# PATENT SPECIFICATION

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# (54) PROCESS FOR THE HYDROGENATION OF CARBON MONOXIDE

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Byandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of n-alkanes by catalytic hydrogenation of carbon monoxide.

Solid catalysts for the synthesis of hydrocarbons by hydrogenation of carbon monoxide have been investigated on a large scale, cf. Kirk-Othmer, "Encyclopedia of Chemical Technology", second edition, Volume 4 (1964), pages 446-489. The heat of reaction generated on these solid catalysts calls for the use of reactors of elaborate construction to ensure the removal of the heat from the catalyst bed and thus to reduce the tendency of the reaction to produce increasing amounts of methane at increasing temperatures.

The present invention provides the use of dissolved catalysts and thus circumvents the heat-transfer problem encountered in the known processes referred to above in which solid catalysts are employed.

Accordingly the invention provides a process for the preparation of n-alkanes, which comprises contacting a gaseous phase containing carbon monoxide and hydrogen with an organic solvent containing a dissolved trinuclear coordination entity comprising (a) a triangular array of ruthenium, of osmium or of cobalt atoms, and (b) either a tridentate ligand bound with the three coordinating atoms to the three ruthenium or osmium atoms or a group $R-C\equiv$, bridged to the triangular array of cobalt atoms to form a tetrahedral grouping $Co_3C$, R representing a substituted or unsubstituted hydrocarbyl group.

The tridentate ligand or the group $R-C\equiv$ mentioned under (b) fits like a "cap" on the triangular array of metal atoms; the trinuclear coordination entities may, therefore, be called "capped catalysts".

In the process according to the present invention methane, ethane, propane and all n-alkanes with 4 to 30 carbon atoms per molecule are usually formed in amounts such that the quotient $C_{n+1}H_{2n+4}:C_nH_{2n+2}$ is constant, n being an integer between 9 and 24 inclusive and the divident and divisor representing the number of moles of the n-alkanes $C_{n+1}H_{2n+4}$ and $C_nH_{2n+2}$, respectively, formed in the same period of time. This quotient is referred to hereinafter as the "regression factor".

Each of the three ruthenium, osmium or cobalt atoms in the triangular array may be bound to three CO groups. One, two or all three of these CO groups may be displaced by other molecules, for example by a trihydrocarbylphosphine, a trihydrocarbylamine, a trihydrocarbyl phosphite or a hydrocarbyl isonitrile. Two or more different molecules may be used for displacement of two or more CO groups.

The triangular array preferably consists of ruthenium or osmium atoms because the trinuclear coordination entities containing such an array do not give rise to inactive species under the reaction conditions. Trinuclear coordination entities containing ruthenium atoms are preferred, because these are more active than those containing osmium atoms.

The tridentate ligand may be any molecule having three atoms each of which is capable of functioning as a donor of electrons in a coordinate bond with a ruthenium or an osmium atom. These three coordinating atoms may be, for example, arsenic or, as is preferred, phosphorus atoms. Each of the three phosphorus atoms may be bound to two hydrocarbyl groups and to one and the same silicon atom. The silicon atom may also be bound to a hydrocarbyl group. The hydrocarbyl groups bound to the phosphorus atoms and the hydrocarbyl group bound to the silicon atom may be, for example, alkyl, cycloalkyl or aryl groups. The hydrocarbyl groups may be substituted, for example by a hydrocarbyloxy group, or unsubstituted. Examples of suitable alkyl groups are methyl, ethyl, propyl, i-propyl and n-butyl groups. The trinuclear coordination entity composed of (a) a triangular array of ruthenium atoms, each of which is bound to three CO groups, and (b) methyltri-(di-n-butylphosphino)silane — for the structural formula see catalyst I on the formula page — proved to be suitable. Another example of a catalyst is the trinuclear coordination entity composed of (a) a triangular array of ruthenium atoms, each of which is bound to three CO groups, and (b) closo-tetrakis-(phenylsilyl)hexakis(phenylphosphine). The compound mentioned under (b) is described in Angew, Chem. Internat. Edit. 1969, *8*, page 989; for the structural formula of the latter catalyst see catalyst II on the formula page.

The group in the group $R{-}C{\equiv}$ may be, for example an alkyl, a cycloalkyl or an aryl group. If desired, the group R may carry a substituent, for example a hydrocarbyloxy group. Examples of suitable alkyl groups are methyl, ethyl, propyl, i-propyl, n-butyl sec-butyl and tert-butyl groups. A methylidyne group which is bridged to a triangular array of cobalt atoms, each of which is bound to three Co groups, is suitable; for the structural formula of this known compound see structure III on the formula page.

