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54 **Process for the production of oxygenated hydrocarbon product containing ethanol.**

57 Oxygenated hydrocarbons such as ethanol, methanol and acetic acid are produced by contacting synthesis gas (carbon monoxide and hydrogen) with a supported mixture of a rhodium component and a zirconium component optionally containing one or more additional components selected from the metals iron, manganese, molybdenum, tungsten, ruthenium, chromium, uranium and thorium. The preferred support is silica. The reaction conditions are typically a temperature in the range from 150 to 450°C, a pressure in the range from 1 to 700 bars and a gas hourly space velocity greater than 10³ per hour.

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PROCESS FOR THE PRODUCTION OF AN OXYGENATED HYDROCARBON
PRODUCT CONTAINING ETHANOL.

The present invention relates generally to a process for the production of an oxygenated hydrocarbon product containing ethanol. In particular the invention concerns the production of such an oxygenated hydrocarbon product containing ethanol by contacting a mixture of
5 carbon monoxide and hydrogen, hereinafter to be referred to as synthesis gas, with a catalyst comprising a supported mixture of a rhodium component and a zirconium component.

Oxygenated hydrocarbons, and in particular C_2 - oxygenated hydrocarbons, such as acetic acid, ethanol and acetaldehyde are
10 valuable industrial products. On a commercial scale acetic acid is generally produced either by oxidation of paraffinic hydrocarbon fractions or by carbonylation of methanol; ethanol is produced either by fermentation of natural products, e.g. molasses or by hydration of ethylene in the presence of an acid catalyst and
15 acetaldehyde is produced by the Wacker process. The dwindling reserves of crude oil from which many of the above feedstocks are derived and the associated need to utilise fully the remaining natural resources such as coal and the vast amounts of gases, e.g. methane potentially available from the exploitation of North Sea oilfields,
20 has stimulated research into the utilisation of synthesis gas which can readily be obtained not only from crude oil but also from both coal and methane gas. Much of the early work on synthesis gas conversion involved the use as catalysts of the iron group metals, ruthenium and various metal oxide systems. One general disadvantage
25 of such systems is that catalysts which possess acceptable activity generally tend to be unselective i.e. they produce a wide spectrum

of products including both hydrocarbons and oxygenated hydrocarbons having a broad distribution of carbon numbers. This not only complicates the recovery of the desired products but also results in the wastage of reactants to undesirable products. On the other hand
5 those catalysts having acceptable selectivity generally have a low activity thereby necessitating recycle of large quantities of unchanged reactants.

In US Application Serial No: 541,661 (Union Carbide Corp) published as a priority document for Netherlands application No:
10 7500916 there is disclosed a process which, it is claimed, overcomes the aforesaid disadvantages of the prior art processes. The process for selectively producing C_2 - oxygenated hydrocarbons involves continuously contacting synthesis gas with a heterogeneous catalyst essentially comprising rhodium metal under reaction conditions
15 correlated so as to favour the formation of a substantial proportion of acetic acid, ethanol and/or acetaldehyde. Subsequent patent applications describe the production of ethanol by contacting synthesis gas with a rhodium/iron catalyst (US Serial No: 541,660 published as a priority document for Netherlands application No: 7500918), a
20 rhodium/manganese catalyst (DT 2628463), a rhodium/molybdenum or rhodium/tungsten catalyst (USP 4096164), a rhodium/ruthenium catalyst (USP 4101450) and a rhodium/uranium/thorium catalyst (USP 4162262). Our own copending UK application No: 79/14253 (BP Case No: 4776)
25 describes the use of a rhodium/chromium catalyst for the production of C_1 to C_4 oxygenated hydrocarbons from synthesis gas.

We have now found that a supported mixture of a rhodium component and a zirconium component is an active catalyst for the selective production of an oxygenated hydrocarbon product containing ethanol.

