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(54) **Noble metal catalysts for hydrocarbon conversion**

(57) Catalysts, useful for performing hydrocarbon conversions such as reforming, production of aromatics, isomerization of paraffinic and aromatic hydrocarbons, hydrocracking, hydrodealkylation and

steamdealkylation, are formed of a carrier such as alumina and, expressed by weight with respect to the carrier, from 0.05 to 0.6% of noble metal of the platinum family, 0.005 to 5% of titanium, 0.005 to 3% of at least one of manganese, technetium and rhenium, and from 0.1 to 15% of halogen. The catalysts are advantageously used as a moving bed.

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SPECIFICATION

New catalysts for hydrocarbon conversion

The invention concerns new catalysts for hydrocarbon conversion.

Catalysts containing a metal of the platinum family deposited on a carrier have been well known
 5 for a long time. However, in spite of numerous improvements to these catalysts, for example by 5
 incorporating one, two or even three other metals in them, it is still worth while making efforts to
 discover new catalysts that would give still better yields than those obtained up to now and would also
 have a longer life than the known catalysts. In addition, efforts are being made to improve the
 mechanical properties of these catalysts in order particularly to make possible their use as a moving bed
 10 of conglomerates, for example balls or extrudates of a substantial size, so as to leave a relatively easy 10
 passage for the gaseous reactants. The wear of the catalysts results in the formation of much smaller
 particles, which progressively obstruct the free space and make it necessary to increase the input
 pressure of the reactants or even to discontinue the operation.

Specific catalysts have now been discovered that have an increased activity and an increased life
 15 as compared with prior catalysts. 15

The catalyst according to the present invention comprises a carrier, and by weight with respect to
 the carrier: (a) 0.05 to 0.6% and more particularly 0.1 to 0.5% of a noble metal of the platinum family,
 (b) 0.005 to 5%, preferably 0.05 to 3% and more particularly 0.4 to 1% of titanium, (c) 0.005 to 3%,
 preferably 0.07 to 2% and more particularly 0.2 to 0.5% of manganese, technetium and/or rhenium and
 20 (d) 0.1 to 15% by weight, with respect to the carrier, of halogen, for example chlorine or fluorine. The 20
 preferred noble metals of the platinum family are platinum, rhodium and iridium. The preferred third
 metal is manganese or technetium.

The carriers are generally oxides of elements from group(s) II, III and/or IV of the periodic
 classification of elements, for example the oxides of magnesium, aluminium, titanium, zirconium,
 25 thorium or silicon, separately or in admixture, and possibly with oxides of other elements, for example 25
 boron and/or antimony. Coal may also be used. It is also possible to make use of zeolites or molecular
 sieves of the X or Y types, of the mordenite or faujasite type or, for example of the type ZMS-5, ZMS-4
 or ZMS-8, as well as mixtures of oxides of metals from groups II, III and/or IV with a zeolitic material.

The catalysts of the present invention are used particularly in a catalytic reforming process and in
 30 a catalytic process for manufacturing aromatic hydrocarbons. These processes are usually operated at a 30
 temperature of from 430 to 600°C under an absolute pressure of from 0.1 to 3.5 MPa, at an hourly
 velocity of 0.1 to 10 volumes of liquid charge per volume of catalyst, the molar ratio
 hydrogen:hydrocarbons ranging from 1:1 to 20:1. The catalysts according to the invention are
 particularly useful for carrying out these two processes under severe conditions.

Thus, they are useful for reforming reactions in order to obtain gasoline having a clear octane
 35 number higher than or at least equal to 102. The severe conditions of catalytic hydroreforming reactions 35
 are particularly the following: average temperature from 510 to 580°C, pressure 0.5 to 1.8 MPa,
 preferably 0.6 to 1.3 MPa, hourly velocity from 1 to 10 volumes of liquid charge per volume of catalyst
 and hydrogen:hydrocarbons molar ratio from 3:1 to 10:1. The charge is generally a naphtha distilling in
 40 the range 60°C to 220°C, in particular a straight run naphtha. 40