The process is preferably conducted at elevated temperatures — for example, at a temperature in the range of from 200° C to 350° C — and elevated pressures, for example at a starting pressure of at least 50 bar, measured at 20° C. Suitable starting pressures are, for example, between 75 and 300 bar, measured at 20° C. The hydrogen is preferably applied in a partial pressure in the range of from 10% to 80% and particularly from 40% to 75% of the sum of the partial pressures of hydrogen and carbon monoxide. The catalyst may be used in very low concentrations, for example, between 0.1 and 10 millimol per litre of the organic solvent.

Examples of solvents which may be used in the process are (1) aliphatic hydrocarbons, for example n-hexane, n-heptane, n-octane, n-dodecane or mixtures of aliphatic hydrocarbons, for example, gasoline and kerosine fractions, (2) cycloaliphatic hydrocarbons, for example, cyclohexane, methylcyclohexane, cycloheptane and decalin (cis and trans), (3) aromatic hydrocarbons, for example, benzene, toluene, o-xylene, m-xylene, p-xylene and tetrahydronaphthalene, (4) ethers, for example tetrahydrofuran, tetrahydropyran, 1,4-dioxane, monomethyl and dimethyl ethers of ethylene glycol, propylene glycol, 1,3-butanediol and 1,4-butanediol; di(2-hydroxyethyl) ether and di(2-hydroxypropyl) ether, (5) ketones, for example, acetone, 2-butanone, methyl, methyl isopropyl ketone, diisobutyl ketone, cyclohexanone and cycloheptanone, (6) esters, for example, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, pentyl acetate, methyl propionate, ethyl butyrate and methyl isobutyrate, and (7) methanol.

Trinuclear coordination entities composed of (a) a triangular array of ruthenium or osmium atoms each of which is bound to three CO groups — of which one, two or all three may be displaced by other molecules — and (b) a tridentate ligand bound with the three coordinating atoms to the three ruthenium or osmium atoms may be prepared by contacting dodecacarbonyl-triangulo-triruthenium or dodecacarbonyl-triangulo-triosmium with the tridentate ligand which is to be bound with three coordinating atoms to the three ruthenium or osmium atoms, in the presence of a solvent. This solvent may be, for example, a hydrocarbon, such as an aromatic or aliphatic hydrocarbon. Optionally, one, two or all three of the CO groups in the trinuclear coordination entity thus prepared may be displaced by other molecules.

Methyltri-(di-n-butylphosphino)silane may be prepared by contacting a methyltrihalosilane with di-n-butylphosphinolithium in a solvent at a temperature below −20° C; "halo" indicating a halogen atom having an atomic number of at least 17. An example of a suitable solvent is diethyl ether. Methyltrichlorosilane is a very suitable starting methyltrihalosilane.

The Examples further illustrate the invention.

The structural formulae of the catalysts used are dipicted on the formula page. Each catalyst is indicated with a Roman numeral. The dotted lines in formulae I and II indicate the three coordinate bonds between the three ruthenium atoms and the three coordinating phosphorus atoms in the tridentate ligand.

The catalysts were tested in a 0.1—1 autoclave consisting of stainless steel type 316. This steel is described in R. H. Perry and C. H. Chilton, Chemical Engineers' Handbook, fifth edition (1973), pages 23—39. During each experiment the contents of the autoclave were stirred vigorously by means of a magnetic pulsating stirrer.

The infrared (IR) and nuclear magnetic resonance (NMR) spectra of the novel compounds prepared were in agreement with the structures shown on the formula page. The abbreviations used in the presentation of the IR data have the following meanings: s = strong, m = medium, and w = weak.

## EXAMPLE I.

### Preparation of methyltri-(di-n-butylphosphino)silane

A flask kept at a temperature of −80° C was charged under argon with a solution of 19.1 mmol of methyltrichlorosilane in 50 ml of diethyl ether and subsequently — over a period of ten minutes with stirring — with a solution of 57.2 mmol of di-n-butylphosphinolithium in 100 ml of diethyl ether. The reaction mixture thus formed was allowed to reach 22° C and left at this temperature for 16 hours. The solid precipitate (lithium chloride) formed during the reaction was removed by filtration. The filtrate was boiled down and the viscous residue obtained was distilled at sub-atmospheric pressure to give the desired silane in a yield of 70%. This silane, a viscous colourless oil, boiled at 150° C at a pressure of 0.05 mm Hg.

