



US009409158B2

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

(10) **Patent No.:** **US 9,409,158 B2**  
(45) **Date of Patent:** **Aug. 9, 2016**

(54) **SYNTHESIS CATALYST AND SYNTHESIS METHOD FOR UNSATURATED CARBOXYLIC ACID AND/OR DERIVATIVE THEREOF**

(71) Applicants: **KABUSHIKI KAISHA SANGI**, Tokyo (JP); **KOCHI UNIVERSITY**, Kochi (JP)

(72) Inventors: **Ayumu Onda**, Kochi (JP); **Yumiko Matsuura**, Kochi (JP); **Kazumichi Yanagisawa**, Kochi (JP); **Jun Kubo**, Tokyo (JP)

(73) Assignees: **KABUSHIKI KAISHA SANGI**, Tokyo (JP); **KOCHI UNIVERSITY**, Kochi (JP)

(\* ) 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.: **14/889,277**

(22) PCT Filed: **May 8, 2014**

(86) PCT No.: **PCT/JP2014/002448**

§ 371 (c)(1),  
(2) Date: **Nov. 5, 2015**

(87) PCT Pub. No.: **WO2014/181545**

PCT Pub. Date: **Nov. 13, 2014**

(65) **Prior Publication Data**

US 2016/0096166 A1 Apr. 7, 2016

(30) **Foreign Application Priority Data**

May 10, 2013 (JP) ..... 2013-100404

(51) **Int. Cl.**

**B01J 27/14** (2006.01)  
**C07C 51/347** (2006.01)  
**B01J 35/00** (2006.01)  
**B01J 27/18** (2006.01)  
**C07C 67/327** (2006.01)  
**B01J 37/10** (2006.01)

(52) **U.S. Cl.**

CPC ..... **B01J 27/18** (2013.01); **B01J 27/1806** (2013.01); **B01J 37/10** (2013.01); **C07C 51/347** (2013.01); **C07C 67/327** (2013.01); **B01J 35/002** (2013.01)

(58) **Field of Classification Search**

CPC ..... B01J 27/1806; C07C 51/377  
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,729,978 A \* 3/1988 Sawicki ..... B01J 27/1806  
502/174  
4,792,620 A \* 12/1988 Paulik ..... B01J 31/0231  
560/232  
2014/0155653 A1\* 6/2014 Dongare ..... C07C 51/377  
562/599

FOREIGN PATENT DOCUMENTS

JP	2000-169417	6/2000
JP	2006-015330	1/2006
JP	2009-067775	4/2009
JP	2012-071267	4/2012
WO	2011/052178	5/2011
WO	2012/063044	5/2012

OTHER PUBLICATIONS

Zaragoza Dorwald, *Side Reactions in Organic Synthesis*, 2005, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Preface. p. IX.\*

Ghantani et al., "Catalytic Dehydration of Lactic Acid to Acrylic Acid Using Calcium Hydroxyapatite Catalysts," *Green Chemistry*, Feb. 27, 2013, vol. 15, No. 5, pp. 1211-1217.

Matsumura et al., "Dehydration of Lactic Acid to Acrylic Acid Using Hydroxyapatite Catalyst," *Journal of Dai 106 Kai Shokubai Toronakai*, Sep. 9, 2010, p. 159. (Partial Translation Included).

Onda et al., *Synthesis of Apatite Compound Microparticles Substituted by Various Elements and Application to Catalyst*, *Journal of the Society of Inorganic Materials*, May 1, 2013, vol. 20, No. 364, pp. 172-182. (Partial Translation Included).

\* cited by examiner

*Primary Examiner* — Paul A Zucker

(74) *Attorney, Agent, or Firm* — Occhiuti & Rohlicek LLP

(57) **ABSTRACT**

Using conventional synthesis methods, when an unsaturated carboxylic acid or a derivative thereof is synthesized from a hydroxycarboxylic acid or a derivative thereof by a dehydration reaction using a catalyst, the yield has been low. Accordingly, an object of the present invention is to provide a catalyst capable of synthesizing unsaturated carboxylic acids or derivatives thereof by a dehydration reaction that produces a high yield. The synthetic catalyst comprises an apatite compound containing an alkali metal in a crystal structure thereof, and the invention further includes methods for synthesizing an unsaturated carboxylic acid and/or a derivative thereof. The methods comprise contacting the aforementioned synthetic catalyst with the hydroxycarboxylic acid and/or a derivative thereof, so as to synthesize the unsaturated carboxylic acid and/or a derivative thereof by a dehydration reaction.

**18 Claims, 4 Drawing Sheets**