



(12) **DEMANDE DE BREVET CANADIEN  
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2018/06/07  
(87) Date publication PCT/PCT Publication Date: 2018/12/27  
(85) Entrée phase nationale/National Entry: 2019/11/29  
(86) N° demande PCT/PCT Application No.: EP 2018/064958  
(87) N° publication PCT/PCT Publication No.: 2018/234045  
(30) Priorité/Priority: 2017/06/23 (DKPA 2017 00375)

(51) Cl.Int./Int.Cl. *C07D 301/08* (2006.01),  
*C07B 33/00* (2006.01), *C07B 41/00* (2006.01)  
(71) Demandeur/Applicant:  
HALDOR TOPSOE A/S, DK  
(72) Inventeurs/Inventors:  
JANSSENS, TON V.W., DK;  
BEATO, PABLO, DK  
(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : PROCEDE D'OXYDATION D'UN ALCENE INFERIEUR A BASSES TEMPERATURES DANS DES  
MELANGES GAZEUX CONTENANT DE L'AMMONIAC  
(54) Title: A PROCESS FOR OXIDATION OF A LOWER ALKENE AT LOW TEMPERATURES IN AMMONIA-  
CONTAINING GAS MIXTURES

(57) **Abrégé/Abstract:**

In a process for the oxidation of a lower alkene, such as ethylene, over a catalyst containing Cu and one or more zeolite or zeotype materials, the oxidation is conducted in the presence of ammonia in the feed gas at a process temperature below 350°C. The oxidation can be performed in a continuous process.

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

(19) World Intellectual Property  
Organization  
International Bureau



(10) International Publication Number  
**WO 2018/234045 A1**

(43) International Publication Date  
27 December 2018 (27.12.2018)

WIPO | PCT

**(51) International Patent Classification:**

C07D 301/08 (2006.01) C07B 41/00 (2006.01)  
C07B 33/00 (2006.01)

**(21) International Application Number:**

PCT/EP2018/064958

**(22) International Filing Date:**

07 June 2018 (07.06.2018)

**(25) Filing Language:**

English

**(26) Publication Language:**

English

**(30) Priority Data:**

PA 2017 00375 23 June 2017 (23.06.2017) DK

**(71) Applicant:** HALDOR TOPSØE A/S [DK/DK]; Haldor  
Topsøes Allé 1, 2800 Kgs. Lyngby (DK).

**(72) Inventors:** BEATO, Pablo; Under Elmene 1, 2.tv., 2300  
Copenhagen (DK). JANSSENS, Ton V.W.; Gunnarsvej 3,  
2880 Bagsværd (DK).

**(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, 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).

**Declarations under Rule 4.17:**

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

**Published:**

- with international search report (Art. 21(3))

**(54) Title:** A PROCESS FOR OXIDATION OF A LOWER ALKENE AT LOW TEMPERATURES IN AMMONIA-CONTAINING GAS MIXTURES

**(57) Abstract:** In a process for the oxidation of a lower alkene, such as ethylene, over a catalyst containing Cu and one or more zeolite or zeotype materials, the oxidation is conducted in the presence of ammonia in the feed gas at a process temperature below 350°C. The oxidation can be performed in a continuous process.



WO 2018/234045 A1

**Title: A process for oxidation of a lower alkene at low temperatures in ammonia-containing gas mixtures**

The present invention relates to a process for oxidation of a lower alkene, such as ethylene or propylene, in ammonia-containing gas mixtures and catalysts for use in the process. The invention is based on the finding that oxygen can be activated by mobile Cu-ammonia complexes formed inside the cavities of a zeolite. The term "lower alkene" refers to an alkene containing from 1 to 5 carbon atoms in the molecule.

Partial oxidation of ethylene ( $C_2H_4$ ) to ethylene oxide ( $C_2H_4O$ ) is industrially catalyzed by silver, and it is an important industrial process with a large production capacity. Due to the global capacity of this process, even slight improvements in the selectivity would have large scale economical benefits. Processes and catalysts for the oxidation of ethylene to ethylene oxide are described e.g. in WO 95/05896 A1, WO 2004/078737 A1, WO 2012/141942 A1 and EP 2 980 082 A1.

