

Description

The present invention relates in general to the production of mono-olefins by the catalytic oxidative dehydrogenation of gaseous paraffinic hydrocarbons having 2 or more carbon atoms and in particular to the production of mono-olefins by the catalytic oxidative dehydrogenation of ethane, propane and butanes.

The prior art on the oxidative conversion of gaseous paraffins to mono-olefins can be broadly divided into two groups, depending on the temperatures employed. At low temperatures, typically below 500 °C, oxidative dehydrogenation is generally a genuinely catalytic process. This is exemplified by US-A-4524236 and EP-A-0189282. In the process of US-A-4524236 ethane/oxygen mixtures are passed over catalysts comprising mixed oxides of molybdenum, vanadium, niobium and antimony (optionally incorporating a wide range of additional metals). Reaction takes place at temperatures in the range from 350 to 400 °C to give high selectivities to ethylene (i.e. 70% selectivity to ethylene at 75% ethane conversion). These catalysts produce only carbon oxides from higher paraffins. EP-A-0189282 discloses the use of a tin/phosphorus oxide catalyst in the production of mono-olefins from ethane, propane or butane in admixture with oxygen. Although reaction temperatures in the range 200 to 700 °C are disclosed, the working embodiment uses a temperature of only 550 °C.

At higher temperatures, for example temperatures greater than 500 °C, it is unlikely that reaction is entirely heterogeneous. At such temperatures thermal cracking and gas phase oxidations are likely to assume increasing importance. An example of prior art relevant to the high temperature reaction is US-A-3541179 which discloses passing a paraffinic gas through an externally heated fluid bed of "fire resistant" particles containing from 0.5 to 20% wt of at least one of the metals copper, manganese or vanadium. An oxygen-containing gas is injected into the fluid bed. The reaction temperature is from 650 to 900 °C and the process is at least partially autothermal. At a molar ratio of $C_2H_6:O_2$ of 2.6:1 and about 840 °C about 90% of the ethane feed is converted to ethylene.

Additionally, US-A-3670044 discloses a process for the dehydrogenation of alkanes, cycloalkanes and arylalkanes wherein the hydrocarbons are mixed with gaseous hydrogen or gaseous hydrogen and oxygen and contacted with a catalyst composition comprising a Group VIII metal. The process of the US document requires a hydrocarbon/gaseous oxygen mixture of 1 to 30 moles of oxygen per 100 moles of dehydrogenatable compound.

There are also a number of processes that do not involve catalysts at all. These are genuine high temperature autothermal cracking reactions and are exemplified by, for example, an article entitled "Autothermal Cracking for Ethylene Production" by R.M. Deanesly in Petrol. Refiner, 29 (September, 1950), 217 and GB-A-794,157.

A desirable objective would be to convert ethane, propane or butanes in a single step to mono-olefins.

Recently, the production of olefins together with carbon monoxide and hydrogen from gaseous paraffinic hydrocarbons, including ethane, by partial oxidation in spouted or fluid bed reactors has been disclosed in, for example, our copending applications EP-A-0164864 and EP-A-0178853. EP-A-0178853 discloses a process for the preparation of synthesis gas (carbon monoxide and hydrogen) from a hydrocarbon feed wherein the saturated hydrocarbon and an oxygen-containing gas are introduced in a ratio of 1.1 to 5 times the stoichiometric ratio of hydrocarbon to oxygen for complete combustion. The process does not require a catalyst for operation.

The present invention provides a process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or a mixture thereof which process comprises partially combusting a mixture of the hydrocarbon(s) and a molecular oxygen-containing gas in a composition of from 5 to 9 times the stoichiometric ratio of hydrocarbon to molecular oxygen containing gas for complete combustion to carbon dioxide and water, in contact with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability.

As the gaseous paraffinic hydrocarbon there may suitably be used either ethane, propane or a butane, or a mixture of two or more thereof. A suitable feedstock hydrocarbon is a mixture of gaseous paraffinic hydrocarbons, principally comprising ethane resulting from the separation of methane from natural gas.

As the molecular oxygen-containing gas there may suitably be used either oxygen or air. It is preferred to use oxygen, optionally diluted with an inert gas, for example nitrogen. It is preferred to pre-mix the oxygen-containing gas and the paraffinic hydrocarbon prior to contact with the catalyst. Additionally, other feed components may be included if so desired to optimise process design. Examples of other suitable feed components include methane, hydrogen, carbon monoxide, carbon dioxide and water.

