(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 October 2015 (01.10.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/147755 A1

(51) International Patent Classification:
B01J 23/42 (2006.01) *B01J 23/68* (2006.01)
B01J 23/648 (2006.01) *B01J 23/89* (2006.01)
B01J 37/02 (2006.01) *C07C 1/20* (2006.01)
B01J 23/56 (2006.01)

(21) International Application Number:
PCT/SG2015/000102

(22) International Filing Date:
30 March 2015 (30.03.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10201401085S 28 March 2014 (28.03.2014) SG

(71) Applicant: **AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH** [SG/SG]; 1 Fusionopolis Way #20-10, Connexis, Singapore 138632 (SG).

(72) Inventors: **WANG, Chuan**; c/o Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, Singapore 627833 (SG). **CHANG, Jie**; c/o Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, Singapore 627833 (SG). **BORGNA, Armando**; c/o Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, Singapore 627833 (SG).

(74) Agent: **VIERING, JENTSCHURA & PARTNER LLP**; P.O. Box 1088, Rochor Post Office, Rochor Road, Singapore 911833 (SG).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2015/147755 A1

(54) Title: CATALYSTS FOR HYDRODEOXYGENATION REACTIONS

(57) Abstract: The invention relates generally to catalysts for hydrodeoxygenation reactions, and a method for preparing the catalysts. Further, the method for preparing a catalyst comprising: mixing a suspension of a solid support and a solution of a transition metal precursor to form a surface modified solid support; drying the surface modified solid support; and adding a solution of a noble metal salt to the dry surface modified solid support to thereby form the catalyst.

CATALYSTS FOR HYDRODEOXYGENATION REACTIONS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of priority of Singapore Patent Application No. 10201401085S, filed March 28, 2014, the contents of which being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

The invention relates generally to catalysts for hydrodeoxygenation reactions, and to methods for preparing the catalysts.

BACKGROUND

Due to the depletion of fossil fuels and rising concern over environmental protection, biomass has attracted more attention as an alternative energy source and chemical feedstock. There are various processes proposed by which biofuels and biochemicals can be obtained, such as direct conversion via pyrolysis, high-pressure liquefaction and solvolysis or indirect synthesis way via gasification followed by Fischer-Tropsch synthesis. Bio-oil, derived from fast pyrolysis of biomass, has been reported as a promising substitute fuel due to the lower cost compared to other biofuels. However, crude bio-oil is not suitable as a transportation fuel owing to its undesired characteristics such as thermal instability (increasing viscosity upon prolonged storage), high acidity and poor heating value. Thus, it is necessary to upgrade bio-oils to improve their quality to meet the requirements of conventional internal combustion engines.

A common upgrading technology of pyrolysis oil is catalytic hydrodeoxygenation (HDO) to achieve partial or total removal of these oxygenated functionalities. Several HDO catalysts have been reported or patented to-date. Generally, HDO catalyst consists of a solid support with high porosity, for instance

alumina, silica, titania, or active carbon, and one or more active elements in the form of metal, oxide, or sulphide, mainly including transition metals. Normally, high hydrogen pressure in the range of 60 to 250 bar is required to reach a reasonable deoxygenation levels and prevent coke deposition over the catalyst surface. The high cost to handle this high pressure both in capital and in operating costs partially makes the process uneconomical.

Therefore, there remains a need to provide for alternative catalysts for hydrodeoxygenation reactions to overcome or at least alleviate the above problems.

SUMMARY

The inventors have surprisingly found that by modifying solid supports with noble metals as active phase, the thus modified catalysts demonstrate high activity for hydrodeoxygenation reaction of pyrolytic lignin under low severity conditions; high selectivity towards aromatic products; decrease in hydrogen consumption and operation cost; production of high value products; and improved stability.

Thus, in a first aspect of the invention, there is provided a method for preparing a catalyst, the method including mixing a suspension of a solid support and a solution of a transition metal precursor to form a surface modified solid support. The method further includes drying the surface modified solid support and adding a solution of a noble metal salt to the dry surface modified solid support to thereby form the catalyst.

Use of the catalyst thus formed by the first aspect in hydrodeoxygenation reactions of oxygen containing chemicals, particularly biomass-derived pyrolysis oils, is also disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

Fig. 1 shows a diagram of present grafting method to prepare a transition metal modified catalyst support.

Fig. 2 shows product selectivity of guaiacol HDO over a series of platinum catalysts.

Fig. 3 shows product selectivity of guaiacol HDO over a series of platinum versus time on stream.