Accordingly, the present invention provides a process for the
30 production of an oxygenated hydrocarbon product containing ethanol which process comprises contacting synthesis gas with a catalyst comprising a supported mixture of a rhodium component and a zirconium component under reaction conditions which result in the formation of an oxygenated hydrocarbon product containing ethanol.
35 Synthesis gas in the form of mixtures of the gases carbon monoxide

and hydrogen is abundantly available. Methods for preparing synthesis gas are well-known in the art and usually involve the partial oxidation of a carbonaceous substance, e.g. coal. Alternatively synthesis gas may be prepared, for example, by the catalytic steam reforming of methane. Although it is preferred to use substantially pure synthesis gas the presence of such impurities as carbon dioxide and nitrogen can be tolerated. On the other hand impurities which have a deleterious effect on the reaction should be avoided. The ratio of hydrogen to carbon monoxide in the synthesis gas may vary widely. Normally the molar ratio of hydrogen to carbon monoxide may be in the range from 20:1 to 1:20, preferably from 5:1 to 1:5 and even more preferably from 1:1 to 2:1. Increasing the molar ratio of hydrogen to carbon monoxide beyond 2:1 generally tends to increase the total rate of reaction but only at the expense of an increase in selectivity to methane. Increasing the molar ratio of hydrogen to carbon monoxide also favours the formation of more highly reduced oxygenated products. Thus, as the ratio increases so the formation of ethanol, rather than acetaldehyde or acetic acid, is favoured. Methods for adjusting the molar ratio by the so-called 'shift reaction' are well-known to those versed in the art.

The catalyst comprises a supported mixture of a rhodium component and a zirconium component. A wide variety of support materials may be employed. Suitable support materials include silica, alumina, silica/alumina, magnesia, thoria, titania, chromia, zirconia and active carbon, of which silica is preferred. Zeolite molecular sieves and in particular the crystalline zeolites may also be employed. Suitably the support has a relatively high surface area. The support may have a surface area up to 350 square metres per gram (BET low temperature nitrogen adsorption isotherm method), preferably in the range 1 to 300 square metres per gram. Whilst the actual form of the rhodium and zirconium components under the reaction conditions is not known with any degree of certainty it is probable that they are either in the oxide form or the metallic form. Under the reducing conditions prevailing it is more likely that the components are in the metallic form. Thus the rhodium and zirconium components may be added in the form of the metals themselves or in the form of metal compounds

and may be added concurrently or sequentially. The rhodium and zirconium components may be deposited on the support by any of the techniques commonly used for catalyst preparation. Although it is possible to add particles of the metals to the support it is preferred to use the techniques of impregnation from an organic or inorganic solution, precipitation, coprecipitation or cation exchange. Conveniently the catalyst may be prepared by impregnating the support with a solution or solutions of a rhodium compound and a zirconium compound which compounds may be organic or inorganic compounds. Suitable compounds are the salts of the metals e.g. the halides, particularly the chlorides and nitrates. Following impregnation the catalyst is preferably dried and calcined. The amount of each of the rhodium component and the zirconium component on the support may suitably be in the range of from 0.01 to 25 weight percent, preferably from 0.1 to 10 weight percent, of each metal based on the combined weight of the metals and the support. The catalyst preferably also contains one or more additional metal components, which may be incorporated in a similar manner to the rhodium and zirconium components. Suitable metals include iron, manganese, molybdenum, tungsten, ruthenium, chromium, uranium, thorium, palladium and iridium. The, or each, additional component may suitably be present in an amount in the range from 0.1 to 25 weight percent based on the combined weight of the metals and the support.

The support may also be activated by the addition of a suitable metal or non-metal component prior to incorporation of the rhodium and zirconium components. Whilst a wide variety of such metals and non-metals may be added, the alkali metals, thorium, manganese, rhodium, iron, chromium, molybdenum, boron and phosphorus are specific examples of materials which may be used. Any of the known techniques for catalyst preparation hereinafter referred to may be used for addition of the activating material. In the case of a metal activator the support is preferably impregnated with a solution of a compound of the metal, suitably the nitrate or chloride, and is thereafter dried, suitably by evaporation and calcined. The activated support is then in a suitable condition for addition of the rhodium and zirconium components and optionally other metal components. The amount of

activator added may suitably be in the range 0.01 to 50 weight percent, preferably from 1 to 25 weight percent, of the activator element based on the combined weight of the activator element and the support.

