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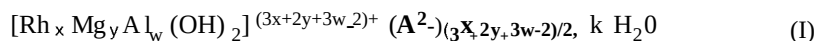
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(54) **Title:** RHODIUM CATALYSTS FOR ETHANOL REFORMING



(57) **Abstract:** Hydrotalcite-like compound of the formula (I): catalyst synthesis process involving such a compound and the use of this catalyst for hydrocarbons reforming and for ethanol reforming.



RHODIUM CATALYSTS FOR ETHANOL REFORMING

The invention relates to new catalysts and their use for the production of synthesis gas.

5 Since a few decades, increasing attention is being paid to the utilization of biomass derived products as renewable energy source. The interest is due to the possibilities to replace oil with a raw material, potentially leading to zero emission of carbon dioxide CO₂ (20-20-20 Renewable Energy UE Directive, 23/01/08, concerning the European Energy Policy and the Kyoto's Protocol). Of great interest is the possibility to produce hydrogen
10 and synthesis gas by ethanol and other oxygenated reforming to be used, as example, in high efficiency fuel cell [F.Aupretre et al., Catal. Communications (2002) (3) 263-267; J. Armor; Appl. Catal. A: General (1999), 176, 159; Dunn S.; Int J. Hydrogen Energy (2002), 27(3), 235-264].

15 Among the oxygenate compounds, ethanol is a good candidate for several reasons:

(i) - It is produced through carbohydrates fermentation;

(ii) - It could easily be decomposed in the presence of water to generate a hydrogen-rich mixture;

(iii) - It is free from catalyst poisons such as sulfur.

20 However, the presences of two carbon atoms and of oxygen lead possible several reactions. The reaction pathway are much more complex than that of methane and ethane partial oxidation and reforming and even more complex than that of methanol, therefore it is very important the role of the catalyst, of the support and their interaction able to select a specific reaction pattern maximizing the hydrogen selectivity at relatively low
25 temperature [A. Haryanto et al.; Energy & Fuels (2005) 19, 2098-2106].

The reaction of steam reforming of ethanol is, from a thermodynamic point of view, feasible above 500 K and at low temperature. It is strongly endothermic in absence of oxygen.

30 Different catalytic system have been studied in this reaction using different metals and various supports, but often a low comprehension about the specificity of each material and the interaction with the support is reported. From these studies it can be evidenced that good catalysts for ethanol steam reforming are supported metals like Co, Ni, Rh, Ru, Pd, Ir and Pt. Most of them promote the dehydrogenation to acetaldehyde and prevent the dehydration to ethylene.

35 However, at a certain level of temperature, these metals decompose the organic substrate to C* and H* (dissociative adsorption), getting close to thermodynamic

equilibrium and giving problems in the effective evaluation of the catalysts selectivity. The coke formation has very often been observed on the surface of the catalysts. The coke formation is even more problematic if the process is carried out with raw ethanol and/or high pressure. Both conditions not only are required for the development of an industrial process and outstanding scientific challenge. Therefore, using these conditions, the possibility to run a process at low temperature with a selective reaction pathway is determinant to inhibit the intermediate which are coke precursors. In particular, the presence of other oxygenated impurities in the raw ethanol (such as butanol or diethyl-ether) can form olefins and promote the coke formation. The study of these effects allows extend the results at different organic substrate of biological origin.

Although the formation of coke at low temperature is still a problem on this catalyst, it can be inhibited through the support modification and the metal support interaction. Recently, structured catalysts based in cobalt and zinc oxide supported on cordierite monoliths and macroporous silicon have been studied. The study of the reaction pathway and the reaction intermediates of the steam ethanol reforming revealed that ethanol and acetaldehyde compete for the same active sites and that water and methane conversion depend on ethanol conversion since water and methane, reaction intermediate, are adsorbed on the same active sites than ethanol. The nature of the active sites greatly modify the catalytic activity, in particular a support with both strong or weak acidic sites mainly favors the C-C breakage and therefore the formation of CO and CH_x, while the presence of only acidic sites favors the acetaldehyde formation.

Few studies are focused on the combined effect of metal and support or the combination in bimetallic catalysts and several aspects of the process are still little understood. Nevertheless, the scientific community agrees that the control of activity and selectivity need to be faced through studies involving the preparation of materials able to tailor the metal support interaction and the chemical environment in the nano-structure. To obtain such materials it is necessary to develop a new approach allowing control the dispersion of the active phase from the first stages of the preparation leading to active sites strongly interacting with the support.

The innovative approach is related to the insertion of the noble metal inside a well defined crystalline structure prepared in the way to give rise to the noble metal dispersed, like in a solid solution, inside an oxide matrix. One of the most promising methods is related to the insertion of metallic cations of active phase inside an hydrotalcite type structure. Recent studies have demonstrated that it is possible to obtain a noble metal dispersed on the surface by a reduction process. Catalysts obtained with this method

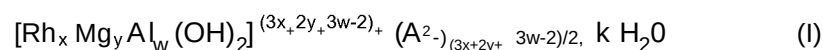
have shown to be active in the partial oxidation and steam reforming of methane to synthesis gas without strong deactivation during reaction conditions.

The invention is related to the possibility to obtain high activity, selectivity and stability of the Rh° obtained by reduction of specific phase distribution of mixed oxides in which the Rh^{3+} is present after calcination of hydrotalcite precursor. The catalysts are obtained from the hydrotalcite structure containing Rh, Mg, Al and having carbonate or silicate as interlayer anions and in the way to obtain a specific phase distribution and an high Rh dispersion after the high temperature reduction treatment.