The composition of the gaseous paraffinic hydrocarbon/molecular oxygen-containing gas mixture is from 5.0 to 9.0 times the stoichiometric ratio of hydrocarbon to oxygen for complete combustion to carbon dioxide and water, but these limits are extendible if desired. Typically, commercial reactors would be

operated at pressures of approximately 1-5 bar above atmospheric.

A catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability is employed. Suitable catalysts comprise supported platinum group metals and mixtures thereof, for example supported platinum or palladium. Although a range of support materials may be used, it is preferred to use an alumina as the support. The support material may be in the form of spheres or other granular shapes, but is preferably in the form of a monolith. Monoliths are continuous multichannel ceramic structures, frequently of a honeycomb appearance. They are commercially available as similar materials are commonly used as catalytic converters in automobile exhausts. A preferred form of alumina-supported platinum catalyst is platinum/gamma-alumina spheres. A more preferred form of supported platinum catalyst is a platinum/monolith, for example a platinum/cordierite or mullite monolith. Cordierite has a material composition of $2 \text{ MgO} \cdot 2 \text{ Al}_2\text{O}_3 \cdot 5 \text{ SiO}_2$ whilst mullite has a material composition of $3 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$. The catalyst may suitably be prepared by impregnating the support with a solution of a soluble compound of the platinum group metal. Using a monolith catalyst, this may suitably be achieved by soaking the monolith in a solution of a soluble compound, for example a salt, of the metal, removing the monolith from the solution and drying, typically at about 120°C . Using the simple soaking method it is difficult to achieve high, i.e. greater than about 0.15% metal loadings. Although such a metal loading is adequate for the performance of the invention, in certain circumstances higher loadings may be desirable. A higher loading may be achieved by wash coating the monolith prior to immersion in the solution of the catalytic metal compound with a material, for example alumina, capable of facilitating the retention of the metal compound. A combustion catalyst in the form of a metallic gauze such as Pt/Rh may also be employed.

The catalyst in the form of spheres may be used as a solids recirculating bed, for example a fluid bed or a spouted bed.

A process for producing synthesis gas, i.e. carbon monoxide/hydrogen mixtures, from a reaction mixture comprising a saturated hydrocarbon and an oxygen-containing gas in a spouted bed, the bed comprising material which is catalytically active for steam reforming reactions, is described in our copending EP-A-0164864. The process described in EP-A-0164864, which is incorporated by reference herein, may be modified by the use of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability, for example a supported platinum group metal(s) as hereinbefore described, instead of the steam reforming catalyst and the conditions modified in accordance with the process of the present invention to produce a mono-olefin as the principal product of the process. In a preferred embodiment of the modified process of EP-A-0164864, hydrogen is co-fed to the process as described in our copending EP-A-0178853 which is also incorporated by reference herein.

It is preferred to use the catalyst in a fixed bed. One reason for this preference is that it largely avoids the attrition problems generally encountered in moving bed operations. In the context of fixed bed operation it is further preferred to use a monolith catalyst. Monolith catalysts are preferred over other forms of fixed bed catalyst because (1) they are capable of sustaining a very low pressure drop along the bed, thereby allowing large gas throughputs, (2) they present a high surface area to the gaseous combustion mixture, (3) they are particularly free from attrition problems, (4) they can result in very low levels of soot formation and as a result require less frequent de-coking and (5) they are available in various cell sizes and shapes and their preparation by the soaking technique is relatively simple.

The elevated temperature employed in the process of the invention may suitably be in the range from 500 to 1200°C , though temperatures in the upper part of this range, for example 800 to 1000°C are preferred.

It is preferred but not essential to co-feed hydrogen gas. By so-doing the yields of and selectivities to desirable products can be improved. It is also preferred but not essential to preheat the feed gas, a suitable temperature being in the range 300 to 500°C .

In a preferred embodiment the present invention provides a process for the production of ethylene from ethane which process comprises contacting a mixture comprising ethane and oxygen in an ethane to oxygen molar ratio of 1.7 to 2.1 with a platinum- or palladium-containing monolith fixed bed catalyst.

