



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C07C 29/16, 31/125, B01J 23/46 B01J 23/83	A1	(11) International Publication Number: WO 87/ 04147 (43) International Publication Date: 16 July 1987 (16.07.87)
(21) International Application Number: PCT/FI86/00155 (22) International Filing Date: 22 December 1986 (22.12.86) (31) Priority Application Number: 855157 (32) Priority Date: 27 December 1985 (27.12.85) (33) Priority Country: FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, SF-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only) : ALVILA, Leila [FI/FI]; Mastotie 4 B 11, SF-80160 Joensuu (FI). PAKKANEN, Tapani [FI/FI]; Koulukatu 34 A 12, SF-80120 Joensuu (FI). KRAUSE, Outi [FI/FI]; Kaunispääntie 3 F 55, SF-00970 Helsinki (FI). JOUTSIMO, Matteus [FI/FI]; Riskutie 25 A, SF-00950 Helsinki (FI).		(74) Agent: FORSSÉN & SALOMAA OY; Uudenmaankatu 40 A, SF-00120 Helsinki (FI). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
(54) Title: CATALYST SYSTEM AND PROCESS FOR PRODUCING ALCOHOLS FROM OLEFINS AND SYNTHESIS GASES (57) Abstract Catalyst system and process for selectively producing alcohols from olefines and synthesis gas. The catalyst system comprises one or several metal cluster compounds belonging to the cobalt group on an inorganic carrier and an amine of the form $NR_1R_2R_3$, where R_1, R_2 and R_3 are either hydrogen or an aliphatic or aromatic group containing 1 to 8 carbon atoms.		

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1 Catalyst system and process for producing alcohols
from olefines and synthesis gases

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The present invention concerns a catalyst system and process by
the aid of which alcohol can be produced from olefines and syn-
thesis gases (H_2+CO). This synthesis belongs to the group of hydro-
10 formylation, or oxo, reactions, by which compounds containing
oxygen, such as aldehydes and alcohols, are usually produced from
olefines. The catalysts to be used in the reaction are typically
homogeneous and they contain rhodium or cobalt either in the form
of carbonyls or phosphines. However, isolation of the catalyst
15 dissolved in the reaction mixture poses a difficult problem, par-
ticularly when catalysts containing rhodium are used, and it affects
the process costs. Endeavours have been made to avoid the drawbacks
of homogeneous catalysis by binding the metal compounds on a solid
carrier, which may be of organic or inorganic origin. However,
20 heterogeneous hydroformylation catalysts are often less active
than homogeneous ones, the metals are solved off the carriers in
reaction conditions, and their thermal durability is limited.

Metal cluster compounds constitute a group of compounds which have
25 favourable properties as catalyst precursors. In the U.S. Patent
No. 4,144,191, a bimetallic carbonyl cluster compound catalyst for
producing alcohols by hydroformylation is disclosed. For cluster
compound, either $Rh_2Co_2(CO)_{12}$ or $Rh_3Co(CO)_{12}$ is used, bound to an
organic polymer containing amine groups. The catalyst operates at
30 low temperature and produces almost exclusively alcohols.

In the Finnish patent application No. 844634 the observation is
made that a mixture of the monometal cluster compounds $Rh_4(CO)_{12}$
and $Co_4(CO)_{12}$ bound to an amine resin carrier serves as the ex-
35 tremely selective catalyst in producing alcohols. An advantage of
the cluster mixture catalyst is that it is simpler to prepare and

1 its activity can be optimized as a function of the mole proportion
of the metals.

Increasing the reaction rate in the hydroformylation reaction
5 would be desirable, and feasible by raising the reaction tempera-
ture, but the thermal sensitivity of amine resin carriers restricts
the raising of the reaction temperature. When using inorganic
carrier materials, the use of higher temperatures would be possible.
It was noted, however, in attempts to use monometal cluster compound
10 mixtures containing rhodium and cobalt, or bimetallic compounds
containing rhodium and cobalt, on inorganic carriers that the
hydroformylation reaction in fact produced aldehydes only.

The object of the present invention is a catalyst system in which
15 the above-mentioned drawbacks are avoided and which thus enables
alcohols to be produced with high selectivity and at relatively
high temperatures. The catalyst system of the invention for pro-
ducing alcohols selectively from olefines and synthesis gases is
characterized in that it comprises one or several metal cluster
20 compounds belonging to the cobalt group on an inorganic carrier
and an amine of the form $NR_1R_2R_3$, where R_1, R_2 and R_3 are either
hydrogen or an aliphatic or aromatic group containing 1 to 8 carbon
atoms.

25 Adding amine either into the reaction mixture, on the carrier, or
to both, is indispensable for achieving sufficient alcohol con-
version. The bimetallic $Co_2Rh_2(CO)_{12}$ mixture as well as a mixture
of monometal clusters $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ bound to aluminium
oxide or silicon dioxide-based carriers produce nothing but alde-
30 hydes if no amines are present.

