07F 15/0086** (2013.01); **C01P**
2002/86 (2013.01)(57) **ABSTRACT**

A functionalized fibrous hierarchical zeolite includes a framework comprising aluminum atoms, silicon atoms, and oxygen atoms, the framework further comprising a plurality of micropores and a plurality of mesopores. The functionalized fibrous hierarchical zeolite is functionalized with at least one terminal amine bonded to a silicon atom. Terminal organometallic functionalities are bonded to a nitrogen atom of the at least one terminal amine, the terminal organometallic functionalities comprising a platinum atom.

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Hodgkins et al.(10) **Pub. No.: US 2023/0078677 A1**(43) **Pub. Date: Mar. 16, 2023**(54) **NON-BRØNSTED FIBROUS HIERARCHICAL
ZEOLITE AND METHOD OF MAKING THE
SAME**

(21) Appl. No.: 17/412,807

(22) Filed: Aug. 26, 2021

(71) Applicants: Saudi Arabian Oil Company, Dhahran
(SA); King Abdullah University of
Science and Technology, Thuwal (SA)**Publication Classification**(51) **Int. Cl.**
C01B 39/02 (2006.01)
C01B 39/40 (2006.01)(52) **U.S. Cl.**
CPC **C01B 39/026** (2013.01); **C01B 39/40**
(2013.01); **C01P 2002/72** (2013.01)(72) Inventors: Robert Peter Hodgkins, Dhahran (SA);
Omer Refa Koseoglu, Dhahran (SA);
Jean-Marie Maurice Basset, Thuwal
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Anissa Bendjeriou Sedjerari, Thuwal
(SA); Sathiyamoorthy Murugesan,
Thuwal (SA); Manoj Kumar
Gangwar, Thuwal (SA); Rajesh
Kumar Parsapur, Thuwal (SA)(57) **ABSTRACT**

A fibrous hierarchical zeolite includes a framework comprising aluminum atoms, silicon atoms, and oxygen atoms, the framework further comprising a plurality of micropores and a plurality of mesopores. The framework comprises no Brønsted acid activity.

(73) Assignees: Saudi Arabian Oil Company, Dhahran
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(54) **NICKEL NANOPARTICLE
FUNCTIONALIZED FIBROUS
HIERARCHICAL ZEOLITE AND METHOD
OF MAKING THE SAME**

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(22) Filed: Aug. 26, 2021

(71) Applicants: Saudi Arabian Oil Company, Dhahran
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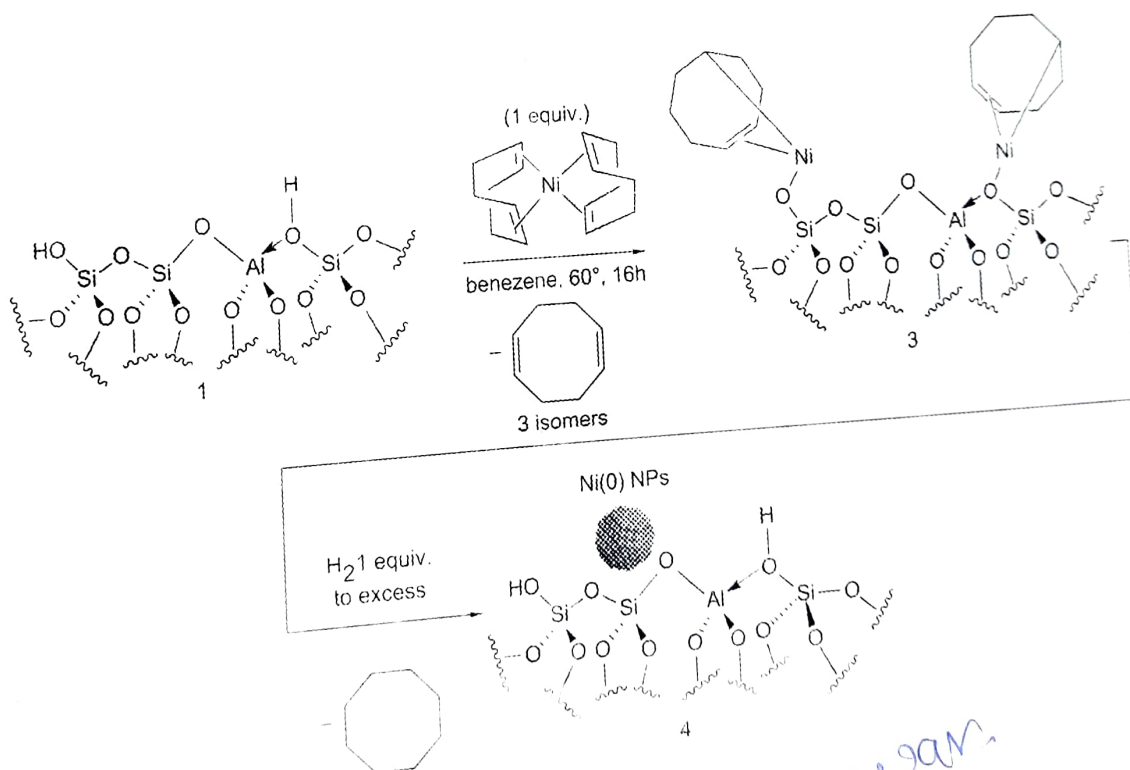
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ABSTRACT

A functionalized fibrous hierarchical zeolite includes a framework comprising aluminum atoms, silicon atoms, and oxygen atoms, the framework further comprising a plurality of micropores and a plurality of mesopores. A plurality of nanoparticles comprising nickel are immobilized on the framework.