DESCRIPTION

The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

Modified noble metal catalysts are disclosed herein. Such modified catalysts are useful, for example, in hydrodeoxygenation reactions of oxygen containing chemicals, particularly biomass-derived pyrolysis oils.

In accordance with a first aspect of present disclosure, a method for preparing the modified noble metal catalyst is disclosed herein. The modified noble metal catalyst generally includes a solid support and a noble metal as active phase, and one transition metal dopant as a promoter to improve its activity and stability.

Thus, the preparation method includes mixing a suspension of a solid support and a solution of a transition metal precursor to form a surface modified solid support. The method further includes drying the surface modified solid support and adding a solution of a noble metal salt to the dry surface modified solid support to thereby form the catalyst.

The solid support employed herein, for example in bio-oil HDO processes, is desirable to have suitable porosity, acid resistance, and hydrothermal stability, according to the specific reaction environment. In various embodiments, the solid support may include active carbon, titania, zirconia, ceria, modified silica-based materials, or a mixture thereof.

In various embodiments, the transition metal precursor may include a transition metal selected from the group consisting of vanadium, iron, cobalt, nickel and zirconium. Preferably, the transition metal is zirconium or vanadium.

In various embodiments, the step of mixing the suspension of the solid support and the solution of the transition metal precursor may further include refluxing the mixture of the suspension of the solid support and the solution of the transition metal precursor. Preferably, prior to the refluxing of the mixture, the respective suspension of the solid support and the solution of the transition metal precursor are separately treated, for example by refluxing in toluene, to remove any absorbed water.

Thereafter, the treated respective suspension of the solid support and the solution of the transition metal precursor are mixed and refluxed at suitable temperatures and for a period of time. For example, the reflux temperature may be between 373 K and 473 K, such as about 373 K, about 378 K, about 383 K, about 388 K, about 393 K, about 398 K, about 403 K, about 408 K, about 413 K, about 418 K, about 423 K, about 428 K, about 433 K, about 438 K, about 443 K, about 448 K, about 453 K, about 458 K, about 463 K, about 468 K, or about 473 K. The reflux period may last between 2 and 10 h, such as about 2 h, about 3 h, about 4 h, about 5 h, about 6 h, about 7 h, about 8 h, about 9 h, or about 10 h.

In present context, the mixing of the suspension of the solid support and the solution of the transition metal precursor is such that the transition metal is grafted to the surface of the solid support. In other words, the surface modified solid support refers to the transition metal grafted to a surface of the solid support.

After forming the surface modified solid support, the solid support is dried, for example, by calcining.

In various embodiments, a noble metal is loaded or introduced into the modified solid support by adding a solution of a noble metal salt to the dry surface modified solid support. For example, the solution of the noble metal salt may be added via an impregnation method, such as an incipient wetness impregnation method.

In preferred embodiments, the noble metal salt may include a platinum salt. The loading of platinum may be in the range of 0.1 to 10% wt. The promoter, i.e. the transition metal, is desired to have strong interaction with platinum to improve its activity and stability during the hydrodeoxygenation process.

In various embodiments, the preparation method may further include calcining the catalyst after formation, at varying calcination temperatures and different periods. For example, the calcining step may

be carried out at between 723 K and 873 K, such as about 723 K, about 728 K, about 733 K, about 738 K, about 743 K, about 748 K, about 753 K, about 758 K, about 763 K, about 768 K, about 773 K, about 778 K, about 783 K, about 788 K, about 793 K, about 798 K, about 803 K, about 808 K, about 813 K, about 818 K, about 823 K, about 828 K, about 833 K, about 838 K, about 843 K, about 848 K, about 853 K, about 858 K, about 863 K, about 868 K, or about 873 K. The catalyst may be calcined for a period of 3 to 10 h, such as about 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, or 10 h.

As mentioned above, the modified catalyst thus formed by present method is useful in hydrodeoxygenation reactions of oxygen containing chemicals, particularly biomass-derived pyrolysis oils.

In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting example.

EXAMPLES

A series of transition metal doped or modified SBA-15 supported Pt catalysts are described herein as non-limiting examples. First, transition metal modified SBA-15 ("M-SBA-15") were prepared by grafting method as illustrated in Fig. 1. Homemade SBA-15 and transition metal precursor (V, Fe, Co, Ni and Zr acetylacetonate) were refluxed separately in toluene to remove any absorbed water, followed by refluxing the mixture of those two solutions at 393 K for 3 h. After filtration and washing, the synthesized M-SBA-15 samples were calcined and ready for the loading of platinum. Pt catalysts supported on M-SBA-15 catalysts were prepared using incipient wetness impregnation method. After impregnation, the samples were dried in air and calcined at 813 K for 5 h.

