

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau

(43) International Publication Date
21 March 2019 (21.03.2019)



(10) International Publication Number
WO 2019/053438 A1

(51) International Patent Classification:

B01J 21/08 (2006.01) **B01J 37/08** (2006.01)
B01J 21/06 (2006.01) **B01J 35/02** (2006.01)
B01J 23/04 (2006.01) **C07C 67/313** (2006.01)
B01J 31/02 (2006.01) **C07C 51/353** (2006.01)
B01J 37/02 (2006.01)

UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/GB2018/052606

(22) International Filing Date:

13 September 2018 (13.09.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1714756.2 13 September 2017 (13.09.2017) GB

(71) Applicant: **LUCITE INTERNATIONAL UK LIMITED**

[GB/GB]: Cassel Works, New Road, Billingham TS23 1LE (GB).

(72) Inventors: **CULLEN, Adam**; Wilton Centre, Wilton, Redcar TS10 4RF (GB). **JOHNSON, David William**; Wilton Centre, Wilton, Redcar TS10 4RF (GB). **YORK, Ian Andrew**; Wilton Centre, Wilton, Redcar TS10 4RF (GB).

(74) Agent: **APPLEYARD LEES IP LLP**; 15 Clare Road, Halifax Yorkshire HX1 2HY (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: A CATALYST AND A PROCESS FOR THE PRODUCTION OF ETHYLENICALLY UNSATURATED CARBOXYLIC ACIDS OR ESTERS

(57) Abstract: A catalyst has a modified silica support and comprises a modifier metal, zirconium and/or hafnium, and a catalytic metal on the modified support. The catalyst has at least a proportion, typically, at least 25%, of modifier metal present in moieties having a total of up to 2 modifier metal atoms. The moieties may be derived from a monomeric and/or dimeric cation source. A method of production: - provides a silica support with isolated silanol groups with optional treatment to provide isolated silanol groups (-SiOH) at a level of <2.5 groups per nm²; contacting the optionally treated silica support with a monomeric zirconium or hafnium modifier metal compound to effect adsorption onto the support; optionally calcining the modified support for a time and temperature sufficient to convert the monomeric zirconium or hafnium compound adsorbed on the surface to an oxide or hydroxide of zirconium or hafnium in preparation for catalyst impregnation. A method of producing an ethylenically unsaturated carboxylic acid or ester, typically, an α, β ethylenically unsaturated carboxylic acid or ester, comprising the steps of contacting formaldehyde or a suitable source thereof with a carboxylic acid or ester in the presence of catalyst and optionally in the presence of an alcohol, wherein said catalyst is used.



WO 2019/053438 A1