Recent studies have demonstrated that it is possible to obtain a noble metal dispersed on the surface by a reduction process. Catalysts obtained with this method have shown to be active in the transformation of methane to synthesis gas without deactivation during reaction conditions. Nevertheless the activity of the best catalyst used in the methane reforming are not suitable catalyst in this reaction due to the metal support interaction, to the structure sensitiveness of the reaction and to the catalyst stability.

That is the reason why the invention concerns new catalysts with enhanced performances in terms of activity, selectivity and stability towards hydrogen and carbon monoxide formation, which are active in a wide range of temperature and which generates C_2 by-products in a very low amount. These catalysts are based on hydrotalcite precursor containing rhodium, both using carbonate or silicate as interlayer anions and having a specific phase distribution after calcination and a high Rhodium dispersion after the high temperature reduction treatment. The catalysts are active and selective at low temperature ($500^\circ C$) with 100% selectivity in C_1 products, with no formation of by product. The catalysts are active and stable at higher temperature and need low residence time reaching equilibrium value below 50 ms at $550^\circ C$.

According to a first embodiment the invention concerns an Hydrotalcite-like compound of the formula (I):



wherein:

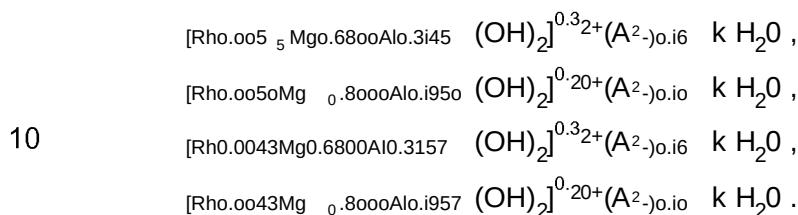
- (A^{2-}) represents either a carbonate anion or a silicate anion,
- $x > 0$,
- $y > 0$,
- $w > 0$,
- $(x+y) = (1-w)$,
- $1 \leq [y/(w+x)] \leq 4$, and
- $1/100 \leq x/w \leq 5/100$.

According to a particular embodiment, in the formula (I) as hereinabove defined, $0.5 \leq y < 0.9$.

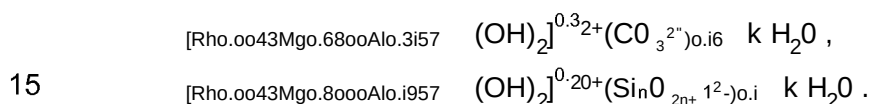
According to another particular embodiment, in the formula (I) as hereinabove defined, $0.1 \leq w \leq 0.4$.

5 According to another particular embodiment, in the formula (I) as hereinabove defined, the atomic ratio: $[y/(w+x)] \geq 2$.

Examples of such Hydrotalcite-like compounds are those of the following formulas:



According to more particular embodiment, hydrotalcite-like compounds are those of the following formulas:



The invention relates to a synthesis process of the Hydrotalcite-like compound of the formula (I) hereinabove defined, comprising the following steps:

- A step A during which an aqueous solution containing together, aluminium nitrate, rhodium nitrate and aluminium nitrate is prepared by mixing said nitrate salts in the
20 desired molar proportions, with water;

- A step B during which, said solution obtained at step A is mixed with an aqueous solution of sodium carbonate or sodium silicate, the pH being maintained between 8 and 10, preferably around 9, to produce a precipitate;

- A step C during which, said precipitate obtained at step B, is isolated by filtration,
25 washed and then dried to form the expected hydrotalcite-like compound of said formula (I)-

The synthesis process as hereinabove defined may further comprise:

- A step D during which, said hydrotalcite-like compound of said formula (I) as hereinabove defined, obtained at step C, is grinded to form a powder of particles of said
30 hydrotalcite-like compound of said formula (I).

The invention also relates to a synthesis process of a catalyst comprising :

- A step E during which, the powder obtained at step D of the hereinabove defined process, is calcined.

The synthesis process of a catalyst as herein above defined, may further
35 comprises :

- A step G during which, the calcined powder obtained at step F is reduced with hydrogen at a temperature preferentially below 230°C.

According to another embodiment, the invention concerns a catalyst consisting in a combination of rhodium (Rh), magnesium oxide (MgO), mixed magnesium and aluminium oxide (MgAl_2O_4), and optionally mixed magnesium and silicon oxide (Mg_2SiO_4), and obtainable by the process as hereinabove defined, wherein:

- The molar ratio $\text{MgO}/\text{MgAl}_2\text{O}_4$ in said combination is less than or equal to 2 and greater or equal to 1,

- The molar concentration of MgAl_2O_4 is greater or equal to 30mole % and less or equal to 50mole %

- The sum of the molar concentrations of MgO and Mg_2SiO_4 is greater or equal to 40mole% and less or equal to 90mole% and

- The molar concentration of rhodium in said combination is greater or equal to 10^{-3} mole% and less or equal to 10^{-2} mole%.

The invention also concerns a synthesis process for the preparation of the catalyst as hereinabove defined, comprising the following steps:

- A step A during which an aqueous solution containing together, aluminium nitrate, rhodium nitrate and aluminium nitrate is prepared by mixing said nitrate salts in the desired molar proportions, with water;

- A step B during which, said solution obtained at step A is mixed with an aqueous solution of sodium carbonate or sodium silicate, the pH being maintained between 8 and 10, preferably around 9, to produce a precipitate;

- A step C during which, said precipitate obtained at step B, is isolated by filtration, washed and then dried to form the expected hydrotalcite-like compound of said formula (I);

- A step D during which, said hydrotalcite-like compound of said formula (I) as hereinabove defined, obtained at step C, is grinded to form a powder of particles of said hydrotalcite-like compound of said formula (I);

- A step E during which, the powder obtained at step D, is calcined;

- A step G during which, the calcined powder obtained at step F is reduced with hydrogen at a temperature of less than 230°C.