Catalytic activity measurements of the HDO of guaiacol as model reaction for HDO of bio-oil, were carried out in a fixed-bed stainless steel reactor at 673 K under a total pressure of 40 bar. Prior to the

reaction, the catalyst was in situ pre-treated under flowing H_2 at 673 K for 1 h. After that, the guaiacol was injected on the top of the catalyst bed using a HPLC pump. In all experiments, the contact time, defined as the ratio of catalyst weight to feed flow rate (W/F), and the molar ratio of H_2 to feed were kept at 0.067 h and 20:1, respectively. The product stream was passed through a condenser to condense all liquid products. Then, the liquid products were collected in a sampling cylinder after accumulating the liquid for each hour of time on stream. The products were analyzed using an Agilent 6890 GC. A GC/MS (Agilent 6890) was also used for product identification.

The product selectivity of guaiacol HDO over a series of platinum catalysts is shown in Fig. 2. All the data are based on the first hour reaction. The products are categorized into three groups: oxygen containing compounds, hydrocarbons and unknown. Hydrocarbons are 100% oxygen removal products including benzene, toluene, cyclohexene, and cyclohexane. It can be seen that all the modified platinum catalysts showed over 70% selectivity towards hydrocarbons for guaiacol HDO under lower severity, 40 bar of total pressure instead of high pressure of 60~250 bar, and higher space velocity, with a value of 15 g/g_{cat} h compared to traditional values in the range of 0.1~2 g/g_{cat} h. Without the transition metal promotion, Pt/SBA-15 catalyst showed about 88% selectivity towards hydrocarbons, which is a quite high level of deoxygenation. However, such high deoxygenation deactivate quickly over time. After 5 hours of reaction, it dropped to 75%, which is about 15% loss during 5 hours reaction, as shown in Fig. 3. When transition metal promoters are introduced, V and Zr modified or doped Pt/SBA-15 catalysts show positive effect on the oxygen removal which has higher amount of hydrocarbons and less oxygen containing compounds, while Fe, Co and Ni modified or doped Pt/SBA-15 showed poorer effect. V and Zr modified or doped Pt/SBA-15 catalysts showed the best performance in terms of oxygen removal. Therefore, the stability of Pt/V-SBA-15 and Pt/Zr-SBA-15 are further tested as shown in Fig. 3.

Without the transition metal promoter, the selectivity towards total oxygen removal products (categorized as hydrocarbons in this disclosure) dropped 15% over 5 hour's reaction. After modification with V, the

stability of Pt/V-SBA-15 catalyst improved significantly. There was less than 2% loss of selectivity towards hydrocarbons after 5 hours, and the total deoxygenation level is over 95%. For the Zr-modified Pt/Zr-SBA-15 catalyst, the deactivation rate is also improved compared to the one with no promoter; but it is less stable than a V-modified catalyst. In summary, both V- and Zr-modified Pt catalysts exhibited much higher stability against deactivation for the guiacol HDO at 673 K under a total pressure of 40 bar.

In conclusion, novel platinum catalyst supported on vanadium and zirconium modified SBA-15 show superior catalytic performance on the guaiacol hydrodeoxygenation reaction. Both activity and stability of platinum catalyst are improved significantly after modification by vanadium and zirconium, which gives Pt/V-SBA-15 and Pt/Zr-SBA-15 the highest potential for industry application. The disclosure provides a good catalyst system for the selective removal of oxygenated functional groups to aromatic or naphthenic hydrocarbons, which can be used as high value chemicals. The high selectivity and stability of present modified catalysts help to improve the economic feasibility of bio-oil upgrading technology significantly.

By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally,

the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Other embodiments are within the following claims and non- limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

CLAIMS

1. Method for preparing a catalyst, comprising:

mixing a suspension of a solid support and a solution of a transition metal precursor to form a surface modified solid support;

drying the surface modified solid support; and

adding a solution of a noble metal salt to the dry surface modified solid support to thereby form the catalyst.

2. Method according to claim **1**, wherein said mixing further comprising refluxing the mixture of the suspension of the solid support and the solution of the transition metal precursor.