The overall reaction comprises three reactions: (1) the selective oxidation of ethylene to ethylene oxide ( $C_2H_4 + \frac{1}{2} O_2 \leftrightarrow C_2H_4O$ ), (2) the unselective oxidation of ethylene to  $CO_2$  and  $H_2O$  ( $C_2H_4 + 3 O_2 \rightarrow 2 CO_2 + 2 H_2O$ ) and (3) the over-oxidation of ethylene oxide to  $CO_2$  and  $H_2O$  ( $C_2H_4O + 2.5 O_2 \rightarrow 2 CO_2 + 2 H_2O$ ).

The industrial catalyst consists of silver particles supported on low surface alumina ( $\alpha-Al_2O_3$ ), with the addition of alkali compounds as promoters. During the

process, chlorine is added in ppm amounts to the feed stream as a promoter in the form of chlorinated hydrocarbons in order to enhance the ethylene oxide selectivity. Today, the ethylene oxide selectivity of the industrial catalyst lies in the range of 80-90%.

One of the challenges of the current process is the high heat of reaction, which limits the conversion of ethylene to below 10% in order to avoid local overheating and hence sintering of the Ag particles, which ultimately leads to a decrease in activity.

Recently, it has been found that Cu-zeolites are able to oxidize methane directly to methanol at around 200°C (M.H. Groothaert et al., *J. Am. Chem. Soc.* **127**, 1394 (2005); P.J. Smeets et al., *Catal. Today* **110**, 303 (2005), E.M.C. Alayon et al., *ACS Catal.* **4**, 16 (2014); Le, H. et al., *ACS Catal.* **7**, 1403-1412 (2017); Markovits, M. A. C. et al., *Top. Catal.* **59**, 1554-1563 (2016)), which are very mild conditions for the activation of methane. However, the procedure for the conversion to methanol requires an activation of the Cu-zeolite which comprises exposure of the Cu-zeolite to oxygen at temperatures above 400 °C to activate the oxygen. The current interpretation of this partial oxidation of methane to methanol is that the oxidation reaction requires the formation of dimeric Cu-O species, such as Cu-O-Cu, Cu-O-O-Cu, or Cu-O<sub>2</sub>-Cu, where the actual oxidation of methane then takes place.

Cu-zeolites are also well known catalysts for the selective catalytic reduction of NO<sub>x</sub> by ammonia (NH<sub>3</sub>-SCR), which is the basis for the current technology for reduction of NO<sub>x</sub>

emissions from diesel engines and power plants. The NH<sub>3</sub>-SCR reaction proceeds according to the equation:



5

According to this reaction equation, the NH<sub>3</sub>-SCR reaction also requires an activation of oxygen. On Cu-zeolites, the NH<sub>3</sub>-SCR reaction proceeds already around 200-250°C (Gao, F. et al. *J. Catal.* **319**, 1-14 (2014); Janssens, T.V.W. et al., *ACS Catal.* **5**, 2832-2845 (2015); Paolucci, C. et al. *J. Am. Chem. Soc.* **138**, 6028-6048 (2016)). As can be inferred from the reaction equation, this reaction also requires an activation of oxygen on the Cu-zeolites, which implies that oxygen activation takes place at around 200-250°C in NH<sub>3</sub>-SCR.

15

In NH<sub>3</sub>-SCR, it has been found that the interaction between NH<sub>3</sub> and Cu plays a special role. Cu forms stable complexes with ammonia, such as Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> and Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complexes. The Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complex is weakly bound in the zeolite (Janssens, T.V.W. et al., *ACS Catal.* **5**, 2832-2845 (2015); Paolucci, C. et al., *J. Am. Chem. Soc.* **138**, 6028-6048 (2016)), which suggests that this complex is mobile under reaction conditions for NH<sub>3</sub>-SCR.