They are also useful for reactions producing aromatic hydrocarbons from unsaturated or saturated
 gasolines (for producing benzene, toluene or xylenes). In the case of an unsaturated charge, i.e. a charge
 containing diolefins and monoolefins, the unsaturated compounds may be selectively or totally
 hydrogenated. Then, the charge, optionally made free by hydrogenation of substantially all its diolefins
 45 and monoolefins, if any, is subjected to a treatment with hydrogen in the presence of a catalyst at a 45
 temperature of 530 to 600°C under a pressure of 0.1 to 1.3 MPa, the hourly volume feed rate of the
 liquid charge being of the order of 1 to 10 times the catalyst volume, the molar ratio
 hydrogen:hydrocarbons being 3:1 to 10:1. The feed charge may consist of pyrolysis, cracking and
 particularly steam-cracking or catalytic reforming gasolines, or may be constituted of naphthenic
 50 hydrocarbons convertible by dehydrogenation to aromatic hydrocarbons. 50

The catalysts according to the invention are also convenient for hydrocracking reactions, which
 are generally performed at a temperature ranging from about 260 to 530°C and under a pressure from
 about 0.5 to 25 MPa. The conversion conditions comprise an hourly space velocity of the liquid or
 VSHL, or volume per hour of liquid charge at 15°C per volume of catalyst, ranging from 0.1 to 10.0,
 55 having preferably 0.4 as upper limit and a hydrogen flow rate of about 1 to 20 moles per mole of 55
 charge.

The catalysts according to the invention are also convenient for the isomerization of aromatic
 hydrocarbons (e.g. xylenes), which is usually carried out at a temperature of 200 to 600°C under a
 pressure of 0.005 to 7 MPa, the hourly flow rate by volume being from 0.1 to 10 times the catalyst
 60 volume. 60

The catalysts according to the invention are further convenient for isomerizing, under hydrogen
 atmosphere, saturated C₄₋₇ hydrocarbons at a temperature of 50 to 250°C, e.g. 100—200°C. The
 operation is preferably conducted under a pressure of 0.5 to 10 MPa and with a space velocity of 0.2 to

10 liters of charge per liter of catalyst and per hour. The molar ratio H_2 :hydrocarbon is for example, from 0.01 : 1 to 20 : 1.

5 The catalysts according to the invention are also convenient for the hydrodealkylation or steam-dealkylation of aromatic hydrocarbons. These reactions are performed under known operating conditions, generally 300 to 600°C, so as to produce, for example, benzene from toluene or from other alkylbenzenes. 5

The catalysts may be used as a moving bed, particularly for the reactions of reforming and aromatic hydrocarbon production, which reactions are preferably conducted in a series of moving bed reactors.

10 The feed charge successively passes through each reactor or reaction zone axially radially (radial flow consisting of a flow from the centre towards the periphery or from the periphery towards the centre). The reaction zones are serially arranged, for example side by side or superposed. Preferably, the reaction zones are placed side by side. The feed charge successively flows through each of the reaction zones, with the provision of an intermediate heating of the charge between the reaction zones; the fresh catalyst is introduced at the top of the first reaction zone where the fresh charge is introduced; it then progressively flows downwardly through the reaction zone and is progressively withdrawn at the bottom by any convenient means (in particular a lift in the case of side-by-side reactors) it is conveyed to the top of the next reaction zone through which it progressively flows also downwardly, and so on to the last reaction zone at the bottom of which the catalyst is also progressively withdrawn to be fed to a regeneration zone. At the output of the regeneration zone, the catalyst is fed back progressively to the top of the first reaction zone. The various catalyst withdrawals are effected "progressively" as above mentioned, i.e. either periodically or continuously. Continuous withdrawals are preferred to periodic withdrawals. 10

25 For the reactions of reforming or aromatic hydrocarbon production and for the reactions of paraffinic or aromatic hydrocarbon isomerization, the preferred carrier is alumina, advantageously of a specific surface ranging from 50 to 400 m²/g, preferably from 100 to 300 m²/g. 25

30 The catalyst may be prepared by conventional methods involving impregnating the carrier with solutions of the metal compounds to be introduced. There can be used either a common solution of these metals or separate solutions of each metal. When using several solutions, intermediate drying and/or roasting steps may be performed. Usually a final calcination is effected, for example at 500 to 1000°C, preferably in the presence of free oxygen, for example by air scavenging. 30

Examples of metal compounds included in the catalyst composition are the nitrates, chlorides, bromides, fluorides, sulphates, and acetates, including ammonium mixed salts and any other salt or oxide that is soluble in water, hydrochloric acid or any other convenient solvent.