3. Method according to claim **1** or **2**, wherein said surface modified solid support comprises the transition metal grafted to a surface of the solid support.

4. Method according to any one of claims **1-3**, wherein said drying comprises calcining.

5. Method according to any one of claims **1-4**, wherein said adding comprises an impregnation method.

6. Method according to claim **5**, wherein said adding is an incipient wetness impregnation method.

7. Method according to any one of claims **1-6**, further comprising calcining the catalyst after formation.

8. Method according to claim **7**, wherein said calcining comprises calcining at between 723 K and 873 K.

9. Method according to claim **8**, wherein said calcining comprises calcining at about 813 K.

10. Method according to any one of claims **7-9**, wherein calcining comprises calcining for a period of 3 to 10 hours.

11. Method according to claim **10**, wherein calcining comprises calcining for about 5 hours.

12. Method according to any one of claims **1-11**, wherein the transition metal precursor comprises a transition metal selected from the group consisting of vanadium, iron, cobalt, nickel and zirconium.

13. Method according to claim **12**, wherein the transition metal is zirconium or vanadium.

14. Method according to any one of claims **1-13**, wherein the noble metal salt comprises a platinum salt.

15. Method according to any one of claims **1-14**, wherein the solid support is selected from the group consisting of activated carbon, titania, zirconia, ceria, and modified silica-based materials.

16. Catalyst obtained by a method according to any one of claims **1-15**.

17. Use of a catalyst obtained by a method according to any one of claims **1-15** in hydrodeoxygenation reactions of oxygen containing chemicals, particularly biomass-derived pyrolysis oils.

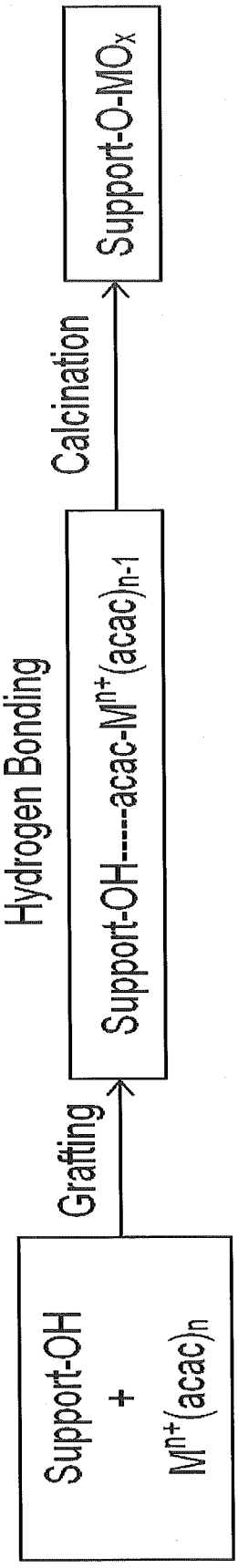

Support-OH
+
$M^{n+}(acac)_n$
Grafting
Support-OH----acac-$M^{n+}(acac)_{n-1}$
Hydrogen Bonding
Calcination
Support-O-MO_x