25

Applicant's patent applications WO 2015/154829 A1, WO 2015/154828 A1 and WO 2015/154827 A1 describe methods for the preparation of Cu-zeolite and Cu-zeotype materials by mixing a given zeolite or zeotype material in the H<sup>+</sup> or NH<sub>4</sub><sup>+</sup> form with CuO or Cu<sub>2</sub>O powder, followed by exposure to NH<sub>3</sub> or a mixture of NH<sub>3</sub> with nitrogen oxides at temperatures below 300°C. The materials prepared in this way show an

30

activity for NH<sub>3</sub>-SCR that is comparable to or exceeds the activity of materials prepared by conventional ion exchange procedures, which means that solid state ion exchange can take place between Cu oxides and zeolites at temperatures  
5 below 300°C in the presence of ammonia. It has been proposed that the ability of performing ion-exchange at low temperatures is due to the mobility of the Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complex (Shwan, S. et al., *ACS Catal.* **5**, 16-19 (2015)). The role of the mobility for the activation of oxygen in NH<sub>3</sub>-SCR in Cu-  
10 zeolites has not been established yet.

The above-mentioned WO 2015/154829 A1 discloses that the efficiency of the solid state ion exchange process decreases at temperatures above 350°C. Following the idea  
15 that the solid state ion exchange process is due to the mobility of the Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complex, it can be deduced from this result that the Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complex is not thermally stable above 350°C. This then leads to a loss of the mobility of the Cu-complex.

20 US 2009/0050535 describes a process for preparing an olefin oxide by reacting a feed comprising an olefin and oxygen. The process, which is carried out as a continuous process, comprises contacting the feed components with an absorbent  
25 comprising copper and an epoxidation catalyst comprising a carrier, which may be based on zeolites. A reaction modifier such as ammonia may be present in the feed. This US document, however, relates to a traditional process, such as an ethylene oxide process, and even though copper  
30 is present as an absorber in the reactor, the process is very different from the present process.

More specifically, the present invention is built on the observations that oxidation of ethylene at around 200°C requires an activation of oxygen on a Cu-zeolite or Cu-zeotype, which probably involves more than one Cu-center, and that the presence of ammonia enhances the mobility of the Cu-centers in a Cu-zeolite or Cu-zeotype.

By substituting silver (15-25% Ag on alumina in the prior art industrial catalyst) by Cu (3-5% in the zeolite), the costs of the catalyst can be reduced by a very large factor.

Thus, the present invention concerns a process for the oxidation of a lower alkene over a catalyst containing Cu and a zeolite or a zeotype material at a process temperature below 350°C, wherein the oxidation is conducted in the presence of ammonia in the feed gas. The presence of ammonia is essential to the oxidation of the alkene on Cu-zeolite or Cu-zeotype materials, even though it does not directly take part in the oxidation of the alkene, and it is not necessarily a part of the reaction product. It is also noted that the process of the invention implies activation of oxygen at temperatures below 350°C, and does not require the oxygen activation above 400°C as described in Le, H. et al., *ACS Catal.* **7**, 1403-1412 (2017) and Markovits, M.A.C. et al., *Top. Catal.* **59**, 1554-1563 (2016).

A lower alkene is a C1-C5 alkene. The preferred lower alkane is ethylene. Another preferred lower alkene is propylene.

A preferred reaction product is ethylene oxide. Another

preferred reaction product is propylene oxide.

Other preferred reaction products are ethylene glycol and acetaldehyde.

5

A first embodiment of the invention is a process in which a gas mixture comprising oxygen, ammonia and a lower alkene is contacted with a Cu-zeolite material at a temperature below 350°C, resulting in an alkene concentration in the product stream that is lower than the concentration in the inlet stream.

Another embodiment of the invention is a process in which a gas mixture comprising oxygen, ammonia and a lower alkene is contacted with a Cu-zeotype material at a temperature below 350°C, resulting in an alkene concentration in the product stream that is lower than the concentration in the inlet stream.

Another embodiment of the invention is a process in which a gas mixture comprising water, ammonia and lower alkene is contacted with a Cu-zeolite material at a temperature below 350°C, resulting in an alkene concentration in the product stream that is lower than the concentration in the inlet stream.

Another embodiment of the invention is a process in which a gas mixture comprising water, ammonia and lower alkene is contacted with a Cu-zeotype material at a temperature below 350°C, resulting in an alkene concentration in the product stream that is lower than the concentration in the inlet stream.

A further embodiment of the invention is a catalyst containing a mixture of a zeolite or a zeotype in the H<sup>+</sup> or NH<sub>4</sub><sup>+</sup> form and an oxide of Cu.

