US009409156B2

(12) **United States Patent**
**Sanchez Valente et al.**

(10) **Patent No.: US 9,409,156 B2**
(45) **Date of Patent: Aug. 9, 2016**

(54) **OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE AND PREPARATION OF MULTIMETALLIC MIXED OXIDE CATALYST FOR SUCH PROCESS**

(71) Applicants: **Jaime Sanchez Valente**, Mexico City (MX); **Jose Manuel Lopez Nieto**, Valencia (ES); **Hector Armendariz Herrera**, Mexico City (MX); **Amada Masso Ramirez**, Valencia (ES); **Francisco Ivars Barcelo**, Valencia (ES); **Maria de Lourdes Alejandra Guzman Castillo**, Mexico City (MX); **Roberto Quintana Solorzano**, Mexico City (MX); **Andrea Rodriguez Hernandez**, Mexico City (MX); **Paz Del Angel Vicente**, Mexico City (MX); **Etel Maya Flores**, Mexico City (MX)

(72) Inventors: **Jaime Sanchez Valente**, Mexico City (MX); **Jose Manuel Lopez Nieto**, Valencia (ES); **Hector Armendariz Herrera**, Mexico City (MX); **Amada Masso Ramirez**, Valencia (ES); **Francisco Ivars Barcelo**, Valencia (ES); **Maria de Lourdes Alejandra Guzman Castillo**, Mexico City (MX); **Roberto Quintana Solorzano**, Mexico City (MX); **Andrea Rodriguez Hernandez**, Mexico City (MX); **Paz Del Angel Vicente**, Mexico City (MX); **Etel Maya Flores**, Mexico City (MX)

(73) Assignees: **Instituto Mexicano Del Petroleo**, Mexico City (MX); **Pemex Petroquimica**, Veracruz (MX); **Universidad Politecnica De Valencia**, Valencia (ES)

( * ) 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.: **13/655,620**

(22) Filed: **Oct. 19, 2012**

(65) **Prior Publication Data**

US 2014/0114109 A1 Apr. 24, 2014

(51) **Int. Cl.**
***C07C 5/48*** (2006.01)
***B01J 23/28*** (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC ..... ***B01J 23/8877*** (2013.01); ***B01J 23/28*** (2013.01); ***B01J 23/30*** (2013.01); ***B01J 23/885*** (2013.01);
(Continued)

(58) **Field of Classification Search**
USPC ..... 585/658; 502/312
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,250,346 A 2/1981 Young et al.
4,524,236 A * 6/1985 McCain ..... 585/658
(Continued)

FOREIGN PATENT DOCUMENTS

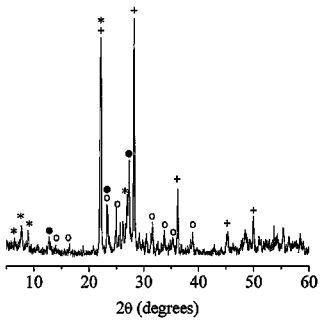
CN 102176966 9/2011
EP 0294845 12/1988
(Continued)

OTHER PUBLICATIONS

Watanabe et al., 2006, Comparative study on the catalytic performance of single-phase MO-V-O-based metal oxide catalysts in propane ammoxidation to acrylonitrile, Ind. Eng. Chem. Res., vol. 45, pp. 607-614.*
(Continued)

*Primary Examiner* — In Suk Bullock
*Assistant Examiner* — Youngsul Jeong
(74) *Attorney, Agent, or Firm* — Dickinson Wright PLLC

(57) **ABSTRACT**

Oxidative dehydrogenation of light paraffins, such as ethane at moderate temperatures (<500° C.) to produce ethylene without the formation of side products such as acetic acid and/or other oxygenated hydrocarbons is achieved using tellurium-free, multimetallic catalysts possessing orthorhombic M1 phase and other crystalline structures that have an important role for obtaining high performance catalysts for the oxidative dehydrogenation of ethane to ethylene. Such catalysts are prepared using thermal and hydrothermal methods.

**14 Claims, 18 Drawing Sheets**