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**WO 01/70660 A1**

(54) Title: PROCESS FOR PREPARING AN ALCOHOL FROM AN OLEFIN

(57) Abstract: A process for the preparation of an alcohol from an olefin, wherein the olefin is reacted with syngas in the presence of a catalyst system comprising a homogeneous hydroformylation catalyst and a heterogeneous catalyst comprising copper on a support.

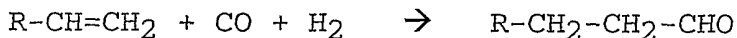
## PROCESS FOR PREPARING AN ALCOHOL FROM AN OLEFIN

Field of the Invention

The present invention relates to a process for preparing an alcohol from an olefin, wherein the olefin is reacted with syngas in the presence of a hydroformylation catalyst.

Background of the Invention

The synthesis of "oxo" alcohols by hydroformylating an olefin followed by the hydrogenation thereof is known. As described in Chapter 1 of Falbe's "New Syntheses with Carbon Monoxide" (Springer-Verlag, 1980), the synthesis involves the preparation of an aldehyde by the following reaction:



The hydroformylation reaction is typically conducted in the presence of a homogeneous catalyst on the basis of a transition metal, such as cobalt, nickel, palladium or platinum. This reaction is also extensively described in Chapter 4 of "Carbonation" by Colquhoun et al (Plenum Press, 1991).

A secondary reaction occurring simultaneously involves the hydrogenation of the oxo-aldehyde into an oxo-alcohol. The extent of this secondary reaction can be increased via various measures, although it must be borne in mind that these measures may lead to many undesirable side-products (Falbe, Chapter 1.5.2.2.1).

Some homogeneous catalysts have sufficient activity to hydrogenate the in-situ formed oxo-aldehyde into the desired oxo-alcohol. However, in most instances a separate post-hydrogenation finishing step of the oxo-alcohol is essential due to quality considerations. It

therefore remains desirable to be able to produce alcohols in a single-step process without the necessity of a post-hydrogenation finishing step.

#### Summary of the Invention

5           Accordingly, the present invention provides a process for the preparation of an alcohol from an olefin, wherein the olefin is reacted with syngas in the presence of a catalyst system comprising a homogeneous hydroformylation catalyst and a heterogeneous catalyst comprising copper  
10 on a support.

#### Detailed Description of the Invention

          Hydroformylation of an olefin in the presence of a homogeneous transition metal catalyst is well documented. Such processes rely for instance on classical catalysts  
15 such as Co-, Rh-, Ir-, Ru- or Os-carbonyls, or on modified catalysts (e.g., wherein the CO ligands are replaced by phosphines). Of particular interest are modified palladium or platinum hydroformylation  
20 catalysts.

          The process of the present invention comprises the modification of such hydroformylation processes by conducting the hydroformylation in the presence of a catalyst system comprising a known homogeneous hydro-  
25 formylation catalyst and a heterogeneous catalyst comprising copper on a support.

          The process of the present invention involves using a catalyst system further comprising a supported copper catalyst. The catalyst comprising copper on a support is believed to be at least partially in a metallic state  
30 under operating conditions. The catalyst may be a sophisticated catalyst wherein the copper is part of an alloy, and/or wherein the catalyst comprises additional, promoter, metals. Suitable alloys can include one or more metals of Groups 8 to 11 of the Periodic Table of

Elements. Suitable promoter metals can include one or more metals of Groups 1 to 7 of the Periodic Table. However, ordinary catalysts, based on copper as the only active component, are quite acceptable.

5           The nature of the catalyst support is not essential. Suitable supports include inert carriers composed of a metallic or glass sponge, or based on an inorganic carbide, or oxide, or carbon. For instance, the support may be based on oxides of Groups 2-6 and 12-14 metal of  
10           the Periodic Table and mixtures thereof e.g. ZnO, titania, alumina, zirconia, silica and/or zeolites. Preferred supports are resistant to an acidic medium. Suitable results in model reactions have been achieved with copper on ZnO, on silica, and on Cr<sub>2</sub>O<sub>3</sub>.

15           The support may be used as fine powder or shaped into mouldings such as, for example, pellets, granules, or extrudates using methods known in the art, such as those described in US-A-5364984 which disclosure is herein incorporated by reference. Alternatively, the support may  
20           be in the shape of a honeycomb, a foam, a sponge or similarly large monolith.

          The amount of copper may also vary widely. For instance, the copper may be present on the support in a quantity of 0.1 to 80 w%, preferably 10 to 50 w%, more  
25           preferably 25 to 35 w%, relative to the support.

          The synthesis of the copper catalyst is conventional, typically involving the co-precipitation of copper and support precursor. Optionally it can also be prepared by doping a carrier with a copper solution, calcining the  
30           loaded carrier, and reducing the same at elevated temperatures under H<sub>2</sub>. Various supported copper catalyst are commercially available, e.g. for use in the hydrogenation of esters to the corresponding alcohols. Copper containing catalysts are also described in

US-A-5096688, in a two-stage process for converting synthesis gas into higher alcohols. This document describes its use for the hydrogenation of undesirable non-alcohol oxygenates and the conversion of water and carbon monoxide in hydrogen gas and carbon monoxide.

The process of the present invention may be a continuous process, a semi-continuous process or a batch process. In the case of continuous processes, liquid hourly space velocities of about 0.1 to about 10 h<sup>-1</sup> are preferred. In batch processes, reaction times varying from about 0.1 to about 10 hours are suitable. The quantity in which the supported copper catalyst may be used, in batch processes, may vary widely, e.g. ranging from about 0.1 to about 50 w%, preferably from about 1.0 to about 10 w%, calculated on the weight of the olefin.