In addition to ethylene, small amounts of higher olefins, acetylenes, aromatics and carbon oxides, i.e. carbon monoxide and carbon dioxide are co-produced.

The process of the invention will now be further illustrated by reference to the following Examples.

Example A - Preparation of Pt/cordierite monolith

A cordierite monolith (ex CORNING) was soaked in a solution of $[(\text{NH}_3)_4\text{Pt}]\text{Cl}_2 \cdot \text{H}_2\text{O}$. After 2 weeks the Pt impregnated monolith was removed from the solution, allowed to drain and dried in air at 120°C . The platinum loading, as determined by X-ray Fluorescence Spectroscopy was about 0.1% w/w.

Example 1

The Pt-loaded monolith (approximately 38 mm diameter x 51 mm length) was placed at the bottom of a quartz, 51 mm diameter, reactor with a baffle placed beneath it. The baffle ensured that the incoming flow of feed gas became evenly distributed through all cells in the monolith. Ethane, oxygen, hydrogen and nitrogen were passed through the monolith catalyst at atmospheric pressure. No preheat of the feed gases was required to effect autothermal operation, substantial heat generation being provided by the highly exothermic combustion of hydrogen/oxygen. Details of the molar proportions of the feed, the flow rates and the results obtained are given in Table 1.

TABLE I

Total Flow nl/min ⁻¹	C ₂ H ₆ /O ₂	H ₂ /O ₂	N ₂ /O ₂	Maximum Temperature (°C)	Conversion (% mol)	Selectivity (% C mol)						
						C ₂ H ₄	C ₂ H ₂	CH ₄	CO	CO ₂	C ₃ /C ₄	C ₆ H ₆
16.0	1.99	1.86	0.65	841	70.0	72.3	0.4	8.3	13.7	1.1	3.7	0.4
27.7	1.90	1.86	0.72	-	72.2	72.8	0.5	8.3	14.0	1.0	3.1	0.3
36.8	1.82	1.88	0.63	855	79.8	70.0	0.9	9.3	15.2	0.9	3.2	0.5

Example 2

Into a 51 mm diameter quartz reactor was placed a catalyst in the form of previously calcined Pt/gamma-alumina spheres (2 mm diameter), supported on a coarse silica sintered disc.

Ethane, hydrogen, oxygen and nitrogen were passed over the catalyst in the molar proportions and under the conditions shown in Table 2. Also tabulated in Table 2 are the experimental results. No soot formation was observed.

5 Example 3

In the following example, 0.5% Pt/Pd loaded alumina spheres (1.7 mm diameter) were placed into a quartz reactor (25 mm diameter). The catalyst was supported on a coarse silica sintered disc.

10 The appropriate paraffinic feedstock, ethane, propane or butane, or mixtures thereof, was co-fed with oxygen and nitrogen over the catalyst in the proportions and under the conditions shown in the following tables (3-4). Methane and hydrogen were also co-fed in some experiments.

The tables also show the experimental results, in which selectivities have been calculated on a soot free basis. Minimal soot formation was observed.

15 Example 4

In the following example, the monolith or gauze was placed in a quartz reactor (25 mm diameter) and the catalyst was supported on a coarse silica disc.

20 Ethane, hydrogen, oxygen and nitrogen were co-fed over the catalyst in the molar proportions and under the conditions shown in the following tables (7-9).

Tables 7 to 9 also show experimental results in which selectivities have been calculated on a soot-free basis. No soot formation was observed.

25

30

35

40

45

50

55

TABLE 2

Bed vol/cm ³	Total Flow nl/min ⁻¹	C ₂ H ₆ /O ₂	H ₂ /O ₂	N ₂ /O ₂	Maximum Temperature (°C)	Conversion (% mol)	Selectivity (%C-mol)						
							C ₂ H ₄	C ₂ H ₂	CH ₄	CO	CO ₂	C ₃ /C ₄	C ₆ H ₆
12	27.8	1.75	2.45	0.76	887	72.1	62.6	-	4.3	29.0	2.1	1.9	0.2
12	37.4	1.78	2.47	0.56	916	79.1	66.3	-	5.7	23.4	1.5	2.1	0.1
12	55.3	1.90	1.99	0.57	922	80.4	68.9	-	6.4	19.8	1.4	2.6	0.1
25	27.3	1.76	2.38	0.75	933	74.9	64.8	-	4.3	26.9	2.0	1.2	0.1
25	37.0	1.78	2.45	0.54	980	81.4	68.8	-	5.7	20.5	1.3	2.3	0.1
25	55.0	1.89	1.96	0.55	983	82.2	71.2	-	5.9	17.3	1.2	3.0	0.2
55	27.7	1.75	2.43	0.74	933	69.1	58.4	-	3.5	33.6	3.2	1.3	-
55	37.8	1.78	2.47	0.65	977	77.3	67.8	-	4.7	23.0	1.8	2.0	0.1