FIG. 1

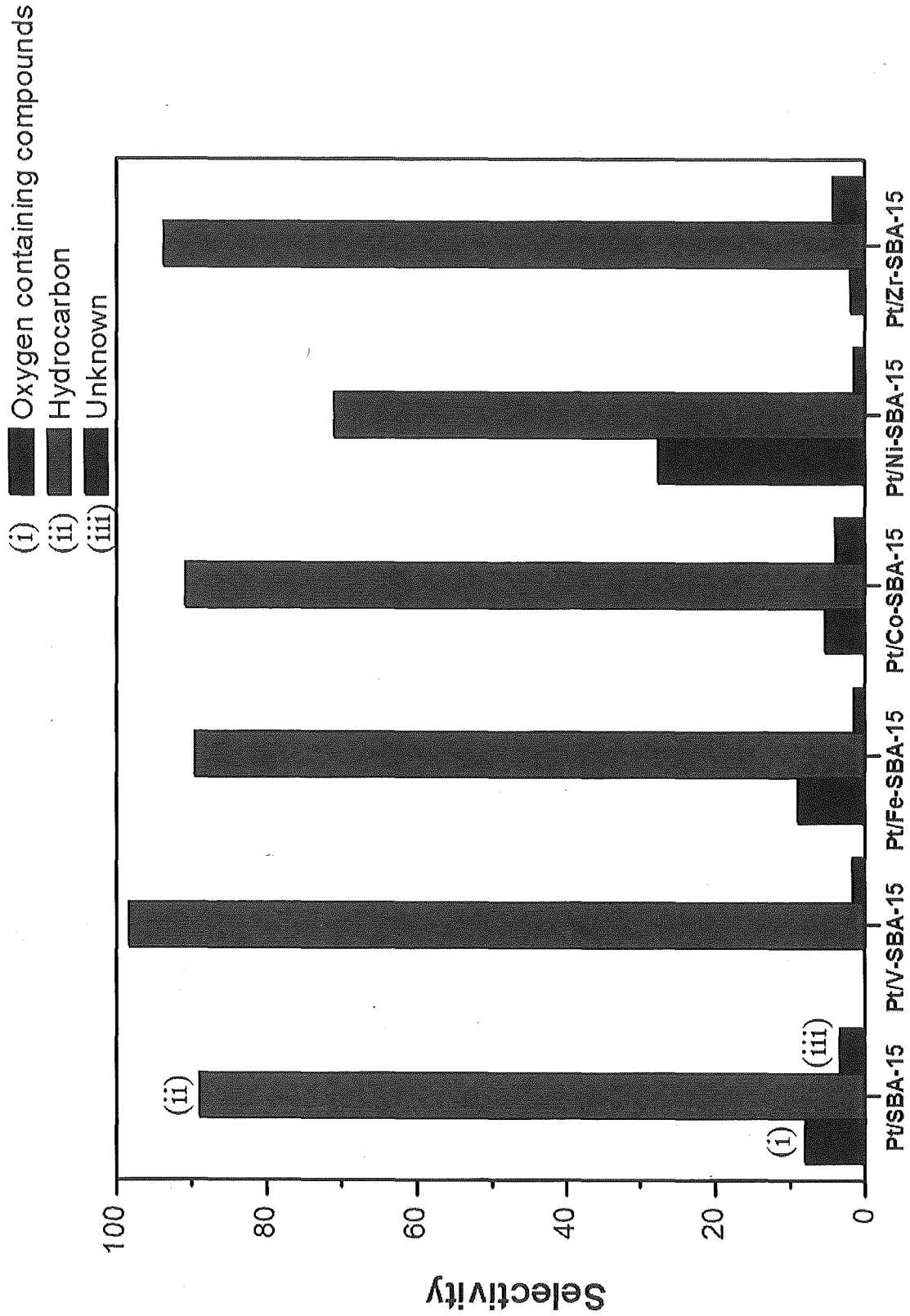

(i) Oxygen containing compounds
(ii) Hydrocarbon
(iii) Unknown
Selectivity
100
80
60
40
20
0
(ii)
(iii)
(i)
Pt/SBA-15
Pt/V-SBA-15
Pt/Fe-SBA-15
Pt/Co-SBA-15
Pt/Ni-SBA-15
Pt/Zr-SBA-15