The most efficient amines have turned out to be tertiary amines
 NR_3 , where R is any aliphatic or aromatic group.

35 The characteristics of the catalyst of the invention are influenced
by factors related both to production technology and reaction

1 technique. The catalyst is prepared by mixing a carrier and a
metal cluster compound in a solvent. After the binding process has
been completed, the solvent is removed, the catalyst rinsed with
pure solvent, and dried in vacuum. The binding depends on the
5 oxide carrier, on the chemical and mechanical characteristics.
Aluminium oxide is one of the best agents for binding cobalt and
rhodium compounds. Binding can also be observed on silicon oxide,
zeolites and several silicates, for instance magnesium silicate.
The binding efficiency of the carrier is also affected by its
10 degree of grinding. The most finely ground carriers bind best, and
they are also the most active in catalytic reactions. In practice,
more coarsely ground materials are easier to handle.

Impregnating a tertiary amine directly into the carrier material
15 prior to binding the cluster compound also results in an active
hydroformylation catalyst producing alcohols. Admittedly, amine-
impregnated aluminium oxide and silicon oxide bind cluster compounds
less well, the consequence being that greater catalyst quantities
have to be used.

20 The amine may also be added, not to the carrier, but directly to
the reaction mixture, or part of the amine may be added to the
reaction mixture and part of it to the catalyst. The quantity of
amine is advantageously 0.1 to 10 % by weight of the reaction
25 mixture.

Secondary and primary amines also act as factors catalyzing the
hydroformylation reaction of rhodium-cobalt cluster compounds
bound on a carrier into alcohols. For instance, the conversion of
30 1-hexylene on adding diethylamine, Et_2NH , is certainly complete,
but C_7 alcohols are produced, even in advantageous circumstances,
only with about 70 % selectivity. Moreover, the diethylamine is
used up completely in hydroformamination with that 1-hexylene
which is not converted into C_7 alcohols. It is thus noted that the
35 metal compound catalyzes also this side reaction.



Primary amines, such as aniline, behave in the same way and form the corresponding hydroformamination products. When the amine is
5 replaced with ammonia in the hydroformylation mixture of 1-hexylene in the presence of $[Co_2Rh_2(CO)_{12}]$ -aluminium oxide, the ability of the catalyst to produce C₇ products ceases altogether.

Adding a tertiary amine to the cluster catalyst mixture is not the
10 only remarkable factor controlling the product distribution. The amount of the cluster compound on the carrier also exerts an influence on the activity and selectivity of the catalyst. Low metal content and longer reaction time result in more selective catalysis than a correspondingly larger catalyst quantity and shorter reaction
15 time.

In producing the catalyst, either a mixed cluster compound $Co_xRh_{4-x}(CO)_{12}$, $x=1,2$ or 3 , or a $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ mixture can be used, without significant difference in catalytic character-
20 istics in similar reaction conditions. In practice, the mixture is simpler and also enables the metal proportions to be optimized.

The performing of the hydroformylation reaction with the catalysts described in the foregoing is not significantly limited by external
25 reaction conditions. Alcohol production takes place in the pressure range 1 to 7 MPa and in the temperature range 300 K to 450 K. The composition of the catalyst and the reaction conditions may be optimized within these limits for a large group of starting material
olefines.

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Example 1

The catalyst was prepared by mixing 1.0 g aluminium oxide (Alumina grades D, dried at 800°C), 0.1 g $Co_2Rh_2(CO)_{12}$ (Martinego, S et
35 al., J. Organomet. Chem. 59 (1973), p. 379) and 0.020 dm³ hexylene in nitrogen atmosphere for 15 hrs. The hexylene containing unbound

1 cluster material was removed. The catalyst was rinsed with hexylene
and dried in vacuum.

Examples 2-4

5 The catalysts were prepared as in Example 1, except that in Example
2 the carrier was zeolite (Zeolon 900 Na), in Example 3 the carrier
was a silicon dioxide (silika grades F 22), and in Example 4 the
carrier was magnesium silicate.

10

Example 5

The catalysts were prepared as in Example 1, except that the quan-
tity of cluster compound $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ was 0.05 g.

15

Example 6

The catalyst was prepared as in Example 1, except that instead of
the mixed cluster compound was used a cluster compound with
20 0.035 g $\text{Co}_4(\text{CO})_{12}$ (Strem Chemicals), and 0.071 g $\text{Rh}_4(\text{CO})_{12}$
(Martinego, S. et al, Inorganic Synthesis, Vol. 20, 1980, p. 209).

Example 7

25 The catalyst was prepared as in Example 1, except that the aluminium
oxide used for carrier was impregnated with 2 ml triethylamine
(16 hrs). The excess was evaporated in vacuum.

Example 8

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The catalyst of Example 1 (0.1 g), 1-hexylene (1.0 dm^3), toluene
(3.0 dm^3), and triethylamine Et_3N ($0.11 \times 10^{-3} \text{ dm}^3$, 0.79 mmol)
were transferred in nitrogen atmosphere into an autoclave
($V=0.075 \text{ dm}^3$), into which 2.5 MPa H_2 and 2.5 MPa CO were added.