35 The halogen of the catalyst may be supplied by introducing a metal as a halide, or it may be introduced in the form of hydrochloric acid, hydrofluoric acid, ammonium chloride, ammonium fluoride, chlorine gas or a hydrocarbon halide, for example CCl_4 , CH_2Cl_2 or CH_3Cl . 35

40 One method of preparation consists of impregnating the carrier by means of an aqueous solution of, for example, titanium nitrate or another titanium compound, drying at about 120°C, roasting in air for a few hours at a temperature of 500 to 1000°C, and thereafter effecting a second impregnation by means of a solution containing the metal of the platinum family and the third metal (manganese, technetium and/or rhenium). 40

Another method consists of impregnating the carrier by means of a solution containing simultaneously the three catalyst metals.

45 Still another method consists of introducing the metal elements by effecting a number of successive impregnations corresponding to the metal elements in the catalyst. 45

50 An important application of the invention consists of producing gasoline of very high octane number, which requires an operation under very severe conditions that the currently used catalysts withstand only with difficulty. The use of bimetallic catalysts has however resulted in a clear improvement. Numerous attempts to associate metals have been made and even recently catalytic compositions containing up to 4 and even 5 metals have been proposed. These compositions are effectively responsible for an improvement but, generally, whereas the used promoters give new and favourable stability, they are also responsible, particularly in the case of noble metals of the platinum family, for a certain tendency to hydrogenolysis, leading finally to a decrease in yields, shortening of the cycle period and a decrease in the number of possible cycles, i.e. ultimately a decrease of the catalyst life time. 50

55 It has been observed that the simultaneous use of titanium and manganese, technetium and/or rhenium, jointly with a noble metal of the platinum family, very substantially attenuates this phenomenon by substantially decreasing this tendency to hydrogenolysis, and it has been observed that the advantages obtained by each of the three metals are optimum in the case of severe operating conditions, particularly when using low pressures, high temperatures and long operating times. 60

The following examples illustrate without limiting the invention. All percentages are by weight unless otherwise stated.

EXAMPLE 1

In order to obtain gasoline having a clear octane number of 103, there is used as feed charge a naphtha having the following characteristics:

	ASTM distillation	80—160°C	
5	Composition: aromatic hydrocarbons	7%	5
	naphthenic hydrocarbons	27%	
	paraffinic hydrocarbons	66%	
	"Clear research" octane number	about 37	
	Average molecular weight	110	
10	Specific gravity at 20°C	0.782	10

This naphtha passes with recycled hydrogen over two catalysts A and B containing 0.4% of platinum and 0.5% of titanium with respect to a carrier which consists of alumina having a surface of 240 m²/g and a pore volume of 0.58 cc/g; the chlorine content of catalysts A and B is 1.12%. Catalyst A further contains 0.3% of manganese and catalyst B further contains 0.3% of technetium.

15 The catalysts A and B have been prepared by adding to 100 g of alumina 100 cc of an aqueous solution containing 1.90 g of concentrated HCl ($d = 1.19$ g/cc), 20 g of an aqueous solution of chloroplatinic acid containing 2% of platinum, 10 g of an aqueous solution containing 5% of titanium as titanium trichloride, and (catalyst A), 1.57 g of manganese nitrate $Mn(NO_3)_2 \cdot 6H_2O$ or (catalyst B) 30 ml of a solution containing 0.61 g of $(NH_4)_2TcO_4$. 15

20 After 5 hours of contact, the product is dried for 2 hours at 100°C, then roasted at 500°C under scavenging with dry air (10 l/hour of air dried by passage through a bed of activated alumina). Then reduction is performed with a dry hydrogen stream (5 l/hour and passage over activated alumina) for 2 hours at 450°C. 20

The obtained catalysts A and B contain (by weight):

25 0.4% of platinum 25

0.5% of titanium

0.3% of manganese (catalyst A), or

0.3% of technetium (catalyst B), and

1.12% of chlorine

30 These obtained catalysts A and B have a specific surface of 230 m²/g and a pore volume of 0.55 cc/g. 30

The operation is conducted in a continuous manner, with a moving bed, in 3 reactors of substantially identical volumes.