5

Preferably the zeolite structure of the Cu-zeolite catalyst is one or more structures selected from the group consisting of AEI, AFX, CHA, KFI, ERI, GME, LTA, IMF, ITH, MEL, MFI, SZR, TUN, \*BEA, BEC, FAU, FER, MOR and LEV. It is especially preferred that the Cu-zeolite catalyst is selected from the group consisting of Cu-CHA, Cu-MOR, Cu-MFI, Cu-BEA, Cu-ZSM-5 and Cu-FER.

10

According to the present invention, the process feed gas mixture comprises oxygen, ammonia and a lower alkene. Other gaseous compounds, such as nitrogen, water, noble gases and other hydrocarbons, can be present in the feed gas mixture as well.

15

An advantage of the present invention is that the process can be conducted continuously without any need of re-activation of the Cu-zeolite or Cu-zeotype material.

20

Another advantage of the present invention is that the process can be conducted isothermally at a process temperature between 150 and 350°C. A preferred embodiment of the invention is a process in which the oxidation is performed at a temperature of 250°C or lower.

25

A further embodiment of the invention is that the catalyst for the process comprises a mixture of a metal-free zeolite or zeotype material and an oxide of Cu.

30

Another embodiment of the invention is a process in which a gas mixture comprising oxygen, ammonia and a lower alkene is contacted with a catalyst containing Cu and one or more zeolite or zeotype materials at a temperature below 350°C, in which the concentration of NH<sub>3</sub> is between 1 and 5000 ppmv.

Another embodiment of the invention is a process in which a gas mixture comprising oxygen, ammonia and a lower alkene is contacted with a catalyst containing Cu and one or more zeolite or zeotype materials at a temperature below 350°C, in which the concentration of oxygen is 10 vol % or lower.

Another embodiment of the invention is a process in which a gas mixture comprising water, ammonia and a lower alkene is contacted with a catalyst containing Cu and one or more zeolite or zeotype materials at a temperature below 350°C, in which the concentration of water is 10 vol % or lower.

**Claims:**

1. A process for the oxidation of a lower alkene over a catalyst containing Cu and one or more zeolite or zeotype materials, wherein the oxidation is conducted in the presence of ammonia in the feed gas at a process temperature below 350°C.
2. Process according to claim 1, wherein a zeolite or zeotype material is mixed with an oxide of Cu.
3. Process according to claim 1 or 2, wherein the zeotype is a silico-alumino phosphate material.
4. Process according to any of the claims 1-3, in which the oxidation is performed in a continuous process.
5. Process according to any of the claims 1-4, wherein the lower alkene is ethylene.
6. Process according to any of the claims 1-5, wherein the reaction product is ethylene oxide.
7. Process according to any of the claims 1-5, wherein the reaction product is ethylene glycol.
8. Process according to any of the claims 1-5, wherein the reaction product is acetaldehyde.
9. Process according to any of the claims 1-4, wherein the lower alkene is propylene.

10. Process according to any of the claims 1-4 and 9, wherein the reaction product is propylene oxide.

11. Process according to any of the claims 1-10,  
5 wherein the content of ammonia in the feed gas is between 1 and 5000 ppmv.

12. Process according to any of the claims 1-10,  
10 wherein the content of oxygen in the feed gas is 10 vol% or lower.

13. Process according to any of the claims 1-10,  
wherein the content of water in the feed gas is 10 vol% or  
lower.

15 14. Process according to any of the claims 1-10,  
wherein the process temperature is 250°C or lower.

15. Process according to any of the preceding claims,  
20 wherein one or more zeolite or zeotype materials in the catalyst have structures selected from the group consisting of AEI, AFX, CHA, KFI, ERI, GME, LTA, IMF, ITH, MEL, MFI, SZR, TUN, \*BEA, BEC, FAU, FER, MOR and LEV.

25 16. Process according to claim 15, wherein the Cu-zeolite catalyst is selected from the group consisting of Cu-CHA, Cu-MOR, Cu-MFI, Cu-BEA, Cu-ZSM-5 and Cu-FER.

30 17. Process according to claim 15, wherein the Cu-based catalyst is Cu-CHA.