TABLE 3

Example	GHSV (h ⁻¹)	C ₃ H ₈	H ₂	N ₂	Conversion (%mol)	Selectivity (%C-mol)											
						CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₆	other C ₃	C ₄	C ₄ ⁻	1,3-C ₄ ⁻	C ₅ ⁺
3A	235200	1.41	—	—	87.3	17.4	3.9	16.7	40.6	3.2	0.9	14.1	0.2	0.1	0.8	2.0	0.1
3B	238800	1.65	—	—	73.6	15.5	4.5	14.8	36.4	3.5	0.5	19.9	0.2	0.3	1.9	2.2	0.3
3C	256800	1.15	1.96	0.44	98.9	13.0	1.1	23.4	47.5	2.4	2.8	4.6	0.6	—	0.3	2.5	1.8
3D	262800	1.29	3.23	0.54	88.8	7.2	0.8	21.8	47.0	3.4	0.9	13.3	0.4	0.3	1.1	1.8	2.0

Autothermal cracking of propane over 0.5% Pt/Pd/Al₂O₃

TABLE 4

Example	GHSV (h ⁻¹)	iC ₄	H ₂	N ₂	Conversion (%mol)	Selectivity (%C-mol)											
						CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	other C ₃	nC ₄	C ₄ ⁻	C ₅ +
3E	194400	1.06		0.37	90.9	18.7	6.1	22.7	17.8	2.1	1.3	0.2	25.2	1.3	-	4.7	-
3F	198000	1.32		0.39	74.9	13.9	6.6	16.1	8.8	1.4	0.4	0.2	30.7	1.6	-	20.0	0.3
3G	235200	1.04	2.13	0.44	94.2	11.8	2.0	28.3	24.3	2.0	1.8	0.2	17.2	1.0	-	10.7	0.7
3H	264000	1.18	2.11	0.43	72.4	9.3	2.3	22.9	14.8	1.7	0.6	0.3	36.6	1.3	0.2	10.0	-

Autothermal cracking of iso-butane over 0.5% Pt/Pd/Al₂O₃

TABLE 5

Exemple	GHSV (h ⁻¹)	nC ₄ — O ₂	H ₂ — O ₂	N ₂ — O ₂	Conversion (%mol)	Selectivity (%C-mol)											
						CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	other C ₃	iC ₄	C ₄ ⁻	C ₅ ⁺
3I	182400	1.00		0.52	98.8	19.0	4.0	14.8	45.5	2.5	1.8	0.4	8.1	0.6	—	3.0	0.3
3J	178800	1.16		0.58	88.1	14.2	4.6	12.5	39.4	3.6	0.8	0.6	18.4	0.5	tr	5.0	0.4
3K	260400	1.17	2.22	0.51	82.8	6.2	1.3	14.6	42.0	3.8	0.4	0.7	22.0	0.2	1.8	6.7	0.3
3L	254400	1.45	2.24	0.54	63.6	4.4	1.2	13.8	36.2	4.1	0.2	0.8	30.5	0.2	0.7	7.4	0.5