The operating conditions are as follows:

35	pressure	1 MPa	35
	temperature	530°C	
	molar ratio H ₂ /hydrocarbons	8	
	hourly flow rate of liquid charge	2 times the catalyst volume.	

40 The operation is also conducted with a catalyst Q, according to the invention, containing, by weight, 1.12% of chlorine, 0.4% of platinum, 0.5% of titanium and 0.3% of rhenium. 40

Various catalysts of the prior art not conforming with the invention, comprising 1, 2 or 3 metal elements are also used. All of these catalysts also contain 1.12% of chlorine.

45 Table I below indicates the C₅₊ yield obtained and the hydrogen percent contained in the recycle gas after 200 hours. 45

50 The results obtained in this example 1, making use of the catalysts according to the invention, may be maintained over very long periods, for example of several months, by operating as indicated, i.e. continuously, with a system of 3 moving bed reactors, the catalyst being withdrawn for example continuously at a rate so adjusted that the whole catalyst bed of the reactor is progressively renewed with fresh catalyst for example in about 500 hours. 50

TABLE I

CATALYST	METAL % WITH RESPECT TO THE CATALYST CARRIER			YIELD OF C ₅ ⁺ (b.w.)	RECYCLE GAS % H ₂ MOLAR
A	0.4 platinum	0.5 titanium	0.3 Manganese	80.2	79.5
F	0.4 platinum	—	—	73.4	72.9
C	0.4 platinum	0.5 titanium	—	76.7	76.2
D	0.4 platinum	—	0.3 Manganese	77.9	77.6
B	0.4 platinum	0.5 titanium	0.3 Technetium	80.2	79.7
E	0.4 platinum	—	0.3 Technetium	74.9	74.5
G	0.4 platinum	0.2 iridium	0.3 Manganese	79.7	78.3
H	0.4 platinum	0.08 iridium	0.3 Manganese	79.7	78.4
I	0.4 platinum	0.2 iridium	0.3 Technetium	79.3	78.8
J	0.4 platinum	0.08 iridium	0.3 Technetium	79.3	78.8
K	0.4 platinum	0.08 iridium	—	75.2	74.9
L	0.4 platinum	0.08 ruthenium	—	75.1	74.9
M	0.4 platinum	0.2 ruthenium	—	75.1	74.7
N	0.4 platinum	0.08 ruthenium	0.3 Manganese	79.6	78.8
O	0.4 platinum	—	0.5 Manganese	77.9	77.5
P	0.4 platinum	—	0.3 Rhenium	76.7	76.2
Q	0.4 platinum	0.5 titanium	0.3 Rhenium	80.2	79.7

EXAMPLE 2

Example 1 is repeated with the use of catalysts containing platinum, titanium, manganese or technetium, while varying the titanium, manganese or technetium content.

5 The metal contents and the obtained results are reported in Table II: All of these catalysts contain 1.12% of chlorine.