Feed and process conditions are entirely conventional. By way of example, the feed may be an olefin or substituted olefin of 2 to 20 carbon atoms, which may be linear, branched or cyclic. The hydrogenation conditions are not very critical. The temperature may vary widely, e.g. from about 10 to about 300 °C, preferably from about 20 to about 150 °C. Similarly, the pressure may vary from about atmospheric to about 30 MPa (300 bar), preferably from about 0.5 to about 7 MPa (5 to 70 bar). The hydroformylation catalyst is employed in conventional quantities too, varying from about 0.001 to about 10.0 mmole per mole olefin. The process may involve the use of a solvent.

Synthesis gas is a blend of hydrogen and carbon monoxide. It typically is made by partial combustion of a petroleum feed. Commercial syngas comprises hydrogen and carbon monoxide in an H<sub>2</sub>/CO ratio of about 1.0-2.0. Syngas with a higher H<sub>2</sub>/CO ratio, e.g. up to about 10.0,

and higher, may be prepared by the so-called water gas shift reaction, and such gases may also be used in the process of the present invention. On the other hand, it is an advantage of the present invention that it may cope  
5 with carbon monoxide-rich gases, at H<sub>2</sub>/CO ratios as low as about 0.5. The preferred H<sub>2</sub>/CO ratio hence varies from about 0.5 to about 10.0, more preferably from about 1.0 to about 5.0.

#### Preparation of nonanol

10 In the following example a hydrogenation catalysts as hereafter described may be used which are provided for illustrative purposes and are not to be construed as limiting the invention.

Cu/Zn a ZnO/alumina catalyst containing ~40 w% of Cu

15 Cu/Si a silica catalyst containing ~29 w% of Cu

Cu/Cr a chromite catalyst containing ~37 w% of Cu

Prior to the reaction, the hydrogenation catalyst should be reduced, for instance, at 300 °C for 11 hours under 0.5 MPa (5 bar) H<sub>2</sub>.

20 Charge a 250 ml magnetically-stirred autoclave with 20 ml 1-octene, 50 ml 2,5,8-trioxanonane, 0.25 mmole of palladium acetate, 0.3 mmole of 1,3-bis(di-n-butyl-phosphino)propane, 2 mmole sodium trifluoroacetate, and 2 g of any of the above hydrogenation catalysts. After  
25 being flushed, pressurize the autoclave with carbon monoxide and hydrogen up to a partial pressure of 30 bar of each. Seal the autoclave, heat to a temperature of 90 °C, and maintain at that temperature for 5 hours.

C L A I M S

1. A process for the preparation of an alcohol from an olefin, wherein the olefin is reacted with syngas in the presence of a catalyst system comprising a homogeneous hydroformylation catalyst and a heterogeneous catalyst  
5 comprising copper on a support.
2. The process of claim 1, wherein the catalyst comprises metallic copper on a support.
3. The process of claim 1 or 2, wherein the carrier is composed of a clay, of a metallic or glass sponge, or  
10 based on an inorganic carbide, or oxide or carbon.
4. The process of claim 3, wherein the catalyst is selected from Cu on ZnO, on alumina, on silica, or on  $\text{Cr}_2\text{O}_3$ .
5. The process of any one of claims 1 to 4, wherein the  
15 copper is present on the support in a quantity of 0.1 to 80 w% relative to the support.
6. The process of any one of claims 1 to 5, wherein the (substituted) olefin has 2 to 20 carbon atoms, and is either linear, branched or cyclic.

## INTERNATIONAL SEARCH REPORT

Int'l Application No

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A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C07C29/16 C07C31/125

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 982 011 A (J.A.A. HANIN) 1 January 1991 (1991-01-01) the whole document ---	1
A	WO 94 06739 A (EXXON CHEMICAL PATENTS) 31 March 1994 (1994-03-31) page 18 -page 20; claims 1,6 ---	1
A	US 5 096 688 A (J.T. MILLER, ET AL.) 17 March 1992 (1992-03-17) cited in the application the whole document -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
US 4982011	A	01-01-1991	AR 240905 A	27-03-1991
			AR 240904 A	27-03-1991
			AT 48990 T	15-01-1990
			AT 60044 T	15-02-1991
			AU 593809 B	22-02-1990
			AU 5763486 A	26-11-1987
			BR 8506001 A	19-08-1986
			BR 8506003 A	19-08-1986
			CA 1273367 A	28-08-1990
			CA 1313681 A	16-02-1993
			DE 3574964 D	01-02-1990
			DE 3581382 D	21-02-1991
			EP 0183545 A	04-06-1986
			EP 0185477 A	25-06-1986
			JP 1858666 C	27-07-1994
			JP 5066932 B	22-09-1993
			JP 61148132 A	05-07-1986
			JP 1959832 C	10-08-1995
			JP 6092336 B	16-11-1994
			JP 61197535 A	01-09-1986
			SG 65392 G	04-12-1992
			SG 66292 G	19-02-1993
			US 4658068 A	14-04-1987
			AR 241119 A	15-11-1991
			AT 44286 T	15-07-1989
			BR 8506002 A	19-08-1986
			CA 1273366 A	28-08-1990
			DE 3571247 D	03-08-1989
			EP 0184382 A	11-06-1986
			JP 61209251 A	17-09-1986
			US 4735743 A	05-04-1988
			US 4656215 A	07-04-1987
			US 4683343 A	28-07-1987
<hr/>				
WO 9406739	A	31-03-1994	NONE	
<hr/>				
US 5096688	A	17-03-1992	CA 2018611 A	13-12-1990
			CA 2018612 A	13-12-1990
			US 5109027 A	28-04-1992
<hr/>				