The invention also concerns the Use of said catalysts, as a catalyst for hydrocarbons reforming and/or as a catalyst for ethanol reforming.

The following paragraphs disclose non-limitative examples of catalysts according to the present invention.

The invention is related to the preparation of an active selective and stable catalyst, by insertion of metallic cations as active phase inside an hydrotalcite type precursor, from which the catalyst can be obtained by calcination at a temperature between 750°C and 1000°C and reduction between 700 and 900°C.

5 Surprisingly among the 4 catalysts prepared with 1,0 wt.% of Rh the catalyst obtained by calcination and reduction of the Rh/Mg/Al 0,5/80/19,5 a.r. hydrotalcite with silicate as interlayer anion (R05M80A) and the Rh/Mg/Al 0,43/68/31,57 a.r. with carbonate (R043MA) are active and selective while the catalyst obtained by hydrotalcite with Rh/Mg/Al/ 0.55/68/31,45 with carbonate as interlayer (R055MA) is poorly selective while
10 the Rh/Mg/Al 0.43/80/19,5 with silicate as interlayer anion (R043M80A) is poorly active and selective towards hydrogen and synthesis gas.

The composition of hydrotalcites is summarized in the following

	R055M	R05M80A	R043MA	R043M80A
Mg	68	80	68	80
Al	31.45	19.50	31.57	19.57
Rh	0.55	0.50	0.43	0.43
Anions	Silicates	Silicates	Carbonates	Carbonates

Table 1

The activity and selectivity of the 4 hydrotalcite (HT)-derived catalysts are reported
15 in **Figure 1** and **Figure 2**, that clearly show that samples R05M80A and R043MA are the best combination in terms of activity and selectivity at 550°C and 700°C.

Figure 1 shows the activity and selectivity of each of the catalysts R055M, R05M80A, R043MA, and R043M80A in an ethanol reforming test, at atmospheric pressure, with a residence time of 6ms at a temperature = 700°C with a steam/ethanol
20 ratio = 5.

Figure 2 shows the activity and selectivity of each of the catalysts R055M, R05M80A, R043MA, and R043M80A in an ethanol reforming test, at atmospheric pressure, with a residence time of 25 ms, at a temperature = 550°C with a steam/ethanol ratio = 5.

25 The selectivity is maximum in the synthesis gas product and minimum in C2 and C3 products, which are coke precursors. In fact, no carbon formation on the catalysts has been observed at low C2⁺ selectivity.

Even more clearly are the specificity of the two R043MA and R05M80A catalysts if the catalyst selectivities are compared at similar conversion.

The selectivity in hydrogen is reported in **Figure 3** and the selectivity in C2 and C3 products are reported in **Figure 4**, as a function of the ethanol conversion for each of the catalysts R055M, R05M80A, R043MA, and R043M80A. The graphs clearly show two different to better enhance the specific selectivity of the catalyst through hydrogen.

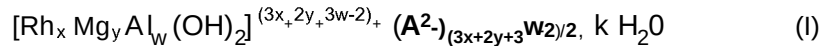
5 The diffraction patterns of the calcined catalysts (**Figure 5** and **Figure 6**) show that, by increasing the Mg/Al, together with the expected increase in the intensity of the MgO phase diffraction lines, the amount of spinel phase decreases. Moreover, the crystalloid of the forsterite phase for the 80/20 is lower. It is worth noting that by reducing the amount of trivalent cations, the charge excess of the hydroxyl layers decreases, as
10 does the silicate content in the structure in order to balance it.

The hypothesis of the phase composition of the matrix containing the active phase are summarized in **Figure 7**. Excluding the forsterite phase which does not contains Rh, it is clear that the two active catalysts have similar composition in terms of $\text{MgO/MgAl}_2\text{O}_4$ related to an optimal Rh distribution in the matrix, in a specific metal support interaction
15 and in specific acid base properties.

The previous catalysts have been tested at temperature between 500 and 600°C showing optimal stability with time on stream. The tests carried out for a period of 65h demonstrate the stability of the performances of the R05M80S with time on stream even using Surfin grade ethanol (commercial grade). The tests show an increase of the methane
20 conversion and Hydrogen selectivity while the ethanol conversion is maintained to 100%. **Figure 8** reports the stability tests in ethanol reforming carried out using surfin ethanol at $T = 520^\circ\text{C}$, $P = 20 \cdot 10^5 \text{ Pa}$ (20 bar), with a EtOH/Steam ratio = 1/5 and a residence time = 1.2 s.

Claims

1. Hydrotalcite-like compound of the formula (I):



5 wherein:

- (A^{2-}) represents either a carbonate anion or a silicate anion,
- $x > 0$,
- $y > 0$,
- $w > 0$,
- 10 - $(x+y) = (1-w)$,
- $1 \leq [y/(w+x)] \leq 4$, and
- $1/100 \leq x/w \leq 5/100$.

2. Hydrotalcite-like compound of the formula (I) according to Claim 1 wherein $0.5 \leq y < 0.9$.

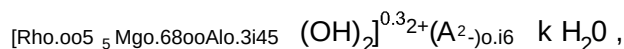
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3. Hydrotalcite-like compound of the formula (I) according to anyone of Claims 1 or 2, wherein $0.1 \leq w \leq 0.4$.