5

TABLE II

CATALYST	METAL % WITH RESPECT TO THE CATALYST CARRIER			YIELD OF C ₅ ⁺ (b.w.)	RECYCLE GAS % H ₂ MOLAR
	0.4 platinum	0.5 titanium			
A ₁	0.4 platinum	0.5 titanium	0.003 manganese	76.7	76.2
A ₂	0.4 platinum	0.5 titanium	0.03 manganese	79.9	78.5
A ₃	0.4 platinum	0.5 titanium	0.10 manganese	80.1	79.3
A	0.4 platinum	0.5 titanium	0.3 manganese	80.2	79.5
A ₄	0.4 platinum	0.5 titanium	1.0 manganese	80.0	79.3
A ₅	0.4 platinum	0.5 titanium	2.5 manganese	79.5	78.6
A ₆	0.4 platinum	0.5 titanium	4 manganese	76.2	75.9
B ₁	0.4 platinum	0.5 titanium	0.003 technetium	76.7	76.2
B ₂	0.4 platinum	0.5 titanium	0.03 technetium	79.5	79.0
B ₃	0.4 platinum	0.5 titanium	0.1 technetium	80.0	79.5
B	0.4 platinum	0.5 titanium	0.3 technetium	80.1	79.7
B ₄	0.4 platinum	0.5 titanium	1.0 technetium	79.9	79.4
B ₅	0.4 platinum	0.5 titanium	2.5 technetium	79.4	78.9
B ₆	0.4 platinum	0.5 titanium	4 technetium	76.0	75.6
Q ₁	0.4 platinum	0.5 titanium	0.003 rhenium	76.6	76.3
Q ₂	0.4 platinum	0.5 titanium	0.03 rhenium	79.4	78.7
Q ₃	0.4 platinum	0.5 titanium	0.10 rhenium	80.0	79.4
Q	0.4 platinum	0.5 titanium	0.3 rhenium	80.1	79.7
Q ₄	0.4 platinum	0.5 titanium	1.0 rhenium	79.9	79.4
Q ₅	0.4 platinum	0.5 titanium	2.5 rhenium	79.4	78.7
Q ₆	0.4 platinum	0.5 titanium	4.0 rhenium	75.9	75.8

TABLE II (continued)

CATALYST	METAL % WITH RESPECT TO THE CATALYST CARRIER			YIELD OF C ₅ ⁺ (b.w.)	RECYCLE GAS % H ₂ MOLAR
R ₁	0.4 platinum	0.003 titanium	0.3 manganese	77.9	77.6
R ₂	0.4 platinum	0.003 titanium	0.3 technetium	76.9	76.5
R ₃	0.4 platinum	0.003 titanium	0.3 rhenium	77.2	77.8
R ₄	0.4 platinum	0.01 titanium	0.3 manganese	79.8	78.4
R ₅	0.4 platinum	0.01 titanium	0.3 technetium	79.4	78.8
R ₆	0.4 platinum	0.01 titanium	0.3 rhenium	79.6	78.9
R ₇	0.4 platinum	0.2 titanium	0.3 manganese	80.0	79.2
R ₈	0.4 platinum	0.2 titanium	0.3 technetium	79.8	79.2
R ₉	0.4 platinum	0.2 titanium	0.3 rhenium	79.7	79.1
R ₁₀	0.4 platinum	2.0 titanium	0.3 manganese	80.0	79.2
R ₁₁	0.4 platinum	2.0 titanium	0.3 technetium	79.7	79.2
R ₁₂	0.4 platinum	2.0 titanium	0.3 rhenium	79.6	79.0

EXAMPLE 3

Catalysts A and B as prepared in Example 1, are used in a process for producing aromatic hydrocarbons.

5 The feed charge, passed with hydrogen over these two catalysts, has the following composition by weight: 5

	— isopentane + n.pentane	:	1.59%	
	— isohexanes + n.hexane	:	24.22%	
	— isoheptanes + n.heptane	:	42.55%	
10	— cyclopentane	:	0.13%	10
	— methylcyclopentane	:	6.72%	
	— cyclohexane	:	5.50%	
	— C ₇ naphthenes	:	15.81%	
	— C ₈ naphthenes	:	0.14%	
15	— benzene	:	1.68%	15
	— toluene	:	1.66%	
	Total		<u>100.00%</u>	

The operating conditions were as follows:

	pressure	:	1 MPA	
	temperature	:	550°C	
5	hourly flow rate of liquid feed charge	:	3 times the catalyst volume	5
	molar ratio hydrogen/feed charge	:	6	

The results are reported in Table III where are indicated, in relation with the catalyst age, the contents by weight of benzene, toluene, benzene + toluene, as a proportion of the initial charge, as well as the C₅⁺ yield by weight.