FIG. 2

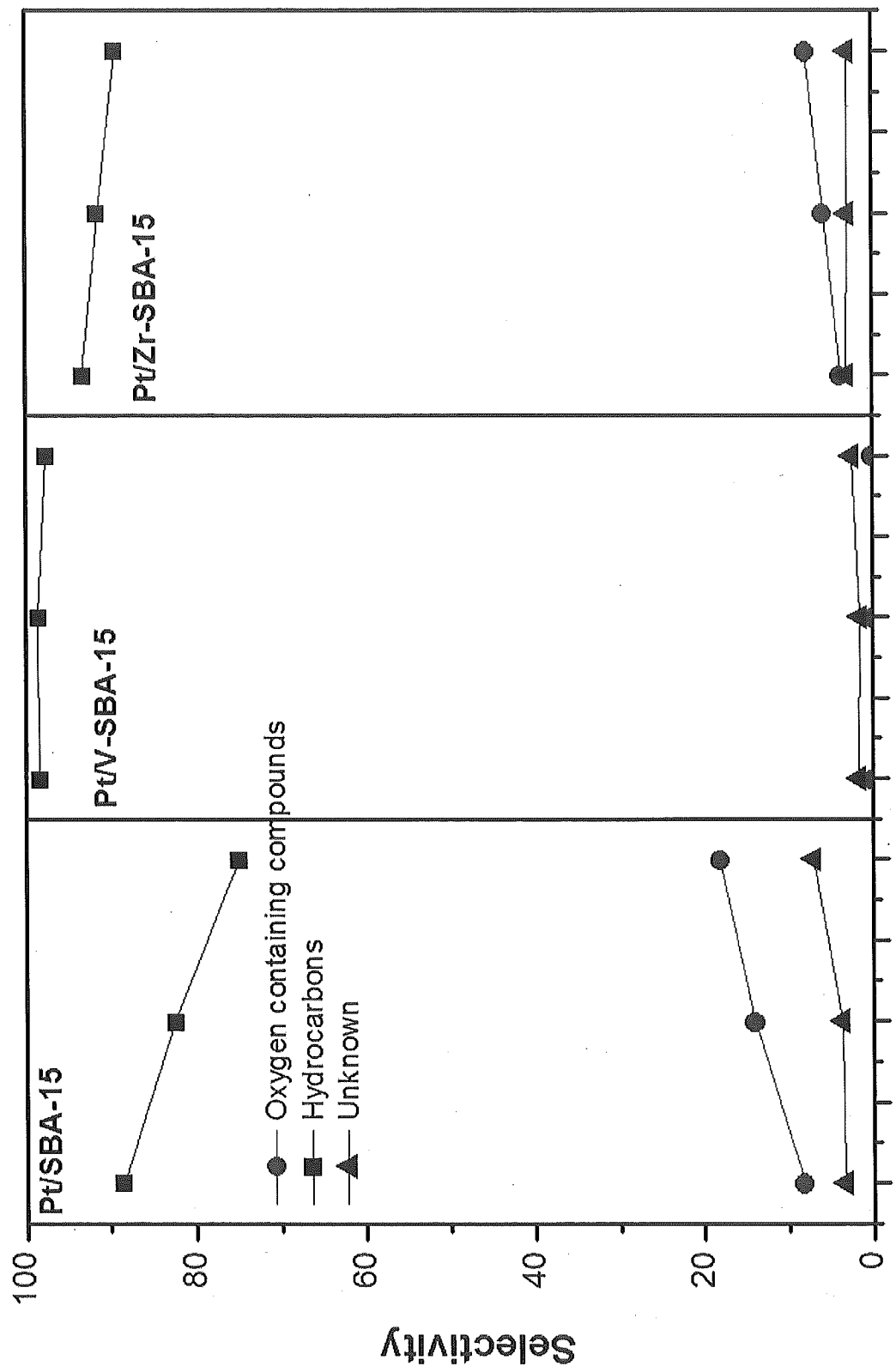

Pt/SBA-15
Pt/V-SBA-15
Pt/Zr-SBA-15
Oxygen containing compounds
Hydrocarbons
Unknown
Selectivity
Time on stream (hour)
0
20
40
60
80
100
1
2
3
4
5

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2015/000102

A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/42 (2006.01) ***B01J 23/648 (2006.01)*** ***B01J 37/02 (2006.01)*** ***B01J 23/56 (2006.01)*** ***B01J 23/68 (2006.01)*** ***B01J 23/89 (2006.01)*** ***C07C 1/20 (2006.01)***

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)

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)

EPODOC and WPI:/IPC/CPC C07C OR B01J AND Keywords (HYDRODEOXYGENATION OR HDO) and Keywords ((impregnat+ w solid+), (noble or platinum or Pt) 2w metal)).Cluster - $PATEN-English full text databases EPODOC, WPIAP, TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXTPEPEA, TXPES, TXPUSE0A, TXPUSE1A, TXPUSEA, TXPUSEB, TXPWOEA and Keywords ((impregnat+ w solid+), (noble or platinum or Pt) 2w metal)) & like terms.

Espacenet and keywords (hydrodeoxygenation AND B01J37).
GoogleScholar and keywords (supported transition noble "HDO catalyst" calcining).

Applicant(s)/Inventor(s) name search in AusPat:
Search query: Applicant name = "AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH" AND Inventor name = "Wang, Chuan"
0 results found and viewed.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 May 2015	14 May 2015

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au

Authorised officer

John Deuis
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262832146

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/SG2015/000102**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/0031546 A1 (Shen et al.) 30 January 2014 See the abstract; para. [0021], [0032]-[0038]; and claims 1-21.	1-15, 16, 17
A	WO 2013/191661 A1 (AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH) 27 December 2013 See the abstract; and para. [0049]-[0051].	1, 16, 17

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2015/000102**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 2014/0031546 A1	30 January 2014	CN 104428060 A	18 Mar 2015
		WO 2014018591 A1	30 Jan 2014
WO 2013/191661 A1	27 December 2013		

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.