5 The reaction conditions which result in the formation of an oxygenated hydrocarbon product containing ethanol are suitably a temperature in the range from 150 to 450°C, preferably from 200 to 400°C, and even more preferably from 200 to 300°C. The use of higher temperatures within the aforesaid range tends to increase the co-production of methane. Because of the highly exothermic nature
10 of the reaction the temperature requires careful control in order to prevent a runaway methanation, in which methane formation increases with increasing temperature and the resulting exotherm increases the temperature still further. In fixed bed operations, temperature control may be achieved by mixing the catalyst with an inert diluent,
15 thereby ensuring that the exothermic heat is more evenly distributed. In this way the catalyst may be protected and its useful life prolonged. Reaction pressure is suitably in the range from 1 to 700 bars, preferably from 20 to 300 bars. The use of higher pressures within the aforesaid ranges increases the production rate of C₂ -
20 oxygenated hydrocarbons.

An important reaction parameter is the conversion. A low conversion, preferably less than 20% of the carbon monoxide favours the formation of acetic acid, ethanol and/or acetaldehyde. A low conversion may suitably be achieved in a continuous process by
25 employing a high space velocity. Suitably the gas hourly space velocity (volume of synthesis gas, at STP, per volume of catalyst per hour) is greater than 10³ per hour; preferably the gas hourly space velocity is in the range from 10⁴ to 10⁶ per hour. Excessively high space velocities result in an uneconomically low conversion while excessively
30 low space velocities result in a loss of selectivity to desirable products.

Although the reaction may be carried out batchwise it is preferably carried out in a continuous manner.

The catalyst may be employed in the form of a fixed or a fluidised bed. The desired oxygenated products may be recovered from the effluent
35 from the reaction by various means, such as scrubbing and/or distillation.

The residual gas which consists mainly of unreacted synthesis gas may be mixed with fresh carbon monoxide and hydrogen to give the required feed ratio and this composite gas then recycled to the reaction.

5 The process of the invention will now be illustrated by the following Examples and by reference to the accompanying Figure which is a simplified flow diagram of the apparatus employed.

10 With reference to the Figure, 1 is a preheater (150°C), 2 is a preheater (200°C), 3 is a bursting disc, 4 is a reactor, 5 is a salt pot, 6 is a knock-out pot, 7 is a water quench, 8 is a water recycle pump, 9 is a water wash tower, 10 is a DP level controller, 11 is a knock-out pot, 12 is a Foxboro valve, 13 is a molecular sieve drier, 14 is a Gyp relief valve, 15 is a back pressure regulator, 16 is an aqueous product receiver, 17 is a gas recycle pump, 18 is a ballast vessel and 19 is a vent.

Catalyst Preparation

Catalyst A

Rhodium/Zirconium/Silica

20 Rhodium trichloride trihydrate (1.3 g) and zirconium tetrachloride (1.3 g) were dissolved in deionised water (25 ml) and added to Davison grade 59 silica (10 g, 8 - 16 mesh granules). The mixture was evaporated to dryness on a steam - bath and dried at 120°C for 16 hours. The catalyst was then reduced in hydrogen at 450°C for 5 hours.

Catalyst B

Rhodium/Zirconium/Chromium/Molybdenum/Silica

25 Ammonium heptamolybdate tetrahydrate (0.42 g), chromium nitrate nonahydrate (3.8 g), rhodium trichloride trihydrate (1.3 g) and zirconium tetrachloride (1.3 g) were dissolved in deionised water
30 (30 ml) and the resulting solution added to Davison grade 59 silica (10 g, 8 - 16 mesh granules). The mixture was evaporated to dryness on a steam-bath and the solid dried at 120°C for 16 hours. The catalyst was reduced in hydrogen at 450°C for 3 hours.

Catalyst CRhodium/Zirconium/Molybdenum/Silica

Ammonium heptamolybdate tetrahydrate (0.21g), zirconium tetrachloride (1.95g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and the resulting solution added to Davison grade 59 silica (10g, 8-16 mesh granules). The mixture was evaporated to dryness on a steam-bath and the solid dried at 120°C for 16 hours. The catalyst was reduced in hydrogen at 450°C for 3 hours.

Catalyst D10 Rhodium/Zirconium/Molybdenum/Silica

Zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and added to Davison silica grade 59 (10g, 8-16 mesh). The mixture was evaporated to dryness on a steam-bath and the solid dried at 120°C for 16 hours and reduced in hydrogen at 450°C for 3 hours. Ammonium heptamolybdate tetrahydrate (0.42g) was dissolved in deionised water (20 ml) and the solution added to the above catalyst. The mixture was evaporated to dryness on a steam-bath, dried at 120°C for 16 hours and treated in hydrogen at 450°C for 3 hours.