Autothermal cracking of n-butane over 0.5% Pt/Pd/Al₂O₃

TABLE 6

Example	GHSV (h ⁻¹)	CH ₄ /C ₂ H ₆ /C ₃ H ₈ O ₂ (Zmol)		H ₂ O ₂	Feed hydrocarbon composition (Zwt)			CONVERSION (Zmol)		Selectivity (ZC-mol)									
					CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₆	C ₃ H ₈	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃ H ₆	other C ₃	C ₄ ⁻	C ₅ ⁺	
3M	388400	1.80			17.6	32.8	49.6	93.2	99.9	30.8	4.1	13.6	45.6	5.2	-	0.2	0.5	-	
3N	340800	2.12			17.4	32.4	50.2	74.4	96.1	24.4	4.4	12.7	53.3	1.5	1.6	0.3	1.8	-	
3P	344400	2.45			17.2	32.2	50.6	54.4	84.4	21.3	5.5	11.1	51.7	0.7	6.4	0.4	2.7	0.2	
3Q	358800	1.98		1.67	18.1	33.3	48.6	85.5	99.3	19.3	1.3	17.4	58.5	1.6	-	0.2	1.4	0.3	
3R	357600	2.46		1.65	17.8	33.0	49.2	61.5	91.1	12.6	1.3	14.9	62.1	1.6	4.5	0.1	2.5	0.4	
3S	352800	2.79		1.69	17.6	33.1	49.4	43.4	75.2	10.4	1.3	13.5	59.6	0.4	10.9	0.3	3.0	0.6	

utothermal cracking of mixed methane/ethane/propane feeds over 0.5% Pt/Pd/Al₂O₃

TABLE 7

Example	Total Flow (l/min)	C ₂ H ₆		H ₂		N ₂		Conversion (%mol)	%C-mol Selectivity							
		O ₂		O ₂		O ₂			CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃ 's	C ₄ 's	C ₅ +
4A	16.9	1.79		-		0.29		94.7	26.8	3.3	10.2	51.9	3.6	1.0	2.2	1.0
4B	16.8	1.98		-		0.31		88.3	23.4	3.6	8.7	58.0	1.5	1.5	2.2	1.9
4C	22.9	1.83		2.16		0.32		89.5	19.3	1.0	10.4	63.2	2.1	0.9	1.6	1.5
4D	22.3	1.83		1.74		0.32		91.1	19.4	1.0	10.5	60.8	2.3	1.1	2.1	2.8

Autothermal cracking of ethane over a Pt/Rh gauze

TABLE 8

Example	GHSV	C ₂ H ₆		H ₂		N ₂		Conversion (%mol)	%C-mol Selectivity							
		—	O ₂	—	O ₂	—	O ₂		CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃ 's	C ₄ 's	C ₅ +
4E 4F	144286	1.73	0.64	—	0.34	—	0.34	95.8	21.7	1.5	9.7	57.5	4.7	0.7	2.9	1.4
	164429	1.90	1.67	—	0.38	—	0.38	89.6	16.6	0.7	9.3	67.4	2.1	0.9	2.5	0.5

Autothermal cracking of ethane over a Pt/Pd loaded MULLITE monolith

TABLE 9

Example	GHSV	C ₂ H ₆ — O ₂	H ₂ — O ₂	N ₂ — O ₂	Conversion (%mol)	%C-mol Selectivity							
						CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃ 's	C ₄ 's	C ₅ +
4G	80124	1.91	—	0.41	94.7	27.7	2.4	12.3	49.5	3.7	0.7	2.2	1.5
4H	80071	2.09	—	0.42	89.9	24.4	2.5	10.9	56.4	1.9	0.9	2.1	0.9
4I	118407	1.83	1.75	0.38	96.2	23.0	1.0	13.3	52.6	5.6	0.5	2.4	1.6
4J	128018	2.24	1.98	0.45	85.2	16.5	0.8	10.1	67.5	1.4	0.9	2.1	0.7

Autothermal cracking of ethane over Lithium Aluminium Silicate (LAS) monolith
(feed pre-heated to 300°C)

Claims

1. A process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or a mixture thereof which process comprises partially combusting a mixture of the hydrocarbon(s) and a molecular oxygen-containing gas in a composition of from 5 to 9 times the stoichiometric ratio of hydrocarbon to molecular oxygen containing gas for complete combustion to carbon dioxide and water, in contact with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability.
2. A process according to claim 1 wherein the catalyst is a supported platinum group metal or a mixture thereof.