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The autoclave was kept at 373 K for 17 hrs. The product mixture
was cooled and analyzed with IR and NMR spectrometers, and by

1 capillary gas chromatography. The reaction product contained 97 %
C₇ alcohols.

Example 9

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As Example 8, but the triethylamine quantity was $0.10 \times 10^{-3} \text{ dm}^3$.
The reaction product contained 79 % C₇ alcohols and 20 % C₇ aldehydes.

10 Example 10

As Example 8, but triethylamine quantity $0.05 \times 10^{-3} \text{ dm}^3$. The
reaction product contained 30 % C₇ alcohols and 55 % C₇ aldehydes.

15 Example 11

As Example 8, but triethylamine quantity $0.025 \times 10^{-3} \text{ dm}^3$. The
reaction product contained 14 % C₇ alcohols and 70 % C₇ aldehydes.

20 Example 12

As Example 8, but no amine was added. The reaction product contained
85 % C₇ aldehydes.

25 Examples 9-12 show clearly that when the amount of amine is reduced
in the catalyst system of the invention, the selectivity of alcohol
forming deteriorates rapidly.

Example 13

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As Example 9, but the amine was Et₂NH (0.79 mmol). The reaction
product contained 62 % C₇ alcohols and 19 % C₇ aldehydes, and 19 %
byproducts containing amine.

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1 Example 14

As Example 8, but using the catalyst of Example 6 (0.353 g) and
for alkene, propylene (0.8 g). The reaction mixture contained 90 %
5 C₇ alcohols.

Example 15

As Example 8, but using the catalyst of Example 3 (0.1 g). The
10 reaction mixture contained 56 % C₇ alcohols and 39 % C₇ aldehydes.

Example 16

As Example 4, but using the catalyst of Example 5 (0.1 g). The
15 reaction mixture contained 55 % C₇ alcohols and 35 % C₇ aldehydes.

Example 17

As Example 8, but using the catalyst of Example 7 (0.1 g). The
20 reaction mixture contained 70 % C₇ alcohols, 16 % C₇ aldehydes and
12 % C₁₄ alcohols.

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1 Claims

1. A catalyst system for selectively producing alcohols from olefines and synthesis gases, characterized in that it comprises one or several metal cluster compounds belonging to the cobalt group on an inorganic carrier and an amine of the form $NR_1R_2R_3$, where R_1, R_2 and R_3 are either hydrogen or an aliphatic or aromatic group containing 1 to 8 carbon atoms.
2. Catalyst system according to claim 1, characterized in that the metal cluster compound is $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ or a mixture thereof.
3. Catalyst system according to claim 1, characterized in that the metal cluster compound is a mixed cluster compound of the form $Co_xRh_{4-x}(CO)_{12}$, where $x=1-3$.
4. Catalyst system according to any one of the preceding claims, characterized in that the amine has been added into the reaction mixture.
5. Catalyst system according to any one of claims 1-3, characterized in that the amine has been added onto the inorganic carrier substance.
6. Catalyst system according to any one of the preceding claims, characterized in that the amine quantity is 0.1 to 10 % by weight of the quantity of the reaction mixture.
7. Catalyst system according to any one of the preceding claims, characterized in that the amine is triethylamine.
8. Catalyst system according to any one of the preceding claims, characterized in that the carrier substance is aluminium oxide, silicon dioxide, zeolite or magnesium silicate.
9. A process for selectively producing alcohols from olefines and

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1 synthesis gas, characterized in that a mixture containing olefine,
hydrogen and carbon monoxide is reacted in the presence of a cata-
lyst system according to claims 1 to 8.

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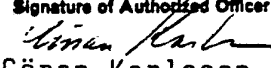
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INTERNATIONAL SEARCH REPORT

International Application No **PCT/FI86/00155**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
C 07 C 29/16, 31/125; B 01 J 23/46, 23/83 4		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC 2-4 US C1	C 07 C 29/16, 31/125; B 01 J 23/46, /83 <u>260</u> :449, 449.5, 632; <u>568</u> :880-883	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
SE, NO, DK, FI classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	Chemical Abstracts, Vol. 91 (1979), abstract No. 157 273t, Jpn. Kokai Tokkyo Koko 79 41, 292.	1-9
Y	Chemical Abstracts, Vol 94 (1981), abstract No. 139 208K, Braz. Pedido PI 79 01, 172.	1-9
Y	US, A, 4 144 191 (THE DOW CHEMICAL COMPANY) 13 March 1979 & US, 4197414	1-9
Y	DE, A, 2 357 645 (MOBIL OIL CORP.) 19 December 1974	1-9
Y	US, A, 4 438 287 (UOP INC.) 20 March 1984	1-9
A	Chemical Abstracts Vol. 92 (1980), abstract No. 110 280y, Fundam. Res. Homo- geneous Catal. 1979, 3, 461-74.	1-9
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
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