20 Catalyst ERhodium/Zirconium/Molybdenum/H-form Aluminosilicate (Mordenite)

Ammonium heptamolybdate tetrahydrate (0.63g), zirconium tetrachloride (1.95g) and rhodium trichloride trihydrate (1.95g) were dissolved in deionised water (16 ml). Half of this solution was then added to H-mordenite (15g, $\frac{1}{16}$ in extrudate) and the mixture dried at 100°C for one hour. The remaining solution was added and the whole evaporated to dryness on a steam-bath and dried at 120°C for 16 hours. The catalyst was reduced in hydrogen at 450°C for 2 hours.

Catalyst F30 Rhodium/Zirconium/Manganese/Silica

Manganous acetate tetrahydrate (0.2g), zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and the resulting solution added to Davison silica grade 59 (10g, 8-16 mesh granules). The mixture was evaporated to dryness on a steam-bath and the solid dried at 120°C for 16 hours and reduced in hydrogen at 450°C for 2 hours.

Catalyst GRhodium/Zirconium/Palladium/Silica

Palladium dichloride (0.2g), zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and the resulting solution was added to Davison silica, grade 59 (10g, 8-16 mesh). The mixture was evaporated to dryness on a steam-bath and the solid dried at 120°C for 16 hours. The catalyst was reduced in hydrogen at 450°C for 2 hours.

Catalyst H10 Rhodium/Zirconium/Iridium/Silica

Ammonium chloroiridate (0.2g), zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20ml) and the resulting solution added to Davison silica, grade 59 (10g, 8-16 mesh). The mixture was evaporated to dryness on a steam-bath and the solid dried at 120°C for 16 hours. The catalyst was reduced in hydrogen at 450°C for 2 hours.

Catalyst IRhodium/Zirconium/Iron/Silica

Ferric nitrate nonahydrate (1.45g), zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and the resulting solution added to Davison silica, grade 59 (10g, 8-16 mesh granules). The mixture was evaporated to dryness on a steam-bath and dried at 120°C for 16 hours. The catalyst was then reduced with hydrogen at 450°C for 3 hours.

25 Catalyst JRhodium/Zirconium/Uranium/Silica

Uranylacetate dihydrate (0.45g), zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and the resulting solution added to Davison silica, grade 59 (10g, 8-16 mesh granules). The mixture was evaporated to dryness on a steam-bath and dried at 120°C for 16 hours. The catalyst was then reduced with hydrogen at 450°C for 3 hours.

Catalyst KRhodium/Zirconium/Tungsten/Silica

35 Ammonium metatungstate tetrahydrate (0.3g), zirconium tetrachloride

(1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and concentrated hydrochloric acid (2 ml) and the resulting solution added to Davison silica grade 59 (10g, 8-16 mesh granules). The mixture was evaporated to dryness on a steam-bath and dried at 120°C for 16 hours. The catalyst was then reduced at 450°C in hydrogen for 6 hours.

Catalyst L

Rhodium/Zirconium/Thorium/Silica

Thorium nitrate hexahydrate (5g) was dissolved in deionised water and added to Davison silica, grade 59 (10g, 8-16 mesh granules) and the mixture was evaporated to dryness on a steam-bath. The support was then heated at 400°C in air for 4 hours.

Zirconium tetrachloride (1.3g) and rhodium trichloride trihydrate (1.3g) were dissolved in deionised water (20 ml) and the resulting solution added to the above support. The mixture was evaporated to dryness on a steam-bath and dried at 120°C for 16 hours. The catalyst was reduced for 6 hours in hydrogen at 450°C.

Synthesis gas conversion

Example 1

With reference to the accompanying Figure a mixture of carbon monoxide and hydrogen in a molar ratio of 1:2 was passed via the inlet manifold through the two preheater coils (1) and (2) maintained at 150°C and 200°C respectively in silicone oil baths. The heated gases were then fed via a heat-traced line to the copper-lined reactor (4) containing a fixed bed of Catalyst A in the form of 8 to 16 mesh (BSS) granules. The reactor was maintained at the desired reaction temperature by immersion in a molten salt bath (5). The product gases were passed via a heat-traced line through a knock-out pot for wax products (6) to a small quench vessel (7) into the top of which water was sprayed. The gases were then passed through a water cooler to the bottom of the water wash tower (9) which was packed with $\frac{3}{8}$ inch Raschig rings. In the tower (9) the product gases were washed counter-current with water. The resulting liquid product was fed into the receiver (16) and any dissolved gases were re-combined with the product gas stream from the back pressure regulator (15). The separated gas stream from the top