10

10

TABLE III

CATALYST	BY WEIGHT COMPOSITION OF THE PRODUCT	AGE OF THE CATALYST IN HOURS		
		30 HOURS	200 HOURS	400 HOURS
A	benzene	27.4%	27.0%	26.6%
	toluene	35.6%	35.3%	34.8%
	benzene + toluene	63.0%	62.3%	61.4%
	yield by weight of C ₅ ⁺	71.9%	72.3%	73.1%
B	benzene	27.8%	27.5%	27.2%
	toluene	34.7%	34.4%	33.9%
	benzene + toluene	62.5%	61.9%	61.1%
	yield by weight of C ₅ ⁺	70.8%	71.0%	71.9%
Q	benzene	27.9%	27.6%	27.3%
	toluene	35.1%	34.8%	34.2%
	benzene + toluene	63.0%	62.4%	61.5%
	yield by weight of C ₅ ⁺	71.4%	71.9%	72.5%

EXAMPLE 4

This Example concerns the use of catalyst A of Example 1 for the hydrocracking of a cut distilling between 330 and 510°C, obtained by hydrotreatment of a vacuum distillate (400—500°C) of crude oil. This cut has the following characteristics:

5	d ₄ ¹⁵	:	0.870 g/cc	5
	nitrogen	:	5 ppm	
	The reaction conditions are as follows:			
	Temperature	:	380°C	
	Total pressure	:	12 MPa	
10	Velocity (vol/vol/hour)	:	1	10
	Hydrogen flow rate (vol/vol of hydrocarbons): 1 000			
	The conversion to C ₁ —C ₂ amounts to 0.30%.			
	The resulting effluent consists of:			
	C ₃ —160°C cut	:	29.9% by weight of the feed charge	
15	160—340°C cut	:	48.3% by weight of the feed charge	15
	cut boiling above 340°C : 27.8% by weight of the feed charge.			
	The 160—340°C fraction constitutes an excellent "Diesel" oil			
	"Diesel" index	:	73	
	Cloud point, lower than -30°C			
20	Freezing point, lower than	:	-63°C	20

EXAMPLE 5

This example concerns the use of a catalyst according to the invention in the isomerization of saturated hydrocarbons.

25	A tubular reactor of stainless steel is provided with a fixed bed of 100 g of the catalyst A, prepared according to Example 1 and previously roasted for one hour in air at 400°C.				25
	The reactor is then scavenged with a dry hydrogen stream at a rate of 50 liters of hydrogen per liter of catalyst and per hour, at a temperature of 50°C under a pressure of 0.2 MPa. After that, one litre of a solution containing 0.2 mole/litre of AlCl ₃ (C ₂ H ₅) in normal heptane is injected, by means of a pump, at a rate of 500 cc/h while recycling the effluent to the reactor.				
30	After 8 hours circulation, the pump is stopped, the solvent discharged and the solid dried in hydrogen.				30
	The analysis of the halogenated solid shows a content by weight of 11.5% chlorine, 0.35% platinum, 0.43% titanium and 0.26% manganese.				
35	The previously used tubular reactor is provided with a fixed bed of 50 cc of the so-prepared catalyst. The reactor is maintained under hydrogen circulation at 150°C and 2 MPa, and a hydrocarbon feed charge containing 50% by weight of normal pentane and 50% by weight of normal hexane, to which is added 1,000 ppm by weight of carbon tetrachloride, is injected. The feed charge is injected at a rate of two litres per litre of catalyst and per hour while maintaining a hydrogen hourly flow rate such that the ratio hydrogen/hydrocarbons is 3 moles/mole.				35

The analysis of the reactor effluent shows that the latter has the following composition:

	iso-pentane	:	28.5% by weight	
	normal pentane	:	21.5% by weight	
	iso hexanes	:	43.8% by weight	
5	normal hexane	:	6.2% by weight	5

$$\text{so that } \frac{iC_5}{\Sigma C_5} = 57\%$$

$$\text{and } \frac{iC_6}{\Sigma C_6} = 87.6\%$$

EXAMPLE 6

This example concerns the use of a catalyst according to the invention in the reactions of aromatic hydrocarbon isomerization. 10

A catalyst with an alumina base is used whose composition by weight is as follows:

Platinum: 0.4%, titanium: 0.5%, manganese: 0.3%, fluorine: 10%, the complement to 100% being alumina forming the carrier.