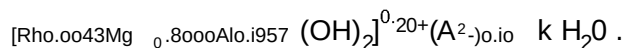
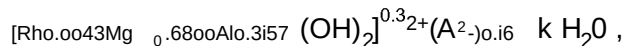
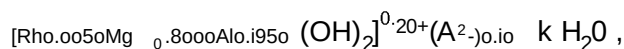
4. Hydrotalcite-like compound of the formula (I) according to anyone of Claims 1 to 3, wherein the atomic ratio: $[y/(w+x)] \geq 2$.

20

5. Hydrotalcite-like compound according to anyone of Claims 1 to 5, of the following formulas:

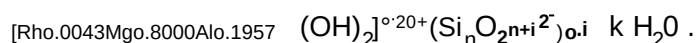


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6. Hydrotalcite-like compound according to Claim 5, of the following formulas:

30



7. Synthesis process of the Hydrotalcite-like compound of the formula (I) according to anyone of Claims 1 to 6, comprising the following steps:

35

- A step A during which an aqueous solution containing together, aluminium nitrate, rhodium nitrate and aluminium nitrate is prepared by mixing said nitrate salts in the desired molar proportions, with water;

5 - A step B during which, said solution obtained at step A is mixed with an aqueous solution of sodium carbonate or sodium silicate, the pH being maintained between 8 and 10, preferably around 9, to produce a precipitate;

- A step C during which, said precipitate obtained at step B, is isolated by filtration, washed and then dried to form the expected hydrotalcite-like compound of said formula (I).

10 8. Synthesis process according to Claim 7, further comprising: a step D during which, said hydrotalcite-like compound of said formula (I) as hereinabove defined, obtained at step C, is grinded to form a powder of particles of said hydrotalcite-like compound of said formula (I).

15 9. Synthesis process of a catalyst comprising a step F during which, the powder obtained at step D of the process according to Claim 8, is calcined;

20 10. Synthesis process according to Claim 9, further comprising a step G during which, the calcined powder obtained at step F is reduced with hydrogen at a temperature of preferentially below 230°C.

11. Catalyst consisting in a combination of rhodium (Rh), magnesium oxide (MgO), mixed magnesium and aluminium oxide (MgAl_2O_4), and optionally mixed magnesium and silicon oxide (Mg_2SiO_4), and obtainable by the process according to Claim 10, wherein:

25 - The molar ratio $\text{MgO}/\text{MgAl}_2\text{O}_4$ in said combination is less than or equal to 2 and greater or equal to 1,

- The molar concentration of MgAl_2O_4 is greater or equal to 30mole % and less or equal to 50mole %

- The sum of the molar concentrations of MgO and Mg_2SiO_4 is greater or equal to 40mole% and less or equal to 90mole% and

30 - The molar concentration of rhodium in said combination is greater or equal to 10^{-3} mole% and less or equal to 10^{-2} mole%.

12. Synthesis process for the preparation of the catalyst according to Claim 11, comprising the following steps:

35 - A step A during which an aqueous solution containing together, aluminium nitrate, rhodium nitrate and aluminium nitrate is prepared by mixing said nitrate salts in the desired molar proportions, with water;

- A step B during which, said solution obtained at step A is mixed with an aqueous solution of sodium carbonate or sodium silicate, the pH being maintained between 8 and 10, preferably around 9, to produce a precipitate;

5 - A step C during which, said precipitate obtained at step B, is isolated by filtration, washed and then dried to form the expected hydrotalcite-like compound of said formula (I) ;

- A step D during which, said hydrotalcite-like compound of said formula (I) as hereinabove defined, obtained at step C, is grinded to form a powder of particles of said hydrotalcite-like compound of said formula (I);

- A step F during which, the powder obtained at step D, is calcined;

10 - A step G during which, the calcined powder obtained at step F is reduced with hydrogen at a temperature preferentially below than 230°C.

13. Use of the catalyst prepared by the process according to Claim 10, as a catalyst for hydrocarbons reforming.

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14. Use of the catalyst according to Claim 11, as a catalyst for ethanol reforming.