of the water wash tower (9) was passed through a water cooler to the knock-out pot (11) and then to the inlet side of the dome-loaded back pressure regulator (15). Recycle gas was recovered from the inlet side of the back pressure regulator (15), passed through a molecular sieve drier (13) and compressed up to 67 bars in the gas ballast vessel (18) using the gas recycle pump (17). The recycle gas was fed back to the inlet manifold. Provision was made to feed spot samples of the inlet gases and the total gas stream to a gas chromatographic analytical unit.

10 The product gas stream leaving the back pressure regulator (15) was measured and samples were withdrawn and analysed by gas chromatography. The liquid product was also sampled and analysed by gas chromatography.

15 After the reactor had reached equilibrium a balance run was carried out over a one hour period at a temperature of 274°C.

Example 2

The procedure of Example 1 was followed using catalyst B in place of catalyst A. The run was carried out at 257°C instead of at 274°C.

20 Example 3

The procedure of Example 1 was followed using catalyst C in place of catalyst A. The run was carried out at 240°C.

Example 4

25 The procedure of Example 1 was followed using catalyst D in place of catalyst A. Runs were carried out at 230°C and 240°C.

Example 5

The procedure of Example 1 was followed using catalyst E in place of catalyst A. Runs were carried out at 250°C and 262°C.

Example 6

30 The procedure of Example 1 was followed using catalyst F in place of catalyst A. Runs were carried out at 261°C, 275°C and 285°C.

Example 7

The procedure of Example 1 was followed using catalyst G in place of catalyst A. Runs were carried out at 280°C and 290°C.

35

Example 8

The procedure of Example 1 was followed using catalyst H in place of catalyst A. Runs were carried out at 233°C, 280°C and 305°C.

Example 9

5 The procedure of Example 1 was followed using catalyst I in place of catalyst A. The run was carried out at 273°C.

Example 10

The procedure of Example 1 was followed using catalyst J in place of catalyst A. The run was carried out at 267°C.

10 Example 11

The procedure of Example 1 was followed using catalyst K in place of catalyst A. The run was carried out at 251°C.

Example 12

15 The procedure of Example 1 was followed using catalyst L in place of catalyst A. The run was carried out at 290°C.

The results of Examples 1 to 12 are given in the Table.

In the Table:-

1. CO Conversion = $\frac{\text{Moles of carbon monoxide consumed}}{\text{Moles of carbon monoxide fed}} \times 100$
- 20 2. Selectivity = $\frac{\text{Moles of carbon monoxide converted to particular product}}{\text{Moles of carbon monoxide consumed}} \times 100$
3. $>C_2$ = Hydrocarbons with carbon numbers greater than 2
4. MeOH = Methanol
5. EtOH = Ethanol
- 25 6. Acet = Acetaldehyde
7. n-PrOH = n-propanol

30

35

TABLE

Reaction parameters: GHSV = 48,000 h⁻¹ H₂ : CO Molar ratio = 2:1
 Pressure = 50 bars Recycle gas ratio = 19:1

Example	Catalyst	Reaction Temp (°C)	CO Conversion (%)	SELECTIVITY (%)							
				CO ₂	CH ₄	>C ₂	MeOH	EtOH	Acet	n-PROH	Acetic Acid
1	A	274	12.2	2.7	34.6	1.1	7.3	39.5	7.6	Nil	7.1
2	B	257	31.2	14.5	30.1	3.5	25.3	21.9	Nil	2.1	3.0
3	C	240	19	11	25	4	22	27	Nil	7	4
4	D	230	25	4	14	3	50	23	Nil	5	1
		240	28	5	22	4	38	24	Nil	4	3
5	E	250	15	3	30	8	26	23	Nil	2	8
		262	22	4	39	8	28	17	Nil	2	2
6	F	261	11	1	29	2	11	36	11	3	6
		275	17	2	35	3	6	40	6	Nil	8
		285	24	2	39	3	5	42	5	2	2
7	G	280	18	4	49	1	11	25	6	Nil	4
		290	20	2	56	1	9	24	3	Nil	5