The catalyst is prepared as in Example 1 by making use of hydrofluoric acid instead of hydrochloric acid. 15

The so-prepared catalyst is used for isomerizing a *meta*-xylene charge to *para*-xylene.

The operating conditions were as follows:

	pressure	:	1.2 MPa	
	temperature	:	430°C	
20	hourly flow rate of liquid feed charge	:	6 times the catalyst volume	20
	molar ratio H ₂ hydrocarbons	:	5	

The obtained conversion rate of *para*-xylene corresponds to 95.5% of the thermodynamic equilibrium with a yield by weight of xylenes amounting to 99.9%.

25 CLAIMS 25

1. A catalyst comprising a carrier and, expressed by weight with respect to the carrier, from 0.05 to 0.6% of a noble metal of the platinum family, 0.005 to 5% of titanium, 0.005 to 3% of at least one of manganese, technetium and rhenium, and from 0.1 to 15% of halogen.

2. A catalyst according to Claim 1, in which the weights with respect to the carrier are 0.1 to 0.5% of the noble metal, 0.05 to 3% of titanium and 0.07 to 2% of manganese, technetium and/or rhenium. 30

3. A catalyst according to Claim 2, in which the weights with respect to the carrier are 0.1 to 0.5% of a noble metal of the platinum family, 0.4 to 1% of titanium and 0.2 to 0.5% of manganese, technetium and/or rhenium.

4. A catalyst according to any one of Claims 1 to 3, in which the catalyst contains (a) an alumina carrier, (b) platinum or iridium, (c) titanium and (d) manganese. 35

5. A catalyst according to any one of Claims 1 to 3, in which the catalyst contains (a) an alumina carrier, (b) platinum or iridium, (c) titanium and (d) rhenium.

6. A catalyst according to Claim 1 substantially as hereinbefore described in Example 1 Catalyst A or B or in Example 2.

7. A process for catalytic hydrocarbon conversion, involving reactions selected from reforming, aromatic hydrocarbons production, isomerization of paraffinic and aromatic hydrocarbons, hydrocracking, hydrodealkylation and steam-dealkylation of aromatic hydrocarbons, in which the catalyst is a catalyst according to any one of Claims 1 to 6. 40

8. A process according to Claim 7, conducted with at least one catalyst moving bed.

9. A process according to Claim 7 or 8 that is a reforming process or a process for producing aromatic hydrocarbons at a temperature from 430 to 600°C under a pressure from 0.1 to 3.5 MPa. 45

10 A process according to Claim 7 or 8 that is a reforming process or in a process for producing

- aromatic hydrocarbons, at a temperature of 510 to 580°C under a pressure of 0.5 to 1.8 MPa with an hourly velocity of 1 to 10 volumes of liquid charge per volume of catalyst, the molar ratio hydrogen:hydrocarbon being in the range 3:1 to 10:1 and the process comprises circulating a charge formed of hydrogen and hydrocarbons through at least two serially arranged reaction zones, each zone
- 5 being of the catalyst moving bed type, the charge circulating successively through each reaction zone and the catalyst also circulating successively through each reaction zone in a downward flow, the catalyst being withdrawn from each reaction zone to be fed to next reaction zone and then withdrawn from the last reaction zone traversed by the charge and fed to an accumulating zone from which the
- 10 reintroduced into the first reaction zone traversed by the charge. 5
11. A process according to any one of Claims 7 to 10, in which the operating conditions are so selected as to obtain a gasoline having a clear octane number higher than or equal to 102. 10
12. A process according to Claim 7 substantially as hereinbefore described in Example 1 (using Catalyst A or B) or any one of Examples 3 to 6.