### EXAMPLE II.
### Preparation of catalyst I

A flask was charged with 2.03 mmol of the methyltri-(di-n-butylphosphino)silane prepared as described above, 1.83 mmol of dodecacarbonyl-tringulo-triruthenium and 50 ml of benzene and the contents of the flask were kept with stirring at a temperature of 80° C for four hours. Then, the contents of the flask were boiled down and the dark residue obtained was triturated with 25 ml of a mixture of 10% vol of diethyl ether and 90% vol of n-pentane to precipitate catalyst I. This catalyst was obtained as yellow-brown crystals in a yield of 16%, calculated on dodecacarbonyl-triangulo-triruthenium. Elemental analysis of the crystals gave the following results: 39.3 %w C (calcd. 39.5 %w) and 5.6%w H (calcd. 5.5 %w).

The infrared data (CsI) of the catalyst were as follows: nu (CO) 2035 $cm^{-1}$(s), 1985 $cm^{-1}$(s), 1948 $cm^{-1}$(w), 1925 $cm^{-1}$(s), 1842 $cm^{-1}$(m), 1800 $cm^{-1}$(s). These absorptions, with the exception of that at 1842 $cm^{-1}$, were broad (width at half height about 25 $cm^{-1}$). The structure of the catalyst depicted on the formula page was confirmed by single crystal X-ray analysis.

### EXAMPLE III.
### Preparation of catalyst II

A flask was charged with 3.08 mmol of $P_6Si_4(C_6H_5)_{10}$ — the ligand bound to dodecacarbonyl-triangulo-triruthenium in catalyst II — 2.77 mmol of dodecacarbonyl-triangulo-triruthenium and 100 ml of benzene and the contents of the flask were kept with stirring at a temperature of 70° C for 16 hours. Then, the contents of the flask were boiled down at a pressure of 15 mm Hg and the brown oily residue obtained was triturated with 50 ml of n-pentane to precipitate catalyst II. This catalyst was obtained in a yield of 93%, calculated on dodecacarbonyl-triangulo-triruthenium. The infrared spectrum of a solution of catalyst II in benzene showed a broad absorption centred at 2000 $cm^{-1}$. Absorptions originating from dodecacarbonyl-triangulo-triruthenium were absent.

### EXAMPLES IV and V.
### Preparation of n-alkanes using catalysts I and II

The autoclave was charged with 50 ml of n-heptane and 0.166 mmol of catalyst I (concentration 3.3 mmol/l), prepared as described in Example II. Then, an equimolar mixture of carbon monoxide and hydrogen was introduced at a temperature of 20° C until the total pressure was 92 bar. The contents of the autoclave were heated over a period of 30 minutes to 300° C — a pressure of 148 bar was observed after this period — and kept at this temperature for 20 hours; a pressure of 110 bar was observed after 10 hours at 300° C. Subsequently, the autoclave was cooled to 20° C and the number of moles of n-alkanes formed per mole of catalyst I and present in the gas phase was determined. The results are presented in Table I (Example IV).

TABLE I

| Example | Catalyst No. | Mol of n-alkanes in gas phase per mol of catalyst | | | |
|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ |
| IV | I | 93 | 2.8 | 0.67 | 0.13 |
| V | II | 18.8 | 1.8 | 0.14 | 0 |

Then, the autoclave was cleaned and charged with 50 ml of n-heptane and 0.33 mmol of catalyst II (concentration 6.6 mmol/l), prepared as described in Example III. Subsequently, an equimolar mixture of carbon monoxide and hydrogen was introduced at a temperature of 23° C until the total pressure was 88 bar. The experiment was further conducted as described above. The pressures at the end of the warming up period of 30 minutes and of the period of 10 hours were 141 bar and 134 bar, respectively. The results are presented in Table I (Example V).

An infrared analysis of the catalyst solutions at the end of the above two experiments (Examples IV and V) showed that no ruthenium pentacarbonyl was present.

The total yield of n-alkanes with 3 to 25 carbon atoms per molecule was less than 0.5 g per g of ruthenium in catalysts I and II.

A blank experiment conducted without catalyst yielded a gas phase containing 0.3%

mol of methane and less than 0.01 % mol of each of the n-alkanes having more than one carbon atom per molecule. For comparison: the gas phases obtained in Examples IV and V contained 6.9% and 1.7% mol of methane, respectively.

### EXAMPLE VI.

Preparation of
n-alkanes and propene using catalyst III

The autoclave was charged with 50 ml of n-heptane and 0.33 mmol of catalyst III (concentration 6.6 mmol/l). Subsequently, an equimolar mixture of carbon monoxide and hydrogen was introduced into the autoclave at a temperature of 22° C until the total pressure was 100 bar, after which the autoclave was heated over a period of 0.75 hours to 300° C — a pressure of 145 bar was observed after this period — and kept at this temperature for 21 hours; a pressure of 106 bar was observed after 10 hours at 300° C. Then the autoclave was cooled to 20° C and the number of moles of n-hydrocarbons formed per mole of catalyst III and present in the gas phase was determined. Table II presents the results.