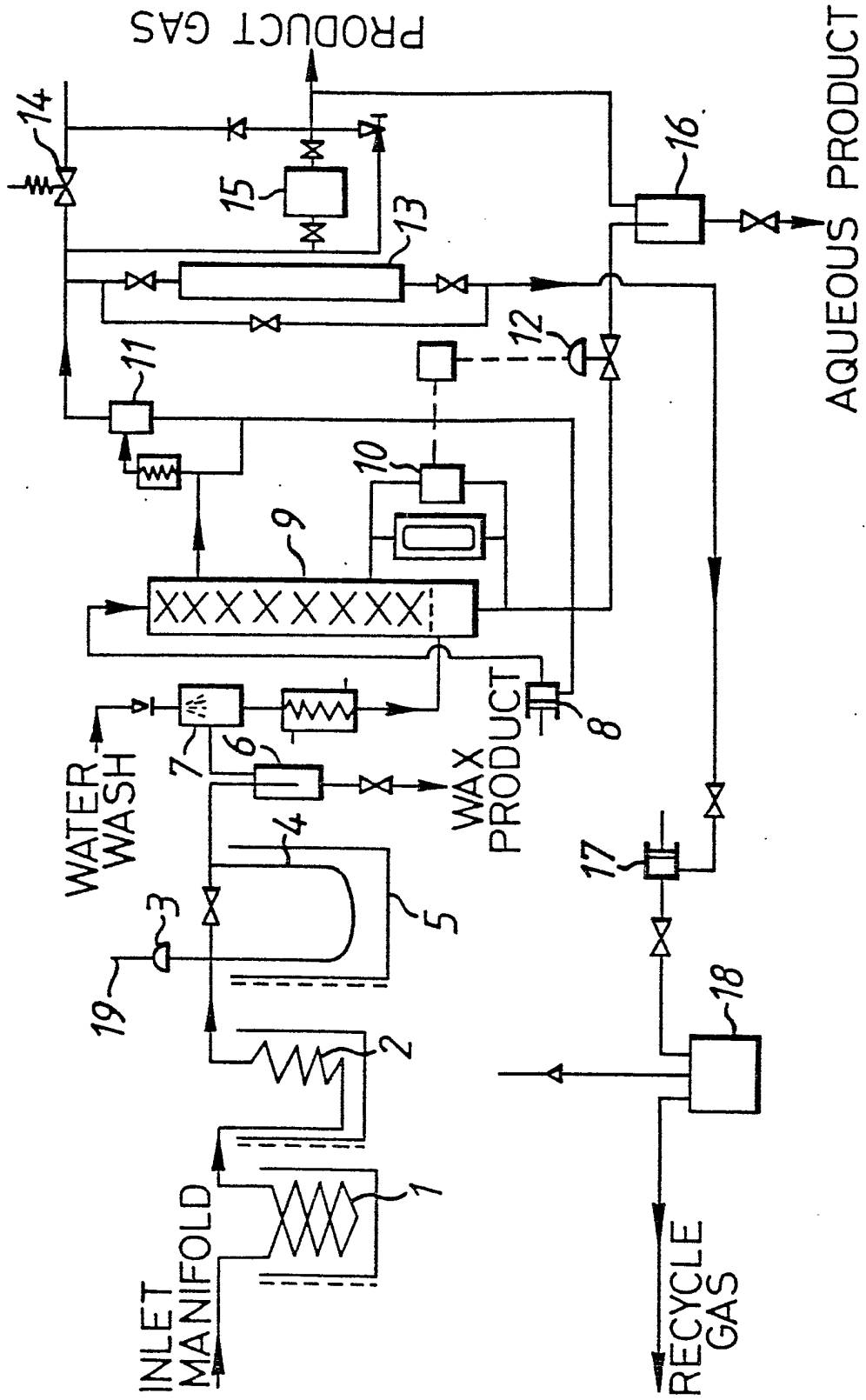
TABLE - continued

Example	Catalyst	Reaction Temp (°C)	CO Conversion (%)	SELECTIVITY (%) 2							
				CO ₂	CH ₄	C ₂	MeOH ⁴	EtOH ⁵	Acet ⁶	n-PrOH ⁷	Acetic Acid
8	H	233	5	3	21	Nil	21	38	9	Nil	8
		280	10	2	39	1	14	29	8	2	5
		305	17	2	56	1	10	25	2	1	3
9	I	273	28	1	34	1	34	27	Nil	2	1
		267	17	1	35	3	13	31	10	2	5
11	K	251	24	2	21	4	22	36	4	4	7
12	L	290	30	1	31	2	13	37	9	3	6