TABLE 9

Example	GHSV	C ₂ H ₆	H ₂	N ₂	Conversion (%mol)	XC-mol Selectivity							
						CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃ 's	C ₄ 's	C ₅ +
4G	80124	1.91	-	0.41	94.7	27.7	2.4	12.3	49.5	3.7	0.7	2.2	1.5
4H	80071	2.09	-	0.42	89.9	24.4	2.5	10.9	56.4	1.9	0.9	2.1	0.9
4I	118407	1.83	1.75	0.38	96.2	23.0	1.0	13.3	52.6	5.6	0.5	2.4	1.6
4J	128018	2.24	1.98	0.45	85.2	16.5	0.8	10.1	67.5	1.4	0.9	2.1	0.7

Autothermal cracking of ethane over Lithium Aluminium Silicate (LAS) monolith
(feed pre-heated to 300°C)

Claims

1. A process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or a mixture thereof which process comprises partially combusting a mixture of the hydrocarbon(s) and a molecular oxygen-containing gas in a composition of from 5 to 9 times the stoichiometric ratio of hydrocarbon to molecular oxygen containing gas for complete combustion to carbon dioxide and water, in contact with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability.
2. A process according to claim 1 wherein the catalyst is a supported platinum group metal or a mixture thereof.



3. A process according to either claim 1 or claim 2 wherein the platinum group metal is either platinum or palladium.
4. A process according to either claim 2 or claim 3 wherein the support is an alumina.
5. A process according to claim 2 or claim 3 wherein the support is a monolith.
6. A process according to claim 2 wherein the catalyst is platinum/gamma-alumina spheres.
7. A process according to claim 2 wherein the catalyst is platinum/cordierite monolith.
8. A process according to claim 5 wherein the catalyst is platinum/mullite monolith.
9. A process according to any one of claims 1 to 3 wherein the catalyst is a metallic gauze containing a platinum group metal.
10. A process according to any one of the preceding claims wherein the gaseous paraffinic hydrocarbon is ethane, propane, butane or a mixture thereof.
11. A process according to any one of the preceding claims wherein the molecular oxygen-containing gas is oxygen.
12. A process according to any one of the preceding claims wherein the gas hourly space velocity of the mixture is at least $80,000 \text{ h}^{-1}$.
13. A process according to any one of the preceding claims wherein hydrogen is co-fed.
14. A process according to any one of the preceding claims wherein the catalyst is in the form of a fixed bed.
15. A process according to any one of the preceding claims wherein the mixture is partially combusted at a temperature in the range from 500 to 1200°C .
16. A process according to claim 15 wherein the temperature is in the range from 800 to 1200°C .
17. A process according to claims 3, 5 and 14 wherein a mixture comprising ethane and oxygen with an ethane to oxygen molar ratio of 1.7 to 2.1 is contacted with the catalyst.

Patentansprüche

1. Verfahren zur Herstellung eines Monoolefins aus einem gasförmigen paraffinischen Kohlenwasserstoff mit wenigstens zwei Kohlenstoffatomen oder einer Mischung davon, das die partielle Verbrennung einer Mischung des Kohlenwasserstoffs (der Kohlenwasserstoffe) und eines molekularen Sauerstoff enthaltenden Gases in einer Zusammensetzung vom 5- bis 9- fachen stöchiometrischen Verhältnis von Kohlenwasserstoff zum molekularen Sauerstoff enthaltenden Gas, das zur vollständigen Verbrennung zu Kohlendioxid und Wasser notwendig wäre, im Kontakt mit einem Katalysator, der zur Unterstützung der Verbrennung über die normale kraftstoffreiche Flammbarkeitsgrenze hinaus fähig ist, umfasst.
2. Verfahren nach Anspruch 1, wobei der Katalysator ein trägergestütztes Metall aus der Platingruppe oder eine Mischung daraus ist.
3. Verfahren entweder nach Anspruch 1 oder Anspruch 2, wobei das Metall aus der Platingruppe entweder Platin oder Palladium ist.
4. Verfahren entweder nach Anspruch 2 oder Anspruch 3, wobei der Träger ein Aluminiumoxid ist.
5. Verfahren nach Anspruch 2 oder Anspruch 3, wobei der Träger ein Monolith ist.