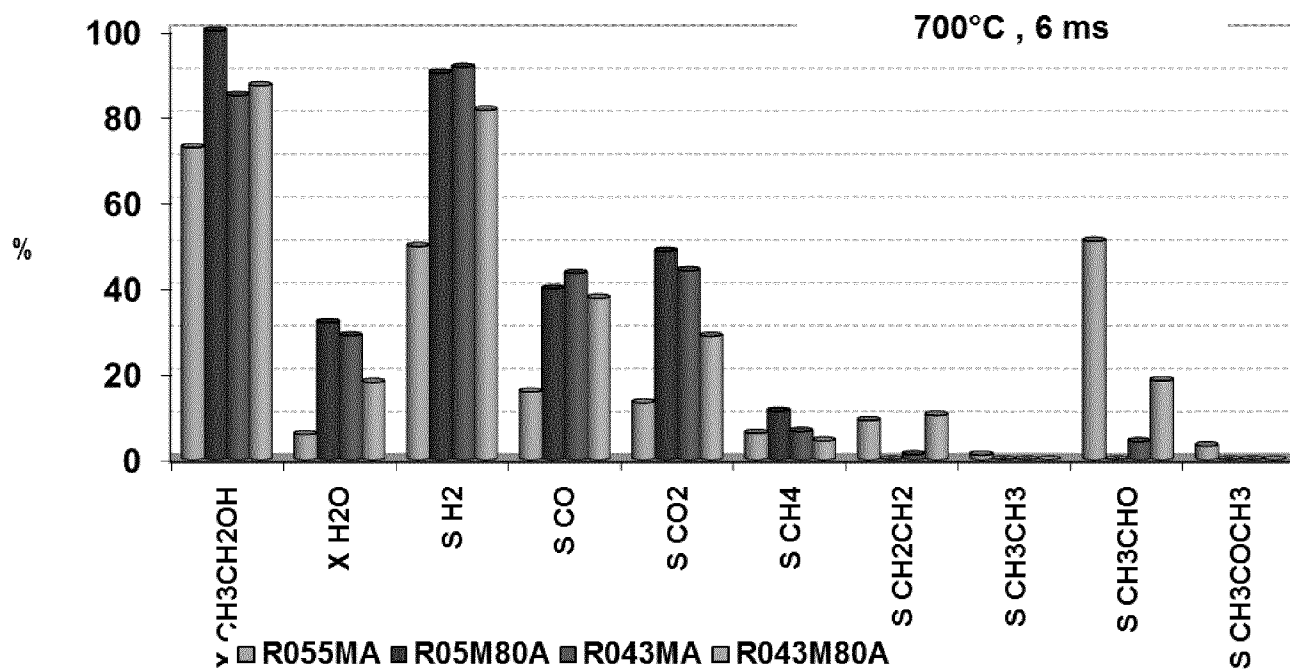


Figure 1

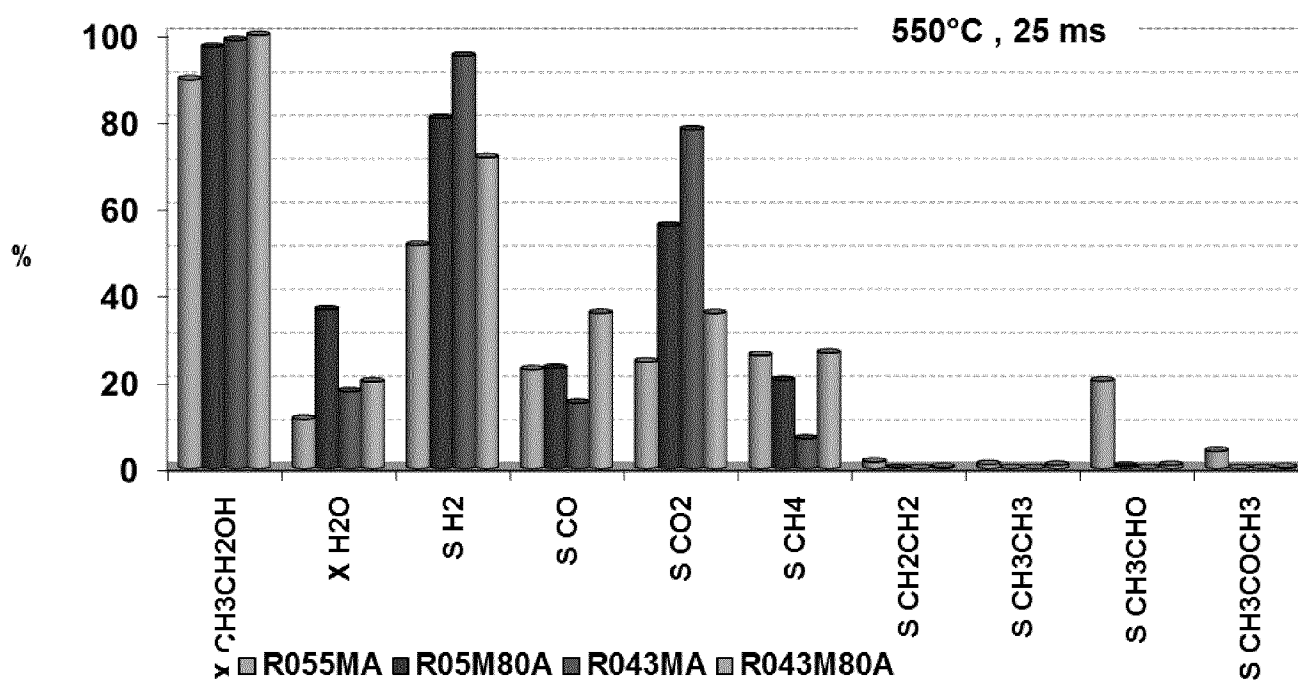


Figure 2

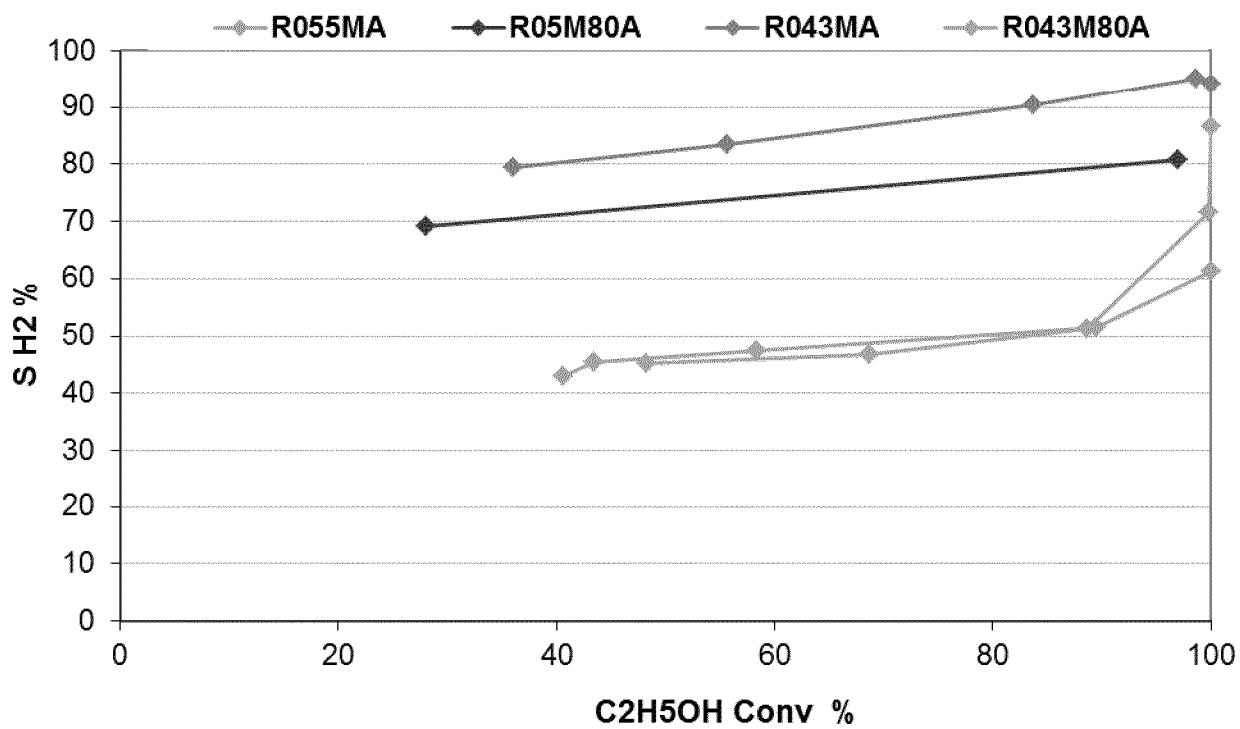


Figure 3

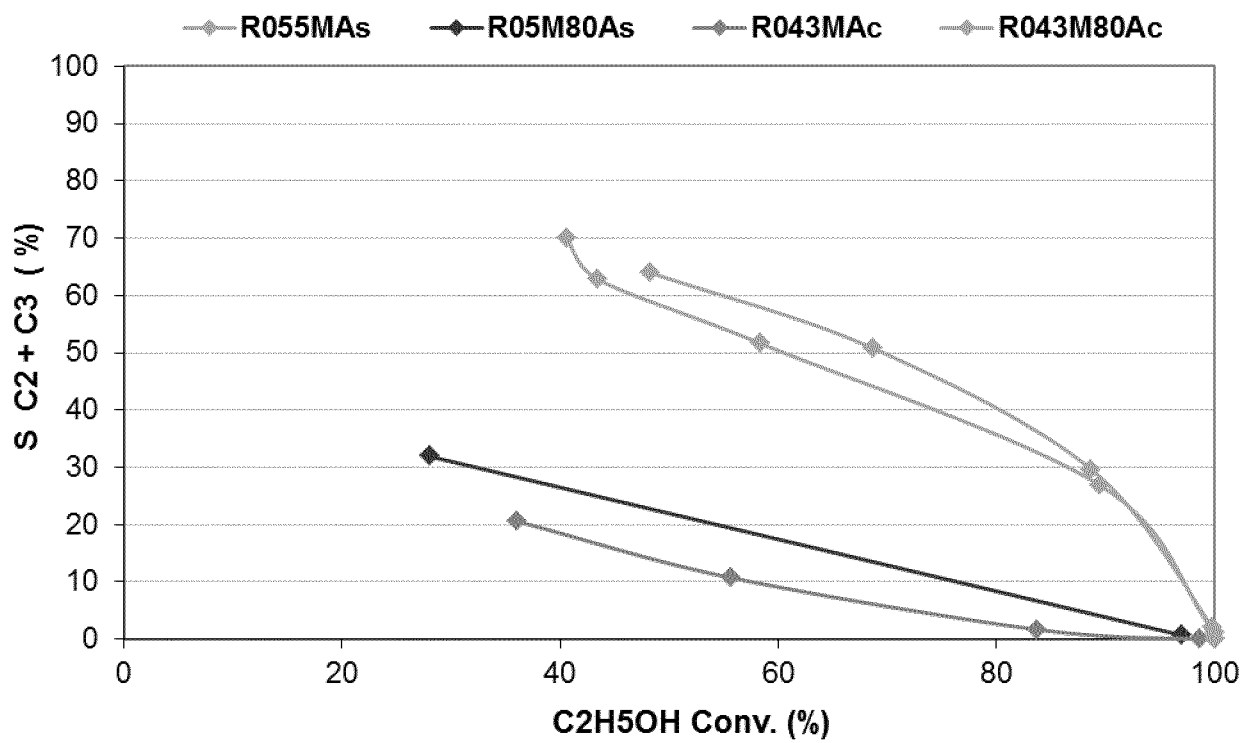


Figure 4

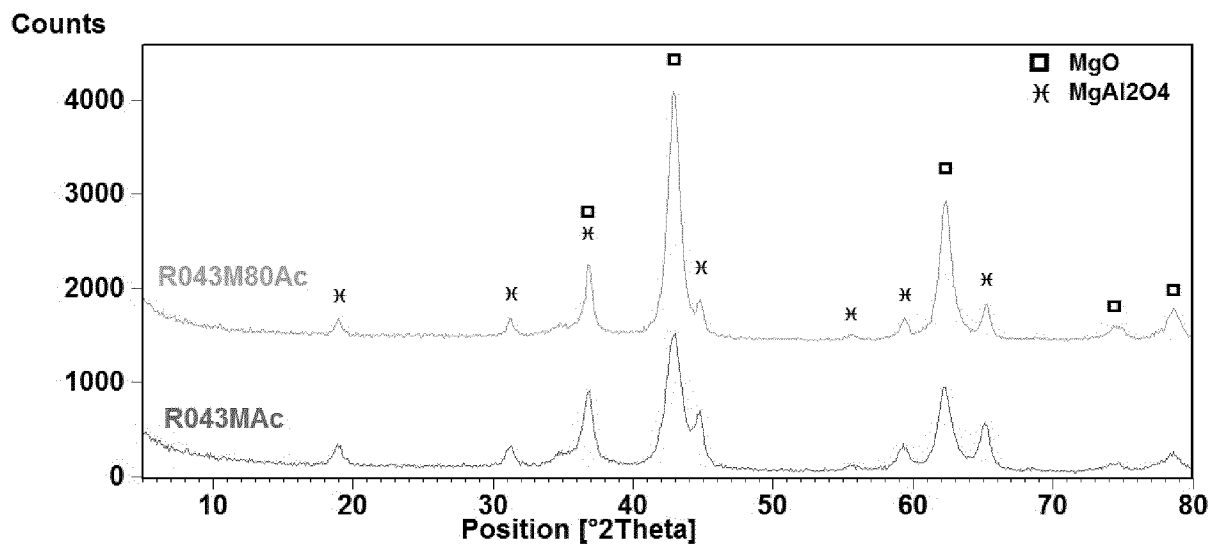


Figure 5

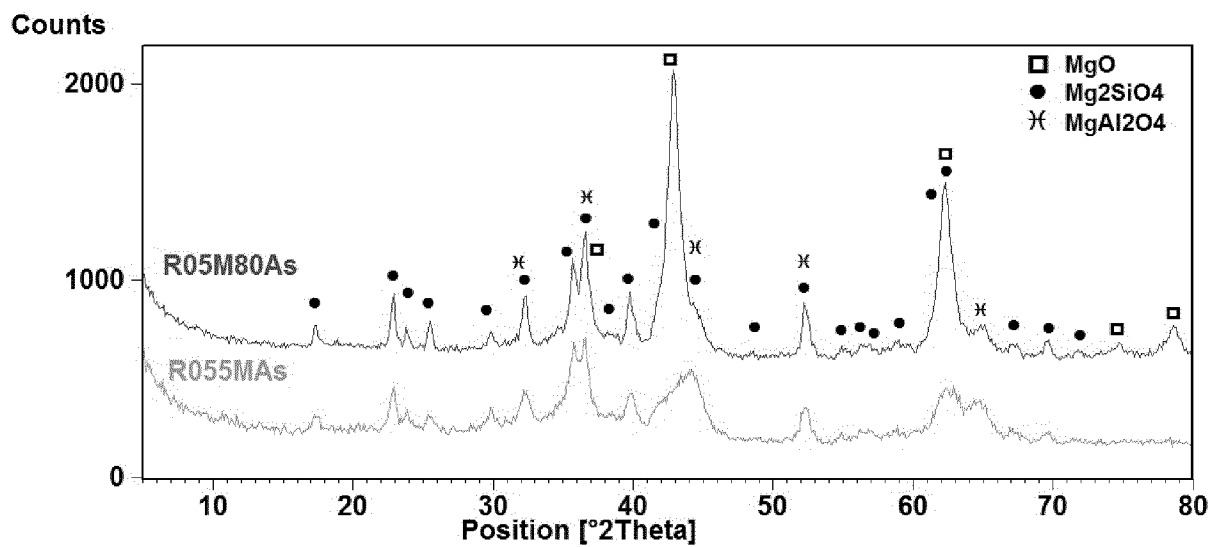


Figure 6

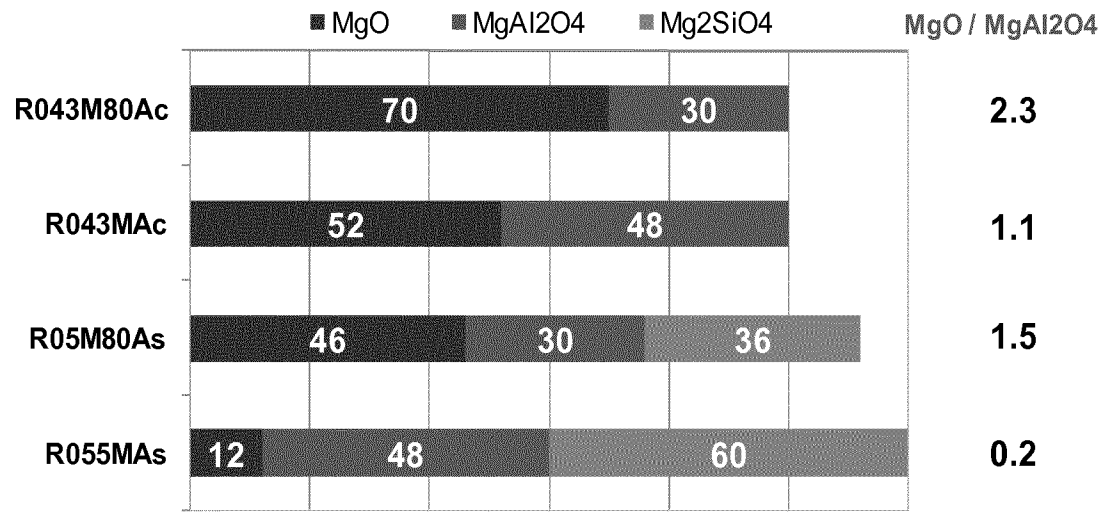


Figure 7

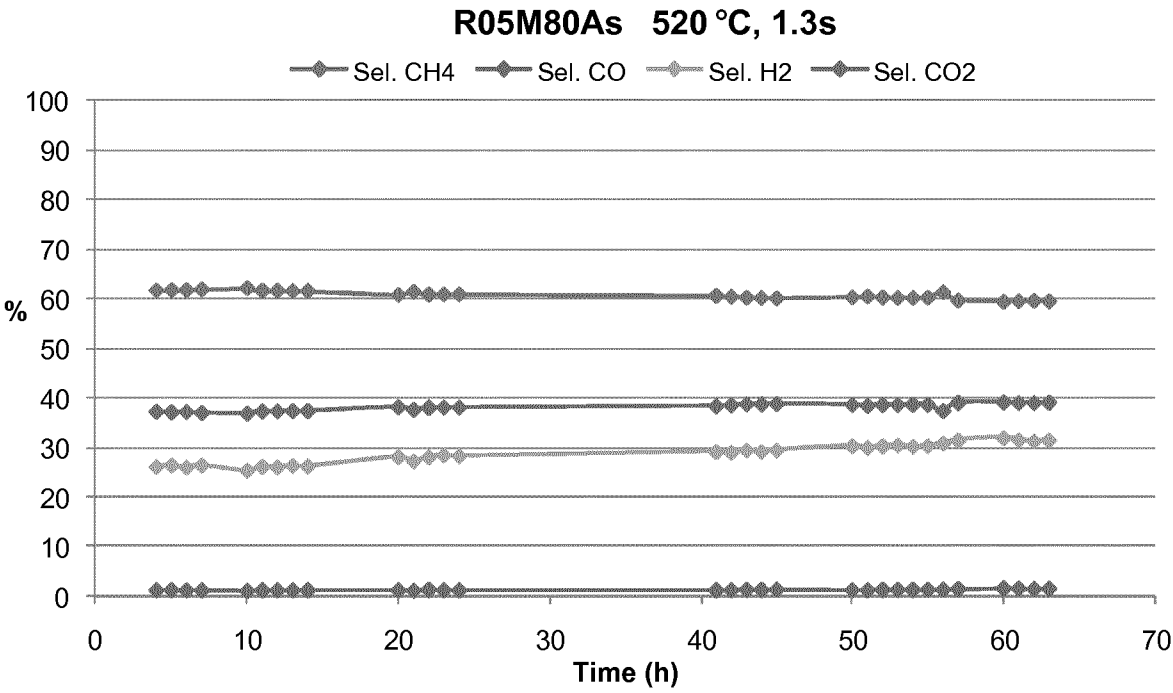


Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/072602

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J21/00 B01J21/16 B01J23/00 B01J23/58 B01J27/236 B01J37/00 B01J37/06 B01J37/08 B01J37/18 C01B3/32 C01F7/00					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01J C01B C01F					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal , WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	EP 0 725 038 A1 (SNAM PROGETTI [IT]) 7 August 1996 (1996-08-07) page 4; example 2 page 7; example 9 -----				1-12