TABLE II

Mol of hydrocarbons in gas phase per mol of catalyst III

| n-alkanes | | | | n-alkenes |
|---|---|---|---|---|
| $CH_4$ | $C_2H_6$ | $C_3H_8$ | n-$C_4H_{10}$ | $C_3H_6$ |
| 49 | 2.5 | 1.2 | 0.2 | 0.1 |

The total yield of n-alkanes with 3 to 25 carbon atoms per molecule was 3.6 g per g of cobalt in catalyst III. The regression factor for the n-alkanes with 10 to 25 carbon atoms per molecule was 0.73.

After reaction none of the catalyst III was present in solution.

WHAT WE CLAIM IS:—

1. Process for the preparation of n-alkanes, which comprises contacting a gaseous phase containing carbon monoxide and hydrogen with an organic solvent containing a dissolved trinuclear coordination entity comprising (a) a triangular array of ruthenium, of osmium or of cobalt atoms, and (b) either a tridentate ligand bound with the three coordinating atoms to the three ruthenium or osmium atoms or a group $R{-}C\equiv$ bridged to the triangular array of cobalt atoms to form a tetrahedral grouping $Co_3C$ and R representing a substituted or unsubstituted hydrocarbyl group.

2. Process as claimed in claim 1, in which the three coordinating atoms in the tridentate ligand are phosphorus atoms.

3. Process as claimed in claim 2, in which each of the three phosphorus atoms is bound to two hydrocarbyl groups and to one and the same silicon atom.

4. Process as claimed in claim 3, in which each of the phosphorus atoms and the silicon atom are bound to alkyl groups only.

5. Process as claimed in claim 4, in which the trinuclear coordination entity is composed of (a) a triangular array of ruthenium atoms, each of which is bound to three CO groups, and (b) methyl-tri-(di-n-butylphosphino)silane.

6. Process as claimed in claim 1, in which the $R{-}C\equiv$ group is a methylidyne group bridged to the triangular array of cobalt atoms, each of which is also bound to three CO groups.

7. Process as claimed in claim 1, substantially as hereinbefore described with reference to Examples IV, V and VI.

8. N-alkanes whenever prepared by a process as claimed in any one of the preceding claims.

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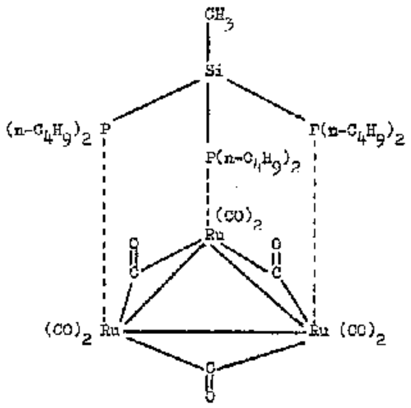
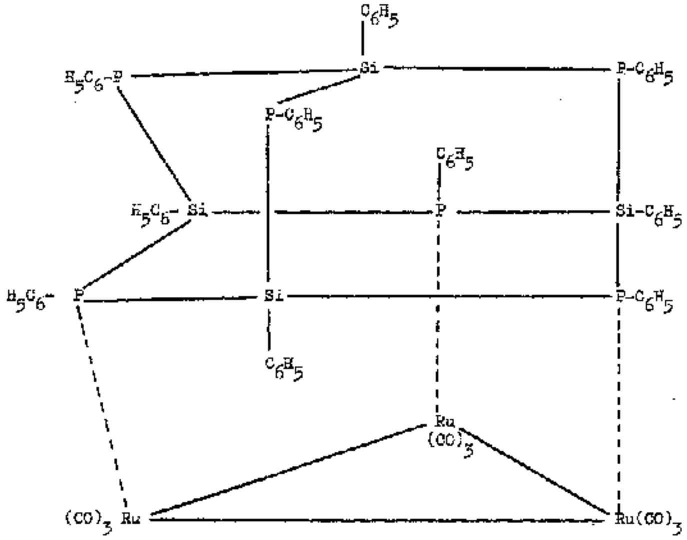

CH3
Si
(n-C4H9)2 P
P(n-C4H9)2
P(n-C4H9)2
(CO)2
Ru
O
C
O
C
(CO)2 Ru
Ru (CO)2
C
O

(I)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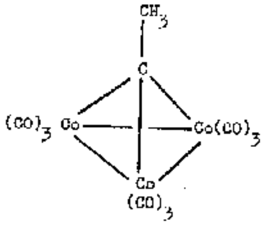
H5C6-P
Si
P-C6H5
P-C6H5
C6H5
H5C6- Si
P
Si-C6H5
H5C6- P
Si
P-C6H5
C6H5
Ru
(CO)3
(CO)3 Ru
Ru(CO)3

(II)

1573422 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2



(III)