6. Verfahren nach Anspruch 2, wobei der Katalysator aus Platin/Gamma-Aluminiumoxid-Kugeln besteht.
7. Verfahren nach Anspruch 2, wobei der Katalysator ein Platin/Cordierit-Monolith ist.
- 5 8. Verfahren nach Anspruch 5, wobei der Katalysator ein Platin/Mullit-Monolith ist.
9. Verfahren nach einem der Ansprüche 1 bis 3, wobei der Katalysator aus einer metallischen Gaze besteht, die ein Metall aus der Platingruppe enthält.
- 10 10. Verfahren nach einem der vorhergehenden Ansprüche, wobei der gasförmige paraffinische Kohlenwasserstoff Ethan, Propan, Butan oder eine Mischung davon ist.
11. Verfahren nach einem der vorhergehenden Ansprüche, wobei das molekulare Sauerstoff enthaltende Gas Sauerstoff ist.
- 15 12. Verfahren nach einem der vorhergehenden Ansprüche, wobei die stündliche Raumgeschwindigkeit des Gases wenigstens $80\,000\text{ h}^{-1}$ beträgt.
13. Verfahren nach einem der vorhergehenden Ansprüche, wobei Wasserstoff mit eingespeist wird.
- 20 14. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Katalysator in Festbettform vorliegt.
15. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Mischung bei einer Temperatur im Bereich von 500 bis $1200\text{ }^{\circ}\text{C}$ teilweise verbrannt wird.
- 25 16. Verfahren nach Anspruch 15, wobei die Temperatur im Bereich zwischen 800 und $1200\text{ }^{\circ}\text{C}$ liegt.
17. Verfahren nach Ansprüchen 3, 5 und 14, wobei eine Ethan und Sauerstoff umfassende Mischung mit einem molaren Verhältnis von Ethan zu Sauerstoff von 1.7 bis 2.1 mit dem Katalysator in Kontakt gebracht wird.
- 30

Revendications

- 35 1. Procédé pour la production d'une mono-oléfine à partir d'un hydrocarbure paraffinique gazeux ayant au moins deux atomes de carbone ou d'un mélange de tels hydrocarbures, procédé qui comprend la combustion partielle d'un mélange du ou des hydrocarbures et d'un gaz contenant de l'oxygène moléculaire ayant une composition de 5 à 9 fois le rapport stoechiométrique de l'hydrocarbure au gaz contenant de l'oxygène moléculaire pour parvenir à une combustion totale en anhydride carbonique et en eau, en contact avec un catalyseur capable d'entretenir la combustion au-delà de la limite normale de richesse en combustible pour l'inflammabilité.
- 40 2. Procédé suivant la revendication 1, dans lequel le catalyseur est un métal du groupe du platine fixé sur un support ou un mélange de tels métaux.
- 45 3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel le métal du groupe du platine est le platine ou le palladium.
4. Procédé suivant la revendication 2 ou la revendication 3, dans lequel le support est une alumine.
- 50 5. Procédé suivant la revendication 2 ou la revendication 3, dans lequel le support est un monolithe.
6. Procédé suivant la revendication 2, dans lequel le catalyseur consiste en platine/sphères de gamma-alumine.
- 55 7. Procédé suivant la revendication 2, dans lequel le catalyseur consiste en platine/monolithe de cordiérite.
8. Procédé suivant la revendication 5, dans lequel le catalyseur consiste en platine/monolithe de mullite.



9. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le catalyseur consiste en une toile métallique contenant un métal du groupe du platine.

5 10. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'hydrocarbure paraffinique gazeux consiste en éthane, propane, butane ou un de leur mélange.

11. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le gaz contenant de l'oxygène moléculaire est l'oxygène.

10 12. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la vitesse spatiale horaire de gaz du mélange est au moins égale à $80\,000\text{ h}^{-1}$.

13. Procédé suivant l'une quelconque des revendications précédentes, dans lequel de l'hydrogène est introduit conjointement.

15 14. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le catalyseur est sous forme d'un lit fixe.

20 15. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le mélange est soumis à une combustion partielle à une température comprise dans l'intervalle de 500 à 1200°C .

16. Procédé suivant la revendication 15, dans lequel la température est comprise dans l'intervalle de 800 à 1200°C .

25 17. Procédé suivant les revendications 3, 5 et 14, dans lequel un mélange comprenant de l'éthane et de l'oxygène en un rapport molaire de l'éthane à l'oxygène de $1,7$ à $2,1$ est mis en contact avec le catalyseur.

30

35

40

45

50

55