X	WO 03/099436 A1 (AIR LIQUIDE [FR] ; BASILE FRANCESCO [IT] ; ALBERTAZZI SIMONE [IT] ; GARY) 4 December 2003 (2003-12-04) page 2, line 22 - page 3, line 21 page 4, line 7 - line 14 page 7, line 5 - line 7 page 11; example 8 -----				9-11 , 13 , 14
X	EP 1 262 224 A1 (RADICI CHIMICA SPA [IT]) 4 December 2002 (2002-12-04) paragraphs [0018] - [0023] , [0026] , [0042] - [0046] ----- -/- .				1-4,7 , 9-11
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.					
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Date of the actual completion of the international search 5 February 2013			Date of mailing of the international search report 15/02/2013		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Schmitt, Christi an		

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/072602

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11 276893 A (MITSUBISHI HEAVY IND LTD; TAKEHIRA KATSUOMI) 12 October 1999 (1999-10-12) paragraph [0006] - paragraph [0010] example 1 -----	1-4,7-9
A	US 5 439 861 A (BHATTACHARYYA ALAKANANDA [US] ET AL) 8 August 1995 (1995-08-08) the whole document -----	1-14
A	EP 1 808 229 A1 (AIR LIQUIDE [FR]) 18 July 2007 (2007-07-18) the whole document -----	1-14
A	JADSON S. MOURA ET AL: "Ethanol steam reforming over rhodium and cobalt-based catalysts : Effect of the support" , INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, vol . 37, no. 4, 9 December 2011 (2011-12-09) , pages 3213-3224, XP055028206, ISSN: 0360-3199 , DOI : 10.1016/j.ijhydene.2011.10.112 the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/072602

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0725038	AI	07-08-1996	DE 69620811 D1 29-05-2002
			DE 69620811 T2 28-11-2002
			DK 725038 T3 19-08-2002
			EP 0725038 AI 07-08-1996
			IT MI950184 AI 05-08-1996

Wo 03099436	AI	04- 12 -2003	EP 1511566 AI 09-03-2005
			Wo 03099436 AI 04-12-2003

EP 1262224	AI	04- 12 -2002	DE 60101461 D1 22-01-2004
			DE 60101461 T2 28-10-2004
			EP 1262224 AI 04-12-2002

JP 11276893	A	12- 10 -1999	JP 4211900 B2 21-01-2009
			JP 11276893 A 12-10-1999

US 5439861	A	08- 08 -1995	US 5439861 A 08-08-1995
			US 5614163 A 25-03-1997

EP 1808229	AI	18-07-2007	CN 101370585 A 18-02-2009
			EP 1808229 AI 18-07-2007
			EP 1976634 AI 08-10-2008
			US 2011017953 AI 27-01-2011
			US 2012149548 AI 14-06-2012
			WO 2007080175 AI 19-07-2007