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Hodgkins et al.(10) **Pub. No.: US 2023/0159343 A1**(43) **Pub. Date: May 25, 2023**(54) **MODIFIED ZEOLITES THAT INCLUDE
TITANIUM-CONTAINING
ORGANOMETALLIC MOIETIES AND
METHODS FOR MAKING SUCH***B01J 35/02* (2006.01)*B01J 37/16* (2006.01)*B01J 37/02* (2006.01)*C01B 39/02* (2006.01)(71) Applicants: **Saudi Arabian Oil Company, Dhahran**
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Science and Technology, Thuwal (SA)(52) **U.S. Cl.***CPC* *C01B 39/40* (2013.01); *B01J 29/405*
(2013.01); *B01J 35/1061* (2013.01); *B01J*
35/1066 (2013.01); *B01J 35/023* (2013.01);
B01J 37/16 (2013.01); *B01J 37/0203*
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2004/64 (2013.01); *C01P 2002/72* (2013.01);
C01P 2004/04 (2013.01); *C01P 2004/03*
(2013.01); *C01P 2002/82* (2013.01); *C01P*
2002/86 (2013.01); *C01P 2006/16* (2013.01);
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14, 2021, now Pat. No. 11,591,229.**Publication Classification**(51) **Int. Cl.** (2006.01)
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B01J 29/40 (2006.01)
B01J 35/10 (2006.01)

Disclosed herein are modified zeolites and methods for making modified zeolites. In one or more embodiments disclosed herein, a modified zeolite may include a microporous framework comprising a plurality of micropores having diameters of less than or equal to 2 nm. The microporous framework may include at least silicon atoms and oxygen atoms. The modified zeolite may further include organometallic moieties each bonded to bridging oxygen atoms. The organometallic moieties may include a titanium atom. The titanium atom may be bonded to a bridging oxygen atom, and the bridging oxygen atom may bridge the titanium atom of the organometallic moiety and a silicon atom of the microporous framework.

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Hodgkins et al.(10) **Pub. No.: US 2023/0174383 A1**(43) **Pub. Date: Jun. 8, 2023**(54) **MODIFIED ZEOLITES THAT INCLUDE
HAFNIUM-CONTAINING
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METHODS FOR MAKING SUCH***B01J 35/10* (2006.01)
B01J 37/02 (2006.01)
B01J 37/16 (2006.01)
C01B 39/02 (2006.01)
B01J 29/40 (2006.01)(71) Applicants: **Saudi Arabian Oil Company, Dhahran
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Science and Technology, Thuwal (SA)**(52) **U.S. Cl.**CPC *C01B 39/40* (2013.01); *B01J 35/023*
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2006/16 (2013.01); *C01P 2002/70* (2013.01);
C01P 2002/82 (2013.01); *C01P 2002/86*
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2004/04 (2013.01); *C01P 2004/62* (2013.01);
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15, 2021, now Pat. No. 11,591,230.**Publication Classification**(51) **Int. Cl.**
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Disclosed herein are modified zeolites and methods for making modified zeolites. In one or more embodiments disclosed herein, a modified zeolite may include a microporous framework including a plurality of micropores having diameters of less than or equal to 2 nm. The microporous framework includes at least silicon atoms and oxygen atoms. The modified zeolite may further include organometallic moieties each bonded to bridging oxygen atoms. The organometallic moieties include a hafnium atom. The hafnium atom is bonded to a bridging oxygen atom, and bridging oxygen atom bridges the hafnium atom of the organometallic moiety and a silicon atom of the microporous framework.

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(54) **MODIFIED ZEOLITES THAT INCLUDE ZIRCONIUM-CONTAINING ORGANOMETALLIC MOIETIES AND METHODS FOR MAKING SUCH**

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See application file for complete search history.

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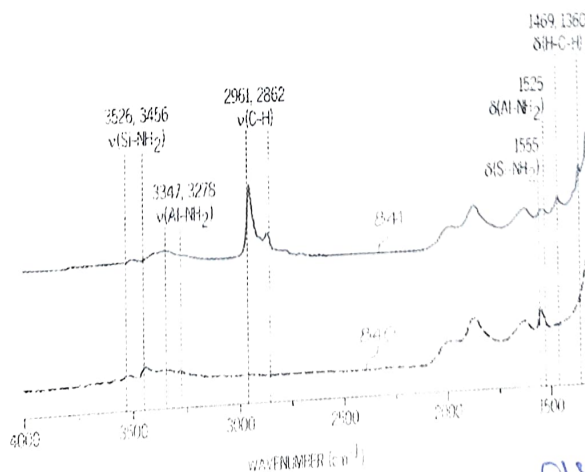
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(57)

ABSTRACT

Disclosed herein are modified zeolites and methods for making modified zeolites. In one or more embodiments disclosed herein, a modified zeolite may include a microporous framework including a plurality of micropores having diameters of less than or equal to 2 nm. The microporous framework may include at least silicon atoms and oxygen atoms. The modified zeolite may further include organometallic moieties each bonded to a nitrogen atom of a secondary amine functional group including a nitrogen atom and a hydrogen atom. The organometallic moieties may include a zirconium atom that is bonded to the nitrogen atom of the secondary amine functional group. The nitrogen atom of the secondary amine function group may bridge the zirconium atom of the organometallic moiety and a silicon atom of the microporous framework.

20 Claims, 14 Drawing Sheets

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