Claims:

1. A process for the production of an oxygenated hydrocarbon product containing ethanol which process comprises contacting synthesis gas with a catalyst comprising a supported mixture of a rhodium component and a zirconium component under reaction conditions which result in the formation of an oxygenated hydrocarbon product containing ethanol.
2. A process according to claim 1 wherein the support is silica.
3. A process according to either one of the preceding claims wherein the amount of each of the rhodium component and the zirconium component on the support is in the range from 0.1 to 10 weight percent of each metal based on the combined weight of the metals and the support.
4. A process according to any one of the preceding claims wherein the catalyst also contains one or more additional metal components selected from iron, manganese, molybdenum, tungsten, ruthenium, chromium, uranium, thorium, palladium and iridium.
5. A process according to claim 4 wherein the, or each, additional metal component is present in an amount in the range from 0.1 to 25 weight percent based on the combined weight of the metals and the support.
6. A process according to any one of the preceding claims wherein the support is activated by the addition of either an alkali metal, thorium, manganese, rhodium, iron, chromium, molybdenum, boron or phosphorus prior to incorporation of the rhodium and zirconium components.

7. A process according to claim 6 wherein the amount of the activator added is in the range from 1 to 25 weight percent based on the combined weight of the activator and the support.
8. A process according to any one of the preceding claims wherein the reaction conditions which result in the formation of an oxygenated hydrocarbon product containing ethanol are a temperature in the range from 200 to 400°C, a pressure in the range 20 to 300 bar and a gas hourly space velocity in the range from 10^4 to 10^6 per hour.





DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p>BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, vol. 51, no. 8, August 1978, Tokyo, JP MASARU ICHIKAWA "Catalysis by supported metal crystallites from carbonyl clusters. II. Catalytic ethanol synthesis from Co and H₂ under atmospheric pressure over supported rhodium crystallites prepared from Rh carbonyl clusters deposited on TiO₂, ZrO₂ and La₂O₃". pages 2273-2277, * Page 2275, table 3, catalyst 3 *</p> <p style="text-align: center;">--</p> <p>JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS July 5, 1978, no. 13, MASARU ICHIKAWA "Catalytic synthesis of ethanol from CO and H₂ under atmospheric pressure over pyrolysed rhodium carbonyl clusters on TiO₂, ZrO₂ and La₂O₃". pages 566-567. * The whole article *</p> <p style="text-align: center;">--</p> <p>PATENTS ABSTRACTS of JAPAN, vol. 3, no. 68, June 13, 1979, page 48 C 48 & JP - A - 54 41291 (SAGAMI CHUO KAGAKU KENKYUSHO) (04-02-1979) * The whole abstract *</p> <p style="text-align: center;">--</p> <p>P <u>EP - A - 0 010 295 (HOECHST)</u> * Claims *</p> <p style="text-align: center;">--</p>	<p>1,8</p> <p>1,8</p> <p>1,8</p> <p>1-8</p>	<p>C 07 C 29/15 31/08 45/49 47/06 53/08 51/10// B 01 J 23/46</p> <p>TECHNICAL FIELDS SEARCHED (Int. Cl.³)</p> <p>C 07 C 29/15 45/49 51/10 51/12 B 01 J 23/46</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p> <p>&: member of the same patent family, corresponding document</p>
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
The Hague	05-03-1981	DELHOMME	



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p><u>EP - A - 0 004 656</u> (HOECHST)</p> <p>* Claims, page 5, lines 10-20; page 4, lines 24-30 *</p> <p>--</p>	1-8	
	<p><u>FR - A - 2 234 256</u> (UNION CARBIDE)</p> <p>* Claims; page 5, lines 1-30; page 20, line 4-23 *</p> <p>--</p>	1-8	
A	<p><u>FR - A - 2 317 260</u> (UNION CARBIDE)</p> <p>--</p>		TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
E	<p><u>EP - A - 0 022 358</u> (SAGAMI CHEMICAL RESEARCH CENTER)</p> <p>* Claims, examples 3, 12-21, 25-34, 42-47 *</p> <p>-----</p>	1-8	